

Functionalized Polymers for Nano- and Microcomposites: Towards Improvement of the Electrochemical Reliability and Humidity Robustness of PCB Assemblies

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„Auch das lauteste Getöse großer Ideale darf uns nicht verwirren und nicht hindern,
den einen leisen Ton zu hören, auf den alles ankommt.“

- Werner Heisenberg

Die vorliegende Dissertation entstand im Zeitraum von Februar 2018 bis Juli 2021 im Arbeitskreis von Prof. Dr. Stephan Förster am Institut für Neutronenstreuung (Jülich Centre for Neutron Science/ Institute JCNS-1 and IBI-8) des Forschungszentrums Jülich in Kollaboration mit der Robert Bosch GmbH unter der Betreuung von Dr. Heiko Elsinger in Schwieberdingen.

ABSTRACT

Functionalized polymer ligands are polymer chains equipped with functional groups that interact with surfaces, molecules or a polymer matrix. Their versatility, ease of processing and tunable molecular weight make them suitable for modern applications. By interacting with nano- or microparticles, composite materials are created which are becoming increasingly important in miniaturized technologies such as optoelectronics, sensors, microelectronics and automotive engineering.

Precise material selection and a thorough understanding of the interactions between the individual components of the composites are essential. Nanocomposites exhibit their optical properties through absorption and scattering at specific resonance wavelengths, provided size and shape remain stable. Microcomposites, which are intended to improve the corrosion resistance and lifetime of electronic components, require strong adhesion to polymer matrices, fillers or interfaces in order to increase homogeneous dispersion, moisture resistance and electrochemical reliability.

This thesis focuses on how functionalized polymer ligands can address these challenges at both the nano- and microscale. Investigations of gold nanoparticles show that by varying the polymer molecular weight of multidentate amino-terminated polymer ligands, the interparticle distances and thus, the nanoparticle optical properties can be precisely controlled. It is demonstrated herein for the first time that the amino functionality and a moderate binding significantly enhance the shape stability of anisotropic particles by preferentially binding to their lateral surfaces. Furthermore, a polymer-assisted synthesis of gold nanoparticles with defined spacings is presented.

Main focus of this work is on the functionalization of micrometer-sized fumed silica for polymer coatings in printed circuit board assemblies. Short-chain conventional organosilanes are found to exhibit migration effects that can lead to interactions with flux residues in solder pastes, resulting in corrosion. Inspired by the success of polymer ligands previously used for nanocomposites, short-chain organosilanes are replaced with glycidyl ether-terminated polymer ligands. Their higher molecular weight shows reduced migration, resulting in improved adhesion. Tests on printed circuit board assemblies confirm their high electrochemical reliability. As a future perspective, neutron imaging is proposed as an innovative method to detect critical defects in polymer coatings, offering a promising approach to evaluate future insulating materials.

KURZZUSAMMENFASSUNG

Funktionalisierte polymere Liganden sind Polymerketten mit funktionellen Gruppen, die mit Oberflächen, Molekülen oder einer Polymermatrix interagieren. Ihre Vielseitigkeit, die einfache Verarbeitung und die Variation des Molekulargewichts machen sie für moderne Anwendungen vielseitig einsetzbar. Durch Wechselwirkungen mit Nano- oder Mikropartikeln entstehen Kompositmaterialien, die für miniaturisierte Technologien in Optoelektronik, Sensorik, Mikroelektronik und Automobiltechnik relevant sind.

Die sorgfältige Materialauswahl und das Verständnis der Wechselwirkungen einzelner Komponenten ist dabei essentiell. Nanokomposite zeigen ihre einzigartigen optischen Eigenschaften durch Absorption und Streuung bei spezifischen Resonanzwellenlängen, sofern Größe und Form stabil bleiben. Mikrokomposite, die Korrosionsschutz und Langlebigkeit elektronischer Bauteile verbessern sollen, benötigen eine starke Haftung an Polymermatrizen, Füllstoffe oder Grenzflächen zur Erhöhung der homogenen Dispersion, Feuchtebeständigkeit und elektrochemischen Zuverlässigkeit.

In der vorliegenden Arbeit wird der Einfluss von funktionellen Polymerliganden auf der Nano- und Mikrometerskala untersucht. Funktionalisierungen an Goldnanopartikeln verdeutlichen, dass deren interpartikuläre Abstände und damit deren optische Eigenschaften durch Variation des Molekulargewichts Amino-terminierter polymerer Liganden gezielt beeinflusst werden können. Erstmals wird gezeigt, dass die Aminofunktionalität und dessen moderate Anbindung an die lateralen Flächen von zylindrischen Nanopartikeln für die Erhaltung der Anisotropie sorgen. Als Ausblick wird eine polymerunterstützte Synthese abstandsdefinierter Goldnanopartikel vorgestellt.

Zentraler Fokus besteht auf der Funktionalisierung pyrogener Kieselsäure für Polydimethylsiloxan-basierte Beschichtungen auf Leiterplatten. Die Funktionalisierung mit kurzkettigen konventionellen Organosilanen zeigt Migrationseffekte, die Wechselwirkungen mit Flussmittelrückständen und Korrosion verursachen. Inspiriert durch den zuvor erfolgreichen Einsatz von Polymerliganden in Nanokompositen werden kurzkettige Organosilane durch Polymerliganden mit Glycidylether-Endgruppen ersetzt, die aufgrund ihres höheren Molekulargewichts ein geringeres Migrationsverhalten aufweisen. Die Untersuchungen an bestückten und beschichteten Leiterplatten bestätigen ihre hohe Isolationseigenschaft. Als Ausblick wird schließlich Neutronenbildgebung als Methode zur Detektion von Defekten in Polymerbeschichtungen vorgeschlagen.

CONTRIBUTION OF AUTHORS

Parts of this work have been submitted for publication. Parts of this work were done in collaboration with others. The contributions of those involved are listed below.

Chapter 3 and Chapter 4

Parts of these chapters have been submitted for publication.

I prepared the samples, planned and performed the UV-Vis-NIR, TEM, and ^1H -NMR measurements, and analyzed the data. Astrid Rauh synthesized gold nanospheres and provided the colloidal solution for further surface modifications. Susanne Seibt, Matthias Karg and Stephan Förster contributed to the scientific discussion.

ABBREVIATIONS

ANTARES	Advanced Neutron Tomography and Radiography Experimental System
APTES	(3-Aminopropyl)triethoxysilane
AR	Aspect Ratio
ASTM	American Society for Testing and Materials
AuNPs	Gold Nanoparticles
AuNRs	Gold Nanorods
AuNSs	Gold Nanospheres
BGA	Ball Grid Array
BSE	Backscattered Electrons
CTAB	Cetyltrimethylammonium bromide
DC	Direct Current
d_i	Interparticle Distance
DLVO	Derjaguin-Landau-Verwey-Overbeek
ECM	Electrochemical Migration
ECUs	Electronic Control Units
EDX	Energy Dispersive X-Ray Analysis
EIS	Electrochemical Impedance Spectroscopy
FEG	Field Emission Gun
FR	Flame-retardant
FT-IR	Fourier Transform-Infrared Spectroscopy
GPS	(3-Glycidoxypentyl)trimethoxysilane
H2	Hydrophobic Fumed Silica
H3	Highly Hydrophobic Fumed Silica
IEC	International Electrotechnical Commission
IPC	Institute for Printed Circuits
LaB ₆	Lanthanum Hexaboride
LSPR	Localized Surface Plasmon Resonance
MPS	3-Methacryloxypropyl)trimethoxysilane
MPTMS	(3-Mercaptopropyl)trimethoxysilane

OSP	Organic Solderability Preservative
PAA	Poly(acrylic acid)
PCBAs	Printed Circuit Board Assemblies
PCBs	Printed Circuit Boards
PDI	Polydispersity Index
PDMS	Polydimethylsiloxane
PDMS di	Diglycidylether-terminated Polydimethylsiloxane
PDMS mono	Monoglycidylether-terminated Polydimethylsiloxane
PEG	Poly(ethylene glycol)
PMMA	Poly(methyl methacrylate)
PNIPAm	Poly(N-isopropylacrylamide)
PS-OH	Hydroxyl-terminated Polystyrene
PS-SH	Thiol-terminated Polystyrene
QFP	Quad Flat Package
SAC	SnAgCu
SE	Secondary Electrons
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SIR	Surface Insulation Resistance
SOP	Small Outline Package
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
UV-Vis-NIR	Ultraviolet-Visible-Near InfraRed Spectroscopy
WCA	Water Contact Angle
WOAs	Weak Organic Acids

TABLE OF CONTENT

ABSTRACT	VII
KURZZUSAMMENFASSUNG	VIII
CONTRIBUTION OF AUTHORS.....	IX
ABBREVIATIONS	X
TABLE OF CONTENT	XIII
1. INTRODUCTION	1
2. THEORY	3
2.1 Nanometer-Scale Au-Based Composites	3
2.1.1 Overview	3
2.1.2 Synthesis of Spherical and Anisotropic AuNPs	4
2.1.3 Surface Functionalization	8
2.1.4 Optical Characteristics	13
2.1.5 Applications	16
2.2 Micrometer-Scale Silica-Based Composites	18
2.2.1 Overview	18
2.2.2 Surface Functionalization	20
2.2.3 Humidity Robustness and Insulation Characteristics	22
2.2.4 Applications	26
2.3 Surface Insulation Resistance	28
2.3.1 Overview	28
2.3.2 Materials and Layout	29
2.3.3 Measurement Modes	31
2.3.4 Humidity Related Failures	31
2.4 Electron Microscopy	33
2.4.1 Overview	33
2.4.2 Transmission Electron Microscopy	34
2.4.3 Scanning Electron Microscopy	36

2.5	Neutron Imaging.....	38
2.5.1	Overview	38
2.5.2	Imaging Techniques	39
2.5.3	Neutron Sources and Applications	40
3.	INFLUENCE OF FUNCTIONALIZED POLYMER AGENTS ON THE STABILIZATION AND INTERPARTICLE DISTANCE VARIATION OF GOLD NANOPARTICLES	52
	Abstract.....	52
3.1	Introduction	53
3.2	Experimental Part.....	55
3.2.1	Materials.....	55
3.2.2	Synthesis.....	55
3.2.3	Characterization Methods	57
3.3	Results and Discussion	58
3.3.1	AuNP Synthesis and PEHA-Functionalization of PS	58
3.3.2	Investigation of the Ligand Exchange with Functionalized Polymer Ligands.....	60
3.3.3	Influence on Optical Properties	66
3.4	Conclusion and Outlook	67
	Acknowledgments	68
	References.....	69
4.	STUDY OF THE STABILIZATION AND GROWTH OF SPHERICAL AND ELLIPSOIDAL AUNPs BY POLYMER COATING	72
	Abstract.....	72
4.1	Introduction	73
4.2	Experimental Part.....	75
4.2.1	Materials.....	75
4.2.2	Synthesis.....	76
4.2.3	Characterization Methods	77
4.3	Results and Discussion	78
4.3.1	Investigation of the Polymer-Assisted AuNP Synthesis.....	79
4.3.2	Comparison between Direct Polymer Stabilization and Ligand Exchange	80
4.3.3	Study of the Polymer-Assisted Anisotropic Growth	84
4.4	Conclusion	87

4.5	Outlook	88
	Acknowledgments	89
	References.....	90
5.	INVESTIGATION OF THE ELECTROCHEMICAL RELIABILITY OF ORGANOSILANE- AND SILICA-BASED MICROCOMPOSITES IN PDMS COATINGS	93
	Abstract.....	93
5.1	Introduction	94
5.2	Experimental Part.....	96
	5.2.1 Materials.....	96
	5.2.2 Sample Preparation.....	96
	5.2.3 Characterization Methods	97
5.3	Results and Discussion	100
	5.3.1 Electrochemical Reliability.....	101
	5.3.2 Investigation of the Electrochemical Migration	107
	5.3.3 Study of the Influence of Humidity Load	109
5.4	Conclusion	116
5.5	Outlook	117
	Acknowledgments	118
	References.....	118
6.	INFLUENCE OF FUNCTIONALIZED POLYMER LIGANDS APPLIED IN PDMS-BASED COATINGS ON THE ELECTROCHEMICAL RELIABILITY AND HUMIDITY ROBUSTNESS OF PCB ASSEMBLIES	121
	Abstract.....	121
	Introduction	122
6.1	Experimental Part.....	124
	6.2.1 Materials.....	124
	6.2.2 Sample Preparation.....	125
	6.2.3 Characterization Methods	126
6.2	Results and Discussion	128
	6.3.1 Accelerated Electrochemical Reliability Assessment of functionalized Polymer Ligands	131
	6.3.2 Investigation of the Humidity Robustness of functionalized PDMS	135
	6.3.3 Approach for Visual Analysis of Coating Defects by Neutron Imaging	139

6.3	Conclusion	142
6.4	Outlook	143
	Acknowledgments	143
	References.....	144
7.	SUMMARY	147
8.	OUTLOOK.....	149
	ACKNOWLEDGMENTS.....	150
	APPENDIX.....	151
	EIDESSTATTLICHE ERKLÄRUNG	155
	CURRICULUM VITAE	156

1 INTRODUCTION

The ongoing miniaturization in nanotechnology and microelectronics—defined as the process of reducing structural dimensions while maintaining or enhancing functionality—is a central focus of current research and development. This effort aims to improve performance, reduce power consumption, and decrease mass and space requirements, and expanding application areas. However, these technologies increasingly encounter fundamental physical limitations, necessitating alternative and interdisciplinary approaches to ensure future technological advancements.

The increasing functionality and complexity of components, coupled with decreasing spacing, has led to increased interest in finely tuned micro- and nanocomposites embedded in polymer matrices. These composites typically combine inorganic nano- or micrometer-sized particles with functionalized organic ligands or agents, combining the advantages of each. This combination imparts enhanced mechanical strength, temperature and moisture resistance, and specific optical properties to the material. In addition, functionalizing agents promote compatibility between particles and the matrix, improve homogeneity, and strengthen bonding, optimizing the transfer of particle properties to the entire material.

In nanotechnology, for example, 2D and 3D assemblies of nanocomposites hold promise for future applications in catalysis, surface-enhanced spectroscopy, and sensing. Microcomposites combined with widely used polymer matrices such as silicones are used in the automotive industry as protective coatings, potting and sealing materials to protect electronic control units from varying temperature and humidity conditions, contamination, and mechanical stress. These properties are particularly relevant to modern technological developments such as act-by-wire systems, where electronic controls replace traditional mechanical connections.

A significant challenge lies in identifying suitable material combinations for composite materials, optimizing them in conjunction with silicones, and applying appropriate analytical methods to ensure that critical and safety-relevant functions of control units operate reliably and possess high longevity. Specifically, the humidity robustness of printed circuit board assemblies within these units is crucial. Moisture can infiltrate through various pathways, such as high humidity, condensation from temperature fluctuations, or inadequate sealing. It may contain conductive contaminants or dissolve

existing ones, especially in soldered connections on PCBs, leading to corrosion between conductors, causing short circuits, and potentially destroying assemblies.

This thesis investigates the use of functionalized polymers, first focusing on nanocomposites and then on microcomposites. Chapters three and four provide a fundamental analysis of particles at the nanometer scale. Gold nanoparticles are synthesized using a silver-assisted seed-mediated growth method in the presence of short-chain ligands citrate and cetyltrimethylammonium bromide. Subsequent functionalization of these nanoparticles is achieved through ligand exchange with amino- and thiol-terminated polystyrene. The study explores how polymer attachment and variations in molecular weight influence the steric stabilization and optical properties of the particles. In addition, Chapter four explores the potential to synthesize nanoparticles during a polymer-assisted seed-mediated growth process that achieves comparable interparticle spacing to the ligand exchange methods discussed previously.

In Chapters five and six, the focus shifts to applied research on polydimethylsiloxane-based coatings for PCBs. Micrometer-sized silica particles are functionalized with short-chain organosilane agents and evaluated for humidity robustness and electrochemical reliability. This assessment includes surface insulation resistance measurements under applied bias and constant temperature and humidity conditions near the dew point, considering varying conductor spacings. Glycidoxypropyltrimethoxysilane and methacryloxypropyltrimethoxysilane serve as adhesion promoters or coupling agents with bifunctionality, that exhibit migration tendencies. Building on previous findings regarding successful polymer stabilization of nanoparticles, in Chapter six these organosilanes are replaced with functionalized polydimethylsiloxane possessing comparable glycidyl ether functionality. These modified systems are subjected to shorter, more sensitive dynamic resistance measurements under varying humidity levels. Finally, in addition to the study of the isolation capability, a new approach using neutron imaging to detect defects in polymer coatings was proposed for future analysis methods based on the first promising results.

This thesis presents an approach to optimize humidity robustness and electrochemical reliability using polymer functionalization agents by integrating findings from the nano- to the microscale, highlighting the importance of interdisciplinary efforts in the development of future advanced technologies.

2 THEORY

2.1 Nanometer-Scale Au-Based Composites

2.1.1 Overview

They are "dwarves" in size, and yet the excitement of every scientist who marvels at them in an Erlenmeyer flask is tremendous: The nanoparticles. Nanoparticles between 1 and 100 nanometers in size exhibit unique properties due to their dimension, high surface-to-volume ratio and quantum effects. Many types of nanoparticles are of interest to scientists. These include metallic nanoparticles made of noble metals such as gold, platinum and silver^[1] as well as metal oxides and magnetic nanoparticles like iron oxide such as magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$)^[2], silicon dioxide (SiO_2)^[3], zinc oxide (ZnO)^[4] and titanium oxide (TiO_2)^[5]. Different synthesis methods, including chemical, physical and biological routes, enable the production of nanoparticles with tailored shapes, sizes and compositions, allowing customization for specific applications.^[6]

Bottom-up and top-down approaches are the two main approaches to synthesize nano-scale particles. The top-down approach utilizes physicochemical processes to shape and size bulk material, while the bottom-up approach mainly involves reducing metal salts (precursors) in the presence of surfactants and reducing agents.^[7] In the latter case, which is the most commonly used, the ratio of chemicals and synthesis conditions plays a crucial role in the nucleation and growth phases of nanoparticles. Nanoparticle growth itself is an important research area, as it directly impacts the properties of the resulting nanoparticles. In addition, the quantity of the added precursor, the type of reducing agent and the choice of capping agents are all critical factors that significantly influence the synthesis of nanoparticles.^[8,9]

Due to their outstanding physicochemical properties, gold nanoparticles (AuNPs) in particular are the subject of scientific research. AuNPs offer a wide range of applications, including catalysis^[10], sensing^[11] and optoelectronics^[12]. Furthermore, AuNPs are commonly used to produce nanocomposites, in which they form the inorganic core and are surrounded by an organic layer, such as a polymer layer. Polymer attachment on AuNPs has several advantages. Firstly, it enhances their stability, preventing from nanoparticle aggregation and degradation over time. Second, it enables the

introduction of physically adsorbed polymers such as polyelectrolytes, microgels consisting of cross-linked polymers as well as the attachment of functionalized ligands to the nanoparticle surface to form brushes in order to control the nanocrystal arrangement as well as optical properties. Finally, polymer coating significantly improves the biocompatibility of AuNPs, making them more suitable for biomedical applications.^[9,13] The various possible combinations of the core, the attached ligands and their arrangement as well as the interparticle distance (edge-to-edge or tip-to-tip) influence the properties of the Au nanocomposites (see Figure 2-1).

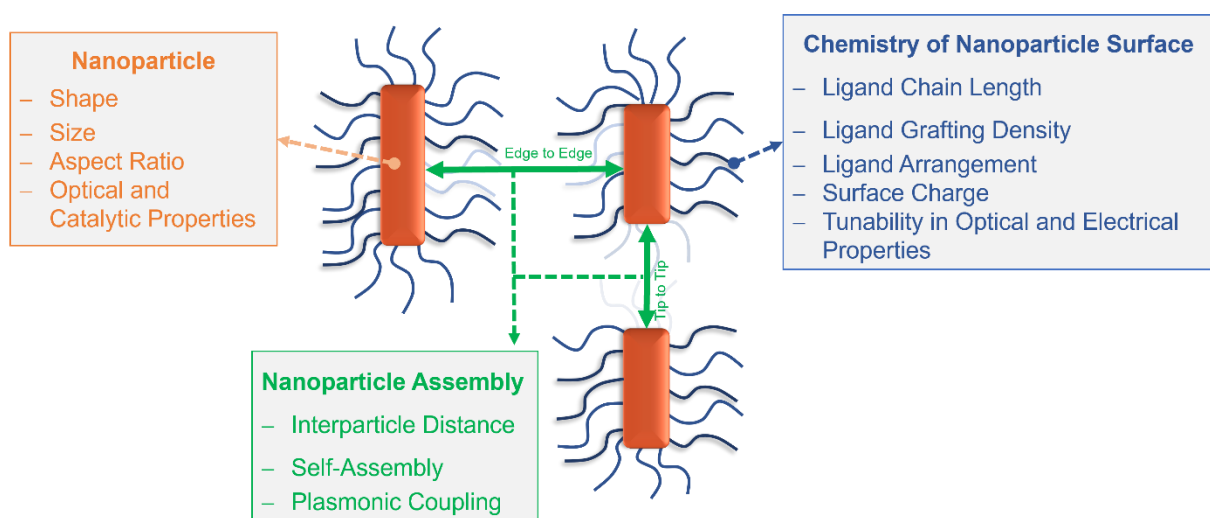


Figure 2-1: Overview of the most important building blocks and the composition in the production of gold nanocomposites, exemplified by cylindrical nanoparticles.

The following sections describe the synthesis of AuNPs and the surface chemistry of the attached ligands in more detail. The effects of the applied ligands on nanoparticle growth and stability, optical properties and applications of AuNPs are further outlined.

2.1.2 Synthesis of Spherical and Anisotropic AuNPs

Since Michael Faraday's discovery of the „beautiful ruby fluid“^[14] which involved reducing chloroauric acid with phosphorus in dissolved form in carbon disulfide, AuNPs have undergone extensive development and several synthesis techniques have been established. The synthesis of nanorods, nanospheres, nanostars, nanocubes,

nanoplates, triangular or hollow nanoparticles demonstrates the diverse possibilities for producing different morphologies, each with unique physical, chemical and optical properties.^[15] The most commonly studied morphologies are spherical and rod-shaped nanoparticles, the syntheses of which are explained in more detail.

On one side, the pioneering and ultimately most popular synthesis of spherical NPs in boiling aqueous solution with a diameter of 20 nm was presented in 1951 by Turkevich *et al.* in the presence of citric acid, which has both a stabilizing and reducing effect (see Figure 2-2 a).^[16] Frens *et al.* improved this approach by adjusting the ratio of chloroauric acid to sodium citrate which enabled them to control the size of the AuNPs ranging from approx. 10 nm – 100 nm.^[17] In line with the approach of Mulvaney *et al.*^[18], the Brust-Schiffrin method is a two-phase synthesis that relies on the strong affinity between gold surfaces and thiol (SH) groups. Here, gold ions are transferred from an aqueous to an organic phase by using tetraoctylammonium bromide (TOAB) as phase transfer agent in presence of the strong reduction agent sodium borohydride (NaBH_4) and nonpolar thiol (originally dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$)), resulting in the formation of thiol-capped AuNPs (see Figure 2-2 b).^[19] The size ranges between 1.5 nm and 5 nm and can be varied by the temperature, the ratio of gold to thiol and the reduction rate.^[20]

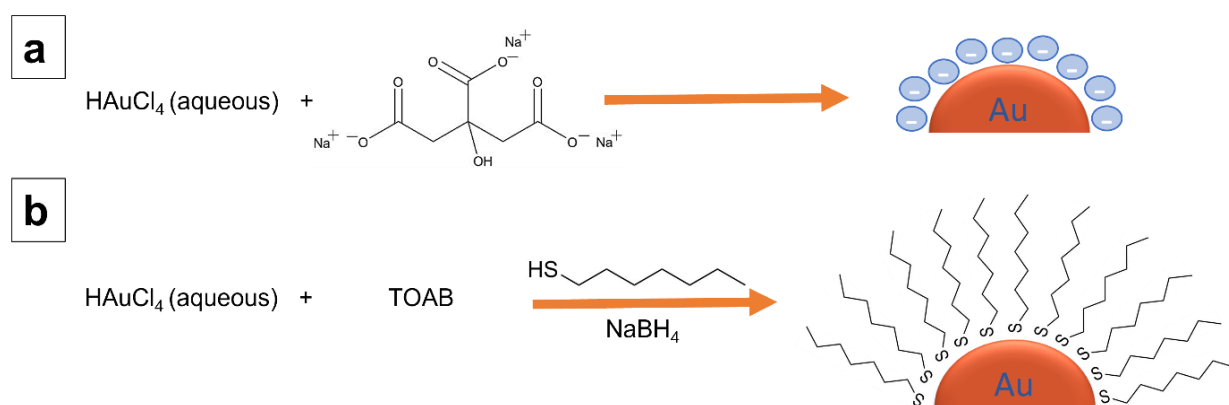


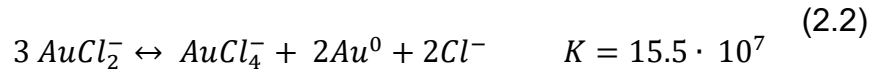
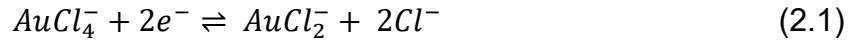
Figure 2-2: Schematic representation of a the Turkevich method using citrate as capping and reducing agent and b the Brust-Schiffrin approach in the presence of a nonpolar thiol for the synthesis of spherical AuNPs.

On the other side, the introduction of anisotropic, rod-shaped nanoparticles has expanded the synthesis possibilities for AuNPs. One of the first syntheses of gold nanorods (AuNRs) were carried out using the electrochemical method introduced by Wang and his research group.^[21,22] This involves using an electrochemical cell with a cathode made of platinum and an anode made of gold. The solution in which the electrodes are located contains cetyltrimethylammonium bromide (CTAB), which prevents aggregation. The solution also contains a small amount of the hydrophobic co-surfactant tetradecylammonium bromide, which contributes to the anisotropy of the AuNPs. After starting the 30-minute electrolysis process by setting the current intensity to 3 mA, the Au-anode is consumed in favor of the formation of AuBr_4^- anions. These interact with the surfactants in the solution, migrate to the Pt-cathode and are finally reduced to AuNRs. By adding a silver plate and thus, silver ions to the system, the aspect ratio of the AuNRs can be controlled.^[21]

These days, the synthesis of nanorods using seed-mediated growth synthesis has become the most widespread method. It offers several significant advantages such as:

- i. Precise controllability of size, shape and structure, enabling homogeneous and reproducible production
- ii. Fine-tuning of the synthesis conditions for optimization of the desired chemical and optical properties
- iii. Efficient large-scale production with increased industrial applicability^[23]

The method's advantages stem from its two-step approach, in which the synthesis is separated into a nucleation and a growth solution in a first step and a defined seed amount is added to the growth solution in a second step to initiate the growth of the AuNRs. In a typical seed-mediated growth synthesis, isotropically grown seeds are produced in the aqueous nucleation solution by reducing tetrachloroauric acid (HAuCl_4) with the strong reducing agent NaBH_4 , usually in the presence of CTAB. The solution for growth comprises an aqueous solution of HAuCl_4 and CTAB along with ascorbic acid, a milder reducing agent that inhibits secondary nucleation events. In detail, ascorbic acid reduces Au^{III} to Au^{I} in the presence of CTAB (see Equation 2.1) without AuCl_2^- -CTAB being disproportionated (see Equation 2.2)^[24]:



In addition, Au^I is reduced by electron transfer at the gold seed surface (see Equation 2.3)^[24]:



Due to the presence of CTAB the reduction can be described as following (see Equation 2.4)^[24]:



with $(CTAB_{mic})$ being CTAB micelles.^[24,25] The $AuCl_2^-$ -anions, which are encapsulated with CTAB, interact with the CTAB-encapsulated gold seeds (both have a Zeta potential of about +90 mV^[26]). The interaction between AuNRs and micelles is regulated by the electrical double layer. The assembly of these components is presumed to be crucial and rapid collision of the micelles at the ends, rather than at the sides, is considered to be essential for the formation of the nanorods.^[24] However, the synthesis method in general has considerable disadvantages in terms of reproducibility, yield and purification capability.^[27]

Significant progress has been made in seed-mediated growth synthesis with the introduction of silver nitrate ($AgNO_3$). It is widely accepted that silver ions are necessary for the preparation of nonspherical AuNPs, although the exact NP growth mechanism has become even more complex and is not yet fully understood. It is known that the presence of silver ions enhances the rod yield and promotes anisotropic structure through symmetry breaking and thus, influences the aspect ratio (length divided by width).^[28,29] It was found out that a higher Ag^+ -concentration results in symmetry breaking at smaller sizes.^[30] Hence, the analysis of the concentration of $AgNO_3$ is decisive for the growth and the resulting aspect ratio of the nanorods (see Figure 2-3), as are other parameters discussed, such as the presence of halides, reducing agents, synthesis conditions (*i.e.* temperature and rate of stirring) and the interplay of these factors.

Furthermore, the quantity, type and surface charge are crucial factors. Also, it is important to consider the size of the seeds since only nanoseeds within a specific size range can produce nanoparticles and ensure a low degree of polymorphism.^[29,31]

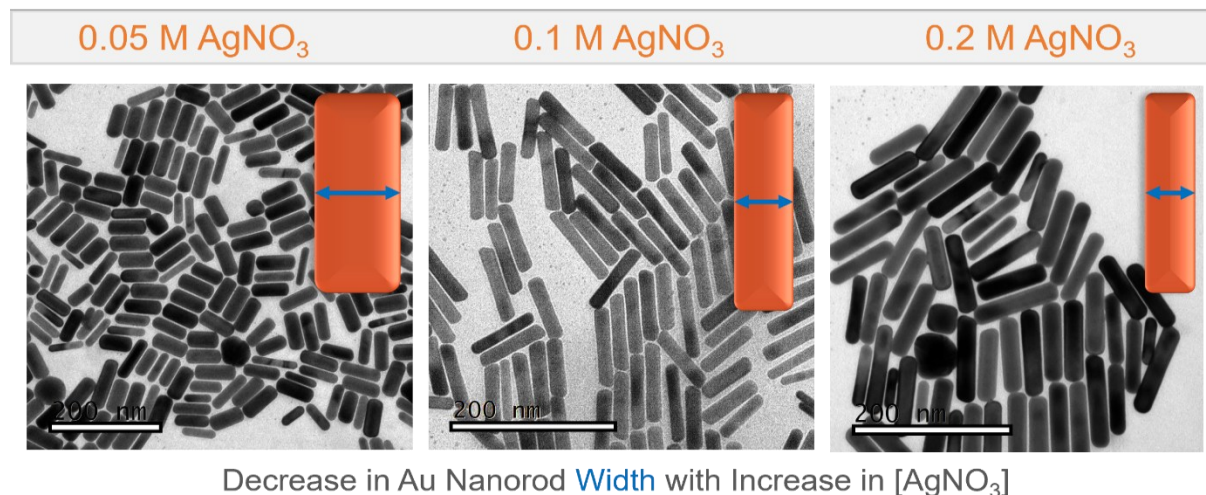


Figure 2-3: Depiction of the influence of $[\text{AgNO}_3]$ on the growth of anisotropic AuNPs. The scale bars correspond to 200 nm.

To explain the reduction in symmetry, three basic mechanisms have been proposed. The first mechanism is based on a micelle soft template, where the interaction of silver with the capping agent CTAB serves to transform the spherical form of CTAB micelles into a non-spherical form.^[32] The second mechanism involves silver under-potential deposition (UPD). On the high-energy facets of isotropic AuNPs, Ag^{I} is reduced to Ag^0 . Anisotropic growth is promoted by depositing a monolayer of Ag^0 on the longitudinal faces.^[28,33] Finally, the third mechanism proposes that the selective binding of CTA- AgBr_2 prevents the addition of further Au^{I} monomer, resulting in directional growth.^[34] The presence of surfactants are thus suggested to have a strong influence on the growth of AuNPs, which will be discussed in more detail in the following section.

2.1.3 Surface Functionalization

Due to the high surface-to-volume ratio, nanoparticles have a natural tendency to aggregate, making surfactants essential. Prior to examining the influence of stabilizing and/or surface functionalizing agents on gold surfaces, it is useful to first consider the stability of AuNPs in general.

The stability of colloidal solutions containing nanoparticles such as AuNPs can be described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. The theory is based on the interplay between van der Waals forces of attraction and electrostatic Coulomb repulsion depending on the charge of the AuNP surface.^[35,36] The total interaction potential between two AuNPs (V_T) can be calculated as the sum of the van der Waals attraction potential (V_{att}) and electrostatic repulsion potential (V_{rep})^[35,37,38]:

$$V_T = V_{rep} + V_{att} \quad (2.5)$$

V_{rep} , which is depending on the particle size and the double layer thickness, can be defined for two colloidal particles with radii R_1 and R_2 in two different Equation 2.6 and 2.7.^[38]

$$\text{for } \kappa R > 5 \quad V_{rep} = 4\pi\epsilon\psi_0^2 \frac{R_1 R_2}{R_1 + R_2} \ln(1 + e^{(-\kappa x)}) \quad (2.6)$$

$$\text{for } \kappa R < 5 \quad V_{rep} = 4\pi\epsilon R_1 R_2 Y_1 Y_2 \left(\frac{k_B T}{e}\right)^2 \frac{e^{(-\kappa x)}}{x + R_1 + R_2} \quad (2.7)$$

$$\kappa = \left[\frac{1000 e^2 N_A (2I)}{\epsilon k_B T} \right]^{\frac{1}{2}} \quad (2.8)$$

$$Y_i = \frac{8 \tanh(e\psi_0/(4k_B T))}{1 + \left[1 - \frac{2\kappa R_i +}{(\kappa R_i + 1)^2} \tanh^2\left(\frac{e\psi_0}{4k_B T}\right) \right]^{\frac{1}{2}}} \quad (2.9)$$

with

κ	= inverse Debye length
ψ_0	= potential at the particle surface (predictable from ζ potential measurements)
ϵ	= medium permittivity
e	= electronic charge
T	= temperature
I	= ionic strength of solution
k_B	= Boltzmann's constant
N_A	= Avogadro number
x	= particle surface closest approach

For the description of the forces of attraction, the Hamaker constant A_H is of crucial importance and is used for the estimation of two separated particles in a continuous medium.^[39] Under the assumption of spherical particle shape and constant ionic strength as well as surface potential, V_{att} can be defined as^[35,37,38]:

$$V_{att} = -\frac{A_H}{6} \left[\frac{2R_1R_2}{d^2 - (R_1 + R_2)^2} + \frac{2R_1R_2}{d^2 - (R_1 - R_2)^2} - \ln \frac{d^2 - (R_1 + R_2)^2}{d^2 - (R_1 - R_2)^2} \right] \quad (2.10)$$

and
$$A_H = \pi^2 C \rho_1 \rho_2 \quad (2.11)$$

with

C	= coefficient of particle-particle interaction
ρ_i	= number of atoms per volume unit
$A_H \text{ for Au}$	= $(1-4) \cdot 10^{-19} \text{ J}$ ^[40]

The removal of the solvent eliminates electrostatic double-layer repulsion, allowing van der Waals attractions to dominate at short interparticle distances. In solution, as in the Turkevich method, there are adsorbed charges on the gold surface that stabilize the colloidal solution by electrostatic repulsion. However, in certain situations, such as solution removal and solution quality reduction, cooling or centrifugation steps, the interaction between AuNPs becomes attractive rather than repulsive, leading to the risk of aggregation.^[23]

In order to prevent aggregation or to shield the van der Waals interactions between the cores of AuNPs, steric stabilization is a suitable method. Short organic ligands, as in the case of the Brust-Schiffrin method, or functional polymer ligands with longer chains provide shielding through elastic and osmotic repulsion between the chains. In this context, the protection ability of the formed layer on the gold surface is dependent on its grafting density as well as its solubility and other factors such as temperature and polymer concentration. An increase in density results in an increase in osmotic repulsion. Higher solubility leads to less aggregation and therefore higher stabilization.^[41]

The Flory-Krigbaum approach is suitable for expressing the free energy of the interpenetration process of two attached chains. It includes the Flory-Huggins interaction parameter χ , which describes the interactions between the polymer chains and the

solvent, as well as between the polymer chains themselves. A low value of the interaction parameter ($\chi < 0.5$) indicates good solubility of the polymer in the solvent, while a high value ($\chi > 0.5$) indicates poor solubility. The complete definition is shown in Equation 2.12^[42]:

$$\Delta G = 2k_B T \frac{v_s^2}{v_i} \left(\frac{1}{2} - \chi \right) \int_V \varphi_1 \varphi_2 dV \quad (2.12)$$

with

v_i	= solvent molecular volume
v_s	= Kuhn segment volume
φ_1, φ_2	= segment density distribution function

Steric stabilization and surface functionalization with functional polymers are pursued for various reasons and can be achieved in different ways. In the field of biology, for instance, the use of AuNPs may be limited by their toxicity and low interaction with biomolecules.^[43] In addition, the functionalization with polymers can enhance temperature- and pressure resistance as well as mechanical strength.^[44] Therefore, in some cases it is necessary to replace the CTAB ligand with a non-toxic, biocompatible or more robust polymer alternative.

The replacement of initial ligands or functionalization of AuNPs typically involves, besides approaches such as single-step functionalization of surfaces^[45], layer-by-layer^[46], silica coating^[47], grafting-to^[48] or grafting-from^[49], a ligand exchange process. This process is a post-synthesis modification step that involves repeated precipitation (by centrifugation) and re-dispersion steps. The cationic surfactant CTAB, which is assumed to form a bilayer structure of about 32 Å on the gold surface^[50] (besides of the assumption of micelles formation^[51]), is replaced by a polymer ligand with a functional group such as thiols, amines, carboxylic or phosphonic acid groups (see Figure 2-4).⁷⁵

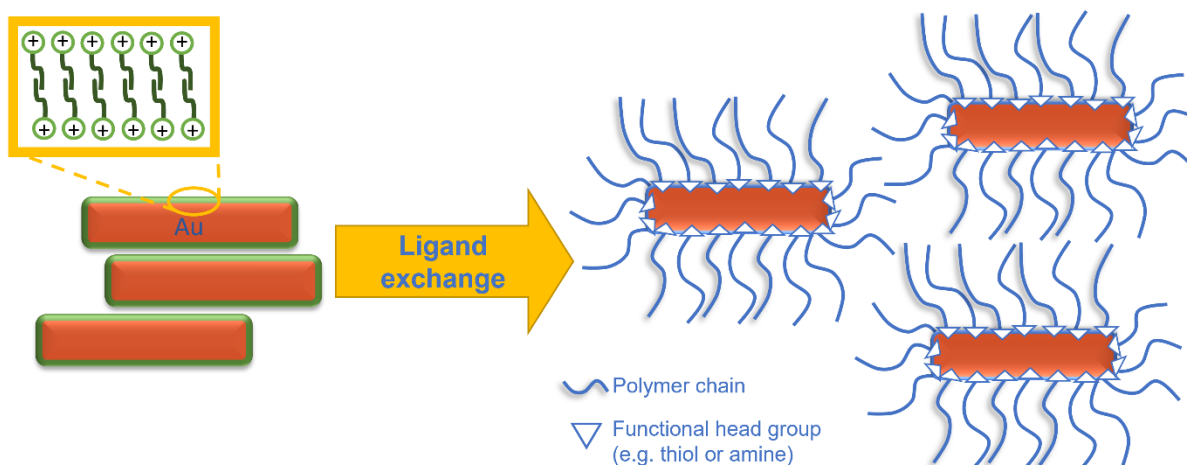


Figure 2-4: Schematic representation of a ligand exchange process in which the amphiphilic molecule CTAB is exchanged with a functionalized polymer.

After ligand exchange, the arrangement of the newly attached ligand may change. Studies have demonstrated that the density of grafted thiolated polymers, such as thiol-functionalized polystyrene (PS-SH) in tetrahydrofuran (THF), is higher at the ends of anisotropic nanocrystals compared to the sides. This contrasts with the behavior of the surfactant CTAB, which exhibits a more uniform distribution along the nanocrystal surface.^[52] In addition, the exchange process typically involves a transition of the medium from an aqueous to an organic phase, which is more suitable for a broad variety of polymers. Based on the high affinity for gold surfaces^[53], SH-terminated polymers and thiolated small molecules are commonly used as polymer ligands in the ligand exchange procedure.^[54] It is assumed that stable adhesion of the PS-SH ligand is highly dependent on this criterion. On the other hand, it is also discussed that the reversibility of surface coordination also plays a role that requires a rather moderate binding. Here, the use of multidentate amines such as pentaethylenhexamine (see Figure 2-5) allows the polymer chains to rearrange more flexibly, which favors the attachment of additional ones. This results in denser brushes around the gold nanocrystals.^[55]

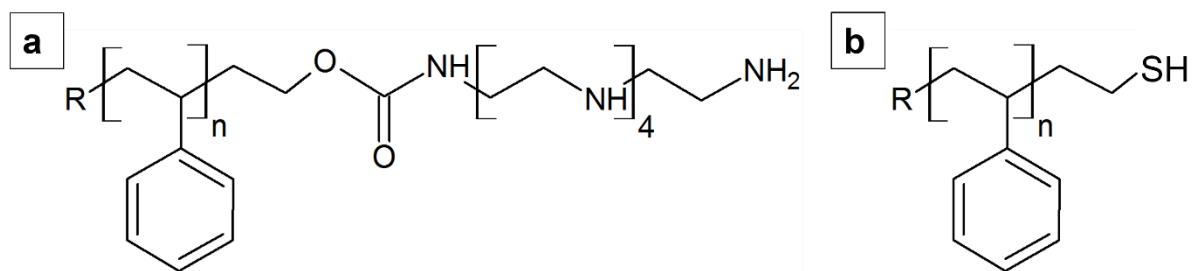


Figure 2-5: Structural formula of a the multidentate amine-terminated PS and, in contrast, b the thiol-terminated PS.

Ligand exchange processes also have disadvantages that should not be neglected. The main one is the critical removal of CTAB during the centrifugation step which can lead to aggregation of AuNP and the thermodynamically more stable spherical form. In addition, especially with cylindrical AuNPs, there is the challenge that CTAB may only be partially exchanged as it binds specifically to the longitudinal surfaces of the AuNPs and tends to be exchanged at the tips.^[56] Studies are therefore being conducted to overcome these difficulties by functionalizing the AuNPs in direct "one-step" or "one-pot" methods with polymers^[57] or by exploiting this very effect to form the AuNPs in a specific arrangement or in self-assembled arrays to achieve specific optical properties.^[52]

2.1.4 Optical Characteristics

Nanoparticle solutions exhibit intense colors due to their absorption and scattering properties in the visible range when interacting with the electromagnetic field.^[14] The interaction possibilities are determined by nanoparticle size as well as the presence of free electrons and are diverse. First, if the dimensions of the nanoparticle are similar to the mean free path of free electrons, scattering occurs. Second, interband transitions occur when electrons move from one occupied bulk band to another empty one. Furthermore, intraband transitions are characterized by a collective oscillation of electrons in the conduction band. This coherent oscillation of the charge clouds of the conduction electrons, known as plasmons, leads to a displacement of the electrons from the nucleus and thus, to a dipole moment. The oscillating charge distributions of the surface

are characterized by a specific resonance energy, the so-called localized surface plasmon resonance (LSPR).^[23,58]

When exposed to a specific frequency, nanoparticles exhibit scattering and/or absorption behavior. This applies in particular to noble metals such as gold or silver, which exhibit strongly pronounced plasmon resonances in the ultraviolet range compared to transition metals. In a diluted solution with metal nanoparticles, the transmitted light intensity can be summarized as the sum of the scattering and absorption modes^[23]:

$$I = I_0 e^{[N \cdot L \cdot (\sigma_{abs} + \sigma_{sca})]} \quad (2.13)$$

with

I	= transmitted light
I_0	= incoming light
N	= number of nanoparticles per unit volume
L	= optical path length in the sample
$\sigma_{sca}, \sigma_{abs}$	= scattering and absorption cross-section

Changes in the shape, size and dielectric function of the medium as well as in the arrangement or distance of the nanoparticles from each other influence the LSPR as well as the position of the surface plasmon absorption maximum λ_{max} . Metal spheres at the nanoscale exhibit a single plasmon mode that lies in the high ultraviolet (UV) region of the UV spectrum, typically in the range of 515 nm to 520 nm (for silver nanoparticles at ~ 400 nm).^[23,59] The relationship between the LSPR band and spherical nanoparticle size can be described by the Mie theory.^[60] One of the most common simplifications of this theory is the quasi-static approximation, which assumes the wavelength of light being much larger than the size of the nanoparticle ($d \ll \lambda$) and a constant field throughout the particle, giving the expressions for the extinction cross-section σ_{ext} and σ_{sca} as follows^[23,61]:

$$\sigma_{ext} = \frac{18\pi\epsilon_{med}^{\frac{3}{2}}V}{\lambda} \cdot \frac{\omega\epsilon_2(\omega, R)}{(\epsilon_1(\omega, R) + 2\epsilon_{med})^2 + \epsilon_2^2(\omega, R)} \quad (2.14)$$

$$\sigma_{sca} = \frac{32\pi^4\epsilon_{med}^2V^2}{\lambda} \cdot \frac{\omega\epsilon_2(\omega, R)}{(\epsilon_1(\omega, R) + 2\epsilon_{med})^2 + \epsilon_2^2(\omega, R)} \quad (2.15)$$

with

R	= radius of sphere
V	= volume of sphere
$\varepsilon_1, \varepsilon_2$	= real and complex parts of dielectric function for metal
ε_{med}	= medium dielectric constant
ω	= angular frequency

Absorption σ_{abs} predominates for smaller AuNS, while scattering dominates for AuNS above 80 nm.^[62] Here, σ_{abs} can be described as^[61]:

$$\sigma_{abs} = \sigma_{ext} - \sigma_{sca} \quad (2.16)$$

For nanorods, two characteristic resonance modes, transverse and longitudinal, are observed due to oscillations along and perpendicular to the nanoparticle longitudinal axis. The Mie theory is not applicable for anisotropic nanocrystals and instead, it can be extended by the theory of Richard Gans.^[63] It describes elongated particles and defines their σ_{abs} as following^[61]:

$$\sigma_{abs} = \frac{\omega \varepsilon_{med}^2 V}{3c} \cdot \sum_j \frac{\varepsilon_2 (1/P_j^2)}{[\varepsilon_1 + [(1 - P_j)/P_j] \varepsilon_{med}]^2 + \varepsilon_2^2} \quad (2.17)$$

with

	consideration of three dimensions of the nanoparticle by $\sum_j$
P_j	= depolarization factors for each nanoparticle axis

Equation 2.17 illustrates the effect of the increase in $[(1 - P_j)/P_j]$ with increasing aspect ratio on the red-shift of the LSPR peak and the impact of the surrounding medium's dielectric constant. Thus, the optical characteristics of AuNPs are also influenced by the dispersion medium, *i.e.* the solvent and furthermore, on coating layers on the surface of nanocrystals.^[64] Silica coatings are the most commonly used inorganic coatings for nanoparticles due to their controllable porosity, chemical inertness, optical transparency and high stability.^[65] The thickness of the silica coating affects the longitudinal plasmon band of anisotropic AuNPs, causing a shift into the near-infrared

range. Additionally, the interparticle distance determines the phenomenon known as plasmon coupling.^[66] Plasmon coupling occurs when two or more nanoparticles are close enough for their plasmon resonances to interact with each other by means of near-field interactions, leading to various effects depending on their arrangement and proximity. These effects include amplifying the electric fields between the nanoparticles and altering their absorption and scattering properties.^[67] The strength of plasmonic coupling increases with the increase in number of AuNPs as well as aspect ratio and the decrease in interparticle distance. This is particularly relevant for cylindrical AuNPs, where edge-to-edge and tip-to-tip distances are considered.^[68] These distances can be set with organic, in particular polymer coatings. Here, the length of the polymer chains and the grafting density are crucial factors. For instance, reducing the molecular weight of the polymer decreases the distance between nanorods, resulting in an increased electric field.^[69] Furthermore, it was shown that 1-D nanochains can be produced through site-specific attachment and polymerization of polymer ligands at the tips of AuNRs. The distance between the tips can be varied by changing the concentration of water and thiolated PS in the presence of an amphiphilic block copolymer and thus, the influence on the longitudinal LSPR coupling can be adjusted.^[70] The interplay between the adjustability of the optical properties and the various polymer coating possibilities of AuNPs enables the application of gold nanocomposites in exciting future-oriented areas.

2.1.5 Applications

AuNP-based plasmonic nanomaterials are used in a wide range of applications including catalysis^[71], photocatalysis^[72], optoelectronics^[73], surface-enhanced spectroscopy^[74] and sensing technology^[75]. When combined with polymers, these materials enable innovative applications. In the following, recent studies on gold nanocomposites based on AuNPs combined with polymer materials, focusing on electrocatalysis, plasmonic nanolasers and sensing are highlighted.

Addressing the growing demand for high-performance, sustainable energy storage and conversion systems, the development of efficient electrocatalytic solutions is crucial. AuNPs contribute significantly to this due to their LSPR-driven electrocatalytic activity and high surface-to-volume ratio, providing many active sites for catalytic reactions.

Xianxian *et al.* demonstrated that varying the molecular weight of SH-terminated PS and application of plasma etching enhances the electrocatalytic activity of 2-D gold nanocomposites. Reducing interparticle distance by decreasing molecular weight from $M_n = 22 \text{ kg} \cdot \text{mol}^{-1}$ to $M_n = 2 \text{ kg} \cdot \text{mol}^{-1}$, as shown in glucose oxidation studies, revealed that LSPR coupling significantly improves catalytic properties.^[76]

In addition, the use of AuNPs as plasmonic nanolasers is being investigated. Spasers, analogous to lasers, generate coherent light through the amplification of surface plasmons, enabling the confinement of electromagnetic energy at scales much smaller than the wavelength of light. The concept employs nanostructured materials such as AuNPs as resonators to amplify and sustain surface plasmons. AuNPs serve as core materials surrounded by an active medium shell with an emission band that overlaps with the LSPR band, forming yolk-shell particles. This configuration results in an efficient light emitter with potential use in high-resolution optical imaging and sensing.^[77] In most cases, the shell material is a silica shell which, however, is limited by low pore capacity. To address this, yolk-shell particles incorporating AuNRs and a polystyrenesulfonate (PSS) layer have been developed. Their synthesis involves a template-based process where a $\sim 35 \text{ nm}$ mesoporous silica layer is formed and later removed *via* hydrolysis after PSS application. These particles are highly stable and efficiently absorb organic dyes making them promising for biomedical applications.^[78]

The use of AuNPs in sensor technology is widespread in the areas of refractive index change detection^[79], fluorescence-based^[80] as well as colorimetric sensor technology^[81]. A promising area for future sensor applications is nanoscale mechanical stress detection, driven by the miniaturization of mechanical and electrical components. Here, key requirements include nanoscale dimensions and reusability under repeated stress. Thus, nano-capsules were developed *via* emulsion templating with spherical AuNPs functionalized with SH-terminated PS in the presence of a plasticizer and embedded in a polydimethylsiloxane (PDMS) matrix. These composites exhibited reversible plasmonic responses to mechanical loading with uniaxial tensile stress causing a plasmon band shift to lower energy due to increased interparticle distance, which regenerated upon stress removal.^[82] This application example shows how (nano)particles in combination with a (semi-) organic matrix such as PDMS can expand their properties and open up new areas of research and application.

2.2 Micrometer-Scale Silica-Based Composites

2.2.1 Overview

Microcomposites, comprising micrometer-sized inorganic particles dispersed in polymer matrices like epoxy, polybutylene terephthalate, or silicone, are vital in electronic packaging, facilitating advanced device designs and enhanced functionalities.^[83]

As the automotive industry continues its transition to electric vehicles and advances in automated driving –accompanied by increasing miniaturization– the importance of robust and reliable material combinations for electronic devices is growing. Modern electric or hybrid vehicles are equipped with approximately 3 km of wiring and up to 200 electrical connections, a significant increase from the 0.18 km of wiring and a few electrical connections that were present in vehicles from the 1960s.^[84] The design of printed circuit board assemblies (PCBAs) in electronic control units (ECUs) relies on protection strategies, including advanced simulation methods and the selection of appropriate composite materials. Thus, composites are used to ensure the reliability and functionality of ECUs and can be used as conformal coatings, potting, underfill or sealing materials.^[85] Moisture resistance is crucial for material performance, necessitating careful selection and analysis of potential failure modes (see Figure 2-6).

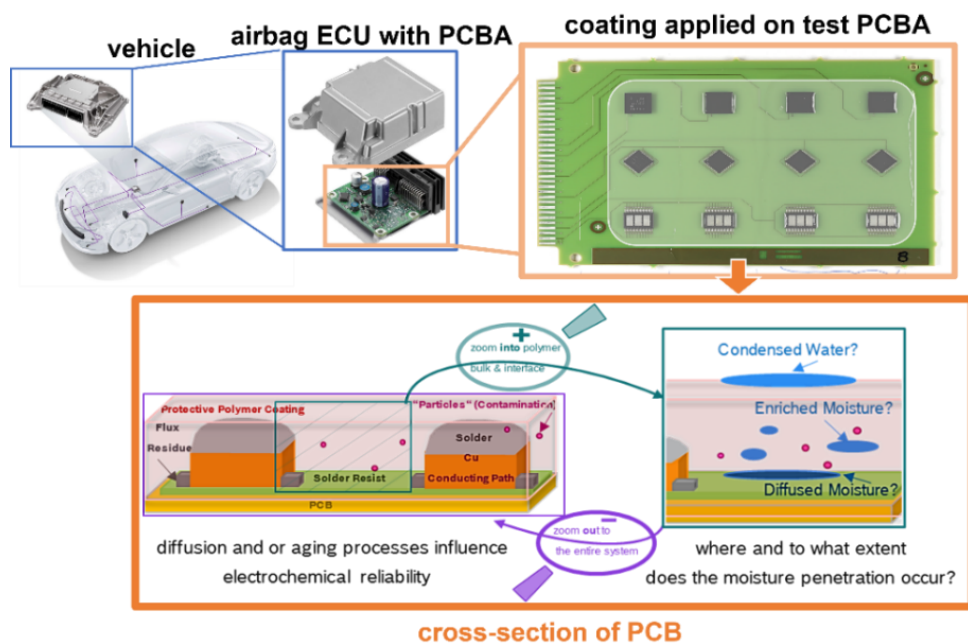


Figure 2-6: Illustration of a PCBA, including housing integrated into an automotive ECU in a vehicle.^[86] Assessing humidity robustness and electrochemical reliability of e.g. coating systems is crucial in ECU development.

Generally, the combination of inorganic particles in the micrometer range and their organic surface modifiers fulfills the specific requirements of automotive electronics, particularly in terms of enhanced humidity robustness, mechanical strength, thermal conductivity and electrical performance. The inorganic core of microcomposites typically consists of inorganic particles such as silica, alumina, titanium dioxide, calcium carbonate, boron nitride, carbon and graphene. The size range of these particles extends from a few to several hundred micrometers.^[87] Silica in particular offers important properties such as increased mechanical strength and electrical insulation, thermal and chemical stability and imparts thixotropic properties.^[88]

In many cases, the surfaces of initially hydrophilic silica particles undergo a variety of post-modification steps. First, fumed silica is often modified with chlorinated silanes or siloxanes to render its hydrophilic surfaces hydrophobic, enhancing moisture resistance. Surface modification can also involve salinization with monofunctional or multifunctional low molecular weight silanes. Silanization with at least bifunctional silanes offers the decisive advantage that a covalent bond is formed between the hydroxyl groups on the silica surface and one part of the functional group of the silane, while the second functional group of the silane bonds to the polymer matrix.^[89] Finally, polymer ligands can be bound to the surface either by adsorption, ligand binding through functional groups or *in-situ* polymerization. This type of surface modification improves compatibility with organic systems and enhances mechanical, thermal and interfacial adhesion properties.^[90]

The incorporation of functionalized silica into the silicone elastomer PDMS enables the initial properties of PDMS, such as its resilience to various environmental factors including temperature, humidity and chemicals to be further refined and thus, improving the performance and reliability of PCBAs. Additionally, the selection of PDMS can be explained by its insulating, flexible, transparent and non-flammable properties which further contribute to its suitability for PCBA applications.^[88,91] PDMS can be crosslinked during the addition cure process without the formation of byproducts such as water or alcohol. Here, a vinyl-terminated siloxane as a prepolymer is crosslinked with a methyl hydroxy-silane-based polymer in the presence of a rhodium- or platinum-based organocatalyst (see Figure 2-7).^[92] In this case, the Pt catalyst facilitates the hydrosilylation reaction, which can be accompanied by a photoinitiator in an UV curing process.^[93]

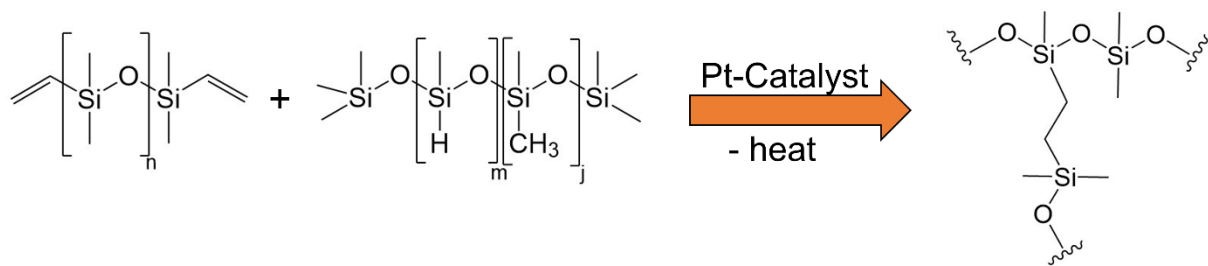


Figure 2-7: Pt-catalyzed addition crosslinking reaction of methyl hydrogen siloxanes and vinyl-terminated siloxane as prepolymer for the formation of PDMS.

Although a variety of factors are considered when selecting protective materials for PCBAs, potential failure modes remain unless the influence and interactions of each material component are fully understood. In addition to mechanical and thermal failure modes such as crack formation, delamination and varying material coefficients of thermal expansion, electrochemical failure modes must also be considered.^[94] Electrochemical failures in its various forms such as lack of humidity and corrosion robustness, (ionic) contamination and electrochemical migration (ECM) have significant influence on the insulation properties.^[95]

In the following sections, the mechanisms of surface functionalization of silica particles with respect to hydrophobic properties, the humidity dependent insulation properties and the applications of microcomposites embedded in a PDMS base material are therefore described in more detail.

2.2.2 Surface Functionalization

Synthetic silica is predominantly produced through two primary methods: The wet chemical process and the pyrogenic process. A widely employed technique within the pyrogenic process is flame hydrolysis, wherein silicon tetrachloride (SiCl_4) undergoes hydrolysis in a hydrogen-oxygen flame. During this process, SiCl_4 decomposes and reacts with hydrogen and oxygen, leading to the formation of fumed silica (SiO_2) and hydrogen chloride (HCl)^[96]:



The resulting ~10 nm primary particles often aggregate and agglomerate to larger effective particle sizes of 100 nm and 5 μm , respectively.^[97] It has a BET surface area typically ranging from 50 to 400 m^2/g and a high surface energy.^[98] Moreover, it is naturally hydrophilic due to the presence of hydroxyl groups (typically 2 SiOH/nm^2) on its surface, which allows it to react with water.^[96] However, if a lower affinity to moisture or other polar components is desired, they are typically subjected to a silylation process. This is commonly accomplished through using surface modifiers such as hexamethyldisilazane and chlorinated silanes (see Figure 2-8 a). This process can be modified to create varying distributions of methyl groups on the silica surface and can be achieved by altering and considering the concentration of the surface modifier, reaction and silica surface conditions.^[99]

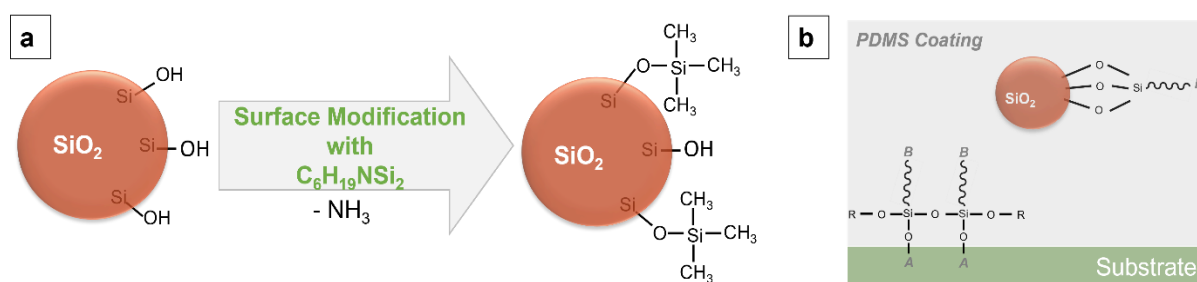


Figure 2-8: Schematic representations of a surface modification of silica with hexamethyldisilazane and b attachment of short-chain silanes to substrate surfaces (A), silica and to a polymer matrix (B), which can represent a PDMS-based coating system.

In addition to the surface modification achieved through the incorporation of hydrophobic groups, low molecular weight or polymer functionalization agents are used to (further) modify the surface of fumed silica. Here, their primary functions are to improve the adhesion of the PDMS matrix to silica and to substrate materials whose surface may consist of e.g. metal hydroxide (see Figure 2-8 b).^[100] The low molecular weight silane agents usually used include (3-glycidoxypropyl)trimethoxysilane (GPS)^[101], (3-Methacryloxypropyl)trimethoxysilane (MPS)^[102], (3-aminopropyl)triethoxysilane (APTES)^[103], (3-mercaptopropyl)trimethoxysilane (MPTMS)^[104] and vinyltriethoxysilane (VTES)^[105]. The structure consists essentially of a hydrolysable functional group such as a methoxy or ethoxy group which can be attached to the silica or a

substrate and a reactive organic group such as an epoxy, vinyl or methacrylic organofunctional group which can be attached to a polymer or a substrate. The reaction types of the reactive groups can be different. For instance, methacrylate-based silanes can be incorporated into unsaturated polymers by radical copolymerization. Epoxy-based silanes, such as the most widely used and commercially available silane GPS, react in an addition reaction with functional groups such as hydroxyl, carboxyl or amino groups of silica or a polymer under ring opening.

Besides of low-molecular silanes, silane- or maleic anhydride-modified polyolefins or block copolymers can serve as polymer ligands, promoting *e.g.* adhesion or crosslinking properties in polymer materials. This relatively new class of adhesives offers the advantage of higher interfacial adhesion and thermal stability.^[89,106] Furthermore, it could be shown that a significant improvement of the mechanical properties of glass fiber reinforced PE can be achieved by the addition of maleic anhydride-grafted Polyethylene (PE) in comparison to short chain silane agents like MPS.^[107] In addition, polymer functionalizing agents provide pH-responsive crosslinking behavior. Diblock copolymers based on poly(*n*-butyl acrylate) and poly(acrylic acid) (PAA) adsorbed onto acrylic latex particles show that ionomeric crosslinking occurs at high pH, resulting in an increase in tack and creep resistance. In the case of low pH, the PAA block is present in a collapsed state on the particle surface.^[108] Finally, due to their higher molecular weight, polymer ligands are less prone to migration, bleeding or weight loss.^[90,109]

2.2.3 Humidity Robustness and Insulation Characteristics

The investigation of the effect of humidity on the electrical insulation properties of silica composites, embedded into a PDMS matrix, is of particular importance when considering the electrochemical reliability of PCBAs. In general, the reduction in insulation properties of PCBAs is facilitated by the presence of ionic contamination (typically a result of the soldering process), condensation, exposure to certain humidity levels and the formation of a conductive path such as a thin electrolyte layer.^[110] If an organic layer in the form of an *e.g.* adhesive, encapsulant or conformal coating (see Chapter 2.2.4) based on *e.g.* silicon elastomers filled with micrometer-scale silica composites is additionally applied and cured onto a PCB, the humidity robustness as well as insulation properties of this layer needs to be considered separately.

Generally, cured PDMS has a high specific resistivity of $4 \cdot 10^{13} \Omega \cdot \text{m}$ and a moderate dielectric constant between 2.3 and 2.8, indicating that it has both the ability to store electrical energy and the quality of an effective insulator. The presence of methyl groups on the cross-linked PDMS surface results in a hydrophobic character, as indicated by a water contact angle (WCA) between 95 and 120 ^[111–113]. Here, the WCA value varies and is highly dependent on the historical factors of the specimen such as pretreatment and sample preparation. Despite its hydrophobic nature, the maximum concentration of water molecules in unfilled and cured PDMS reaches about 0.03 M and the diffusion coefficient is approx. $2 \cdot 10^{-9} \text{ m}^2/\text{s}$, which is in the range of the self-diffusion coefficient of water ^[114]. Moreover, when exposed to long periods of moisture or high levels of humidity, PDMS can undergo a slight swelling effect. However, the swelling is significantly less than other solvents, such as those based on hydrocarbons ^[111,112].

The relatively low water affinity and high electrical insulating properties of PDMS can be altered by the use of silica composites. As previously stated, the surface of fumed silica is inherently hydrophilic. Modifications to the surface, such as silylation, can increase the number of hydrophobic groups, thereby reducing the affinity of silica for water. To define the water affinity of functionalizing agents located on the surface of fumed silica is more challenging. In the field of polymer functionalizing agents, which are still the subject of research, it is primarily the functional groups that determine the interaction with the polymer matrix, the silica surface and the substrates as well as the interaction with moisture and water. For example, the increase in hydrophobicity could be demonstrated by the use of bio-based and UV-curable methacrylated monomers on cardanol basis in protective coatings in comparison to purely diacrylate-based base material ^[115]. In conventional formulations, the short chain silanes GPS with $236.3 \text{ g} \cdot \text{mol}^{-1}$ and MPS with $248.4 \text{ g} \cdot \text{mol}^{-1}$ are typically used in Pt-curing or radically curing polymer formulations (see Figure 2-9) ^{[116],[117]}.

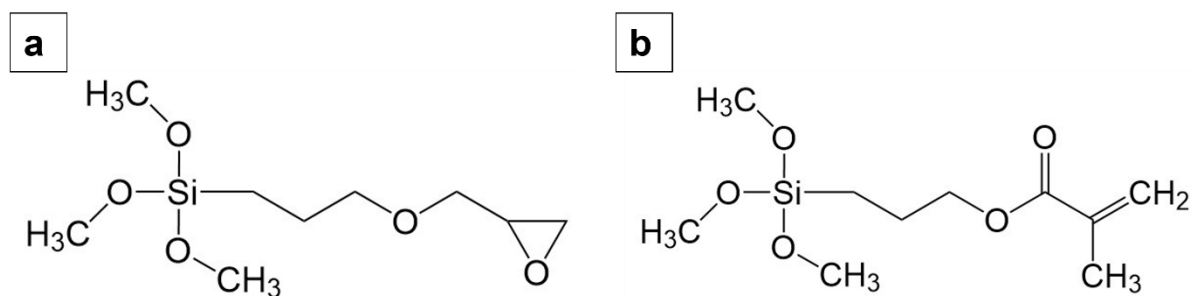
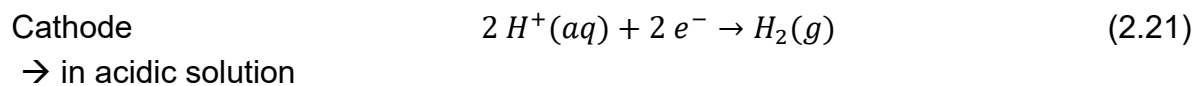
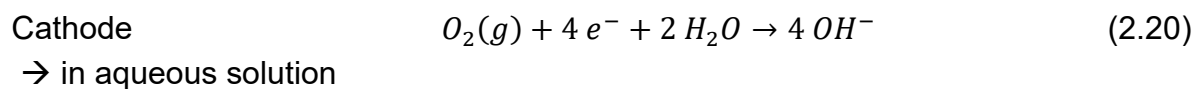
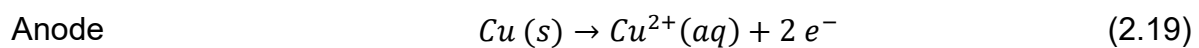


Figure 2-9: Chemical structure formula of a GPS and b MPS.

The utilization of GPS as *e.g.* adhesion promoter is well described in the literature, with particular attention paid to its behavior in various media including aqueous media. Although the complete reaction mechanism of short chain silanes has not been fully understood, it can be stated that partial reactions (simultaneously) occur including (partial) hydrolysis, condensation, formation of hydrogen bonds, and condensation with the filler or substrate as well as reaction with the polymer network.^[89] In aqueous solution, the methoxy groups ($-\text{OCH}_3$) gradually hydrolyze to silanol groups ($-\text{Si}-\text{OH}$) alongside the formation of alcohol as a by-product. The required water can originate from the atmosphere, from adsorbed water on the surface of a substrate or filler, or from controlled exposure to humidity levels near the dew point in *e.g.* climate chambers. Here, the dew point is the temperature at which air becomes fully saturated with water vapor. If the air temperature drops to or below this point, condensation occurs. Moreover, the formed silanol groups can also condense to $\text{Si}-\text{O}-\text{Si}$ bonds under release of water or alcohol and polymerize to a sol-gel network.^[118] Overall the rate of reaction for both hydrolysis and condensation of the alkoxy groups is primarily influenced by the pH and temperature of the surrounding environment. It was demonstrated that hydrolysis occurs at a faster rate than condensation at ambient temperature and in an acidic environment. Furthermore, ring opening of the epoxy ring from GPS occurs at a slower rate than hydrolysis. As the temperature increases from 26 °C to 70 °C, all three reactions proceed at a faster rate.^[119] By using NMR spectroscopy, a rapid hydrolysis and condensation reaction in strongly alkaline aqueous solutions and the formation of silica cages could be demonstrated. The ring opening and thus the formation of diols, dioxanes, methyl ether end groups as well as the formation of polyether occurs slowly under these conditions.^[120] On the one side, the formation of these reaction products may

result in improved integration of silica composites into a polymer matrix and enhanced adhesion to substrate surfaces. On the other side, an increase in material's hygroscopicity represents a potential cause for the enhanced affinity of these species for water uptake.

In electronic applications, the humidity robustness of the organic layer is not the only decisive factor for maintaining the insulating properties. In the case of corrosion, *i.e.* in general material degradation under the influence of the environment (temperature, salts, gases, etc.) and the medium involved in the degradation process, it is indeed necessary, especially for the electrochemical corrosion of metals, for oxygen and water to reach the metal surface and form corrosion products that can lift the organic layer. Here, the corrosion mechanism can be divided into two processes, the anodic reaction (oxidation) and the cathodic reaction (reduction). For metallic conductors such as copper, the two reactions proceed as follows^[121]:



However, as indicated above for PDMS, water diffusion in organic layers is significant with a corrosion rate comparable to that of uncoated surfaces. Therefore, oxygen and water diffusion cannot be considered the only cause of failure.^[122] In fact, the organic layer successfully acts as a diffusion barrier for ion permeability. This effect can either be enhanced by increasing the degree of cross-linking of the polymer matrix and the addition of pigments or reduced by possible damages to the organic layer.^[123] Potential damage that can degrade the insulating properties include crack and pore formation, delamination as well as chemical degradation by UV radiation or exposure to harsh environments.^[123] The consideration of diverse influencing factors in addition to selection of appropriate materials can extend the lifetime and application possibilities of silica composites embedded in polymer base materials.

2.2.4 Applications

Micrometer-sized silica composites in a silicone rubber matrix have found a wide range of applications in electronics, particularly in automotive and semiconductor industries. In general, the continuous reduction of spacing and weight of electronic components leads to an increasing relevance of (functionalized) silica in protective, adhesive and sealing materials. Conformal coatings and potting materials provide protection against mechanical stress, environmental influences, corrosion and (ionic) contamination. Adhesives and sealants are used for component fixation, sealing of housings and heat transfer. They also provide a barrier to moisture and contamination. Typically, the polymer base of these materials can be a silicone elastomer, acrylate, epoxy, parylene, polyamide, polyurethane or synthetic rubber. The primary differences between conformal coatings and potting materials are thickness, deposition method and addition of short chain silanes. In the case of potting material, the use of adhesion promoters such as GPS and MPS is common (see Figure 2-10). Conformal coatings, which conform to the topography of the surface on which they are deposited, are applied in thicknesses ranging from a few to several hundred micrometers. This is achieved by a variety of techniques, including spraying, dipping, or jetting. In contrast, potting materials, which are typically several millimeters thick, are poured and used to encapsulate the entire electronic device.^[89,92,124]

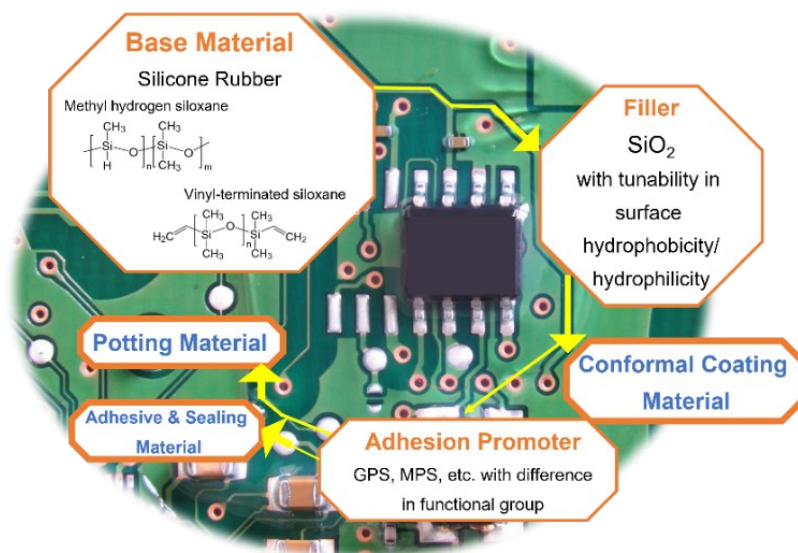


Figure 2-10: The basic building blocks of conformal coatings, adhesives, sealing and potting materials, applied to electronic components in the automotive electronics industry are depicted on PDMS as the base material.

In the field of electromobility, protective, adhesive and sealing materials based on silicone elastomers have become highly relevant. Silicone elastomers provide a reliable sealing against moisture, road salt or dust. In addition, their low compression set makes them attractive for fuel cell production. Accordingly, they have the potential to serve as an effective sealant for the fuel cell system, which is comprised of a stacked configuration of membrane electrode assemblies interconnected by bipolar plates.^[84] Moreover, the capacity of silicone elastomers to provide electrical and physical stability across a wide temperature range (from -45 °C to 200 °C) makes them a crucial component in the operation of power electronic devices that shall be able to switch and control high voltages and currents with high efficiency and minimal loss.^[125] Moreover, silicone elastomers are widely used in the semiconductor industry, especially for pressure sensors. The principle of pressure sensors is based on the conversion of mechanical pressure changes into electrical signals through piezoelectric, capacitive or resistive effects. Silicone elastomers are used to protect the sensor from chemicals, moisture and temperature fluctuations. Their high elasticity and low thermal expansion ensure the sensor's functional stability.^[126]

However, the growing reliability demands for hydrophobicity, adhesive strength and corrosion resistance require continuous optimization of these materials. For instance, modifying PDMS-silica coatings with methyl, phenyl and amino groups in the siloxane chains significantly improved corrosion protection of aluminum substrates compared to untreated ones.^[127] Additionally, PDMS-functionalized nanosilica has gained importance, offering higher hydrophobicity than octyl-silane-functionalized silica. This resulted in superhydrophobic coatings (water contact angle (WCA) > 150 °) with strong substrate adhesion and resistance to leakage current.^[128] Thus, in electronics the study of insulation resistance, alongside adhesion and chemical stability, is crucial for material performance.

2.3 Surface Insulation Resistance

2.3.1 Overview

Surface insulation resistance (SIR) measurement is essential for assessing the reliability of printed circuit boards (PCBs) and PCBAs. It is applied for the identification of insulation deficiencies caused by aging, contamination or moisture and prediction of long-term reliability across industries such as automotive, aerospace, telecommunications and consumer electronics.^[129]

To meet the growing challenges associated with the miniaturization of PCBs, research and development is also focused on analytical methods that can identify potential material weaknesses in advance. The SIR test is important in this context because it enables testing of various materials and PCB layouts and can assist in the identification of possible failure mechanisms. In order to assess the potential for failure mechanisms, methodologies and standards have been developed by various organizations, including the American Society for Testing and Materials (ASTM), the Institute for Printed Circuits (IPC) and the International Electrotechnical Commission (IEC).^[130] The IPC, a global trade association for the electronics industry, develops and publishes standards and specifications. The standards cover various aspects of processes in connection with the manufacture, assembly and testing of electronics. In the automotive electronics sector, for example, the IPC 9202 norm is used, which mainly focuses on the testing of materials and processes used in the printed circuit board assembly. This norm provides guidelines for testing and evaluating the solderability of electronic assemblies, solder residues and processes after soldering. It is also used to evaluate changes in the assembly process, such as changes in the solder material, solder mask or conformal coating supplier. Finally, the norm also incorporates characterization of the process when a new process needs to be developed or an existing one needs to be improved.^[131] The investigation *via* SIR measurements entails the exposure of various materials and test layouts, measurement modes to controlled environmental conditions, including elevated temperatures and humidity levels, to accelerate the identification of potential failure mechanisms.

2.3.2 Materials and Layout

In the context of a SIR measurement, a defined voltage is applied to a PCB surface and the subsequent current flow is monitored. It provides insight into the quality of the surface insulation, with a higher reading indicating better insulation. A PCB can be constructed in a variety of ways, with the simplest form being a single-layer and single-sided board and the more complex form being a double-sided board with components assembled on both sides or a multi-layer board. The main parts of a PCB include substrate material, conducting tracks, solder mask, solder paste and coating materials. A layout of a test PCB is shown in Figure 2-11.

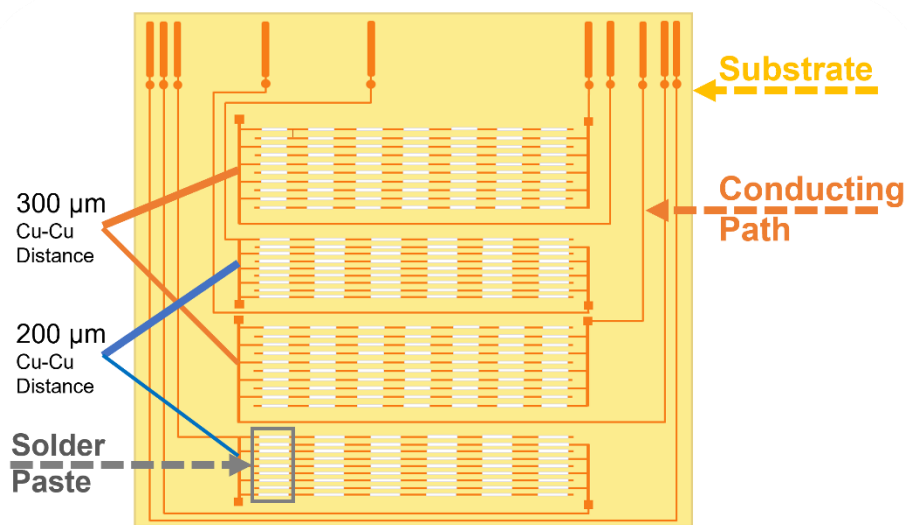
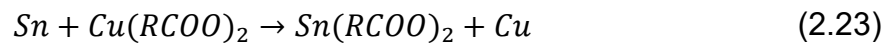
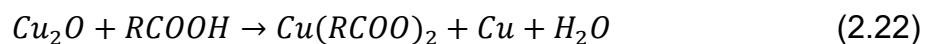


Figure 2-11: Drawing of a test layout with 200 μm and 300 μm Cu-Cu comb structures on which solder paste is applied (without solder mask).

The substrate material is typically a flame-retardant (FR)-4 type material reinforced with glass fibers, which exhibits high mechanical strength, thermal stability and electrical insulation properties.^[132] Depending on the requirements and applications such as power modules, the substrate can also be made of ceramic or polyimide.^[133] The conducting tracks are typically made of copper due to its high electrical conductivity, good adhesion to the substrate material and corrosion resistance. The distance between copper traces or conductors in SIR measurements may vary depending on the test setup, with values ranging from 0.1 mm or lower to 5-10 mm. To protect the Cu conducting tracks from oxidation, a layer of chemical Sn or Au or an organic solderability preservative (OSP) layer based on e.g. imidazole derivatives is applied. Without this

protection, the solderability would be adversely affected. Moreover, the attachment of surface-mount components (SMC) such as Small Outline Package (SOP), Quad Flat Package (QFP) or Ball Grid Array (BGA) to conducting pads on a FR-4 substrate is achieved through the use of Pb-free solder pastes, comprising pre-alloyed metallic powder and flux. The metallic component is typically composed of In, Zn, Sb, Sn, Ag, and Cu up to a content of 85-90 wt.%.^[121,132] Due to the restrictions on the utilization of Pb, solder pastes based on SnAgCu (SAC) are increasingly favored which forms a near-eutectic system with a melting point of approximately 217 °C (Cu content of 0.5-1.0 wt.% and Ag content of 2.0-4.0 wt.%).^[134] The flux in solder pastes primarily serves to remove surface oxidation and to enhance the wetting of the solder joints. It consists of more than 90 % solvents such as alcohol and up to 10 % of activators based on e.g. chloride and weak organic acids (WOAs) $R-COO^-$ such as carboxylic acid as well as additives and surfactants like polyglycols and organic amines.^[135] Weak organic acids are preferred due to their low ionic decomposition and reactivity and are used to remove metal oxides that lead to salt formation (see Equation 2.22 and 2.23)^[136]:



The soldering process may be executed in a variety of ways including reflow soldering, wave and selective wave soldering. Among these methods, reflow soldering, which utilizes a reflow oven with distinct temperature zones, is associated with the lowest levels of residue accumulation on PCBs.^[136] To circumvent the cleaning step subsequent to soldering, the utilization of "no-clean" fluxes is a practicable option. The resins or rosins contained in the flux are supposed to prevent re-oxidation and to cover the remaining activators after soldering.^[121] Finally, a solder mask comprising a polymer resin such as polyurethane or epoxy, solvents, pigments and additives, is applied to a PCB. The solder mask is used to insulate, protect and prevent unintentional solder bridges on PCBs by covering and defining the areas to which the solder is applied during the assembly process.^[132]

2.3.3 Measurement Modes

In general, two primary measurement modes are used for direct current (DC) SIR testing: Constant/long-term and dynamic/short-term measurements. The choice between these test modes depends on the specific requirements of the application. These include the expected lifespan of the product, the environmental conditions to which the product is exposed and the desired level of precision in evaluating the product's insulation performance.

The short-term SIR measurements are conducted in the dynamic mode over a relatively brief period, typically within a few hours and are therefore short-term. The objective of these tests is to assess the immediate performance or reliability of an insulating material or connection. The primary function of short-term SIR measurements is to facilitate the accelerated evaluation of a limited number of new materials in a screening-like test, prior to a more comprehensive examination over an extended period. Here, short-term SIR measurements enable the study of the influence of defects, hygroscopic components and contamination on the leakage current.^[121] The standardization of climatic conditioning tests represents a fundamental element of SIR measurements. However, for specific investigations, including the analysis of contamination and condensation effects, customized climatic conditioning tests are conducted. Consequently, temperature and humidity cycles are employed as a means of corrosion study of electronic components, with the temperature and humidity levels as well as the duration of active and passive resistance measurements, being varied.^[135] In contrast to dynamic SIR tests, constant tests involve the measurement of insulation resistance over an extended period, ranging from days to months or even years. The objective of these tests is to assess the long-term stability and reliability of insulating materials under realistic operational conditions. In this context, the effects of aging, humidity, temperature fluctuations and other environmental factors on the insulation resistance over time can be investigated.^[121]

2.3.4 Humidity Related Failures

SIR measurements allow the investigation of the resistance between two electrical conductors on a PCB surface and, in reverse, the measurement of the leakage current.^[129] A resistance value of $>10^8 \Omega$ indicates a low leakage current through the PCB

surface, representing good insulation. Modification of the dielectric material which separates two electrical conductors will reduce the SIR values and consequently increase the leakage current.^[121]

Exposure of a PCB to a certain voltage, high humidity and elevated temperatures, such as 85 °C and 85 % RH, 100 V for 168 h or 65 °C and 88 % RH, 100 V for 500 h according to IPC standards (e.g. IPC-TM-650), can result in the formation of a conductive layer of water, the thickness of which can vary from small molecular layers to the micrometer range.^[121] The leakage current can flow either through the adsorbed water layer, the substrate material or the PCB surface. The impact of the latter two leakage pathways is considered comparatively minor compared to the adsorbed water layer, unless the substrate material itself is capable of absorbing moisture that can lead to conductive anodic filament (CAF) formation. In addition, unfavorable PCB types and layouts with decreasing spacing between electrical conductors, the presence of flux residues and hygroscopic material components can result in an increase in leakage current that paves the way for ECM.^[121] ECM refers to the movement of positive ions from the anode to the cathode when an electric field is applied and their deposition in the form of metallic tree structures known as dendrites. The ongoing miniaturization and increasing complexity of PCBs result in a gradual reduction of the distances between conductors, leading to an increase in the electric field strength at equal voltages and an acceleration of the ECM process. The process of ECM failure was observed to occur at a slower rate for conductor distances of 640 µm in comparison to shorter distances of 160 µm.^[137] Although no-clean flux do not require further cleaning after soldering, residual ionic contamination can remain, which is a significant contributing factor to failure.^[135] Ionic contaminants are typically characterized by a composition that contains SO_4^- , Br^- , Cl^- , Na^+ , NH_4^+ , Na^+ ions and R-COO^- .^[135] In this context, it was demonstrated that an increase in the solubility and acid value of the activator based on carboxylic acid results in an increase in leakage current.^[138] Moreover, it was shown that the chain length, the degree of symmetry and the number of polar functional groups in case of WOAs play a crucial role with regard to the interaction with moisture. The incorporation of longer-chain palmitic acid with fewer carboxylic acid groups compared to adipic acid was shown to decrease hygroscopicity and thus, corrosion events.^[139] Consequently, it is important to consider hygroscopic components that may

have a negative impact on SIR values and, where appropriate, explore alternative solutions with less affinity to moisture.

The test boards are frequently subjected to analysis prior to and subsequent to SIR measurements, including analysis *via* electrochemical impedance spectroscopy (EIS), light microscopy, contact angle measurements, Fourier Transform-Infrared Spectroscopy (FT-IR) and electron microscopy such as Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX).

2.4 Electron Microscopy

2.4.1 Overview

Electrons with a mass of $9.109 \cdot 10^{-31} \text{ kg}$ ^[140] are used in electron microscopy which is a powerful method for imaging and analyzing materials at a microscopic and nanoscopic scale. Electron microscopy is an integral part of the study of various materials, especially micro- and nanoparticle-based composites. It utilizes the interaction of the samples with an accelerated electron beam to obtain information about the sample's structure, composition and morphology.

The fundamentals of electron microscopy can be understood by considering the underlying physical principles of electrons. According to their wave-particle nature, as described by de Broglie, the wavelength λ of electrons can be defined as follows^[141]:

$$\lambda = \frac{h}{p} \quad (2.24)$$

and $p = h \cdot k \quad (2.25)$

with

h	= Planck's constant with $6.626 \cdot 10^{-34} \text{ J} \cdot \text{s}$
p	= (magnitude of the) momentum of the
k	particle
	= wave vector with $ k = \frac{1}{\lambda}$

When an electron moves through a potential difference V , it is accelerated to the velocity v . The wavelength of the electron depends on the potential difference or the

acceleration voltage and Equation 2.24 can be extended to Equation 2.25, as follows^[141]:

$$\lambda = \frac{h}{p} = h \cdot \left[2m_0eV + \left(\frac{eV}{c} \right)^2 \right]^{-\frac{1}{2}} \quad (2.26)$$

with

m_0	= rest mass of electron
c	= speed of light in vacuum

For example, a 10 kV acceleration voltage can result in electrons with λ of 0.122 nm, while a 100 kV acceleration voltage results in λ of 0.037 nm.^[141] The specific formulation of the question determines the acceleration voltage and the type of signals investigated which result from the interaction between the electron beam and the sample. Different interactions between primary electrons and the specimen are utilized in electron microscopy investigations. In general, these interactions can be classified into two primary categories: Elastic and inelastic scattering. In the context of elastic scattering, which can be described as an interaction between electron and nucleus, particles retain their kinetic energy and momentum after a collision. In contrast, inelastic scattering, which is an electron-electron interaction, results in a loss of energy. Electrons can also be diffracted or absorbed by the sample, which depends on its thickness and composition. In transmission electron microscopy (TEM), a fixed electron beam is transmitted through an ultrathin specimen to generate an image. In contrast, SEM employs a focused electron beam that scans across the surface of the specimen to produce detailed surface images.^[141]

2.4.2 Transmission Electron Microscopy

In a transmission electron microscope, invented by Ruska and Knoll in the 1930s, an electron beam is passed through the sample, providing insight into the specimen's morphology.^[142]

Compared to a light microscope, which uses light sources and optical lenses, transmission electron microscopes further use electron optics to produce high-resolution images. The basic setup of such a microscope is shown in Figure 2-12.^[143]

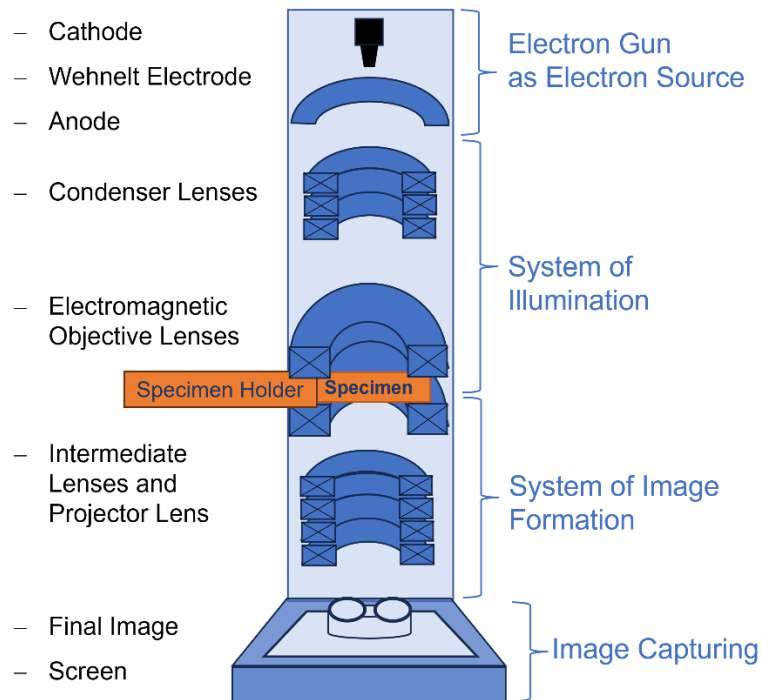


Figure 2-12: Schematic representation of the main components of a transmission electron microscope.

The generation of the electron beam can be accomplished by either a thermionic or a field emission gun. In the former case, the material of the filament typically comprises tungsten or lanthanum hexaboride (LaB_6). In the field emission gun, electrons are emitted from a metal tip, e.g. zirconium oxide, by applying a strong electric field (Schottky effect). The advantage of a field emission gun (FEG) over conventional thermal electron guns is its ability to generate a brighter, finer, and more stable electron beam. This enables better resolution and contrast in TEM images as well as greater beam stability over longer periods of time. Following the extraction of electrons, their acceleration towards the anode is initiated. This process involves traversal of a series of lenses, comprising both electrical and magnetic components. The lenses serve to focus the electron beam and to regulate its dimensions and intensity, thus ensuring high resolution and image quality. The resulting electron beam is then guided through the sample. Some of the electrons penetrate the sample, while others are scattered or absorbed. The transmitted electron image is finally recorded on a detector to create an image of the sample.^[141,144]

2.4.3 Scanning Electron Microscopy

Electrons used in SEM measurements interact with the atoms in the sample, resulting in different interaction possibilities that reveal details about the sample's properties. In contrast to TEM, the SEM method utilizes secondary electrons (SE) and backscattered electrons (BSE) in order to generate images. Moreover, elemental analysis can be conducted *via* EDX. The investigation of this interaction is feasible, as the scanning of the sample in a raster pattern with primary electrons from the electron beam results in a multitude of secondary signals, including cathodoluminescence signals and Auger electrons. The detection of these signals is primarily dependent on the specimen interaction volume (see Figure 2-13 a).^[145]

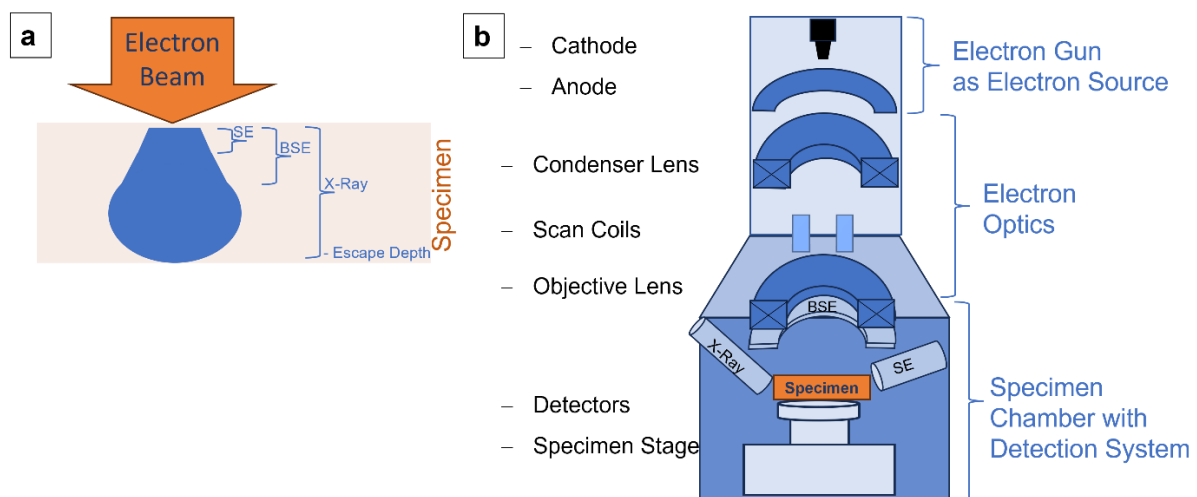


Figure 2-13: Schematic representation of a specimen interaction volume and b main components of a scanning electron microscope.

The formation of the interaction volume depends on a number of factors including the energy of the primary electrons and thus the penetration depth, the sample material and the angle of incidence. Due to inelastic scattering, electrons may be emitted from the surface of the specimen material. These electrons, designated as SEs, may possess kinetic energies up to 50 eV. However, the most common energies are in the range of a few eV (typically 2 to 5 eV). Due to the fact that SEs are emitted from the sample at shorter distances from the surface, it is possible to gain detailed information about the surface morphology and topography of the specimen. As the primary electrons penetrate deeper into the material, they can interact with the sample resulting in

elastic scattering. This process leads to backscattering of electrons. In general, BSEs possess higher energies than SEs, which enables a more detailed analysis of the sample. This is due to the direction and number of BSEs depend on the average atomic number Z of the sample. Furthermore, in the event of an interaction between the electron beam and the surface of the specimen, characteristic X-rays are emitted from the atoms within the specimen. This occurs when the primary electrons undergo inelastic scattering in interaction with the electron of the inner electron shell, resulting in ionization. The vacancy resulting from the interaction of the electron beam with the specimen's surface is filled by an electron from an outer shell, resulting in the emission of a photon. These photons, designated as X-rays, are characteristic of the respective elements and can be quantified by means of EDX detectors, thereby providing insights into the elemental composition and concentration of the elements present in the sample.^[145,146]

The setup of a scanning electron microscope is illustrated in Figure 2-13 b. The generation of electrons is initiated in the electron source. For this process, thermal or field emission sources are typically employed, such as a tungsten filament or a LaB₆ crystal source that shares certain similarities with the TEM. Following the generation of the electrons, they are shaped into a focused electron beam by means of electromagnetic lenses (condenser lens and objective lens) and apertures. This process enables the attainment of high spatial resolution. Subsequently, the electrons are directed towards the surface of the specimen, which is positioned on a three-dimensional movable sample stage. The data acquisition process employs a variety of detection systems, including SE-detectors such as the Everhart-Thornley detector, BSE-detectors, Inlens detectors and X-ray detector such as silicon drift detector (SDD). The acquired signals are then analyzed by a computer system, which generates a visual representation of the surface of the specimen as a two-dimensional image or a spectral display.^[145–147]

2.5 Neutron Imaging

2.5.1 Overview

Neutrons with a mass of $1.675 \cdot 10^{-27}$ kg, a spin of $\frac{1}{2}$ and magnetic moment of $-1.913 \mu_n$ ^[148,149] have become widely used in neutron scattering and imaging experiments and provide an important complementary analytical approach to X-rays. Neutron experiments provide insight into the internal structure and composition of materials and are particularly useful in modern engineering and science.

There are many reasons why neutrons are important for scientific and technical issues. First, neutrons interact with atomic nuclei, enabling the visualization of light elements such as hydrogen, boron and lithium. Due to their sensitivity, neutrons allow to distinguish between neighboring elements in the periodic table. Moreover, isotopic substitution techniques, such as using deuterium instead of hydrogen, can be used to increase contrast. Second, the interaction between neutrons and matter is governed by either the nuclear force or the magnetic moment. Therefore, neutrons can be utilized for detecting the nuclear spin and allow for the study of the dependence of nuclear forces on spin through their interaction with the nuclei. The use of polarized neutron beams enables the investigation of the magnetic properties of various materials. Third, neutrons, being electrically neutral according to the standard model, are ideal for investigating materials where large penetration depth is required. Also, thermal and cold neutrons are suitable for the study of diffuse atomic motions because of the energies in the meV and μ eV range required for the thermal excitation of random atomic motions in liquids and solids. Furthermore, neutrons can be classified by their energy range and wavelength. In this context, it should be noted that the scattering and absorption processes involved in the interaction between neutrons and atomic nuclei are influenced by the energy of the neutrons.^[149] Roughly defined, they range from ultracold neutrons with an energy range ≤ 300 neV to cold neutrons with 0.12 -12 meV, thermal neutrons with 12-100 meV, fast neutrons with 1-20 MeV and high-energy neutrons > 20 MeV.^[149,150] Finally, neutron diffraction and inelastic neutron scattering provide the ability to study atomic or molecular structures and molecular vibrational modes.^[149]

2.5.2 Imaging Techniques

Neutron imaging, a non-destructive technique, uses the transmission of neutrons through a specimen. The neutron imaging technique can be divided into four fundamental categories, which are: Attenuation-based, phase contrast, polarized neutron imaging and Bragg edge imaging. The attenuation method of nuclear imaging is based on the reduction of the intensity of neutron radiation as it passes through a material that exhibits incoherent scattering cross-section or a high neutron absorption property. Given that the incoherent cross section is the highest for ^1H , this method is particularly well suited to address questions related to this element. Neutron beam attenuation is proportional to the material density and thickness through which it passes and can be expressed using the Lambert-Beer law, as follows^[149]:

$$I = I_0 \cdot e^{(-\mu x)} \quad (2.27)$$

with

I	= intensity of incident light
I_0	= intensity of transmitted light
μ	= attenuation coefficient of neutron beam
x	= length of the neutron beam that passes through the material

The described procedure enables the structural analysis of density, composition and any irregularities in a material, incorporating elements with high atomic number Z . Moreover, in analogy to the electromagnetic waves of an electron, neutrons can also be regarded as waves to which a phase can be assigned. Phase contrast imaging utilizes the phase change of neutron beams as they pass through a material and is especially suited for materials with attenuation cross sections being low. Furthermore, due to the negative magnetic moment of neutrons and their ability to interact with the magnetic moment of atoms, they are advantageous for investigating magnetic properties of samples. In this context, polarized neutron imaging represents a viable option, whereby the neutron beam is polarized with a ^3He -polarizer or supermirror. For instance, to visualize DC magnetic fields, the measured alterations in neutron polarization can be employed to determine the spatial distribution and intensity of the field. Finally, Bragg-edge imaging or neutron radiography with wavelength dependency, is a technique that enables the acquisition of quantitative spatial data regarding the atomic

structure of solid materials, especially those with crystalline structure. The underlying theory can be derived from neutron scattering. When neutrons pass through a crystalline material, they interact with the atoms within the material. The neutrons are scattered by the atomic lattices of the crystal, with the scattering angles being dependent on the interatomic distances. When the conditions for constructive interference are met, Bragg reflections occur. These reflections occur when the neutron incidence angle and the crystal lattice with spacing d (with the Miller indices hkl) of the crystalline material are aligned in such a way that the phases of the scattered waves constructively interfere, resulting in an increase in the scattering angle with λ in following relationship^[149]:

$$n\lambda = 2 \cdot d \cdot \sin \theta \quad (2.28)$$

with

n	= integer representing the order of diffraction
λ	= incident wavelength
θ	= angle of the incident beam relative to the crystal surface

Wavelengths that do not satisfy the Bragg condition lead to a decrease in material attenuation. This phenomenon is known as the Bragg edge, whose investigation provides information about phase fractions and lattice strains.^[149]

2.5.3 Neutron Sources and Applications

The generation of neutrons can be achieved through a number of different processes, including photoneutron, photofission, spallation, nuclear fission and nuclear fusion. Nuclear reactors based on nuclear fission continue to represent the primary source of neutrons for neutron imaging applications. Nevertheless, there are also approaches based on accelerators (fusion reactions such as deuterium-deuterium) or radioisotope (e.g. ^{252}Cf) that would enable more portable and cost-effective neutron generation, suitable for e.g. industrial applications. The principal disadvantage of these approaches is that they result in a lower neutron flux (number of neutrons per unit area per unit time) than that of research reactors.^[149]

The 20 MW thermal power of the FRM II research reactor at the Maier-Leibnitz-Zentrum in Garching enables the generation of a high neutron flux, with neutrons

produced through the nuclear fission of ^{235}U . The advanced neutron tomography and radiography experimental system (ANTARES), situated at the research reactor's cold neutron beam port, employs these neutrons for radiographic and tomographic procedures with a neutron flux of $6 \cdot 10^7 \text{ n cm}^{-2} \text{ s}^{-1}$ at a collimation $L/D = 500$ (ratio of length L of the collimator to its aperture diameter D). The main components of the ANTARES instrument are the following: Beam shutter, collimator, velocity selector, flight tubes, apertures, sample positions, detectors and beam stop. Here, the collimator serves to align the neutron beam and to limit its divergence, thereby facilitating more precise imaging. Moreover, a velocity selector permits the selection of neutrons with a specific velocity or energy, thereby ensuring a controlled and specified energy distribution. Depending on the specific inquiry, additional components may be incorporated, such as a double-crystal monochromator, a neutron-beam interferometer or other apparatus^[151,152]:

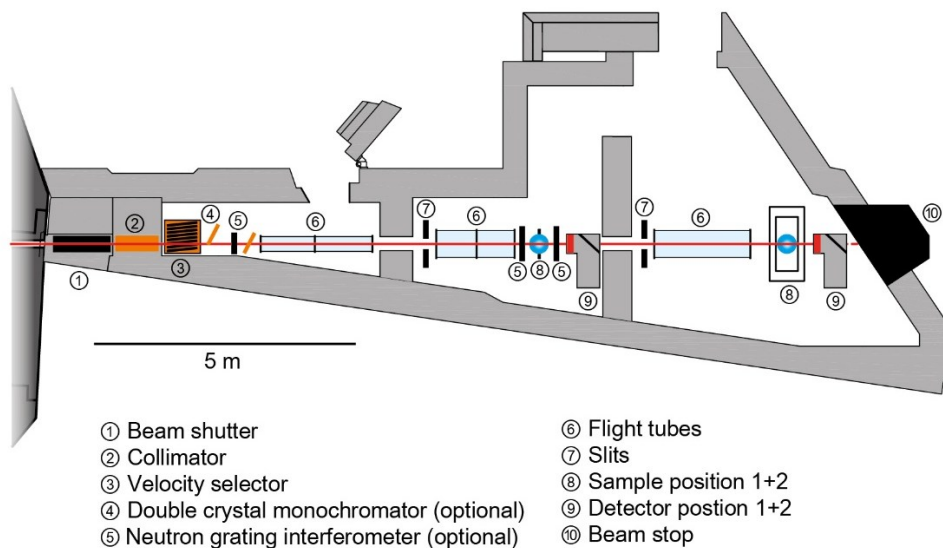


Figure 2-14: Instrument configuration of ANTARES.^[151]

Due to their sensitivity to light elements and their permeability to heavy elements such as Al and Fe, neutrons are particularly suited to illustrating the properties of sealing fluids, liquids and polymers in industrial products. Here, contrast agents such as those based on gadolinium can be utilized due to their high neutron absorption cross-section to detect voids and cracks.^[153] In practice, the use of neutron imaging enabled the visualization of sealing agents, O-rings and residual oil within a diesel injection pump,

which would not have been possible with conventional methods based on X-rays.^[154] Moreover, in the area of fuel cell technology, 4-D neutron computed tomography was used to investigate the local and quantitative water dynamics in a polymer electrolyte fuel cell during operation, which represents a new characterization method for next-generation cell designs.^[155]

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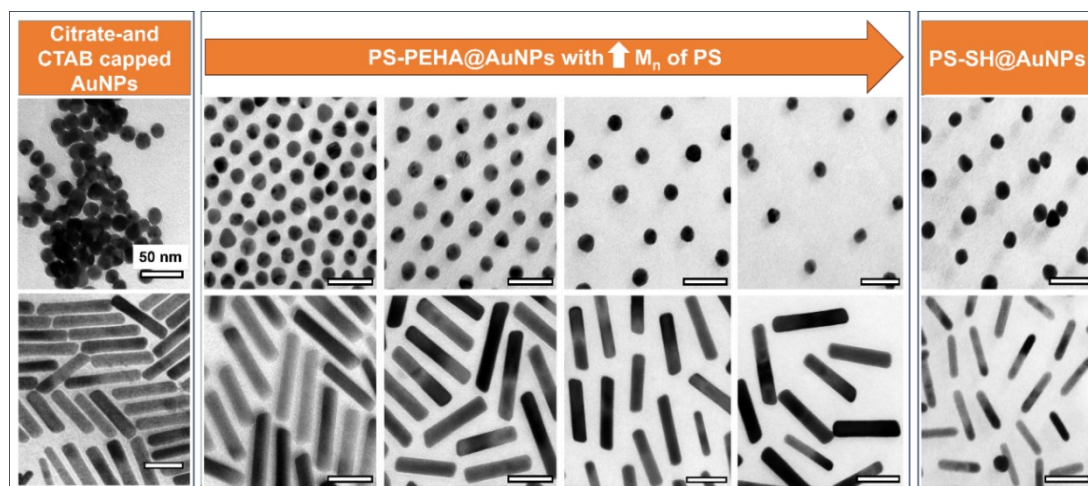
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3 INFLUENCE OF FUNCTIONALIZED POLYMER AGENTS ON THE STABILIZATION AND INTERPARTICLE DISTANCE VARIATION OF GOLD NANOPARTICLES



Abstract

Current research focuses on improving the gold nanoparticle stability and controlling nanoparticle assembly by surface modification and functionalization with polymer agents. Attaching end-functionalized polymers to gold surfaces provides a versatile approach for colloidal stability and structurally well-defined polymer shells. This study investigates the ligand exchange method to attach end-functionalized polystyrene (PS) chains with narrow molecular weight distribution to spherical and anisotropic gold nanoparticles. Gold nanoparticles (AuNPs) initially capped with citrate and cetyltrimethylammonium bromide (CTAB) ligands are exchanged with thiol- and multidentate amino-terminated polystyrene. A systematic variation in interparticle distances (nanoparticle surface-to-surface distances) in both spherical and cylindrical nanoparticle forms, correlated with polymer molecular weight, is shown. Moreover, gold nanorods demonstrate polymer binding primarily to the lateral circumference, with a lower affinity for the cylinder tips, consistent with changes in longitudinal and transverse plasmonic resonances. Finally, a tendency for reduction in rod length when replaced with thiolated polystyrene is discussed. The results of this work offer insights into the process of functionalizing spherical and cylindrical nanoparticles with polymer ligands to enhance stability and control interparticle spacing, paving the way for tunable and stable nanoparticle assembly.

3.1 Introduction

AuNPs represent an interesting field of research with great potential for application such as in the fields of catalysis^[1], solar cells^[2,3], biochemical and chemical sensing^[4] as well as therapeutics and medical diagnostics^[5]. The main motivation is predominantly based on the optical properties of metallic nanoparticles which are attributed to their sensitivity to changes in the dielectric environment, interparticle distance (d_i), size and shape. These changes manifest as shifts in the characteristic localized surface plasmon resonance (LSPR) peaks upon excitation by an electromagnetic field.^[6] Optical absorption spectra distinguish spherical AuNPs, which exhibit a transverse LSPR band around 510–520 nm, from anisotropic AuNPs like gold nanorods (AuNRs).^[7] The latter display an additional longitudinal LSPR band at higher wavelengths with its position varying according to the aspect ratio^[8], surrounding medium and neighboring nanoparticles^[9,10]. Since chemical and physical properties of AuNPs such as plasmonic coupling^[11] depend on their d_i ^[3], uniform shapes and sizes^[9], colloidal stability as well as uniform size distribution are essential.

Metal nanoparticles, especially anisotropic nanocrystals, tend to aggregate due to their high surface-to-volume ratio and therefore require stabilization. The stabilization mechanisms generally involve both electrostatic and steric stabilization which are achieved through electrical double layer repulsion and coordination of bulky groups, respectively.^[12] Based on this, a wide range of synthetic pathways were proposed. These methods involve surfactants, such as sodium citrate^[13,14] CTAB^[15] and alkanethiols^[16,17] as well as the formation of organic or inorganic shells around the nanocrystals. Mosquera *et al.* developed a method for enhancing the stability of AuNPs in biological systems. Thiol groups of 3-mercaptopropyltrimethoxysilane (MPTMS) were attached to the Au surface of NPs and subsequent condensation reactions between MPTMS and APTES resulted in the formation of a silica monolayer. This approach effectively enhanced the stabilizing effect.^[18]

Moreover, colloidal stability can be achieved by using functionalized polymer agents as stabilizers. The encapsulation of an inorganic hard core with a polymer soft shell forms nanocomposites that offer additional advantages, including improvement of homogeneity, colloidal stability and enhanced plasmonic properties^[19] as well as the

ability to change dispersion media using amphiphilic polymer materials^[20,21]. Furthermore, the use of polymer ligands with functional groups generally leads to (self-)assembly of nanoparticles into superstructures and hence, to an extension of the application possibilities.^[22] AuNPs have a strong affinity for thiol groups^[23], leading to the functionalization of polymers such as poly(ethylene glycol) (PEG)^[24], poly(N-isopropylacrylamide) (PNIPAm)^[25] and PS^[26,27] with SH-linkage groups for attachment onto the nanoparticle surface. Thiol-mediated polymer attachment provides versatility, as shown by Wang *et al.*, who used an electric field and anodic alumina template to align AuNRs and enhance interparticle distances by replacing CTAB ligands with SH-terminated PS. The edge-to-edge spacing increased from ~7.1 nm to 17.6 nm and tip-to-tip spacing from ~6.0 nm to 28.4 nm.^[27] Moreover, recent studies emphasized the arrangement of highly anisotropic PS-SH@AuNRs in directional supracolloidal structures, considering factors such as NP surface charge^[28] and solvent quality^[29]. However, the majority of investigations have focused on the study of SH-terminated polymers, while other functional groups have received less attention. In addition, the high affinity of thiolated polymers to gold surfaces is discussed as less optimal for the stabilization of AuNPs compared to moderate levels of affinity.^[30]

In order to fill this gap, this study investigates the surface modification of spherical and anisotropic AuNPs using narrowly dispersed PS ligands with both multidentate amino and thiol functional groups. Specifically, the exchange of citrate and CTAB capping agents with pentaethylenhexamine- (PEHA) and SH-functionalized polystyrene is described. Transmission electron microscopy (TEM) was employed to establish correlations between the functional ligands, their molecular weight and interaction with the gold surface. This work further outlines the protection of AuNRs against aggregation and shape loss for both functional groups. Furthermore, changes in optical properties within the ultraviolet-visible-near infrared (UV-Vis-NIR) spectral range due to surface functionalization were analyzed, showing the sensitivity of AuNPs to surface modifications. This research provides fundamental understanding of the stabilization and control of interparticle spacing in spherical and rod-like AuNPs which will contribute to the design of polymer shells for next-generation functional materials.

3.2 Experimental Part

3.2.1 Materials

The following chemicals were utilized without further purification: Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, supplied by Alfa Aesar), cetyltrimethylammonium bromide (CTAB, supplied by Sigma-Aldrich), sodium borohydride (NaBH_4 , supplied by Sigma-Aldrich), hydroquinone (HQ, supplied by Sigma-Aldrich), silver nitrate (AgNO_3 , supplied by Sigma-Aldrich), sodium citrate dehydrate ($\geq 99\%$, supplied by Sigma-Aldrich), pentaethylenhexamine (PEHA, technical grade, supplied by Sigma-Aldrich) and 1,1'-carbonyldiimidazole (CDI, reagent grade, supplied by Sigma-Aldrich). Hydroxyl-terminated polystyrene (PS-OH) samples with different M_n values (*i.e.*, PS-OH 1 at $11.5 \text{ kg} \cdot \text{mol}^{-1}$, PS-OH 2 at $22.8 \text{ kg} \cdot \text{mol}^{-1}$, PS-OH 3 at $33.3 \text{ kg} \cdot \text{mol}^{-1}$ and PS-OH 4 at $58.3 \text{ kg} \cdot \text{mol}^{-1}$) were procured from Polymer Source, Inc. Likewise, thiolated polystyrene with M_n value of $53.9 \text{ kg} \cdot \text{mol}^{-1}$ was procured from the same supplier. To functionalize PS-OH, the solvent used was tetrahydrofuran (THF, Sigma-Aldrich, with 250 ppm BHT as stabilizer and purity $\geq 99.9\%$), chloroform (CHCl_3 , Sigma-Aldrich, anhydrous, purity $\geq 99\%$ and with amylenes as stabilizer) and deuterated chloroform (CDCl_3 , Roth, purity 99.8 atom% and stabilized with Ag). All three solvents were used without any modifications upon receipt.

3.2.2 Synthesis

AuNS synthesis. AuNS were synthesized according to the methods of Turkevich *et al.*^[13] and Rauh *et al.*^[31]. Prior to synthesis, the glassware and magnetic stirrer underwent cleaning with aqua regia and ethanol followed by drying in an oven. Subsequently, a 500 mL solution containing $5 \cdot 10^{-4} \text{ M}$ HAuCl_4 was heated until boiling, at which point 25 mL of a hot aqueous solution comprising of 1 wt.% sodium citrate dihydrate was vigorously stirred and added. The resulting solution, which exhibited a dark red hue, was slowly cooled with stirring over a period of 20 min. After a 20-min reaction time, the solution turned dark red and was slowly cooled while being stirred.

AuNR synthesis. The silver-assisted seed growth method was used for the synthesis of AuNRs according to the protocol of Vigderman *et al.*^[32] To prepare the seed solution, 0.5 mM HAuCl_4 was added to 5 mL of a 0.2 M CTAB solution and stirred vigorously at

210 rcf for 10 min until the mixture turned yellow. Subsequently, 0.6 mL of ice-cold 0.01 M NaBH₄ was added and the solution was stirred at 210 rcf for about 2 min. The solution was allowed to rest for 1 h. To prepare the growth solution, 12.5 μ L of 0.1 M HAuCl₄ was added to 2.5 mL of 0.1 M CTAB. Subsequently, 12.5 μ L of 0.1 M AgNO₃ and 125 μ L of 0.4 M HQ were added and the mixture was stirred at 35 °C. 100 μ L of seed solution was added to generate AuNRs with a length of 79.6 nm $\pm$ 5.6 nm and a width of 16.8 nm $\pm$ 0.8 nm. 175 μ L of seed solution was added to the growth solution to produce AuNRs with a length of 48.1 nm $\pm$ 4.7 nm and a width of 9.7 nm $\pm$ 0.6 nm. The mixtures were centrifuged twice at 14500 rcf for 60 min and then dispersed again in Milli-Q water.

PEHA-functionalization of PS-OH. The conversion of PS-OH to PS-PEHA was generally accomplished in two steps: Activation of the hydroxyl group of PS followed by its addition to an activated organic PEHA solution. First, 25-fold excess of CDI was slowly dissolved in CHCl₃ and stirred in an inert environment for 24 h. The solution was then prepared by extraction steps with demineralized water and its drying under vacuum. A 25-fold excess of PEHA was then dissolved in chloroform to which the redissolved activated polymer was added dropwise. Again, the solution was stirred for 24 h in an inert environment and the same preparation steps as described above were carried out. In order to monitor the conversion of PS-OH to PS-PEHA, ¹H-NMR measurements were performed, which are presented in the Appendix (Figure A-1 and Figure A-2).^[33]

Ligand exchange. Ligand exchanges were carried out following the procedure outlined by Grzelczak *et al.* with minor alterations.^[21] To a 10 mL solution of THF containing PS-SH or PS-PEHA ($\frac{5 \text{ molecules PS-SH or 5 molecules PS-PEHA}}{\text{nm}^2 \text{ surface of Au}}$), 1 mL of Au dispersion was added dropwise under sonication. The gold dispersion consisted of 0.4 mM citrate-stabilized gold nanospheres (AuNSs) or 4.6 mM CTAB-capped AuNRs. The ultrasound treatment lasted for 15 min and the solution was allowed to stand for 24 h. The final solution underwent two cycles of centrifugation at 7120 rcf for 30 min before redispersing the Au NPs in THF.

PS-*b*-PAA Encapsulation. For application of the PS-*b*-PAA layer, 450 μL of PS-PEHA@AuNRs dissolved in THF was combined with 50 μL of 6 mg/mL PS-*b*-PAA, also dissolved in THF. Then, 250 μL of Mili-Q water was added while stirring magnetically. The solution was left undisturbed for 30 min after reaching a temperature of 75 $^{\circ}\text{C}$ and a 50 wt.% increase in water content was achieved. Finally, it was centrifuged at 4400 rcf for 20 min and dissolved in water.

3.2.3 Characterization Methods

^1H -NMR. To study the functionalization process of PS-OH towards PS-PEHA, 10 mg of PS-PEHA were dissolved in 0.7 mL CDCl_3 and analyzed using a Bruker AC 250 (300 MHz).

SEC. Size Exclusion Chromatography (SEC) was performed mainly using an Agilent 1260 Infinity pump (G1310B), the autosampler (G1329B) and the detectors Wyatt Optilab T-rEX differential refractive index detector and a Wyatt DAWN Heleos-2 light scattering detector. The eluent was a THF-DMA-AcOH mixture with a flow rate of 1 $\text{mL} \cdot \text{min}^{-1}$. Data analysis was performed using the ASTRA 6.1 software.

TEM. A Zeiss CEM902 (80 kV EFTEM with thermal tungsten cathode; Carl Zeiss Microscopy GmbH) transmission electron microscope was used to create TEM images.

UV-Vis-NIR. The UV-Vis absorption spectra were recorded using an Agilent Technologies Cary 5000 spectrophotometer with a wavelength range of 400 to 900 nm and 1100 nm, respectively.

3.3 Results and Discussion

In AuNP wet chemical synthesis, chloroauric acid is reduced by a reducing agent in an aqueous or organic medium with a stabilizing agent. The innovative synthesis method conducted by Turkevich *et al.*^[13], subsequently extended by Frens *et al.*^[34], illustrates the use of sodium citrate as a stabilizing and reducing agent in the aqueous reduction of gold salt. Anisotropic AuNPs are typically prepared using the positively charged surfactant CTAB, which adsorbs onto the surface of Au.^[35] This surfactant plays a crucial role in the synthesis of AuNRs with the prevalent approach being the Ag-assisted seed-mediated growth synthesis.^[36] The synthesis routes for spherical and rod-shaped AuNPs are schematically shown in Figure 3-1.

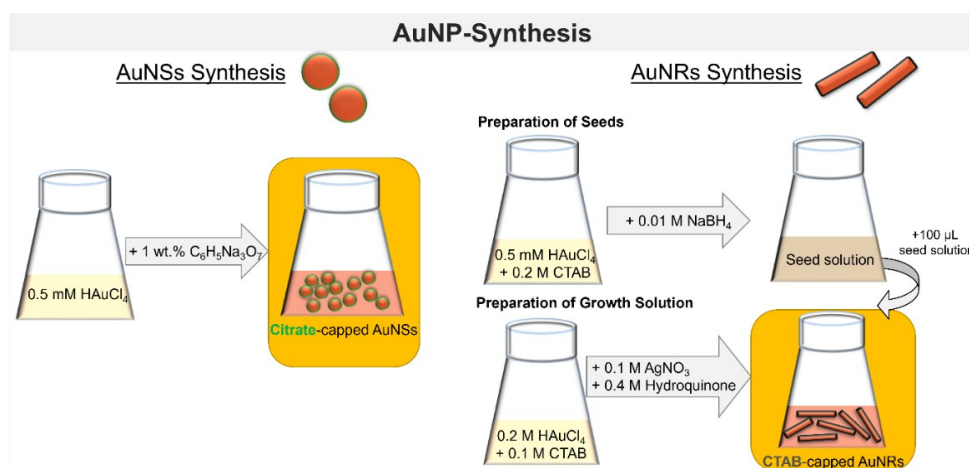


Figure 3-1: Schematic illustration of the syntheses of citrate-capped AuNSs and CTAB-capped AuNRs.

3.3.1 AuNP Synthesis and PEHA-Functionalization of PS

Capping agents like CTAB and sodium citrate, which exhibit weak surface adsorption, are suitable for ligand exchange due to electrostatic interactions with AuNP surfaces.^[17,35] To investigate the geometric dependence and interchangeability of capping agents with polymer ligands, citrate-stabilized AuNSs and CTAB-stabilized AuNRs were synthesized. Using the synthesis protocol of Rauh *et al.*^[31], citrate@AuNSs with an average diameter of $17.9 \text{ nm} \pm 1.5 \text{ nm}$ were produced (see Figure 3-2 a.0). Furthermore, two distinct sizes of nanorods were synthesized by modifying the amount of seed

solution. As a result, AuNRs with aspect ratio (AR) of approximately 5.0 (100 μ L seed solution) as well as an AR of roughly 4.9 (175 μ L seed solution) were synthesized (see Figure 3-2 b.0 and c.0).

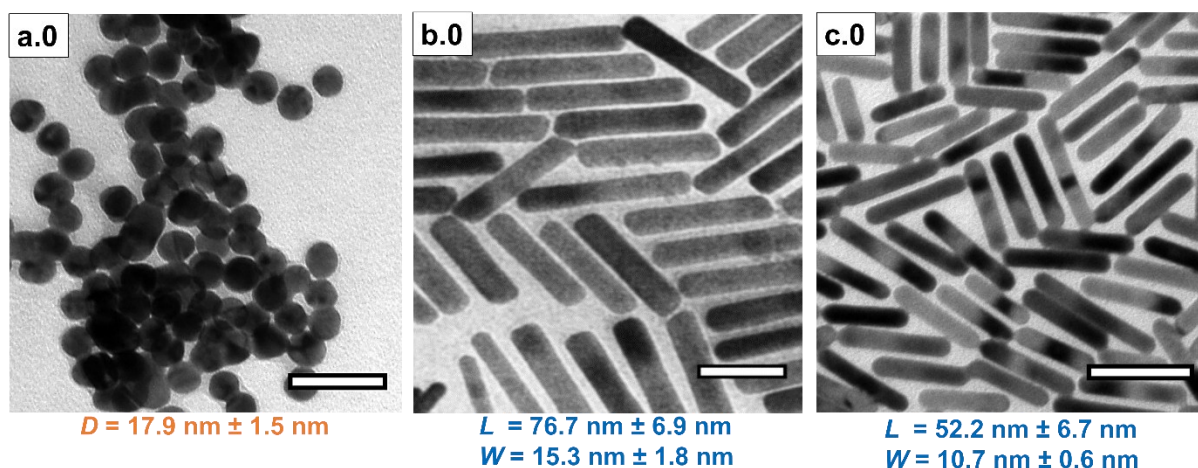


Figure 3-2: TEM images of a.0 citrate@AuNSs, b.0 CTAB@AuNRs with AR~5.0 and c.0 CTAB@AuNRs with AR~4.9. Scale bars correspond to 50 nm.

Subsequently, ligand exchange of the low molecular weight capping agents with PS containing multidentate amino- and SH-end groups is performed. Prior to this, four different molecular weights of OH-terminated PS and SH-terminated PS as reference were selected for PEHA functionalization which are summarized in Table 3-1.

Table 3-1: Distinction in number average M_n and polydispersity index (PDI) between PS-PEHA and PS-SH ligands, along with their respective designations.

OH-terminated PS functionalized towards→ PEHA-terminated PS	$M_n / \text{kg} \cdot \text{mol}^{-1}$	PDI
PS-OH 1 → PS-PEHA 1	11.6	1.01
PS-OH 2 → PS-PEHA 2	23.2	1.02
PS-OH 3 → PS-PEHA 3	34.8	1.06
PS-OH 4 → PS-PEHA 4	58.7	1.02
SH-terminated PS	$M_n / \text{kg} \cdot \text{mol}^{-1}$	PDI
PS-SH	54.2	1.06

3.3.2 Investigation of the Ligand Exchange with Functionalized Polymer Ligands

The spherical and non-spherical nanocrystals depicted in Figure 3-2 a.0 and b.0 underwent a ligand exchange process using PS-PEHA, as illustrated in Figure 3-3 a.1-a.4 and b.1-b.4. Moreover, the same AuNSs and also rods shown in Figure 3-2 c.0 were treated with PS-SH to enable a comparative analysis of the interchangeability between the two polymer ligands (see Figure 3-3 a.5 and c.5). Au dispersions consisting of citrate-capped nanoscale spheres or CTAB-stabilized anisotropic nanocrystals were introduced into organic solutions under sonication as described in detail by Grzelczak *et al.*^[21] to achieve approximately 5 molecules of PS-SH or PS-PEHA per nm² of AuNP surface.

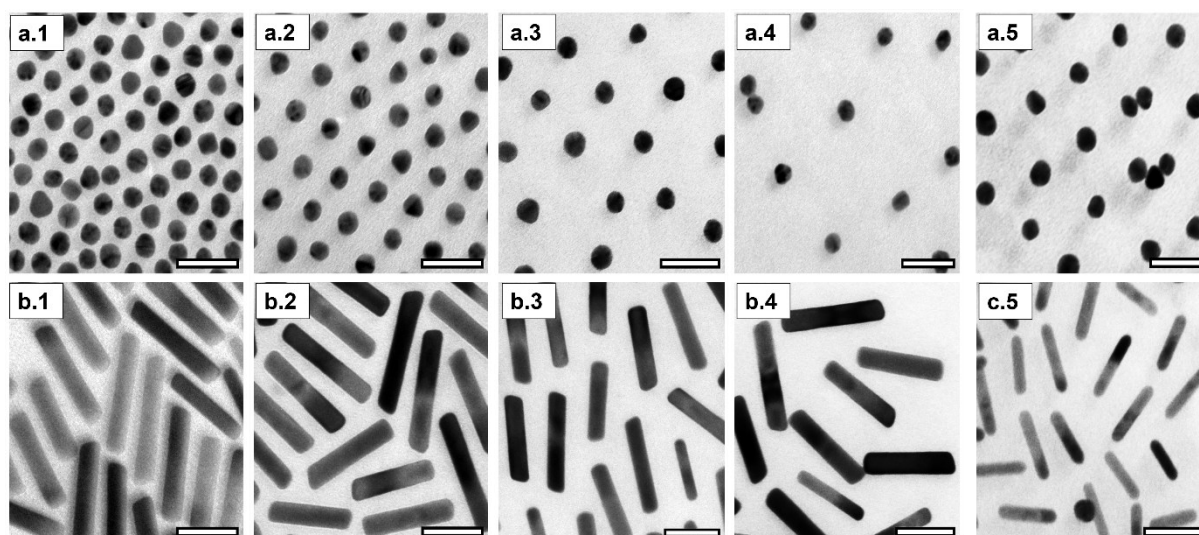


Figure 3-3: TEM images in a.1-a.4 show AuNSs and b.1-b.4 display CTAB-stabilized AuNRs after ligand exchange with PS-PEHA. Increasing M_n of the polymer ligand correlates with enlarged di. Additionally, a.5 spherical and c.5 rod-like AuNPs, exchanged with PS-SH ($M_n \text{ PS-SH} = 54.2 \text{ kg} \cdot \text{mol}^{-1}$), exhibit increased interparticle spacing. Scale bars correspond to 50 nm.

After performing ligand exchange on both PS-PEHA and PS-SH, it becomes apparent that the separation between AuNPs increases proportionally to M_n of the polymer, regardless of the initial stabilizing agent employed. A comparison of the citrate-stabilized nanospheres shown in Figure 3-2 a.0 reveals the formation of well-defined, hexagonally ordered arrays as the M_n of PS increases from $M_n \text{ PS-PEHA } 1 = 11.6 \text{ kg} \cdot \text{mol}^{-1}$ till

$M_n \text{ PS-PEHA } 4 = 58.7 \text{ kg} \cdot \text{mol}^{-1}$. Figure 3-3 b.1-b.4 shows evidence of equivalent success in the ligand exchange process for AuNRs with an AR ~ 5 and an enlargement of side-to-side and tip-to-tip distances. These AuNRs retain their size and anisotropy. Additionally, Figure 3-3 a.5 and c.5 demonstrate an increased separation among AuNPs after exchange with PS-SH. However, the functionalization of the highest M_n of the polymer for both amino and SH groups indicates limitations, as evidenced by the presence of particles in close proximity to each other. For comprehensive analysis, d_i obtained from at least 50 to 100 measurements extracted from TEM images in Figure 3-3 were plotted against M_n of the polymer (see Figure 3-4). Furthermore, specific distinctions were made for AuNRs, differentiating between tip-to-tip and edge-to-edge distances.

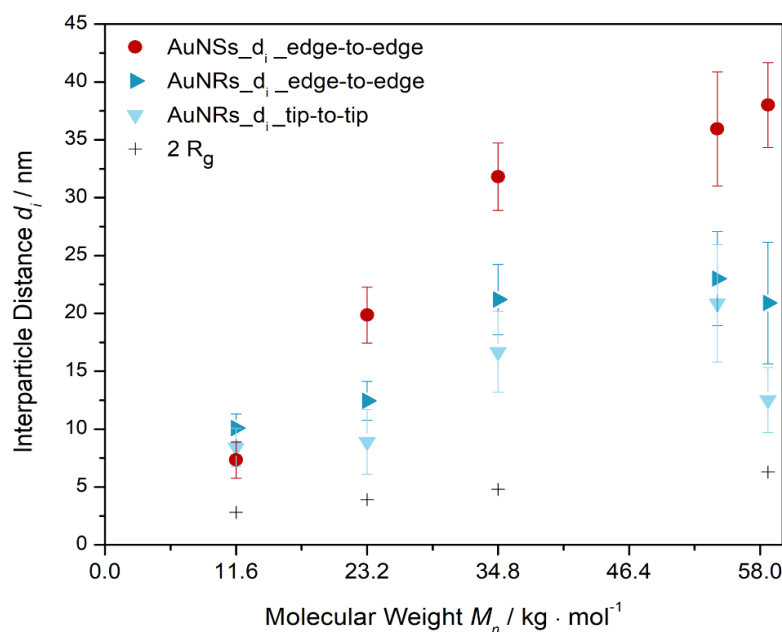


Figure 3-4: Plot shows the interparticle spacing between spherical and anisotropic AuNPs in relation to M_n of PEHA- and SH-terminated PS with values of R_g calculated in accordance with the equation $R_g = 0.25 \cdot M_n^{0.51}$.^[37]

As illustrated in Figure 3-4, the analysis of the edge-to-edge distance between spherical AuNPs as a function of M_n of the polymer demonstrates a systematic increase. For $M_n \text{ PS-PEHA } 1$, d_i is $7.3 \text{ nm} \pm 1.6 \text{ nm}$, increasing progressively from $19.9 \text{ nm} \pm 2.4 \text{ nm}$ to $31.8 \text{ nm} \pm 2.9 \text{ nm}$ and $35.9 \text{ nm} \pm 4.9 \text{ nm}$ for the PS-SH ligand, finally reaching a

plateau at $38.2 \text{ nm} \pm 3.7 \text{ nm}$ for $M_n \text{ PS-PEHA } 4 = 58.7 \text{ kg} \cdot \text{mol}^{-1}$, representing the highest observed value. Similarly, for PS-SH exchanged AuNSs, the edge-to-edge distances also increase with molecular weight and reach a plateau at the highest M_n of PS. The influence of nanoparticle geometry is further explored in the case of ligand exchange with anisotropic AuNPs. For $M_n \text{ PS-PEHA } 1$, the edge-to-edge distance is $10.1 \text{ nm} \pm 1.2 \text{ nm}$, while the tip-to-tip distance is $8.4 \text{ nm} \pm 1.6 \text{ nm}$, which are values comparable to those observed for AuNSs. This indicates effective replacement of both citrate and CTAB ligands by PS-PEHA ligands. However, for AuNRs the increase in edge-to-edge distances with increasing M_n is less pronounced than for spherical nanoparticles, plateauing at $54.2 \text{ kg} \cdot \text{mol}^{-1}$ and decreasing slightly at $58.7 \text{ kg} \cdot \text{mol}^{-1}$. Notably, the tip-to-tip distance decreases to $12.5 \text{ nm} \pm 2.8 \text{ nm}$ at this higher molecular weight of PS.

Overall, Figure 3-4 reveals the trend $d_i(\text{AuNS}) > d_i(\text{AuNR, edge-to-edge}) > d_i(\text{AuNR, tip-to-tip})$ for equivalent ligand molecular weights. Furthermore, as indicated by the crosses in Figure 3-4, the interparticle distances generally exceed twice the radius of gyration of the polymer ligands ($d_i > 2 R_g$). This suggests that the polymer chains in both cylindrical and spherical ligand shells are highly stretched, except in the case of the tip-to-tip distance at $M_n \text{ PS-PEHA } 4$, whereby d_i approximately equals to $2 \cdot R_g$.^[37] The increase in M_n of PS chains is commonly associated with a decline in grafted polymer chain density on Au surfaces.

Consequently, increased molecular weight leads to a decrease in both the grafting density and the degree of polymer chain extension with increasing molecular weight, leading to a plateau in the layer thickness at high M_n . Equally, the discrepancy in the rate of spatial distance increase between spherical and cylindrical nanocrystals can be ascribed to variations in the density of the polymer shell. In this context, the curvature of the nanoparticle surface plays a significant role: Spherical surfaces exhibit a radial r^2 -dependent increase in the area per chain which decreases to r^1 -dependence for rod-shaped surfaces and an r^0 -relation for the planar surfaces of rod tips. This difference in surface accessibility implies that higher surface curvature allows more polymer chains to reach the gold surface with less steric hindrance, as already seen in the

grafting of PS-SH chains onto initial citrate-stabilized spheres from the work of Yockell-Lelièvre.^[38]

To provide a more detailed view of the PS-PEHA polymer shell in terms of shape and thickness, AuNRs were additionally treated with polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) with $M_{n\text{ PS}} = 41 \text{ kg} \cdot \text{mol}^{-1}$ and $M_{n\text{ PAA}} = 4.2 \text{ kg} \cdot \text{mol}^{-1}$ to enhance the contrast in the TEM images (see Figure 3-5). This coating process primarily relies on hydrophobic interactions between the PS block of the copolymer and the PS chains grafted onto the AuNRs.^[21]

According to Figure 3-5, the polymer shell thickness increases predominantly along the sides of the PS-PEHA-coated nanorods and is particularly pronounced at the central region of the nanocrystals. For AuNRs in which the CTAB ligand was replaced with PS-PEHA 3 (Figure 3-5 b.3), a polymer shell increase is also observed at the tips of the nanorods.

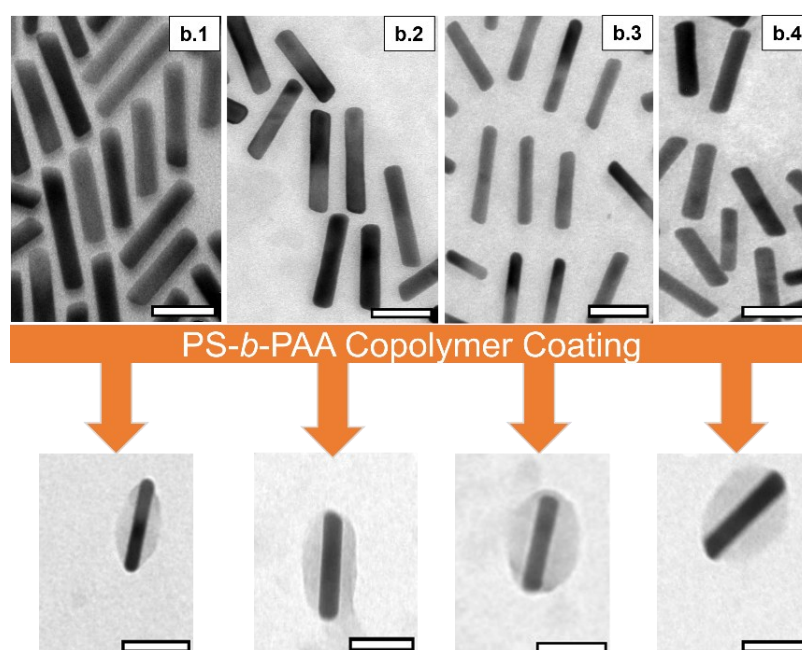


Figure 3-5: TEM images show PS-PEHA@AuNRs that were further coated with PS-*b*-PAA copolymer to highlight the polymer shell. Scale bars correspond to 50 nm.

In conclusion, as the M_n increases, the thickness of the polymer shell primarily grows almost linearly before reaching a plateau at higher molecular weights. The observed initial linear dependence ($d_i \sim M_n^1$) suggests an extended chain configuration within densely packed polymer shells, whereas a weaker dependence ($d_i \sim M_n^{1/2}$) would be expected for less dense polymer shells. These results align with the findings of Wang *et al.*, who demonstrated that both edge-to-edge and tip-to-tip distances increase with the molecular weight of PS-SH. The strong affinity between Au surfaces and SH groups^[23], as well as their preferential binding to the tips of AuNRs during two-dimensional assembly or self-assembly processes^[39], has been widely discussed as a contributing factor to these spatial variations. Although the preferential attachment of SH groups to AuNR tips cannot be conclusively determined from a single reference measurement, the findings indicate that the PS-PEHA ligand primarily stabilizes the central region of the nanorods rather than their tips. This preferential attachment to the central region of the AuNRs, even at higher M_n is likely responsible for the effective stabilization against shrinkage and shape deformation of the nanorods, despite undergoing multiple centrifugation steps during sample preparation. The effectiveness of polymer ligands in mitigating shape deformation, particularly the undesired transformation of nanorods into spherical nanoparticles, was further analyzed by examining the width and length of AuNRs following ligand exchange (see Figure 3-6).

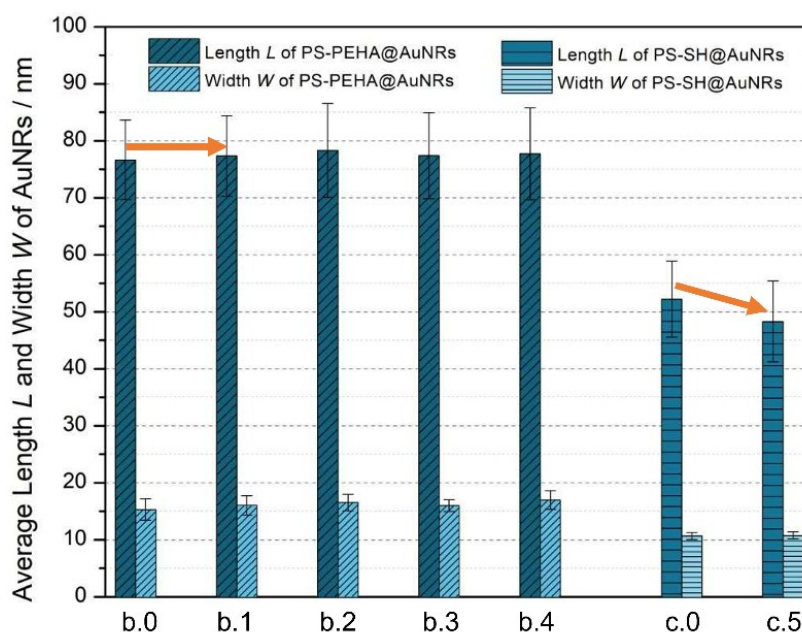


Figure 3-6: Bar graphs display the widths and lengths of anisotropic AuNPs that were exchanged with PS-PEHA, indicating no reduction in either parameter, but when exchanged with PS-SH a slight decrease in the length of AuNRs.

Figure 3-6 clearly illustrates that surface modification with PS-PEHA preserves both the width and length of the initially CTAB-stabilized anisotropic AuNPs with no observable reduction in dimensions. After stabilizing the AuNRs (c.0) with PS-SH, a slight decrease in the average length from $L = 52.2 \text{ nm} \pm 6.7 \text{ nm}$ to $L = 48.3 \text{ nm} \pm 7.1 \text{ nm}$ is observed, although the width remains the same. Thus, in line with Pearson's Hard and Soft Acids and Bases (HSAB) concept^[40], besides of strongly binding SH ligands, also moderately binding PEHA ligands can also effectively stabilize AuNPs, especially nanoparticles of cylindrical shape. Observations from graphene liquid cell electron microscopy reveal comparable findings, indicating that robust stabilization at the central region of AuNRs and/or dynamic diffusion along the Au surface are effective approaches for preserving anisotropy.^[41]

3.3.3 Influence on Optical Properties

The impact of PS ligand exchange on nanoparticle optical characteristics is evident in Figure 3-7. To provide a thorough comparison of changes with respect to SPR positions, the UV-Vis-NIR absorbance spectra were normalized. The influence of nanoparticle morphology on plasmon resonances is well known, such that spherical NPs exhibit a single TSPR peak, while anisotropic nanocrystals exhibit an additional LSPR peak. These peaks can be modified based on specific requirement, using their sensitivity to interparticle spacing, dielectric environment, particle size and arrangement.^[42]

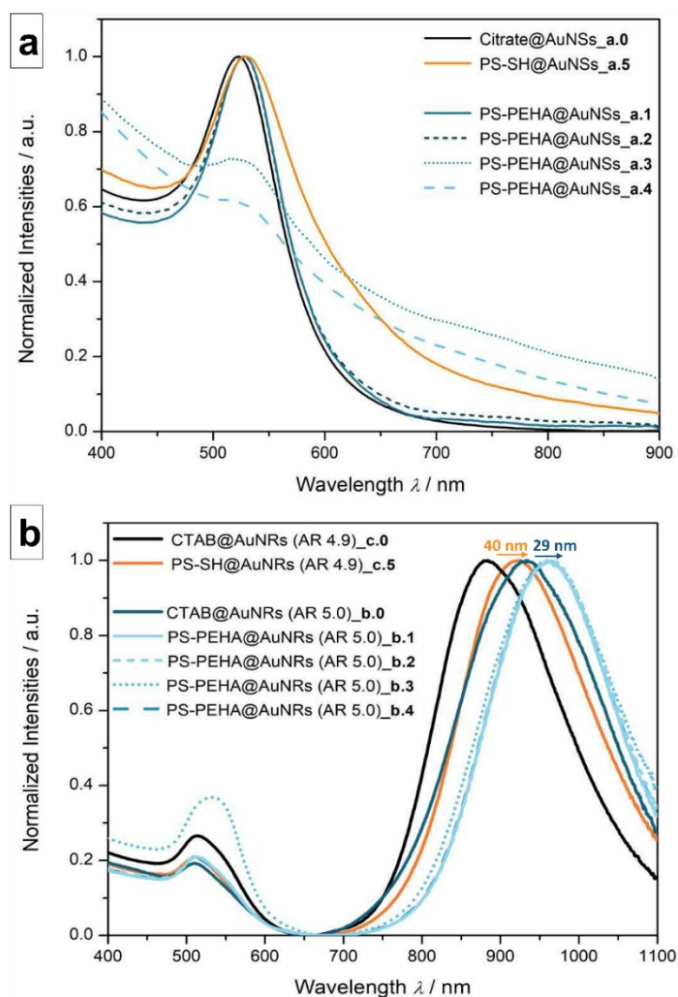


Figure 3-7: Normalized UV-Vis-NIR spectra of a AuNSs and b AuNRs pre and post ligand exchanges with PEHA and SH-functionalized PS. Due to the change in the dielectric environment, red shifts in the transverse and longitudinal plasmons of AuNPs are observed.

As depicted in Figure 3-7 a, the transverse LSPR peak for citrate-stabilized AuNSs appears at 522 nm and undergoes a slight shift to 527 nm after ligand exchange with PS-SH. Notably, a marginal broadening of the peak is evident for PS-SH@AuNSs and this broadening, along with the appearance of the characteristic Rayleigh λ^{-4} scattering, is evident upon exchange with PS-PEHA 3 and PS-PEHA 4, whereas no broadening of the LSPR peak is observed after ligand exchange with PS-PEHA 1 and PS-PEHA 2. All PS-PEHA ligands show a minor but detectable red shift to 535 nm, suggesting that the polymer ligand chains are tightly attached to the surface.

Additionally, the impact of the polymer attachment is distinctly noticeable for both sizes of cylindric nanoparticles, primarily demonstrated through the red shift observed in the longitudinal plasmon as shown in Figure 3-7 b. Specifically, a LSPR peak shift from 882 nm to 922 nm for AuNRs with AR~4.9 is observable and similarly, AuNRs with AR~5.0 exhibit a red shift from 933 nm to 962 nm. Considering AuNRs, differences are noticeable in the transverse plasmons and after the PS-PEHA 3 exchange, a shape change and a red-shift to 536 nm can be seen in both sizes of nanorods. This might be due to the higher polymer shell thickness at the ends of the anisotropic nanocrystals as seen in Figure 3-5 b.3.

3.4 Conclusion and Outlook

In conclusion, this study examines the attachment of polymer shells through ligand exchange methods. The stabilizing agents of the AuNSs and AuNRs were initially citrate and CTAB, respectively. These agents were subsequently replaced with polymer ligands, specifically PEHA- and SH-terminated PS. By systematically tuning the molecular weight of PS, the particle spacings for both spherical and cylindrical nanoparticles can be adjusted, eventually reaching plateau values at the highest molecular weights of the polymer. The UV-Vis-NIR spectra reveal significant red-shifts in the surface plasmon resonances due to polymer ligand binding on the surfaces of spherical and lateral surfaces of rod-like AuNPs. These results, together with TEM studies, suggest that PS-PEHA preferentially binds to the lateral surface rather than the tips of the nanorods, thereby stabilizing AuNRs against morphological changes. Hence, our findings suggest that a more moderate and therefore flexible binding to Au surface, as well

as the attachment concentrated in the center of AuNRs, is recommended for ligand exchange processes. The observed differences in polymer ligand attachment may provide insight into current challenges, such as the inconsistency between translational and rotational diffusion coefficients for thermoresponsive PNIPAM ligands tethered to AuNRs.^[43] Moreover, the results of this study are expected to expand the possibilities of using other functional group-terminated polymers as polymer ligands and hold promise for the development of new 2-D and 3-D assembly materials.

After successful exchange with the polymer ligand PS-PEHA, the next step involves the potential use of PS-PEHA directly as a stabilizing ligand for both spherical and non-spherical AuNPs. This perspective will be further discussed in the following Chapter 4. In particular, with respect to the two-step synthesis of anisotropic nanocrystals, both the seed and growth solutions can be directly stabilized with the polymer ligand, allowing the comparison of the sizes and morphologies of the resulting AuNPs with those already described in the literature. Here, the grafting densities of the polymer ligands on the Au surfaces are to be determined using thermogravimetric analysis.

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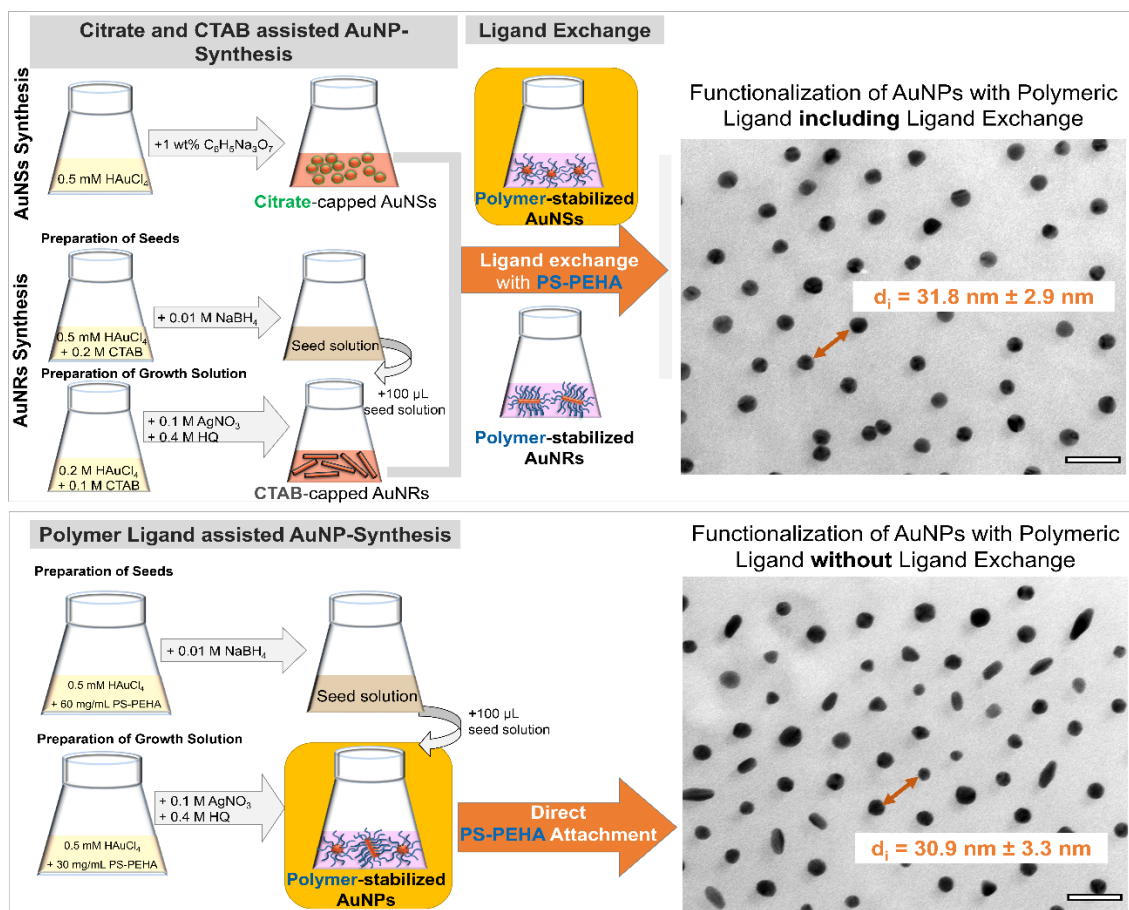
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4 STUDY OF THE STABILIZATION AND GROWTH OF SPHERICAL AND ELLIPSOIDAL AUNPs BY POLYMER COATING



Abstract

The integration of nanoparticles with tunable interparticle distances *via* polymer shells presents new opportunities for functional material design and is a key area of current research. This study explores the attachment of an amino-functionalized polymer to nanosized gold nanocrystals to form Au nanocomposites. Spherical and ellipsoidal nanoparticles were synthesized using the Ag-assisted seeded-growth method. Specifically, pentaethylenehexamine-functionalized polystyrene (PS-PEHA) with a molecular weight of 34.8 kg · mol⁻¹ was used as a capping agent, replacing the conventional short-chain cetyltrimethylammonium bromide (CTAB). The primary goal of this approach is to reduce the synthesis time of Au nanocomposites while preserving the desired interparticle spacing, thereby eliminating the need for additional surface

modifications and minimizing the risk of altering shape and size stability. The nanocomposites were analyzed *via* transmission electron microscopy (TEM) and UV-Vis-NIR and compared to conventionally ligand-exchanged AuNPs. The results demonstrate that interparticle distances between CTAB-capped AuNPs are comparable for both PS-PEHA post-modified AuNPs and directly synthesized PS-PEHA@AuNPs, indicating equally effective polymer attachment in both cases. Additionally, this halide-free synthesis pathway facilitates the study of the effects of long-chain polymer ligands and silver ions on gold nanoparticle (AuNP) growth. A growth model for anisotropic gold nanoparticles in the presence of polymer ligands is proposed, with early growth stages examined to enhance understanding of nanocomposite assembly and inform the design of advanced nanocomposite materials.

4.1 Introduction

The study of AuNPs and their use in the fabrication of functional nanocomposite materials continues to be an exciting and diverse area of research. Anisotropic AuNPs possess the capability to absorb and scatter light in the near-infrared region, a property that is particularly dependent on their aspect ratio.^[1] Consequently, there is a fundamental interest in comprehending their stabilization mechanisms during the nucleation and growth phases, as well as in developing shorter synthesis routes that incorporate the desired surface functionalization and assembly.^[2,3] In order to design the surface of the NPs in favor of an improved colloidal stability, compatibility and functionality, polymer grafting is a suitable method. By preparing Au nanocomposites with a gold core on the inside and a polymer shell on the outside, the arrangement and interparticle distance can be modified to influence the optical and plasmonic performance of AuNPs.^[4] Spherical and anisotropic NPs with a polymer coating offer exciting applications in recently discussed areas such as surface-enhanced spectroscopy and sensing.^[5]

Au nanocomposite syntheses are mainly based on AuNP synthesis routes, which generally involve the use of gold acid, reducing agents, silver nitrate in the case of anisotropic nanocrystals and the addition of capping agents of organic or inorganic nature^[6,7], whose influence on morphology and size of NPs are widely discussed.^[8,9,10]

The growth mechanisms of nanoparticles, particularly anisotropic ones, are typically described by adjusting the conditions of the reagents. In the well-known seed-mediated synthesis of AuNRs, CTAB is commonly used as a stabilizing agent, while Ag^+ ions act as symmetry-breaking agents.^[11] For example, the stabilizing effect of CTAB against oxidation of a silver layer on the Au surface^[12], the formation of a CTA-Ag-Br complex and the order of addition of reagents^[13] as well as the need for a dense stabilization layer consisting of CTA^+ and Br^- ^[14], are considered essential for a well pronounced anisotropic growth. On the other hand, the need for bromide ions for anisotropic growth is also a matter of controversy^[15] and little is known about alternative Br-free methods. Furthermore, discussions on NP growth are mainly based on time-dependent analyses using spectroscopy, scattering methods as well as computational modelling^[16], as it is challenging to arrest the growth process and analyze the state of particle growth using imaging techniques. The key challenge is to optically visualize the early stages of anisotropic growth without procedures such as further addition of arresting sulfide^[17] or thiolated^[18] ligands to understand the initial adsorption of the primary arrangement of surfactants on the Au surface.

To extend functionality, AUNPs are typically post-modified *via* ligand exchange to form Au nanocomposites. This process is preferred for grafting various functional polymer ligands through the partial exchange of initial ligands such as citrate or CTAB and for the transfer of nanocrystals to different media.^[19] A wide variety of SH-terminated polymers such as poly(methyl methacrylate) (PMMA), poly(ethylene glycol) (PEG) and polystyrene (PS) are used in ligand modification techniques to investigate, for example, capping density^[20], catalytic properties^[21], electrical conductivity^[22] and the ability to regioselectivity modify the NP surface^[23]. However, subsequent modifications are time-consuming and may compromise shape stability, particularly for anisotropic AUNPs due to potential loss of the stabilization layer during purification. Therefore, a shorter and more robust synthesis of nanoparticles with the desired surface functionality is preferred.

One approach to a shortened Au nanocomposite synthesis is demonstrated in a study by Wang *et al.* Both CTAB- and citrate-stabilized seeds are added to a growth solution containing PS-SH, PMMA-SH, PEG-SH and SH-terminated poly(2-

(dimethylamino)ethyl methacrylate) (PDMAEMA-SH) and used as seeds in a re-growth synthesis step containing an additional amount of HAuCl_4 to produce different sized polymer-attached AuNPs.^[24] Nevertheless, open questions remain regarding whether seeds can be directly polymer-stabilized and if the distance between directly polymer-stabilized seeds and the polymer-stabilized growth solution results in similar grafting behavior and interparticle distance as with ligand exchange.

This work addresses three key points, primarily through the presentation of an AuNP synthesis derived from the "classical" seed-mediated growth approach. First, a halide-free synthesis method is proposed, where both seed and growth solutions are stabilized with multidentate amino-terminated PS ligands, resulting in polymer-coated seeds and subsequently spherical and ellipsoidal AuNPs. Second, this study compares conventionally grown anisotropic AuNPs using CTAB surfactants with their subsequent ligand exchange to functionalized polymer versus direct polymer ligand attachment to the seed and growth solution, using TEM and UV-Vis-NIR analysis. A high molecular weight PS-PEHA ($34.8 \text{ kg} \cdot \text{mol}^{-1}$) was used in both approaches. Lastly, the polymer ligand serves as steric hindrance to study the early stages of anisotropic growth by TEM, eliminating the need for additional growth inhibitors. This method enables the study of nanoparticle growth in the presence of silver ions and the polymer stabilizer, free from the influence of bromide ions. Based on the observations, a growth model for anisotropic crystal formation in the presence of polymer ligands is proposed.

4.2 Experimental Part

4.2.1 Materials

For the seed-mediated growth syntheses of both spherical and ellipsoidal AuNPs, hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3 \text{ H}_2\text{O}$, Alfa Aesar), sodium borohydride (NaBH_4 , Sigma-Aldrich) and hydroquinone (HQ, Sigma-Aldrich) were utilized as received. Cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich) and silver nitrate (AgNO_3 , Sigma-Aldrich) were additionally used in the synthesis of anisotropic nanocrystals. The chemicals for the preparation of polymer stabilizing agents included hydroxyl-terminated polystyrene (PS-OH with $M_n \text{ PS-OH} = 33.3 \text{ kg} \cdot \text{mol}^{-1}$, Polymer Source, Inc.; PDI = 1.06), 1,1'-carbonyldiimidazole (CDI, Sigma-Aldrich, reagent grade),

pentaethylenhexamine (PEHA, Sigma-Aldrich, technical grade), chloroform (CHCl_3 , Sigma-Aldrich, anhydrous, $\geq 99\%$, contains amylenes as stabilizer), tetrahydrofuran (THF, Sigma-Aldrich, $\geq 99.9\%$, contains 250 ppm BHT as a stabilizer) as well as deuterated chloroform (CDCl_3 , Roth (99.8 atom %, stabilized with Ag) and were used without further purification steps.

4.2.2 Synthesis

CTAB-stabilized AuNR Synthesis. The protocol of Vigderman *et al.* was applied for the synthesis of AuNRs.^[6] The process of functionalizing PS-OH to PS-PEHA is detailed in Chapter 3.2.2. Initially, a mixture of 0.5 mM HAuCl_4 and 5 mL 0.2 M CTAB was stirred at 210 rcf for 10 min. Afterwards, 0.6 mL of ice-cold 0.01 M NaBH_4 was added to the mixture under vigorous stirring and the resulting seed solution was allowed to rest for 60 min. In parallel, growth solution was prepared by mixing 12.5 μL 0.2 M HAuCl_4 , 2.5 mL 0.1 M CTAB, 12.5 μL 0.1 M AgNO_3 and 125 μL of 0.4 M HQ and the solution was heated up to 35 °C. To initiate AuNR growth, 125 μL of seed solution was added to the growth solution and the final solution was centrifuged twice at 14500 rcf for 60 min.

Citrate-stabilized AuNS Synthesis. Spherical nanoparticles were synthesized following the procedures described by Turkevich *et al.*^[25] and Rauh *et al.*^[26]. A 500 mL solution containing $5 \cdot 10^{-4}$ M HAuCl_4 was heated until reaching a boiling point. At this stage, 25 mL of a hot aqueous solution, consisting of 1 wt.% sodium citrate dihydrate, was added while vigorously stirring. The solution was cooled slowly under stirring for 20 min. Following a reaction time of 20 min, the solution turned dark red and finally the solution was then allowed to cool under stirring.

Ligand Exchange. Following a modified synthesis protocol from Grzelczak *et al.*^[27], the redispersed AuNP solutions in Milli-Q water were then used for ligand exchange. Moreover, the polymer ligand PS-PEHA with a molecular weight of $34.8 \text{ kg} \cdot \text{mol}^{-1}$ was utilized. 1 mL AuNP dispersion was added to 10 mL THF solution. The solution was

sonicated for 15 min, centrifuged twice at 7120 rcf for 30 min and dispersed again in THF.

PS-PEHA stabilized NP Synthesis. For the preparation of both ellipsoidal and spherical nanocrystals, a modified version of the seed-mediated growth synthesis described above was used. For the seed solution, 0.5 mM HAuCl₄ and 1 mL of a 60 mg/mL PS-PEHA solution were stirred for 10 min at 210 rcf. After 120 μ L of 0.01 M NaBH₄ was added, the solution was stirred for further 2 min before being allowed to stand for 1 h. Then, 2.5 μ L of 0.2 M HAuCl₄, 2.5 μ L of 0.4 M HQ and 2.5 μ L of 0.1 M AgNO₃ were mixed with 0.5 μ L of 30 mg/mL PS-PEHA. Finally, the growth solution was supplemented with 125 μ L of the seed solution and the mixture was centrifuged twice for 30 min at 14500 rcf.

4.2.3 Characterization Methods

TEM. The Zeiss CEM902 (80 kV EFTEM with thermal tungsten cathode) and JEOL JEM-2200FS TEM microscopes (200 kV EFTEM with Schottky FEG) from Carl Zeiss Microscopy GmbH and JEOL GmbH were used to take TEM images.

UV-Vis-NIR. A Cary 5000 spectrophotometer (Agilent Technologies, wavelength range for 400 nm to 900 nm) was used to record UV-Vis-NIR absorbance spectra.

4.3 Results and Discussion

The synthesis methods including citrate, CTAB and alkanethiol as capping agents of the most established studies on AuNPs are based on those of Turkevich^[25], Brust and Schiffrin^[28] for spherical AuNPs whereas the Ag-assisted seed-induced growth method developed by Murphy *et al.*^[29] and Nikoobakht *et al.*^[11] is mainly used for the synthesis of AuNRs. Given the great interest in understanding the influence of capping agents especially of CTAB adsorption on the anisotropic growth of AuNPs, parameters such as the presence of additives^[30], but also the arrangement^[31,32], adsorption on specific NP crystal facets and their chemical nature, such as the presence of halides^[14], are discussed in scientific works. Molecular dynamics simulation reveals that the packing density of CTAB is higher at the (110) and (100) faces than at the tip of the AuNRs, the (111) face.^[32] It is therefore assumed that the ends of the nanorods, which have the highest curvature and high-energy surface, are accessible for deposition of further Au ions as well as further interaction with functional groups, such as SH groups. The high affinity of the SH groups to the gold surface^[33] and especially to the tips of AuNRs^[34] is exploited in most polymer functionalization methods to provide the AuNPs with SH-terminated polymers in a further step, e.g. by ligand exchange^[24,35]. Direct stabilization of AuNP with SH-terminated polymers^[36] as well as block copolymers^[37] and homopolymers^[38] with amino groups in so-called one-pot syntheses have been described, but are more restricted to spherical AuNP. Here, both seed and growth solutions were stabilized by the use of PEHA-terminated PS with $M_n = 34.8 \text{ kg} \cdot \text{mol}^{-1}$ and by modifying the synthesis protocol of Vigderman *et al.*^[6] (see Figure 4-1). First, a seed solution was prepared by mixing a solution containing hydrogen tetrachloroaurate hydrate with PS-PEHA as a stabilizer and then adding the reducing agent NaBH_4 . The growth solution was then prepared by similarly stabilizing the gold solution with the polymer ligand and adding silver ions in combination with a stronger reducing agent, hydroquinone, to promote anisotropic growth. Finally, 100 μL seed solution was added to the growth solution.

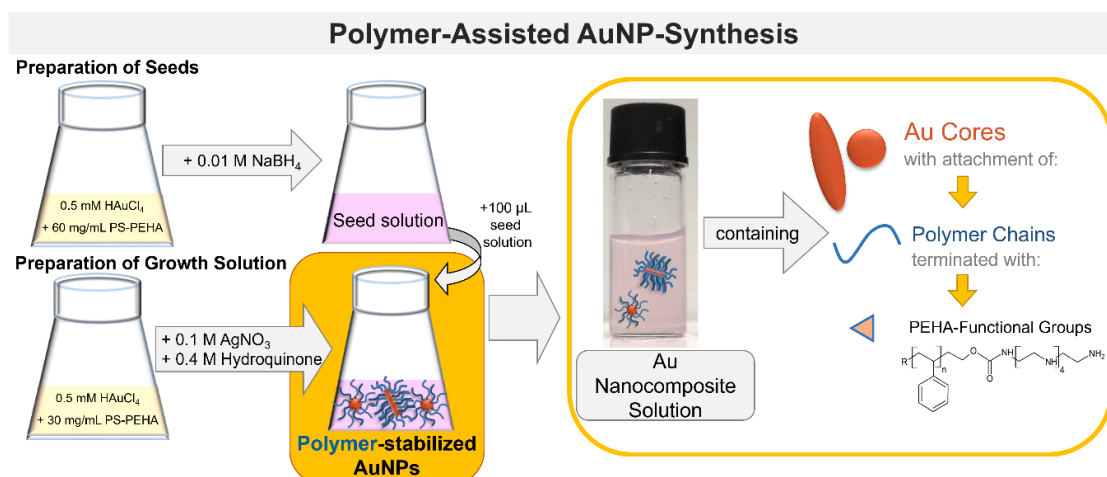


Figure 4-1: Schematic illustration of AuNP-synthesis using the polymer-based stabilizing agent PS-PEHA.

4.3.1 Investigation of the Polymer-Assisted AuNP Synthesis

To investigate the influence of the polymer capping agent on size and shape of seeds, 4 μ L of the pinkish turbid seed solution was applied to a TEM grid and the size of seeds was measured (see Figure 4-2).

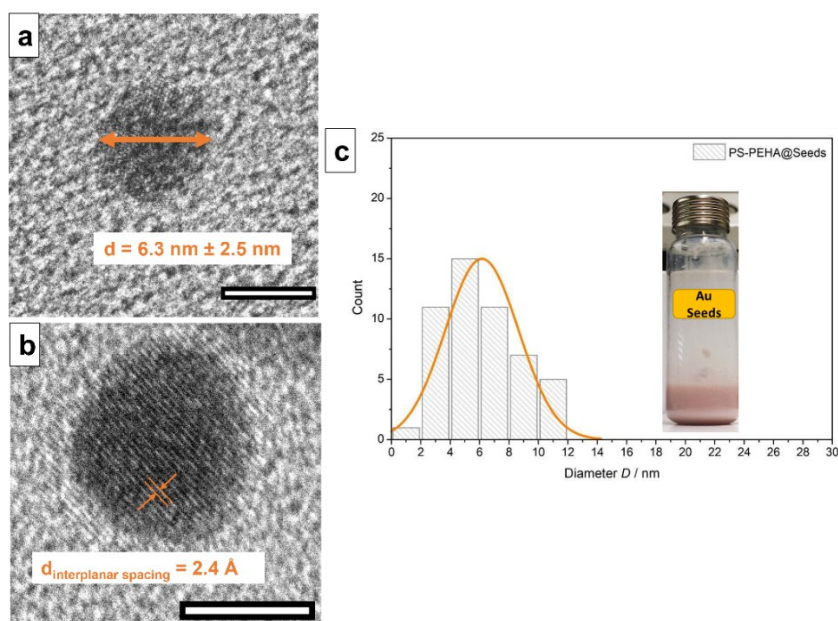


Figure 4-2: a TEM image of a single PS-PEHA-stabilized seed and b higher magnification TEM image showing the single crystalline structure of the Au seed. Histogram in c shows the size distribution of the seeds' diameter with integrated photograph of the pinkish turbid Au seed solution. Scale bars correspond to 5 nm.

The measurement of 50 seed particles resulted in a mean diameter of $6.3 \text{ nm} \pm 2.5 \text{ nm}$ (see Figure 4-2 a). Compared to the nucleus size of $< 4 \text{ nm}$ from the unmodified synthesis recipe from the work of Nikoobakht *et al.*^[11] this results in seeds with slightly larger diameters. Determining the size of the nucleus is crucial since the aspect ratio of anisotropic NPs is known to be affected by the size of the nucleus together with its charge and the reducing agents used in the synthesis. An increase in the nucleus size and consequently a reduction of the surface energy and thus a lower reactivity can lead to a reduction in the aspect ratio, as has been shown in particular for various CTAB-stabilized nucleus sizes.^[39] In addition, the type of capping agent has an influence on the interaction with the surfaces of the seeds to which it is adsorbed or bound. Here, the stabilization of the gold nanoseeds with PS-PEHA reveals a well-defined single-crystalline structure, as shown by the lattice planes in Figure 4-2 b with an interplanar spacing (lattice parameter) of $2.4 \text{ \AA}$. In comparison, the seeds are reported to have a single-crystalline structure in the presence of CTAB^[9], whereas a multiply twinned structure is observed in the presence of citrate^[40] and PVP ligands^[10]. After the Au seeds were prepared and characterized, the seed solution was added to the growth solution and the grown AuNPs were analyzed.

4.3.2 Comparison between Direct Polymer Stabilization and Ligand Exchange

The ligand exchange process is a modern approach for the post-modification of nanocomposites. However, this process is both time-consuming and critical for the stability of the nanoparticles. Therefore, direct stabilization is compared to ligand exchange of AuNPs using a polymer ligand. First, the direct polymer-coated PS-PEHA@AuNPs were examined by TEM (see Figure 4-3).

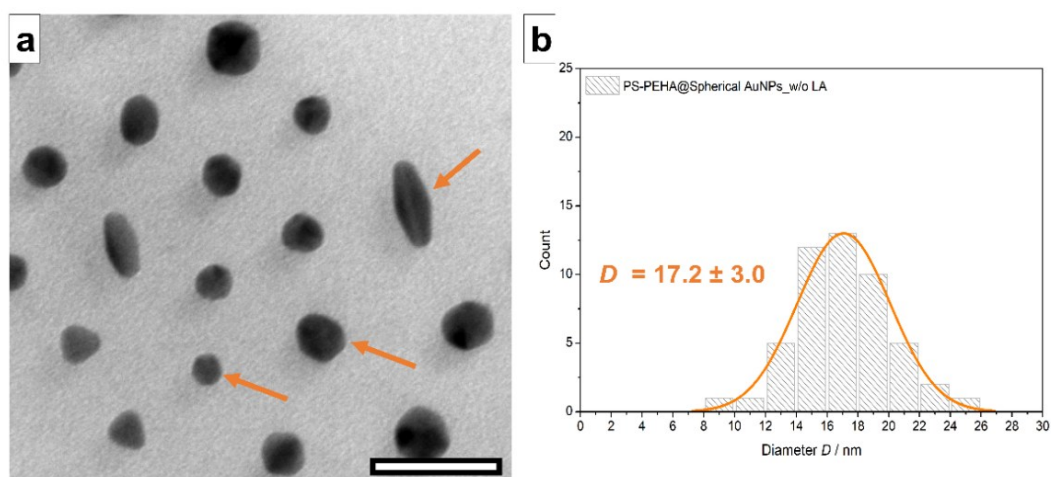


Figure 4-3: TEM image in a shows grown PS-PEHA-stabilized AuNPs with differences in size and morphology (scale bar corresponds to 50 nm). The histogram and the average sphere diameter are depicted in b.

Figure 4-3 a illustrates that the polymer-assisted synthesis resulted in the formation of predominantly spherical AuNPs. Despite their different sizes, it can be demonstrated that spherical AuNPs with a size of $17.2 \text{ nm} \pm 3.0 \text{ nm}$ (see Figure 4-3 b) can be produced using the polymer-stabilized method, similar to the average diameter of $17.9 \text{ nm} \pm 1.5 \text{ nm}$ synthesized with the citrate ligand (refer to Chapter 3.3.1 Figure 3-2 a.0). A smaller number of anisotropic, ellipsoidal AuNPs are also clearly observable. However, they appear shorter and more irregular than those observed with the CTAB ligand (refer to Figure 3-2 b.0 and c.0). The appearance of small or not fully grown nanocrystals may be due to the fact that the polymer ligand already adheres to the gold surface and thus acts as a “barrier” for the uptake of further gold atoms from the growth solution. The chance that already growing particles will continue to grow is higher, indicating a phenomenon similar to a bimodal growth. However, to address the question of whether direct coating with a polymer ligand leads to comparable results in terms of interparticle distance as post-modification procedures such as ligand exchange, three approaches were compared: Direct polymer-stabilized AuNPs as well as AuNRs and AuNSs that were subjected to an exchange of their initial capping agents with PS-PEHA with $M_n = 34.8 \text{ kg} \cdot \text{mol}^{-1}$ (see Figure 4-4 a-c). Non-spherical AuNPs used were of length $L = 63.5 \text{ nm} \pm 6.3 \text{ nm}$ and width $W = 12.6 \text{ nm} \pm 0.8 \text{ nm}$.

Citrate-stabilized spheres with a diameter of $17.9 \text{ nm} \pm 1.5 \text{ nm}$ were chosen as previously described in chapter 3.3.1 (Figure 3-2 a.0).

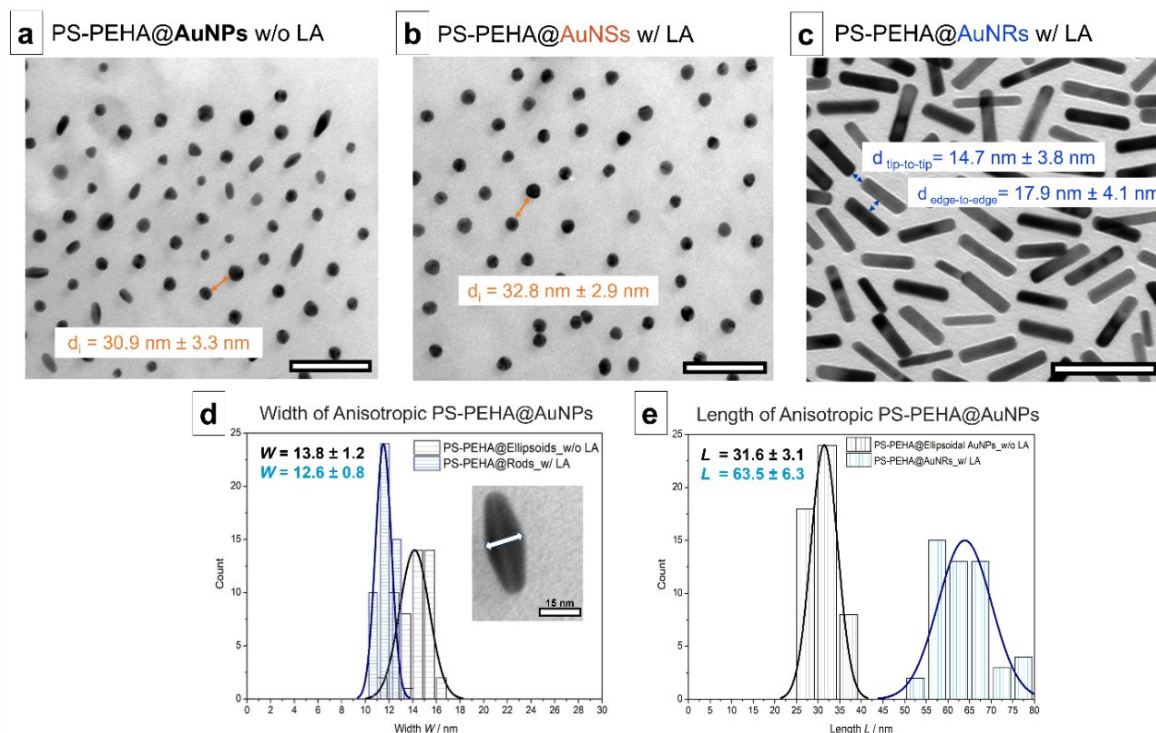


Figure 4-4: TEM images show different interparticle spacings for a PS-PEHA@AuNPs without ligand exchange, b PS-PEHA@AuNRs and c PS-PEHA@AuNSs including ligand exchange (scale bars correspond to 100 nm). Histograms show the d width and e length of the anisotropic PS-PEHA@AuNPs without and including ligand exchange.

AuNPs whose seed and growth solutions were both supported by a polymer ligand exhibit an interparticle distance of $30.9 \text{ nm} \pm 3.3 \text{ nm}$. This value agrees well with the distance obtained for PS-PEHA@AuNSs after ligand exchange and indicates comparable binding of the ligand to the Au nanoparticle surface. There are closely positioned particles in the case of ligand-exchanged AuNSs, which may indicate incomplete PS-PEHA covering. Therefore, direct polymer stabilization could be a good alternative to achieve uniform coating and steric separation of AuNPs. The interparticle distances of the AuNPs after ligand exchange are only comparable to a limited extent. The tip-to-tip and edge-to-edge distances of $14.7 \text{ nm} \pm 3.8 \text{ nm}$ and $17.9 \text{ nm} \pm 4.1 \text{ nm}$ are significantly smaller than those of the directly polymer-stabilized AuNPs. Nevertheless, it was

not possible to produce fully grown nanorods using the polymer-assisted method, thus a direct comparison of the interparticle distances is difficult.

However, it is possible to compare the dimensions of the anisotropic AuNPs with and without ligand exchange. For this purpose, the length and width distributions of 50 directly polymer-stabilized and 50 modified anisotropic AuNPs were measured and summarized in Figure 4-4 d and e. The ellipsoidal AuNPs' widths were measured at their largest position, *i.e.*, in the center. Comparable values in terms of width were obtained in both cases: $13.8 \text{ nm} \pm 1.2 \text{ nm}$ for directly polymer-stabilized and $12.6 \text{ nm} \pm 0.8 \text{ nm}$ for ligand exchanged AuNPs. This similarity can be attributed to the same synthesis and reaction conditions. After initiating the growth process with seed addition and self-nucleation, some nanocrystals switch to anisotropic growth once they reach a size of approximately 14 nm. This finding is especially relevant as in the case of the directly stabilized ellipsoidal AuNPs it is shown that this point can also be reached in the presence of a polymer ligand without the presence of halides in the reaction solution, which among others are considered necessary in this step.^[41] Chapter 4.3.3 provides a more detailed discussion of anisotropic growth. Moreover, differences are evident in the length of the anisotropic nanocrystals. The length is $63.5 \text{ nm} \pm 6.3 \text{ nm}$ for the fully grown AuNRs after ligand exchange and only half that, namely $31.6 \text{ nm} \pm 3.1 \text{ nm}$, for the directly stabilized ellipsoids. As already mentioned, this can be due to the polymer ligand acting as a barrier, limiting gold ion transport after attachment to the nanoparticle surface. This finding shows a difference between polymer-assisted growth and, for instance, the proposed “zippering”^[42] mechanism, where CTAB with longer hydrocarbon chains resulted in longer AuNRs through van der Waals stabilization. Long polymer chains may not promote anisotropic growth to the same extent and show limitations.^[42]

The optical properties of AuNPs are determined by their shape and size. To measure these properties, the PS-PEHA@AuNPs were analyzed *via* UV-Vis-NIR (see Figure 4-5).

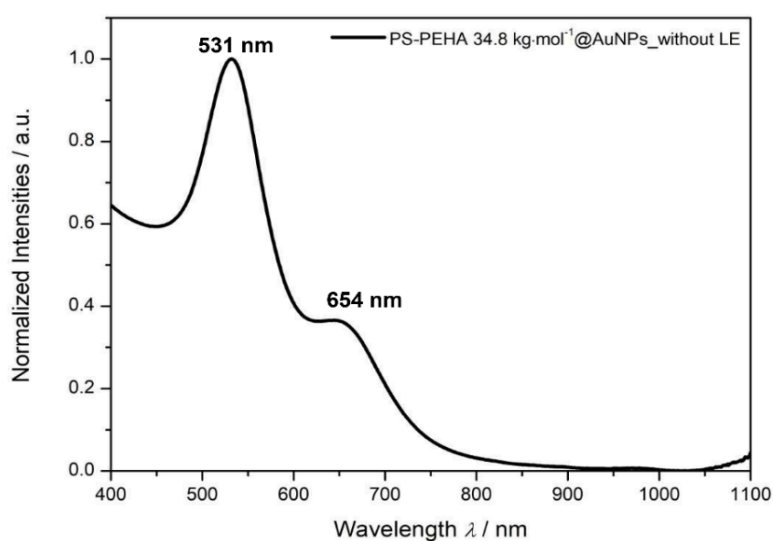


Figure 4-5: Normalized UV-Vis NIR absorption spectra of AuNPs directly stabilized with the polymer ligand PS-PEHA.

The measurement shows a well pronounced transverse plasmon peak at 531 nm, which is in line with expectations as predominantly spherical AuNPs were formed. Compared to the citrate spheres and their red shift from 522 nm to 535 nm after the exchange with PS-PEHA from Chapter 3.3.3, this could indicate that the direct AuNPs have a similarly good adhesion of the polymer chains as after the ligand exchange process. Moreover, it is known that the position of the LSPR peak changes proportionally to the length of the nanorods. As the aspect ratio of AuNRs decreases, the LSPR peak shifts to shorter wavelengths, resulting in a blue-shift in the spectrum.^[11] The LSPR peak of ellipsoidal AuNPs is positioned at 654 nm, which may be attributed to their short length. In addition, it can be seen that the peak is weakly pronounced. This can be due to the early stages of AuNP growth, which is also supported by the TEM images (see Figure 4-3 a). Since the nanocrystals may be in the initial stages of growth, the chosen polymer ligand may be a suitable tool to study the different growth of cylindric Au nanocrystals in more detail.

4.3.3 Study of the Polymer-Assisted Anisotropic Growth

In view of the presented results, there is the demand to explain the mechanism behind the formation of anisotropic AuNPs. Understanding nanoparticle growth dynamics is

essential for refining synthesis parameters, increasing stability and achieving better uniformity control, but is not yet fully understood. The starting point of anisotropic growth and the associated moment of symmetry breaking are considered crucial, with the presence of silver ions and the ratio of $[\text{HAuCl}_4]$ to $[\text{AgNO}_3]$ being essential.^[43] From previous findings on the most commonly used surfactant CTAB, it can be deduced that the symmetry breaking point depends on three key parameters: Directional growth of AuNRs is achieved by the attachment of halides and surfactants and the underpotential deposition of Ag^+ .^[32,41,44]

Park *et al.* suggested a growth model for cylindric AuNPs in the presence of CTAB, silver nitrate and an 'arresting' ligand SH-PS with a molecular weight of $53 \text{ kg} \cdot \text{mol}^{-1}$. Hereby, the AuNPs go through a total of five phases: 1) Isotropic growth of spherical nanocrystals, 2) anisotropic growth, 3) heterogeneous growth of nanorods, 4) equilibrated growth of the sides and finally, 5) achievement of the stable state. The growth was stopped by solvent transfer and ligand exchange for different periods of time.^[18] Since no halides were present here, the explanation of the anisotropic growth is limited to the role of the Ag^+ ions and the surfactant. The individual phases of PS-PEHA-assisted anisotropic growth are compared with the phases in the presence of PS-SH. For this purpose, five different polymer-coated AuNPs were selected, which are assumed to be at different early growth stages (see Figure 4-6).

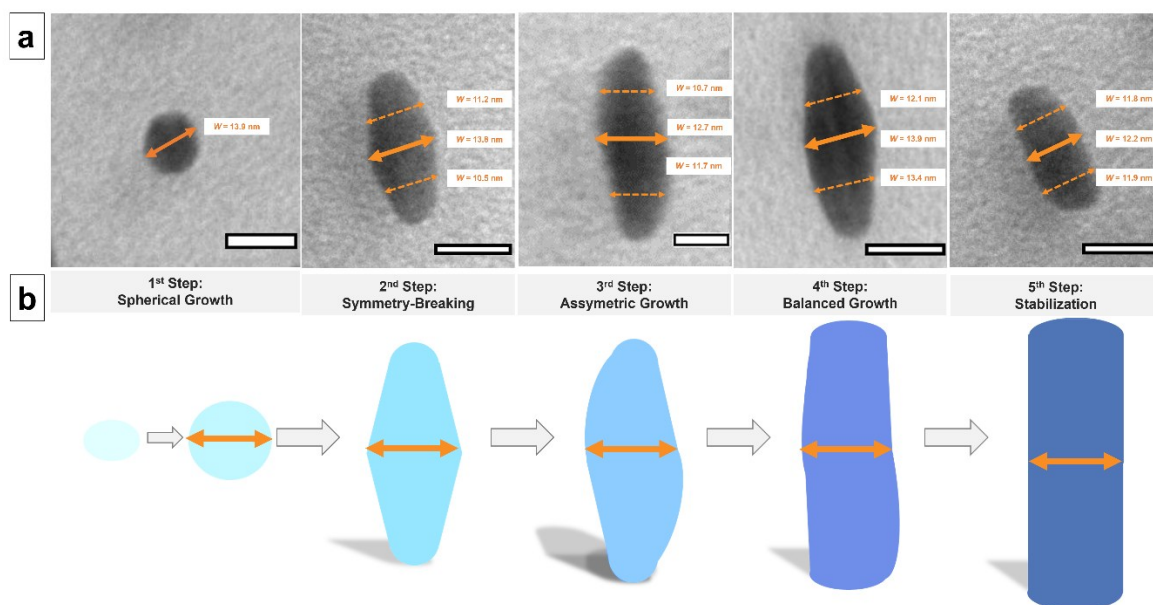


Figure 4-6: a TEM images of different growth stages of AuNPs, whose widest point (center) and two widths near the tips were measured (scale bars correspond to 15 nm). b Schematic representation of the sequential steps in the anisotropic growth of polymer-stabilized AuNPs derived from TEM investigations.

In the first phase, it can be seen that after the addition of the seed solution to the growth solution, an isotropic growth initially takes place, as overall larger spherical particles are formed compared to the seed diameter of ~ 6 nm. As already mentioned, the diameter of the ellipsoidal forms is about 14 nm, from which further growth could continue. In contrast, the arresting method with PS-SH produces isotropically grown nanoparticles of up to 6 nm, *i.e.* significantly smaller particles, from approx. 2 nm large seeds.^[18] In the second growth phase, both methods exhibit one-dimensional length growth after the symmetry break. The width in the center of the AuNPs remains relatively constant throughout the different phases in this study. This supports the hypothesis that a silver monolayer could be formed on the gold surface, inhibiting growth at certain facets.^[45] In contrast, the PS-SH synthesis method initially exhibits slower growth in width than in length, but this effect is reversed over time.^[18] It is also noteworthy that, in contrast to the needle-like ends described in the literature, in this study round ends are formed in the presence of silver ions.^[46] In the third stage, slightly asymmetric growth is observed in addition to the anisotropic growth. The width of the

tips remains constant. Unlike the PS-SH^[18]- or Na₂S^[17]-arresting methods, here, the nanocrystal tips do not adopt a dumbbell shape. The formation of the dumbbell shapes may be due to the preferential binding of thiol groups to the ends of the nanorods.^[34,47] Instead, the sides grow asymmetrically from both halves of the middle of the nanocrystals. In the fourth step, both the PEHA- and the SH-terminated PS exhibit balanced growth. The difference between the methods using PS-PEHA or PS-SH as polymer ligand is that in the former, the compensation or balanced growth occurs from the center outwards, while in the latter, it occurs in reverse.^[18] Finally, in the fifth phase, it is suggested that the stability phase of the nanocylinders is achieved. The polymer ligand PS-PEHA shows moderate binding affinity to gold surfaces and likely adheres preferentially to the lateral sides of anisotropic AuNPs, similar to CTAB.^[32] Therefore, it can be hypothesized that once the optimal synthesis protocol for polymer-assisted AuNPs is established, further growth at the ends of the nanocrystals can be achieved.

4.4 Conclusion

In summary, it has been demonstrated that it is possible to produce gold nanoparticles in a polymer-assisted seed-mediated growth synthesis by using a polymer ligand instead of a conventional low-molecular-weight ligand such as CTAB or citrate. The study showed that spherical seeds grow to an average diameter of approximately 6 nm in the presence of amino-terminated PS with a molecular weight of 34.8 kg · mol⁻¹. After adding the seed solution to the Ag-assisted growth solution, spherical and ellipsoidal morphologies were observed. The spherical AuNPs stabilized with a polymer ligand showed diameters that were similar to those of the AuNSs stabilized with citrate. Additionally, the interparticle distances for both ligand-exchanged AuNPs and directly polymer-stabilized AuNPs are comparable. It can thus be assumed that the polymer adheres in a similar manner in both methods and that direct polymer attachment represents a valid alternative to ligand exchanges. However, differences were found in the preparation of polymer-stabilized anisotropic AuNPs. In the case of direct polymer stabilization, fully grown AuNPs could not be produced. Therefore, a direct comparison with the post-modified AuNRs regarding the interparticle spacing was not possible. In comparison to the CTAB-stabilized AuNPs, which exhibit comparable widths to the

directly polymer-stabilized AuNPs, the polymer-based AuNPs are observed to be of a shorter length. This effect can be attributed to the long polymer chains and the steric barrier, whereby further gold ion deposition is prevented. However, this finding led to the assumption that the AuNPs might be present in different stages of growth. A comparison with fully grown and ligand depleted AuNRs described in the literature was attempted. Overall, the similarities and differences between AuNPs undergoing ligand exchange processes and direct polymer stabilization show that the stabilization ability of the capping agents is strongly correlated with the type and amount of the chemicals added. The anisotropic growth of the nanocrystals is assumed to be dynamic and adaptive within the first few minutes. Overall, the findings of this study contribute to the understanding of the direct attachment of polymer ligands to AuNPs and provide alternatives to previous synthesis protocols for Au nanocomposites.

4.5 Outlook

After the primary question of the possibility of achieving similar interparticle distances by direct polymer stabilization of AuNPs in comparison to the ligand exchange method could be answered positively, points remain which require an improvement or extension of the synthesis. Particularly for polymer-stabilized AuNPs, the optimal balance of chemicals must be systematically analyzed. This includes the correct adjustment of the amount of silver ions, the concentration of chloroauric acid as well as the surfactant. For the latter, the next step can be a systematic study of the relationship between the molecular weight and the anisotropic structure of the nanoparticles. This can be analyzed in more detail by an *in-situ* UV-Vis-NIR study, similar to a study of CTAB-assisted nanorod growth (see Figure 4-7). The longitudinal LSPR peaks that occur after the first few minutes can be compared to those of the conventionally CTAB-stabilized AuNRs.

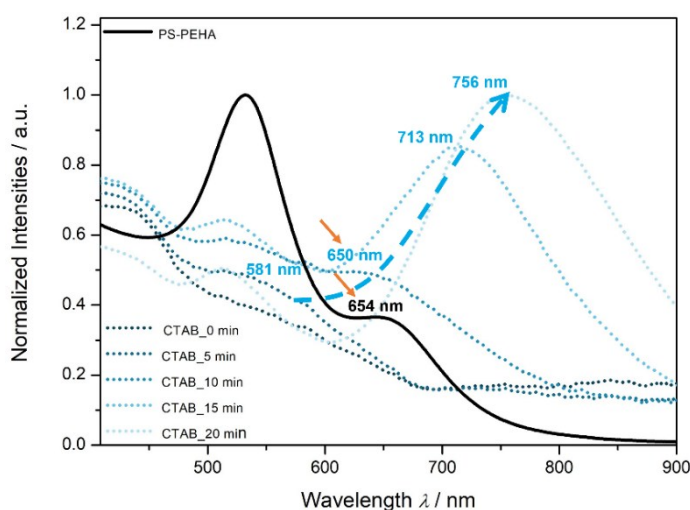


Figure 4-7: Normalized *in-situ* UV-Vis-NIR absorption spectra of CTAB@AuNRs with the position of the longitudinal peaks highlighted after every 5 min and of PS-PEHA@AuNPs with the position of the longitudinal LSPR peak at 654 nm, which may indicate the onset of anisotropic growth, compared to that at 650 nm after 10 min growth of CTAB-stabilized AuNRs.

By using shorter polymer chains, it can also be investigated whether seed diameters < 6 nm can be achieved to achieve a higher seed reactivity which can result in longer nanorods. In order to be able to identify the crystal structure of the seeds and the grown AuNPs, X-ray diffraction (XRD) and high-resolution TEM studies are helpful. These can be complemented by small-angle X-ray scattering (SAXS), similar to the work of Seibt *et al.* [3], since here the transition from spherical to ellipsoidal to rod-like AuNPs can be studied in a time-resolved manner. With all the data collected, an attempt can be made to carry out computer modeling similar to the work of Edgar *et al.* [48], only this time not with Cryo-REM, but with polymer ligands, in order to "freeze" the various early growth stages of the nanoparticles, in order to be able to predict the growth under defined conditions.

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93

5.1 Introduction

The miniaturization of electronic devices—reducing size while maintaining or enhancing functionality—offers benefits such as lower weight, power consumption and material costs, but also poses challenges like overheating and reduced electrochemical reliability. In automotive electronics, ensuring the robustness of electronic control units (ECUs) and printed circuit board assemblies (PCBAs) is crucial to meet the high safety standards of increased vehicle electrification and automation.^[1,2] Critical components of PCBs including connectors, conductive paths and solder joints often experience prolonged exposure to mechanical stress, corrosive environments and fluctuating humidity as well as temperature levels.^[3] These conditions facilitate corrosion, potentially compromising functionality or causing failure, emphasizing the necessity of validating and ensuring PCB reliability.^[4]

The reliability of PCBAs is influenced not only by external factors but also by design parameters such as layer thickness, conductor and pitch spacing, material selection, and cleanliness.^[5] Residues from improper storage, packaging and process-related contamination significantly affect PCB reliability, particularly soldering flux residues produced during PCB assembly.^[6] Previously, PCB surfaces were cleaned after soldering to remove residual contamination. Modern assembly processes primarily use solder pastes including "no-clean" flux systems, eliminating the need for post-cleaning procedures. However, process variations and short exposure times may leave flux residues partially undecomposed, potentially containing ionic or (non-) ionic impurities, such as weak organic acids (WOAs) as activators or halogens (e.g. chloride and bromide).^[7,8] Flux residues, in combination with electric fields and humidity, significantly increase the risk of metal corrosion. Especially their ionic nature favor interactions with humidity, leading to water film formation on PCBAs. Higher residue concentration, hygroscopicity and dissociation constants enhance electrolyte conductivity, reducing electrochemical robustness.^[8] Thus, the interaction between contamination and humidity is a critical factor in corrosion risk for electronics.

The application of polymers as sealing, potting or conformal coating materials is an effective strategy to mitigate corrosion and improve PCBA humidity resistance. Materials like epoxies, acrylics, parylenes, polyurethanes, fluoropolymers, synthetic rubber

and silicones are favored for their chemical inertness, thermal stability, high insulation and ease of application, serving as barriers to ionic movement and water absorption.^[9] In this context, PDMS is a widely used organosilicon polymer coating material known for its hydrophobic nature, thermal stability and curing versatility.^[1] To enhance its mechanical, adhesive, water-repellent and rheological properties, polymers like epoxy resin and polyurethane, composites (e.g., SiO₂, CaCO₃, TiO₂, carbon nanotubes) and functionalizing agents such as short-chain silanes are often incorporated.^[10] For example, it was shown that adding epoxy resin *via* coupling agents and modifying silica with 3-aminopropyl)triethoxysilane (APTES) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane enhances mechanical strength and produces superhydrophobic silicone-based composite coating (WCA) > 150 °).^[11] Moreover, SIR measurements are usually performed to evaluate the electrochemical and insulating properties^[12] of PDMS coatings. Zhan *et al.* showed that silicone coatings prevent SIR degradation and ECM under temperature, humidity, and voltage stress but promote dendritic growth at the coating-substrate interface in the presence of no-clean flux residues.^[13] In a recent study, Li *et al.* found that the presence of flux residues, poor adhesion and delamination of conformal coatings degrade their insulation capabilities.^[14] However, while flux residues in no-clean solder pastes are well known to increase ECM risk^[15], the interactions between different silicone coating components and flux residues as well as their impact on moisture, surface insulation and corrosion resistance, remain poorly understood.

This study systematically investigates the effect of PDMS-based coatings incorporating fumed silica and the functionalizing agents GPS and MPS on the electrochemical robustness of no-clean soldered PCBs using SIR measurements. Test structures with comb patterns, featuring 200 µm and 300 µm Cu-Cu spacing on FR-4 laminates, were used to evaluate the influence of conductor spacing. The SIR tests were conducted under conditions of 1000 h at 100 V, simulating near-dew-point environments at 65 °C and 93 % *R.H.* Additionally, light microscopy and SEM/EDX analyses were performed to identify corrosion products and determine their elemental composition. Finally, to assess the impact of humidity load, FT-IR, WCA, GC-MS, and gravimetric investigations were carried out.

5.2 Experimental Part

5.2.1 Materials

An UV-curable, two-component PDMS was used in a 10:1 ratio (component A: SEMI-COSIL® 912 and component B: ELASTOSIL® CAT PT, Wacker Chemie AG). The density of the cured base material PDMS at 23 °C is typically around $0.97 \text{ g} \cdot \text{cm}^{-3}$.^[16] In addition, both fumed hydrophobic fumed silica – abbreviated as H2 below – and highly hydrophobic fumed silica – abbreviated as H3 below – were used (HDK® H20 and HDK® H2000, Wacker Chemie AG). Furthermore, glycidoxy- and methacrylic-functionalized propyltrimethoxysilanes were utilized as functionalizing agents (GENIOSIL® GPTM and GENIOSIL® MPTM, Wacker Chemie AG).^[17,18] The summary of the components used for PDMS-based coatings is depicted in Table 5-1.

Table 5-1: Overview of the components, including their properties and quantities, used for formulations consisting of functionalized silica dispersed in PDMS.^[16–20]

Chemical	Abbreviation	Mass Fraction / wt. %	Density ^[16–20] / $\text{g} \cdot \text{cm}^{-3}$	Residual silanol ^[19,20] / %
Polydimethylsiloxane	PDMS	86.0	0.97	-
Pt-Catalyst	UV-Cat	8.6	-	-
SiO ₂	H2	4.3	~2.20	50
SiO ₂	H3	4.3	~2.20	25
Epoxy-functionalized alkoxy silane	GPS	1.2	1.07	-
Methacryl-functionalized alkoxy silane	MPS	1.2	1.05	-

5.2.2 Sample Preparation

Test Layout and Material Application for SIR. The test layout for SIR tests involves a halogen-free FR-4 resin laminate reinforced with glass fibers, with a layer thickness of ~1.5 mm. A protective organic solderability preservative (OSP) was applied to the comb pattern, consisting of a 200 µm-thick copper layer. A no-clean SAC305 solder

paste (Sn96.5-Ag3-Cu0.5) was deposited using a solder mask designed for test PCBs. Different PDMS formulations (see Table 5-2) were mixed using a Hauschild DAC 150 SP speed mixer (1300 rcf, 50 s) and applied as 1 mm layers *via* doctor blade. The coatings were UV-cured for 2 min at 250 nm with a dose of $1.5 \text{ J} \cdot \text{cm}^{-2}$.

Table 5-2: Overview of the different test PCBs for SIR measurements, including their designations and the composition of the PDMS-based coatings.

Sample Designation	Coating Components
Copper- and Solder Paste- Reference	No PDMS Coating
PDMS	Pure PDMS
B2	Addition of H2
B5	Addition of H3
C3	Addition of GPS
D4	Addition of GPS and H2
F2	Addition of GPS and H3
C4	Addition of MPS
D5	Addition of MPS and H2
F3	Addition of MPS and H3

5.2.3 Characterization Methods

ATR-FTIR Measurements. Attenuated total reflectance (ATR)-FTIR measurements were conducted using a NICOLET iN10 spectrometer equipped with a germanium ATR crystal (Thermo Fisher Scientific). Spectra were recorded in the $4000\text{--}700 \text{ cm}^{-1}$ range at a 4 cm^{-1} -resolution with 64 scans accumulated per spectrum.

Light Microscopy. The optical analysis was conducted using an Olympus SZX16 microscope.

GC-MS Measurements. A gas chromatograph (Agilent 7890) coupled with a mass spectrometer (Agilent 5977, SOP GCH-02) was employed to analyze outgassing

behavior. For GPS containing PDMS analysis, 10–12 mg of the solder paste or PDMS layer coated on test PCBs was placed in pretreated thermal desorption tubes and heated at 130 °C for 15 min. A few test boards coated with PDMS and the functionalizing agents were additionally subjected to 65 °C as well as different humidity levels and exposure time. Mass spectra were recorded for compound identification.

SEM/EDX. The coated PCBs were sputter-coated with Au using a BAL-TEC SCD 050. Surface imaging was performed with a Zeiss EVO 60 ESEM (Carl Zeiss AG) and the elemental composition of corrosion products was analyzed using an X-MaxN EDX spectrometer (Oxford Instruments).

SIR. The climate chambers VC³ 4034 (Weiss Technik GmbH; see Figure 5-1) and PR-3J (ESPEC Corp.) were used to perform SIR measurements under controlled conditions of temperature and humidity. Each channel was pre-tested at room temperature. During the constant SIR test, constant temperatures of 65 °C and humidity level of 93 % *R.H.* were maintained.

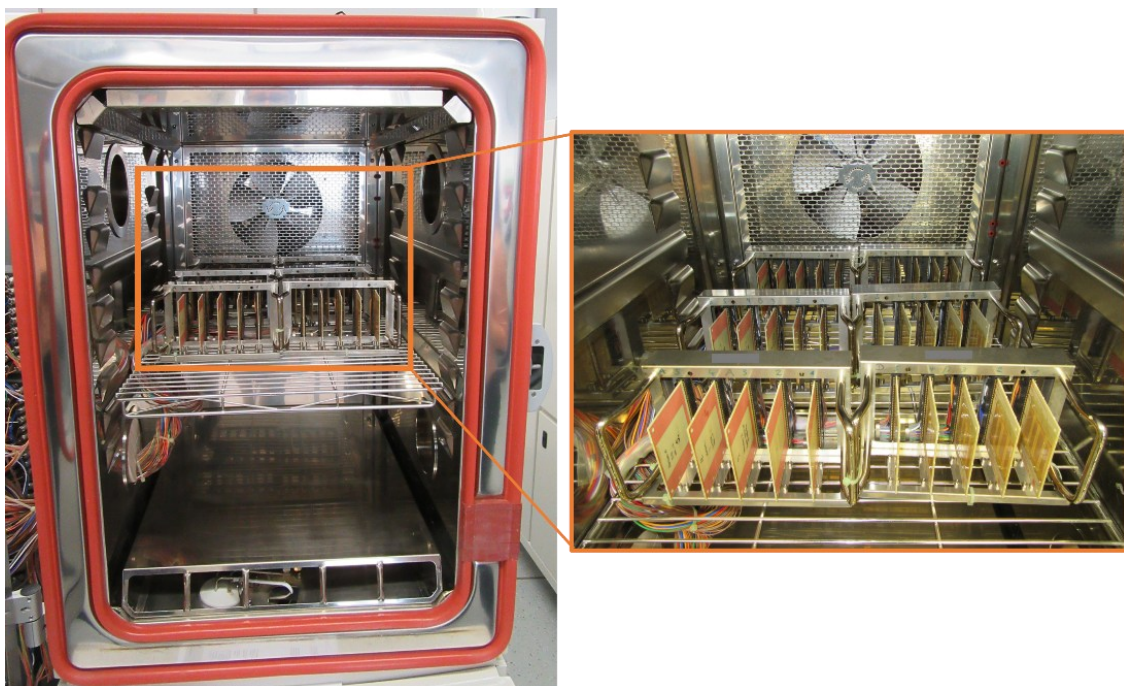


Figure 5-1: Photographic images of a Vötsch climate chamber with coated PCBs which are installed in an integrated PCB plug-in system.

WCA Measurements. The wetting behavior was determined using contact angle measurements with the Drop Shape Analyzer DSA25 (Krüss GmbH). A quantity of 5 μL Millipore water was applied to the sample to determine the contact angle between the sample surface and the drop shape. The measurements were repeated five times.

Moisture Sorption Measurements. Moisture sorption was measured using the SPSx-1 μ -Advance dynamic multi-sample device (ProUmid GmbH & Co. KG) (see Figure 5-2), comprising a climatic chamber, a 23-dish sample tray with an aluminum reference dish, and a microbalance (1 μg resolution). Cured PDMS samples (2 cm $\times$ 2 cm $\times$ 0.1 cm) were placed on perforated aluminum trays to ensure uniform temperature and humidity distribution. The temperature was set at 25 $^{\circ}\text{C}$ and the moisture content was elevated from 50 % *R.H.* to 60 % *R.H.*, and subsequently to 70 % *R.H.*



Figure 5-2: Setup of the SPSx-1 μ -Advance water vapor sorption system from ProUmid GmbH & Co. KG, featuring a sample tray with 23 positions in a climate chamber with an integrated microbalance.

5.3.1 Electrochemical Reliability

5.3.1.1 Influence of PDMS Coating

To evaluate the effect of PDMS coating on electrochemical reliability, test PCBs underwent constant SIR measurements for 1000 h at 100 V. Testing was conducted under near-dew-point conditions with 65 °C and 93% *R.H.* to simulate critical long-term reliability scenarios. Measurements were terminated if the $10^6 \Omega$ limit (orange dashed line) was exceeded five times.

First, three different configurations were tested: Copper conductive paths without solder paste (“Copper-Reference”), soldered paths (“Solder Paste-Reference”), and PDMS-coated PCBs (“PDMS”) (see Figure 5-4). Overview images of the 200 μm and 300 μm comb structures are provided in Appendix Figure A-3.

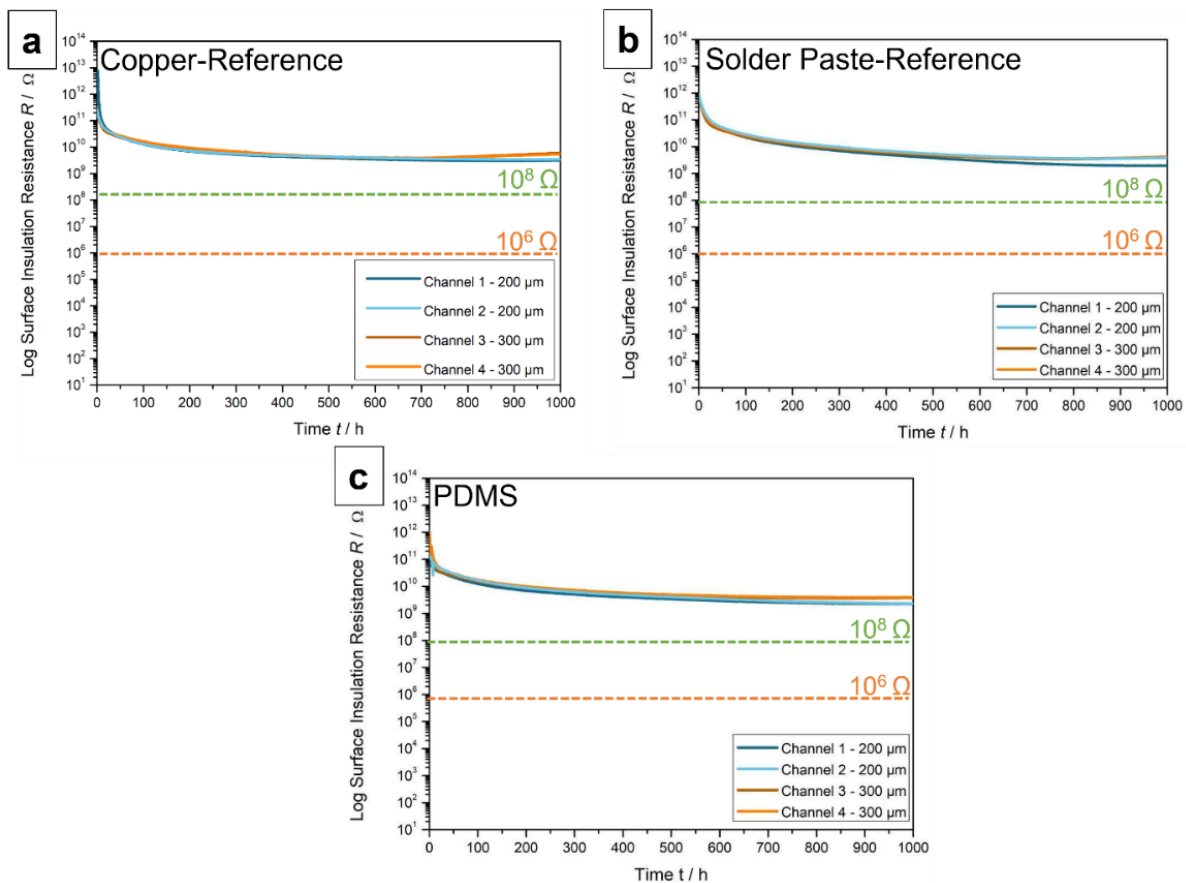


Figure 5-4: Plot of the SIR values of 200 μm and 300 μm Cu-Cu comb structures versus time for reference measurements of a copper conducting tracks, b no-clean SAC305-soldered PCB with c an additional PDMS layer. All three cases show comparable SIR values.

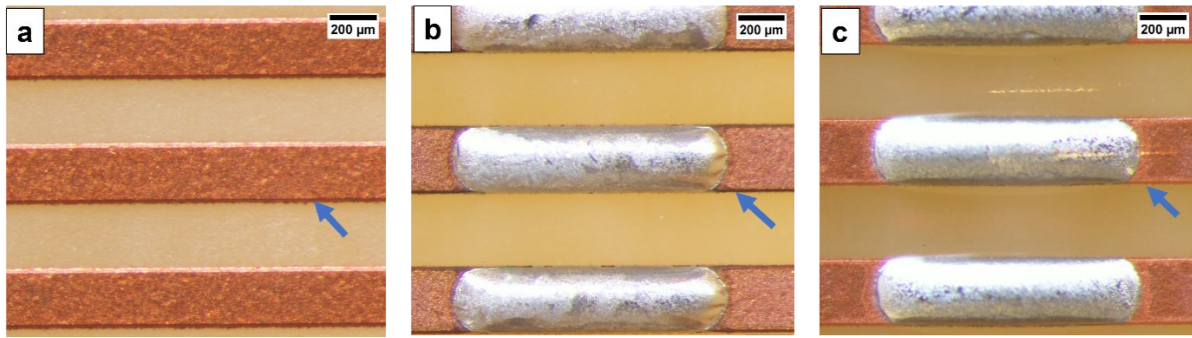


Figure 5-5: The light micrographs in a-c show slightly corroded 300 μm -comb structures after SIR measurement.

As illustrated in Figure 5-4, the resistance values of the comb structures of bare copper, soldered as well as soldered and additionally PDMS-coated PCBs initially reach $10^{11} \Omega$ up to $10^{13} \Omega$. Thereafter, they undergo a slight decline before ultimately stabilizing at a value between $10^{10} \Omega$ and $10^9 \Omega$. In addition, in all three cases, there are no significant differences between the insulation values of the 200 μm and 300 μm comb structures. The SIR value remains consistently above the critical insulation value of $10^8 \Omega$, indicating a good insulation capability of the PDMS coating layer.^[21] The decline in the early stages, followed by a period of stability, is a typical behavior observed in constant SIR measurements. The initial decline in surface resistivity can be attributed to water adsorption until an equilibrium between adsorption and desorption is established.^[22] Consequently, in all three reference measurements, no significant decrease in surface resistivity were observed which could indicate the formation of a continuous monolayer of water molecules and the presence of a critical amount of hygroscopic compounds leading to ECM.^[23] This observation is supported by light microscopy analysis, which revealed no visible evidence of filament growth (see Figure 5-6). Slight traces of copper corrosion can be seen on the edges of the conducting tracks (marked by blue arrows), which is expected under such harsh climatic test conditions.^[24]

5.3.1.2 Influence of Fumed Silica Addition

In the next step, H2 and H3 were added to the PDMS coating and their influence on the surface resistance value was measured (see Figure 5-6).

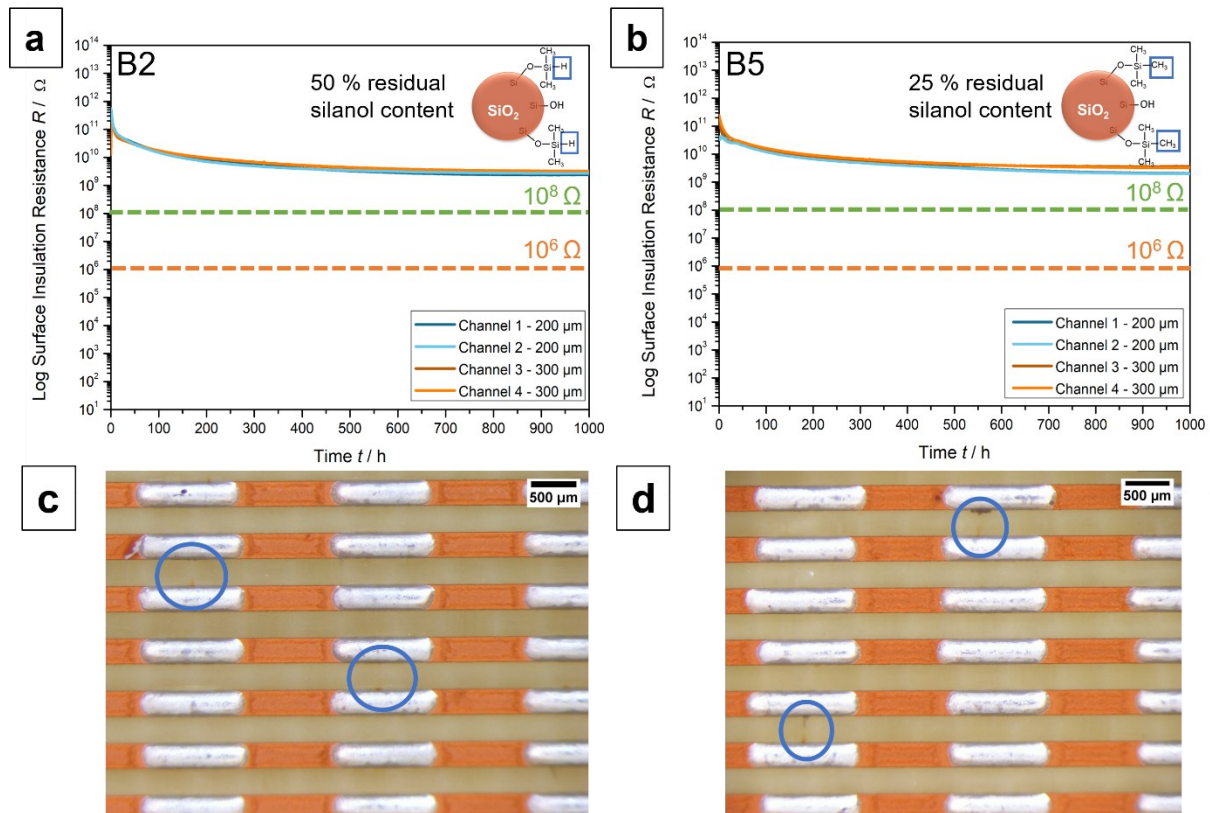


Figure 5-6: Plots of the SIR values versus time for the PDMS-coated test PCB filled with a H2 and b H3 fumed silica. The light micrographs show 300 μm -comb structures after SIR measurement of PDMS-coated PCB including c H2 and d H3. Both test boards show the beginning of corrosion in a few areas (marked with blue circles).

The SIR curves in Figure 5-6 also show a pattern similar to that in Figure 5-4 a. The resistance value for PDMS coatings including both H2 and H3 reaches a maximum in the first few hours and lies between $10^{11} \Omega$ and $10^{12} \Omega$, declines slightly in the first time and shows a constant pattern until the end of the measurement at 1000 h. Similarly, there is no difference between the two different Cu-Cu spacings. The results clearly show that the incorporation of fumed silica has no negative effect on the insulation resistance value, confirming the effectiveness of its insulating properties. In addition, it can be concluded that the residual silanol content has no adverse impact on the SIR values. The images in Figure 5-6 c and d show traces of corrosion after SIR measurement in a few areas without continuous filament formation. However, these traces do not seem to adversely impact the SIR values of the entire comb structures.

5.3.1.3 Influence of Short Chain Silane Addition

After examining the surface insulation properties of test PCBs including copper conducting tracks, soldering addition of PDMS as well as fumed silica, the impact of short-chain silanes was systematically analyzed (see Figure 5-7).

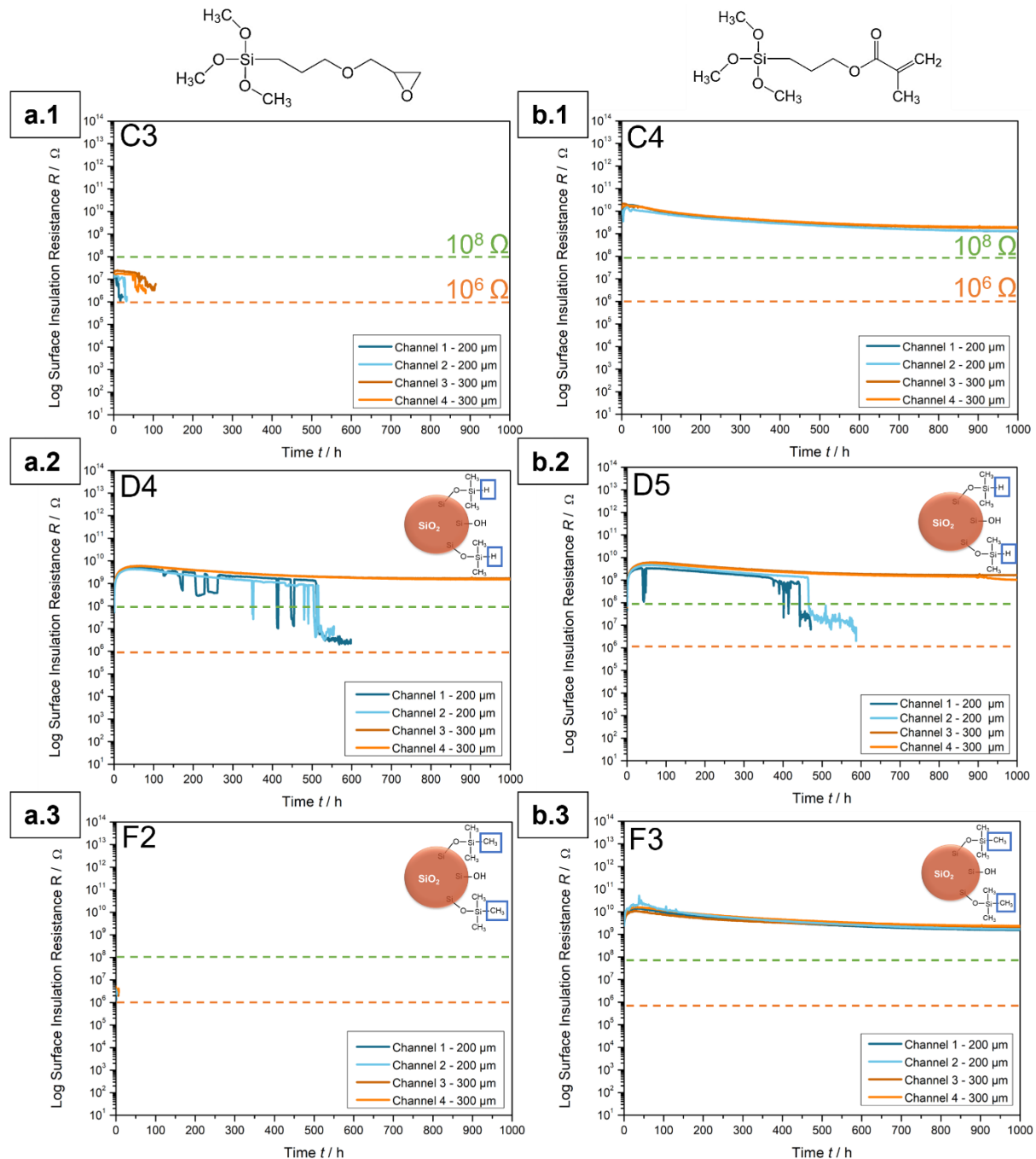


Figure 5-7: Time dependent SIR plots for PDMS based organic layers for both 200 μm and 300 μm Cu-Cu spacings including a.1 GPS, a.2 GPS+H₂, a.3 GPS+H₃ and b.1 MPS, b.2 MPS+H₂ and b.3 MPS+H₃.

Here, GPS and MPS were individually incorporated into the PDMS matrix, followed by the addition of fumed silica to assess the effects of functionalized silica.

The SIR measurements reveal significant differences in insulation performance based on coating composition. First, the addition of GPS led to low initial resistance ($10^7 \Omega$ and $10^8 \Omega$) and rapid failure of both 200 μm (after ~ 40 h) and 300 μm structures (after ~ 100 h - 120 h) (see Figure 5-7 a.1). The formation of dendritic structures is clearly evident on the microscopic images of the test PCB after the SIR test (see Figure 5-8). Conversely, the addition of H₂ improved insulation indicated by higher initial resistance and delayed failure for 200 μm comb structures (after ~ 600 h) as well as no failure for 300 μm Cu-Cu spacings (see Figure 5-7 a.2). In accordance with this observation, the light microscopy images in Figure 5-8 show minimal corrosion for 300 μm copper spacings and more pronounced corrosion for 200 μm Cu-Cu distances. Here, the higher corrosion susceptibility of the smaller copper conductor spacings is clearly visible. However, combining GPS with H₃ showed no improvement, as the test PCB failed immediately, with conductive corrosion bridging copper tracks for both Cu-Cu distances (see Figure 5-7 a.3 and Figure 5-8). The impact of the functional group of short-chain silanes is obvious in the case of MPS. The methacrylic organofunctional group slightly reduces SIR values for both comb structures, starting at $10^{10} \Omega$ and $10^{11} \Omega$ and stabilizing at $10^9 \Omega$ (see Figure 5-7 b.1). This indicates a shift in SIR values compared to pure PDMS with fumed silica, though remaining well above the critical threshold of $10^8 \Omega$. Notably, there are less failures with MPS, in contrast to GPS. But the addition of H₂ produces similar effects to GPS with 200 μm comb structures failing between 450–600 h and 300 μm comb structures that pass the whole measurement period of 1000 h (see Figure 5-7 b.2). However, when H₃ is added to MPS, both Cu-Cu spacings fulfill the failure criterion of $10^8 \Omega$, contrasting with the significant failures observed in GPS-H₃ formulations (see Figure 5-7 b.3). All PCBs exhibit corrosion traces after SIR measurements, with varying severity (see Figure 5-9). Specifically, the 200 μm comb structures with H₂ addition show pronounced bridged gaps between copper tracks which is in accordance to the drop in surface insulation.

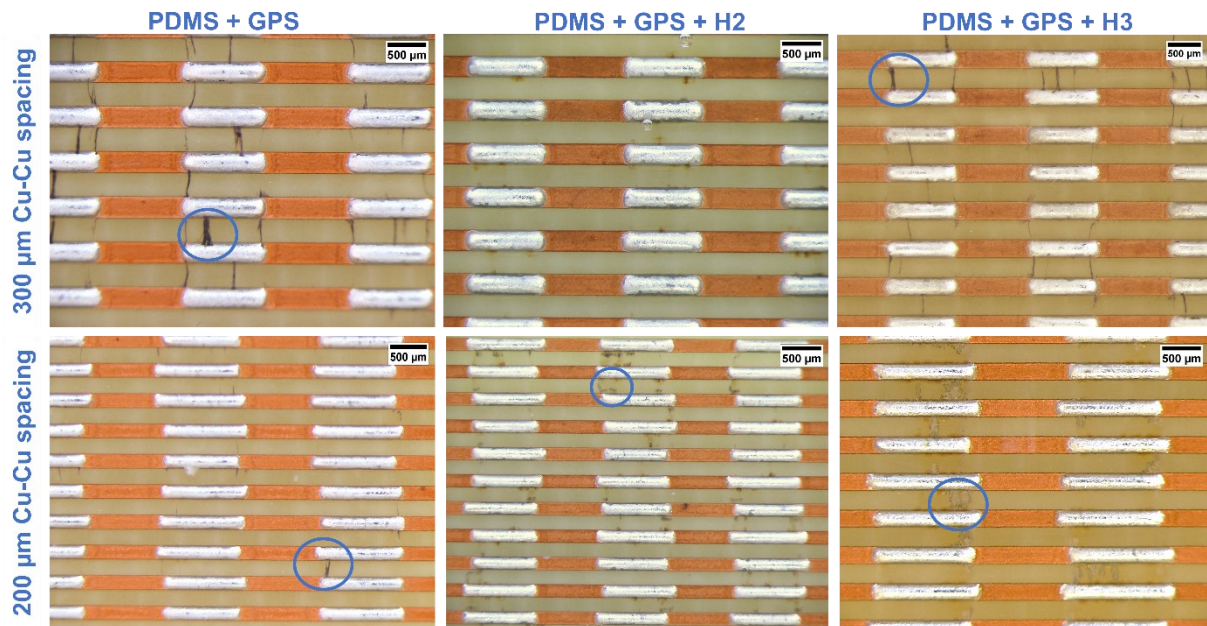


Figure 5-8: Light micrographs of PCBs coated with PDMS containing GPS, GPS+H2 and GPS+H3 after constant SIR measurements show corrosion differences in 300 μm (top) and 200 μm (bottom) Cu-Cu spacings. Blue circles exemplarily highlight bridged gaps between Cu tracks.

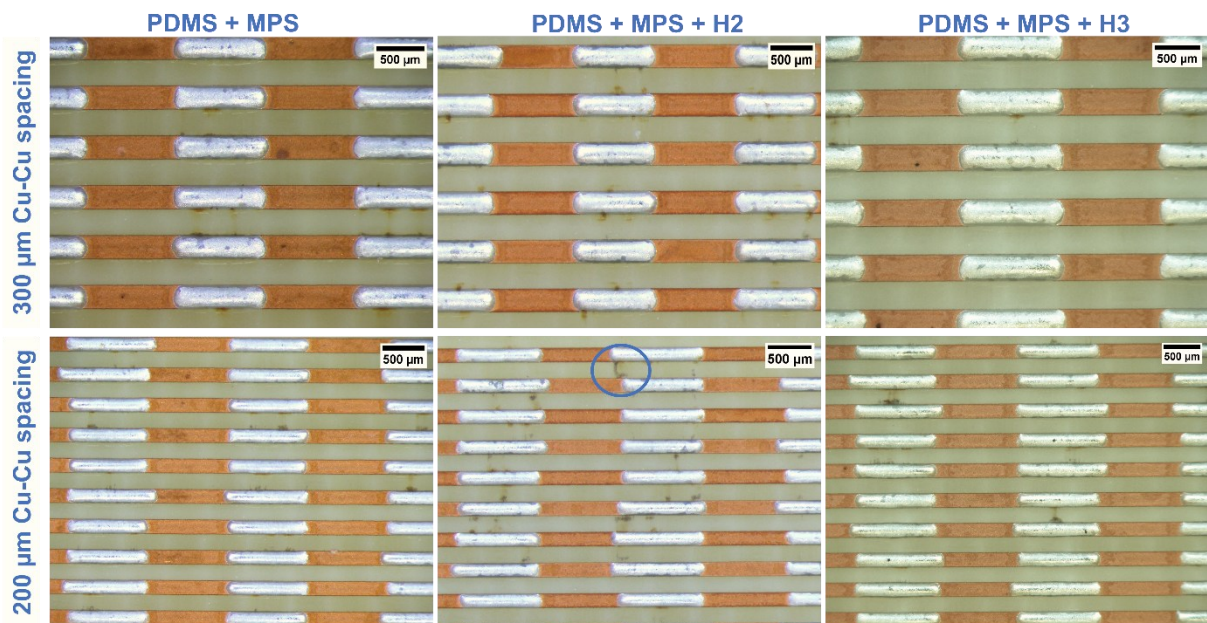


Figure 5-9: Light micrographs of PCBs coated with PDMS including MPS, MPS+H2 and MPS+H3 after SIR tests. The comb structures with 300 μm (top) and 200 μm (bottom) Cu-Cu spacings exhibit different corrosion severity. The blue circle exemplarily highlights a bridged gap between Cu paths.

Consequently, the components of a polymer coating influence both the electrochemical stability and the presence of corrosion. The application of the polymer PDMS, along with the addition of hydrophobic and highly hydrophobic silica, does not adversely affect the insulating properties, even after 1000 h of SIR measurement. However, short-chain silanes, especially glycidoxo-functionalized silane, significantly reduce surface insulation resistance and cause short circuits.

5.3.2 Investigation of the Electrochemical Migration

The tested PCBs exhibit significant corrosion, particularly with GPS as a short-chain silane. To analyze the elemental composition of the corrosion products, representative SEM/EDX measurements at 20 kV acceleration voltage were performed on two PCBs C3 und D4 from constant SIR measurements. The PDMS layer was partially removed mechanically and the PCBs were subsequently coated with a conductive Au layer.

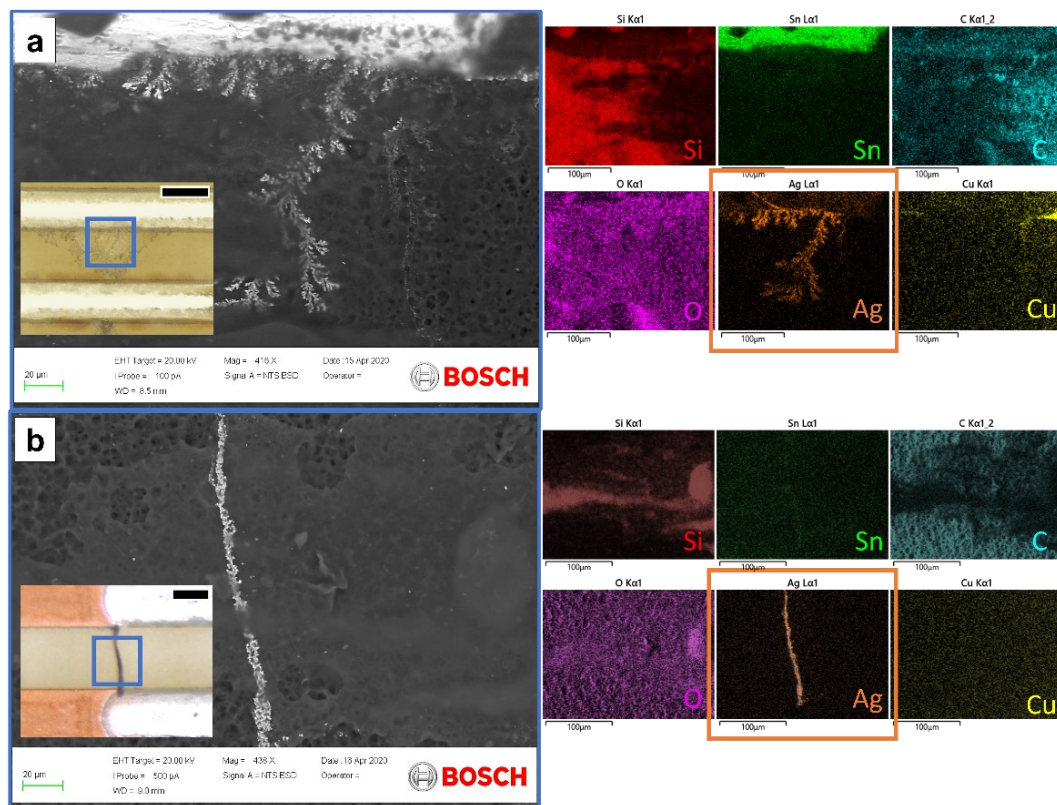
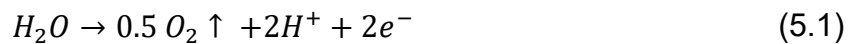
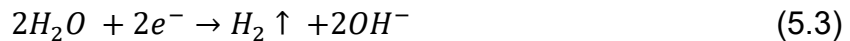


Figure 5-10: BSD-SEM images and integrated light micrographs (scale bars correspond to 200 µm) of the PDMS-coated test PCBs including a GPS-functionalized H2 and b GPS. The corresponding elemental mappings clearly indicate silver corrosion.

As depicted in Figure 5-10, the investigation of the elemental composition of the corrosion products clearly identifies silver dendrites bridging the conductors from silver corrosion of the SnAgCu-based no-clean solder paste. This finding shows that the short circuits detected by SIR measurements are caused by silver dendrites. Dendrite formation generally requires that metal ions can freely migrate from the anode to the cathode without precipitating as insoluble compounds. The ECM process occurs through a sequence of steps: Path formation (water adsorption), electrodisolution (dissolution of Ag from the anode), ion transport (movement of dissolved silver ions through the medium), electrodeposition (re-deposition of Ag at the cathode), and filament growth (the formation of Ag dendritic structures). The oxidation process and metal dissolution occur at the anode, accompanied by the generation of H^+ ions^[25]:



And at the cathode, the reduction process initiates dendrite growth, leading to the formation of OH^- ions^[25]:



It is further assumed that the standard reduction potential determines the propensity of a metal to form dendrites.^[25] However, silver presents an exception here, as shown in Figure 5-8, indicating that this factor alone is not decisive. Hence, dendrite formation is also influenced by surface conditions, including the pH level and the presence of ionic and hygroscopic contaminants.^[26] Copper dendrites form at pH levels below 5, and tin oxidizes to tin(II) and tin(IV)—both of which require low pH to avoid precipitation as hydroxides. Instead, the silver(I) ions remain soluble at higher pH levels which might explain their tendency to form dendrites when exposed to humidity. Moreover, it is known that, flux residues such as WOAs in no-clean fluxes can increase the amount of ionic and hygroscopic contamination.^[26,27] Given the fact that the failure of the comb structures occurred after the addition of the short-chain silane, particularly GPS, it can be derived that a synergistic effect occurs between the flux residues, the functionalizing agent, and humidity load causing corrosion.

5.3.3 Study of the Influence of Humidity Load

To analyze surface material changes under elevated temperature and humidity and assess risk factors for ECM formation, ATR-FTIR, WCA, GC-MS, and gravimetric measurements were performed on PDMS coatings containing GPS, MPS, and fumed silica applied to test PCBs.

ATR-FTIR analyses were conducted before and after SIR testing on PCBs with SAC305 alone (see Figure 5-11 a) and those with both solder paste and a PDMS layer containing GPS (Figure 5-11 b). In the latter, the Ge crystal was placed in both the solder paste and substrate areas to assess local chemical variations in the PDMS layer due to temperature and humidity exposure. Subsequently, GC-MS, WCA, and gravimetric analyses were performed to identify and quantify volatile substances and evaluate mass changes induced by environmental conditions.

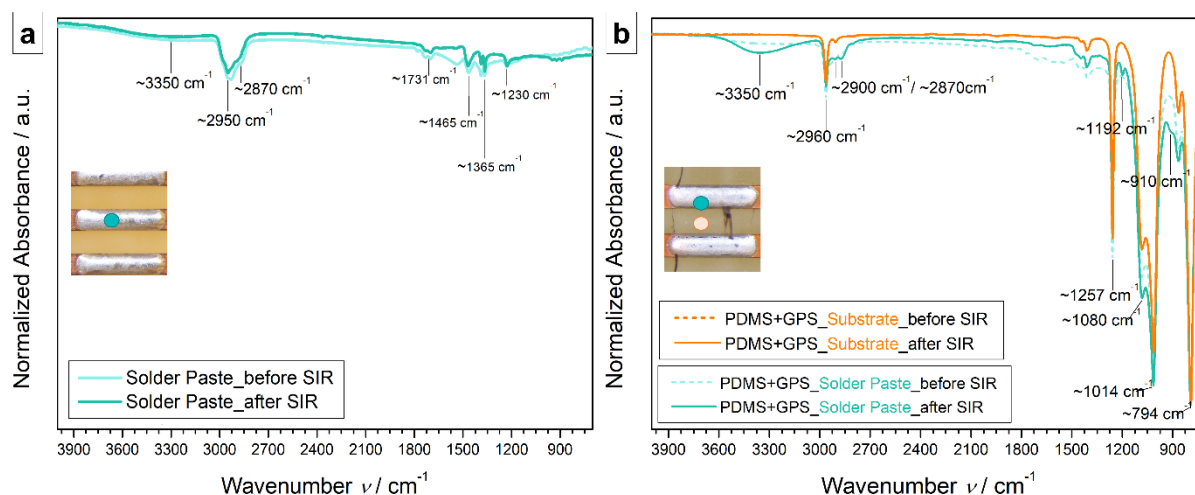


Figure 5-11: ATR-FTIR spectra of test PCBs before and after SIR measurements at 65 °C and 93 % *R.H.* of a no-clean SAC305 and b additionally applied PDMS layer containing GPS. The inserted microscope images show the Ge crystal measuring positions.

The ATR-FTIR spectrum of SAC305 no-clean solder paste (see Figure 5-11 a) reveals characteristic peaks associated with the organic flux components. Key features include the O–H stretching vibration at 3350 cm^{-1} , aliphatic C–H stretching vibrations between 2950 cm^{-1} and 2870 cm^{-1} , and the C=O stretching vibration at 1731 cm^{-1} . Additional

peaks in the fingerprint region correspond to CH_3 -deformation vibrations at 1465 cm^{-1} and 1365 cm^{-1} , as well as C–O stretching at 1230 cm^{-1} . Combined with gas chromatographic data (see Figure A-4 in the Appendix), these findings confirm the presence of residual flux components, including activators (WOAs) and rosin/resin materials, with an estimated residual content of approx. 2.5 to 5 wt. %/ vol. %.^[28] Minimal spectral changes were observed before and after SIR testing.

Conversely, significant spectral changes become evident after the application of a GPS-containing PDMS layer (see Figure 5-11 b). Prior to SIR measurement at $65\text{ }^\circ\text{C}$ and 93 % *R.H.*, characteristic peaks of PDMS are observed. These include the asymmetric and symmetric C–H stretching vibrations of methyl groups at 2960 cm^{-1} and 2900 cm^{-1} , the asymmetric vibration of Si–C at 1257 cm^{-1} and $\sim 794\text{ cm}^{-1}$, the Si–O stretching vibrations at 1080 cm^{-1} and 1014 cm^{-1} ,^[29] which remains unchanged before and after the SIR test. However, in the solder paste region, particularly after SIR, a broad O–H stretching vibration at 3350 cm^{-1} emerges, indicating hydroxyl group formation. Notably, the C–H stretching and Si–O vibrations in the fingerprint region intensify, while the Si–C peak at 1257 cm^{-1} decreases. Additional peaks at 1192 cm^{-1} and 910 cm^{-1} appear, corresponding to C–O stretching of methoxy groups and the epoxide ring of GPS, respectively.^[30] These results confirm that GPS is primarily detectable in the SAC305 solder paste region and only after climatic exposure during SIR testing. Based on this, further investigations focus on PDMS layer compositions in the solder paste area, particularly on test PCBs that mostly remained functional (see Figure 5-12 a) and those containing GPS that failed under SIR conditions (see Figure 5-12 b). Despite a slight increase in C–H stretching vibrations in the solder paste region compared to the substrate (see Figure 5-11 b), Figure 5-12 a confirms that the ATR-FTIR spectra of PDMS remain unchanged before and after SIR, demonstrating the structural integrity and low water absorption of the PDMS layer. The addition of fumed silica (B2, B5) initially does not significantly alter the FT-IR spectrum of pure PDMS. However, after SIR, the O–H stretching vibration at 3350 cm^{-1} and C–H stretching bands exhibit broadening, alongside increased peak intensity at 1080 cm^{-1} and 1014 cm^{-1} (Si–O bonds). This indicates the presence of residual silanol groups in fumed silica, which are highly reactive with flux residues and exhibit high wettability in conditions of high

humidity.^[31] Moreover, MPS functionalization of hydrophobic fumed silica becomes evident after SIR, as indicated by C=O and C=C stretching vibrations at 1731 cm^{-1} and 1630 cm^{-1} , along with fingerprint region peaks characteristic of methacrylic-functionalized silane. In addition, C–O stretching vibrations of the methoxy groups at 1192 cm^{-1} (highlighted in orange) are evident (D5).^[32]

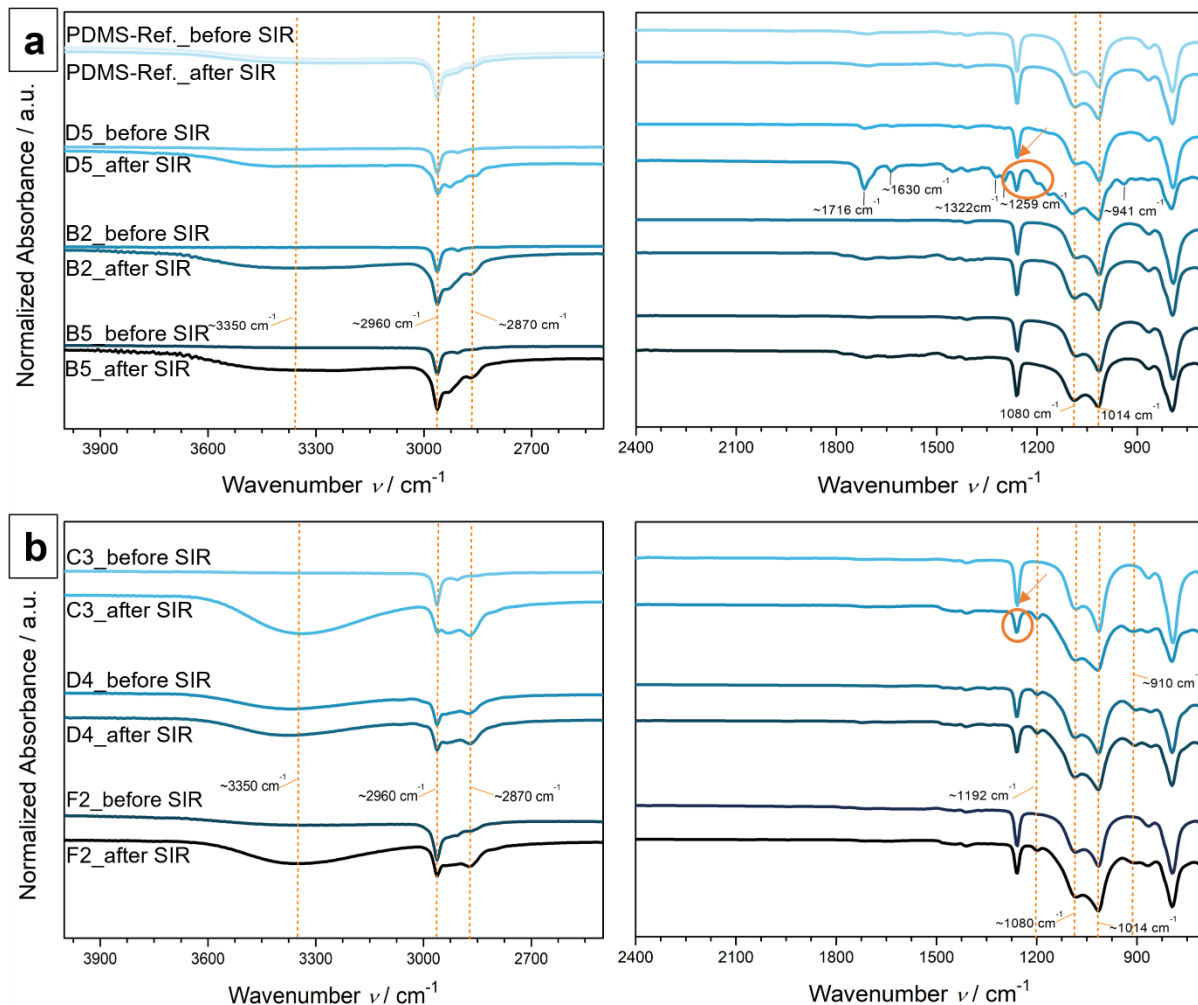


Figure 5-12: Normalized ATR-FTIR spectra of test PCBs before and after SIR measurements in the area of SAC 305 solder paste including distinct coating compositions. The FT-IR spectra are classified into two categories: a Solder paste with the addition of PDMS, fumed silica, and MPS. b Solder paste with the addition of PDMS, fumed silica, and GPS.

A similar effect is observed with GPS addition (Figure 5-12 b). Prior to the SIR measurements, the characteristic PDMS peaks remain unchanged, except in the presence of H2. Here, GPS-characteristic peaks, particularly C–O stretching vibrations at 1192 cm^{-1} and 910 cm^{-1} , confirm that the hydrophobic surface modification of fumed silica influences GPS functionalization (D4). After SIR, significant broadening of O–H and C–H stretching vibrations, along with the emergence of GPS-specific peaks, is observed. Peak intensity is highest for GPS addition (C3), followed by GPS with H3 (F2) and H2 (D4). Additionally, the asymmetric Si–C vibration at 1257 cm^{-1} decreases notably in the presence of GPS—and of MPS—after treatment with elevated temperature and humidity, indicating methoxy group hydrolysis (highlighted with orange arrows).

Consequently, the ATR-FTIR measurements clearly show that organic flux residues and their interaction with short-chain functionalizing agents in PDMS strongly influence SIR values under elevated temperature and humidity. The organofunctional silanes MPS and GPS contain trimethoxy groups that hydrolyze in moisture, releasing methanol and forming silanol groups through condensation.^[33] These silanols interact with polar surfaces, such as hydroxyl groups present on the silica surface. When GPS attaches to the surface of SiO_2 with a residual silanol content of 50 % and a dimethylsiloxo surface modification, failure in 300 μm comb structures can be prevented. However, 200 μm comb structures fail within a similar timeframe (450–600 h) for both GPS and MPS in combination with H2. The ATR-FTIR measurements suggest that the (slow) hydrolysis of methoxy groups and the resulting formation of silanol groups increase the hydrophilic property of the polymer coating, ultimately leading to a reduction in SIR values and failure.

Generally, the methacrylic organofunctional group in MPS is incorporated into the polymer *via* radical grafting. Since such reactions do not apply here, MPS appears to have greater mobility. In contrast, the epoxy functionality in GPS features an epoxide ring that can undergo acid- or base-catalyzed nucleophilic ring-opening with amines or alcohols, with the ability to form methyl ethers, polyether networks, dioxanes, or diols.^[34] These products can contribute to hydrophilicity and hence, to failures of the comb structures.

The influence of the interactions of functionalizing agents with moisture, temperature, and fumed silica on surface wettability and the extent of MPS and GPS volatility are reflected in the WCA and GC-MS measurements (see Figure 5-13 a and b).

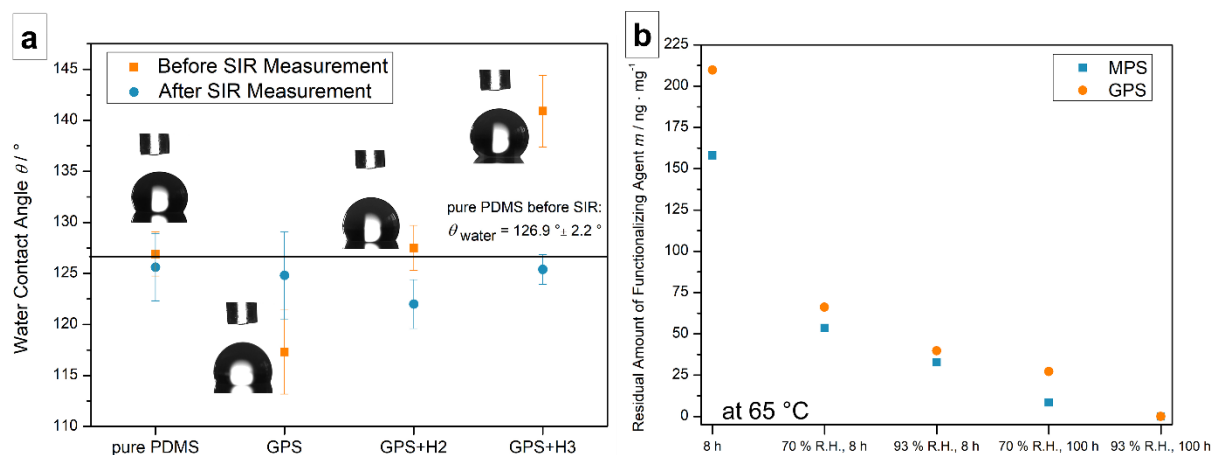


Figure 5-13: a WCA of pure PDMS with GPS and fumed silica before and after SIR measurement. b Exponential decrease in the amount of GPS and MPS as a function of exposure time and humidity pre-treated at 65 °C.

The wettability of pure PDMS remains mainly unchanged, with a WCA of $\Theta = 125.6^\circ \pm 3.3^\circ$ after SIR, indicating its typical hydrophobic behavior.^[35] Adding GPS decreases the WCA to $\Theta = 117.3^\circ \pm 4.1^\circ$ before, but after the SIR measurements, it recovers at $\Theta = 124.8^\circ \pm 4.3^\circ$, similar to pure PDMS. In addition, GC-MS analysis clearly identified the short-chain silanes as GPS and MPS within the corresponding PDMS formulations (see Figure A-5 in the Appendix). Quantitative evaluation revealed an exponential decrease in the concentrations of GPS and MPS as a function of humidity and exposure time. After 100 h of exposure at 65 °C and 93 % *R.H.*, neither MPS nor GPS are detectable (see Figure 5-13 b). Adding hydrophobic silica slightly increases the WCA, which drops to $\Theta = 122.2^\circ \pm 2.4^\circ$ after SIR testing. Similarly, after the addition of highly hydrophobic silica and SIR test, the WCA reduces from $\Theta = 140.9^\circ \pm 3.6^\circ$ down to $\Theta = 125.4^\circ \pm 3.6^\circ$. Here, the distinction in the interaction of GPS with H2 and H3 becomes apparent. The 25 % residual silanol content and

trimethylsiloxy-modification of H3 result in lower GPS attachment to its surface, resulting in GPS migration.

The desorption of GPS and MPS is also evident in gravimetric investigations of silica and short chain silane containing PDMS layers. Based on the rapid decrease in MPS and GPS levels observed from GC-MS measurements, the moisture sorption test was initiated at 25 °C and 50 % *R.H.*, then increased to 60 % *R.H.* and finally, 70 % *R.H.* once equilibrium was reached in case of GPS+H2 (see Figure 5-14).

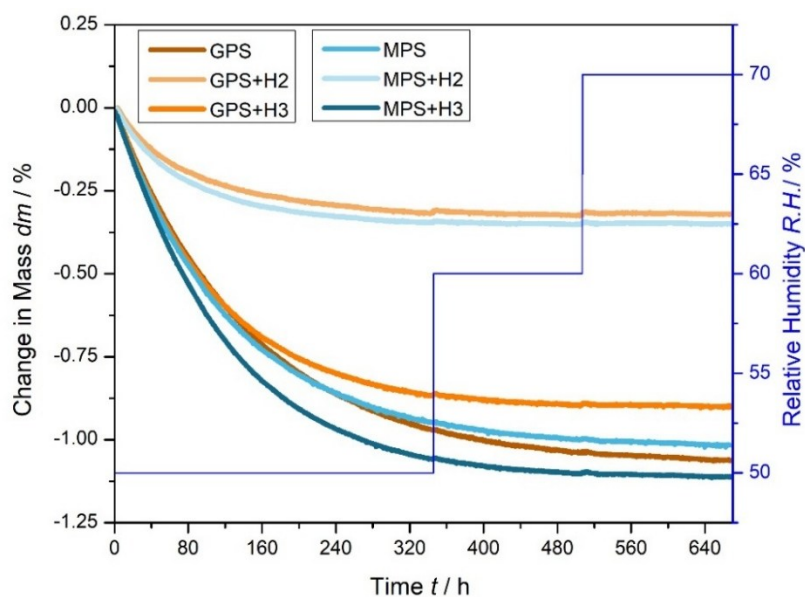


Figure 5-14: Mass change vs. relative humidity as a function of time. The mass loss shows variations depending on the composition of the PDMS layer.

Generally, Fick's law describes diffusion-limited, reversible processes where the mass transport is driven by a concentration gradient and follow characteristic $\sqrt{t}$ -behavior of diffusion.^[36] However, the percentage mass change versus time plot in Figure 5-14 reveals that mass loss occurs, also regardless of the applied humidity levels, indicating that Fick's second law does not apply here. Instead, irreversible desorption occurs which results in a first-order kinetic process:

$$m(t) = m_0 \cdot e^{-k_D t} \quad (5.5)$$

with

$$\begin{array}{ll} m(t) & = \text{mass at time } t \\ m_0 & = \text{initial mass} \\ k_D & = \text{desorption rate constant} \end{array}$$

Accordingly, the desorption rate constant k_D were determined for GPS and MPS as well as fumed silica in PDMS formulations for each humidity level set (see Figure 5-15).

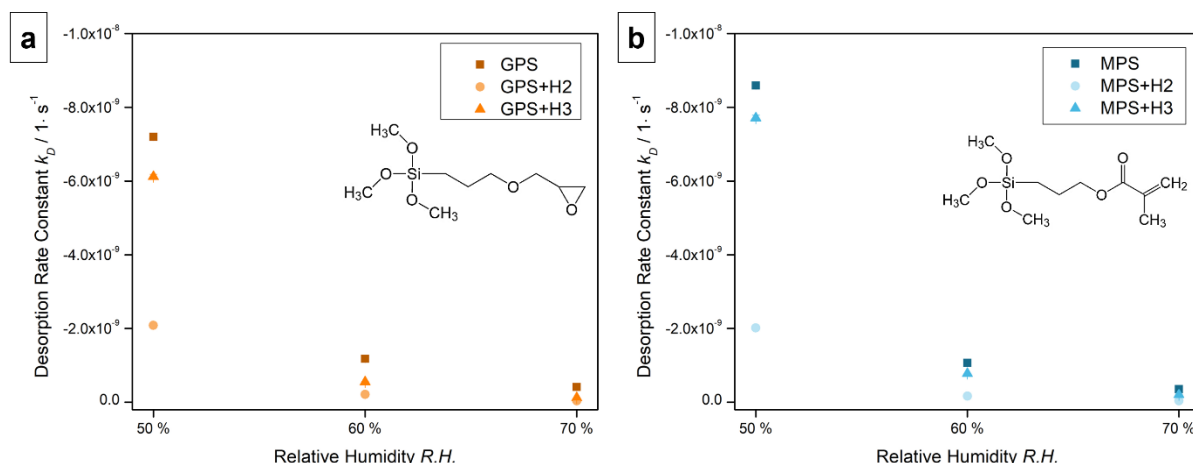


Figure 5-15: Plot of the desorption rate constant k_D versus different relative humidity levels. A significant decrease of k_D is evident as the relative humidity increases from 50 % to 70 % *R.H.*

As demonstrated in Figure 5-15, the desorption rate constant k_D for GPS decreases as relative humidity increases from 50 % to 70 % *R.H.*, with the highest desorption observed at 50 % *R.H.*—a trend also seen for MPS. This behavior is attributed to the release of GPS and MPS from the PDMS matrix, with desorption rates declining at higher humidity levels because most of the short chain organosilanes are already desorbed. The presence of H2 and H3 modifies desorption kinetics. The functionalizing agents attach to H2 which results in a delayed desorption compared to pure GPS or MPS in PDMS. Here, it is likely to be a combination of a retarded desorption of the short chain silanes and a moisture uptake by SiO_2 . The comparable k_D -values for GPS+H2 and MPS+H2 indicate comparable attachment efficiencies, driven by the predominant hydrolysis of methoxy groups and subsequent reaction with the silanol groups of fumed silica. In contrast, the lower hydroxyl content of H3 reduce its capacity

for functionalization, leading to rapid desorption of short-chain silanes already at 50 % *R.H.* While k_D for GPS+H3 and MPS+H3 remains slightly lower than for pure GPS and MPS, H3 does not reduce their migration to the same extent as H2.

The investigation of humidity loads correlates with the surface insulation resistance of PDMS formulations. Rapid failures in GPS-containing systems are attributed to its fast desorption and migration to the PDMS surface, which are intensified by elevated temperature, humidity, and interactions with flux residues, leading to the formation of hydrophilic GPS-derived products. While MPS also migrates quickly, its methacryloxy functionality does not degrade insulation properties as severely as the glycidoxo functionality of GPS. The residual silanol content and the degree of hydrophobic modification of SiO₂ surfaces influence the interaction with GPS and MPS, either promoting attachment of the functionalizing agents or, in the case of highly hydrophobic fumed silica, facilitating migration.

5.4 Conclusion

In conclusion, the insulating properties of polymer coatings applied on test PCBs are strongly influenced by their composition and interactions, both intrinsic and extrinsic. PDMS-based coatings, including hydrophobic and highly hydrophobic surface-modified fumed silica, initially exhibited stable insulation resistance for 300 μm and 200 μm Cu-Cu comb structures, with only minor, neglectable corrosion traces observed. However, the incorporation of short-chain silanes, particularly GPS, led to a rapid failure of both types of comb structures due to the formation of silver dendrites that bridged the gap between the Cu paths. The failure was attributed to both GPS desorption and the high reactivity of its epoxy functionality, identified as critical factors by ATR-FTIR, GC-MS, and gravimetric measurements. Moreover, functionalizing hydrophobic fumed silica with GPS has demonstrated that PCB failures can be significantly reduced. However, the failure of 200 μm comb structures in both GPS- and MPS-containing coatings suggests that the slow hydrolysis of methoxy groups increases the hydrophilic property of the PDMS-based coating, leading to failure, particularly at smaller Cu-Cu distances. The assumption that highly hydrophobic silica inherently improves insulation properties was contradicted, as GPS showed rapid desorption and weak interactions with highly

hydrophobic SiO_2 , leading to similar degradation effects of the SIR values as an unfilled system under elevated temperature and humidity conditions. These findings highlight the critical role of each component in enhancing corrosion resistance of polymer coatings for electronic components, especially as their miniaturization advances. The study also introduces an analytical method to identify and interpret material property synergies, offering insights for optimizing polymer formulations to improve corrosion resistance and long-term humidity robustness in PCBs.

5.5 Outlook

Future research should focus on optimizing reliability assessments for polymer coatings by adopting accelerated SIR testing procedures. In cases where the materials are either unknown or only partially known, it is suggested that shorter SIR tests with *e.g.* varying humidity levels should be used as a preliminary screening method. This would enable earlier detection of reduced insulation properties and thus, inappropriate coating materials as well as reducing time and cost, while enhancing the accuracy of failure predictions. Additionally, enhancing the attachment efficiency of functionalizing agents to both the polymer matrix and filler is crucial to prevent desorption. Increasing the molecular weight and further incorporation of functional groups of functionalizing agents can help to improve the material reliability. Finally, investigating metals and metal ions in corrosion products derived from solder pastes in PDMS coatings can offer insights into the degradation mechanisms of electronic components, particularly as these metals are difficult to access using methods such as SEM/EDX, especially for traces of Cu corrosion. A suitable method could be inductively coupled plasma optical emission spectroscopy (ICP-OES), which ionizes the sample in a high-temperature plasma and detects the characteristic light emitted by metal ions, allowing precise qualification and quantification of metal and metal ions. This could include a leaching process to release the metal ions, which are then analyzed qualitatively and – assuming the establishment of a successful leaching procedure – quantitatively to gain a better understanding of the corrosion process on polymer-coated PCBs.

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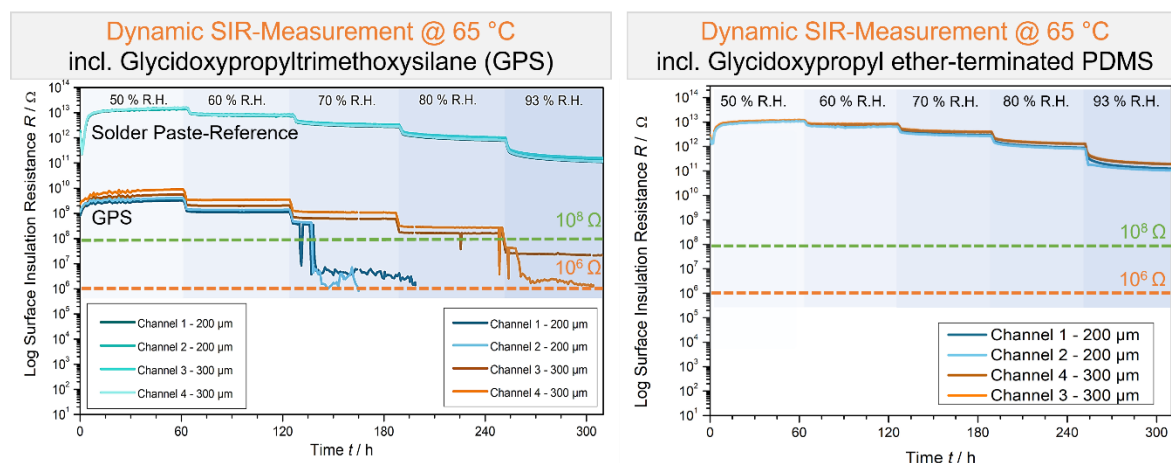
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6 INFLUENCE OF FUNCTIONALIZED POLYMER LIGANDS APPLIED IN PDMS-BASED COATINGS ON THE ELECTROCHEMICAL RELIABILITY AND HUMIDITY ROBUSTNESS OF PCB ASSEMBLIES



Abstract

This study evaluates the electrochemical reliability and humidity resistance of polydimethylsiloxane (PDMS)-based polymer coatings incorporating functionalizing agents and micrometer-sized silica particles with varying surface silanol group densities. Dynamic surface insulation resistance (SIR) tests were performed on soldered test printed circuit boards (PCBs) featuring 200 μm and 300 μm Cu-Cu comb structures, subjected to a constant temperature of 65 °C and varying relative humidity levels. Shorter Cu-Cu spacings treated with the conventional short-chain organosilane 3-glycidoxypyltrimethoxysilane (GPS) exhibited increased leakage currents, leading to comb structure failure at 65 °C and 70 % *R.H.* Energy-dispersive X-ray (EDX) analysis identified silver corrosion from the no-clean solder paste as the cause of the shorts. In contrast, coatings containing functionalizing agents including monoglycidyl and diglycidyl ether-terminated PDMS ($M_n = 5000 \text{ g} \cdot \text{mol}^{-1}$ / $M_n = 800 \text{ g} \cdot \text{mol}^{-1}$) maintained stable insulation values. Further investigations using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, water contact angle (WCA) measurements, and gravimetric assessments revealed minimal moisture uptake and low migration tendencies of the polymer ligands. The results indicate that the higher molecular weight of the polymer ligands improve electrochemical stability and moisture

resistance. Finally, the study proposes neutron imaging, owing to its sensitivity to light elements, to detect polymer coating defects that facilitate moisture ingress and contamination, highlighting this technique's potential for future investigations.

Introduction

The electronics industry is confronted with the challenge of developing increasingly miniaturized electronic devices in a variety of fields, including wearable technologies, medical devices, the Internet of Things (IoT), industrial automation, and mobility.^[1] These devices are typically exposed to mechanical, chemical, environmental, and electrical influences, thus demanding materials which are reliable and support long-term performance. In this context, the protection against corrosion—defined as material degradation caused by interactions with external environmental factors^[2]—plays a key role, and polymer coatings are increasingly being used for this purpose.^[3]

PDMS represent a crucial class of materials applied for the protection of PCBAs.^[4] The silicon-oxygen backbone (Si–O–Si) in PDMS, bonded to nonpolar groups such as methyl groups, exhibits reduced water interaction, making it suitable for anticorrosive coatings. Compared to traditional anticorrosive agents or anodized layers containing Cr⁶⁺, PDMS-based coatings are non-toxic.^[5] Moreover, the bond angle between silicon and oxygen ranges from 100 ° to 180 °, thereby imparting flexibility, while the Si–O bond's energy of 452 kJ · mol⁻¹ ensures thermal stability up to 200 °C. These properties render PDMS ideal for high-temperature application in the field of automotive electronics.^[6] The material's low intermolecular forces and free segmental rotations result on the one side in low surface tension and high gas permeability.^[7] On the other side, its mechanical and adhesive strengths are therefore limited, necessitating the addition of nano- or micro-based inorganic additives or fillers and organic components.^[7]

Functionalized organosilanes such as aminopropyltriethoxysilane (APTES), methacryloxypropyltrimethoxysilane (MPS) and GPS enhance adhesion due to their ability to form strong covalent bonds with reinforcing fibers, fillers, substrates, and polymer matrix.^[8] Key performance factors include effective force transmission, compound stability, and controlled migration of organosilanes to the substrate surface. However, short-chain silanes were observed to migrate to the air interface and cause loss of

adhesion.^[9] This migration in polymer formulations is attributed to an exclusion mechanism during curing, causing phase separation and accumulation at high-energy interfaces, like substrates or air. Additionally, the mobility of silanes can cause a chemical potential gradient, driving their migration from areas of high to low concentration.^[10] The study of Comyn *et al.* of a titanate-catalyzed, alkoxysilane-crosslinked silicone sealant on glass showed that cohesive failure occurred at the surface while adhesive failure was present in the material's core after curing in humid conditions. It was found that crosslinking density and elastic modulus were greater near the surface, indicating that curing agents and the 1.0 wt.% reaction product of GPS, MPS and APTES migrated outward, depleting the core and causing adhesion failures.^[11] Furthermore, partially or complete organosilane desorption can interact with flux residues of the solder pastes of PCBs, reducing the insulation resistance of PDMS-based coatings and causing corrosion (see Chapter 5).

The use of functionalized polymer agents with functional groups offers an opportunity to overcome these challenges. For example, copolymers formed from acetate-protected vinyl catechol and glycidyl methacrylate *via* RAFT radical polymerization are discussed to enhance interfacial interactions between epoxy adhesives and metal substrates through catechol units.^[12] Additionally, the study of Salazar-Hernández *et al.* synthesized PDMS-silica hybrid coatings through a sol-gel reaction involving tetraethyl orthosilicate (TEOS) and PDMS with various functional groups showed an improvement of the hardness, adhesion, and corrosion resistance of aluminum surfaces.^[13] The insulation properties of polymer coatings are typically assessed through electrochemical techniques or accelerated corrosion studies, including constant SIR measurements, Electrochemical Impedance Spectroscopy (EIS), and advanced methods such as Scanning Electrochemical Microscopy (SECM). However, these methods can be time-consuming, less sensitive to varying humidity levels, or require complex modeling.^[14] Moreover, directly visually detecting cracks or voids, that can result in the diffusion of contaminants or moisture within polymer coatings, is challenging.

This study examines PDMS-based polymer coatings incorporating homopolymers with glycidoxy functionality as polymer agents and varying molecular weights. Their insulation properties are assessed *via* dynamic SIR tests at 100 V and 65 °C under humidity

levels from 50 % *R.H.* to 93 % *R.H.* on soldered test PCBs with 200 μm and 300 μm Cu-Cu spacings. The effect of fumed silica with difference in hydrophobic surface modification is also analyzed, as well as the impact of conventional short-chain silane GPS. As a proof of concept, dynamic SIR tests are conducted on polymer coated test PCBs with solder mask and QFP components. Additionally, ATR-FTIR and gravimetric studies were performed to investigate the humidity robustness and sorption processes. Finally, neutron imaging is proposed for detecting defects in aged polymer coatings. This research explores alternatives to conventional functionalizing agents and testing methods, emphasizing the need for precise alignment of polymer coating components with PCBA constituents to ensure electrochemical reliability.

6.1 Experimental Part

6.2.1 Materials

The PDMS layer consist of an UV-curable, two-component formulation mixed in a 10:1 ratio, where component A (SEMICOSIL® 912) was combined with component B (ELASTOSIL® CAT PT), both supplied by Wacker Chemie AG.^[15] Moreover, two types of fumed silica were added as already described in Chapter 5: Hydrophobic silica (H2) and highly hydrophobic silica (H3) (corresponding to HDK® H20 and HDK® H2000, Wacker Chemie AG, respectively). Both types of fumed silica were incorporated into the PDMS layer at 4.3 wt. %. Functionalized polymers were added to the PDMS matrix. First, PDMS-based homopolymers with monoglycidyl ether functionality and $M_{n \text{ PDMS mono}} = 5000 \text{ g} \cdot \text{mol}^{-1}$ (abbreviated as “PDMS mono”, Sigma-Aldrich) as well as diglycidyl ether functionality with $M_{n \text{ PDMS di}} = 800 \text{ g} \cdot \text{mol}^{-1}$ (abbreviated as “PDMS di”, Sigma-Aldrich) were used as received. As a reference, low molecular weight functionalizing agents glycidyl ether-terminated propyltrimethoxysilane was used (GENIOSIL® GPTM, Wacker Chemie AG). An overview of the utilized components is shown in Table 6-1. For the neutron imaging experiment, the test PCBs were additionally coated with a synthetic rubber.

6.2.2 Sample Preparation

Test Layout and Material Application for SIR analysis. A halogen-free FR-4, ~ 1.5 mm thick resin laminate reinforced with glass fibers was used for SIR measurements. A protective organic solderability preservative (OSP) coating was applied to the comb pattern, which consisted of a 200 µm thick copper layer. In addition, no-clean SAC305 solder paste (Sn96.5-Ag3-Cu0.5) was applied. PDMS-based formulations (see Table 6-1) were prepared using a Hauschild DAC 150 SP high speed mixer at 1300 rcf for 50 s. Additionally, test PCBs based on polymer based laminate, soldered with SAC305 solder paste, coated with a solder mask, and assembled with QFP0.4 components were used.

Table 6-1: Overview of the components used in PDMS formulations, including their mass fractions, densities, and molecular weight.^[15–22]

Chemical	Abbreviation	Mass Fraction / wt. %	Density ^[15–22] / g · cm ⁻³	Molecular Weight ^[15–23] / g · mol ⁻¹
Polydimethylsiloxane	PDMS	83.1/ 62.9	0.97	-
Pt-Catalyst	UV-Cat	8.3/ 6.3	-	-
SiO ₂	H2	4.3	~2.20	60.1
SiO ₂	H3	4.3	~2.20	60.1
Homopolymer: Diglycidyl ether-term. PDMS	PDMS di	4.3	0.99	800
Homopolymer: Monoglycidyl ether-term. PDMS	PDMS mono	26.5	0.97	5000
Epoxy-functionalized alkoxysilane	GPS	1.2	1.07	236

These formulations were then applied as 1 mm thick layers using a doctor blade and UV-cured for 2 min at a wavelength of 250 nm with a dose of 1.5 J · cm⁻². A summary of the individual components of the PDMS-based coatings used on the test boards is shown in Table 6-2.

Table 6-2: Overview of the different test PCBs used for dynamic SIR measurements, including sample designation and composition of the PDMS-based coatings.

Sample Designation	Coating Components
Copper-Reference	No Coating
Solder Paste-Reference	No Coating
PDMS-Reference	Pure PDMS
A1	Addition of GPS
B1	Addition of PDMS mono
B2	Addition of PDMS mono and H2
B3	Addition of PDMS mono and H3
C1	Addition of PDMS di
C2	Addition of PDMS di and H2
C3	Addition of PDMS di and H3

Test Layout and Material Application for analysis *via* Neutron Imaging. For the neutron imaging studies, two test PCBs with solder masks featuring different types of integrated circuit packages and coatings were utilized. The coatings comprised PDMS and fumed silica, both with as well as without GPS and were applied manually to the PCBA. Additionally, a coating consisting of a styrene-butadiene rubber (synthetic rubber) was applied using jet dispensing. One of the test PCBs underwent thermal shock testing for 50 cycles between -60 °C and +150 °C.

6.2.3 Characterization Methods

ATR-FTIR Measurements. ATR-FTIR spectroscopy was used to collect spectra in the range of 4000-700 cm^{-1} with a resolution of 4 cm^{-1} -resolution, accumulating 64 scans per spectrum. The measurements were performed using a Thermo Fisher Scientific Nicolet iN10 spectrometer equipped with a germanium ATR crystal.

Light Microscopy. The optical analysis was performed with the stereo microscope SZX16 (Olympus Corporation).

Moisture Sorption Measurements. The SPSx-1 μ -Advance dynamic multi-sample device (ProUmid GmbH & Co. KG) was used for moisture sorption measurements, which features a climatic chamber, a 23-dish sample and a microbalance with a 1 μ g resolution. PDMS samples with the dimensions of 2 cm $\times$ 2 cm $\times$ 0.1 cm were placed on perforated aluminum trays. The temperature was maintained at 25 °C, and the relative humidity level was sequentially increased from 50 % *R.H.* to 60 % *R.H.* and finally to 70 % *R.H.* after equilibrium was reached at each step.

Neutron Imaging. The neutron imaging experiments were performed at the neutron imaging facility ANTARES at the FRM II Reactor of the Heinz Maier-Leibnitz Center (operated by the Technical University of Munich).

SEM/EDX. The coated PCBs underwent gold sputter-coating using a BAL-TEC SCD 050 sputter coater and measurements by means of a Zeiss EVO 60 Environmental Scanning Electron Microscope (ESEM). The elemental composition of corrosion products was analyzed utilizing an X-MaxN Energy-Dispersive X-ray (EDX) spectrometer from Oxford Instruments.

SIR. The climate chamber VC³ 4034 (Weiss Technik GmbH) was used to perform dynamic SIR measurements at 100 V. The temperature was maintained at 65 °C, while humidity was sequentially increased from 50 % *R.H.*, 60 % *R.H.*, 70 % *R.H.*, 80 % *R.H.* to finally 93 % *R.H.* Each humidity level was maintained for 63 h.

WCA Measurements. The wetting behavior was evaluated by measuring the contact angle with a Drop Shape Analyzer DSA25 (Krüss GmbH). A 5 μ L Millipore water droplet was deposited on the sample surface and measurements were repeated five times.

6.2 Results and Discussion

SIR measurements are usually long-lasting, making (new) polymer coating evaluations slow and costly. To address the industry's need for accelerated testing, shorter dynamic SIR studies were conducted on test PCBs at a constant temperature of 65 °C, with humidity levels increasing from 50 % *R.H.* to 93 % *R.H.* at 100 V. If the $10^6 \Omega$ limit (orange dashed line) was exceeded five times, the measurement was terminated.

First, reference PCBs without solder paste, with solder paste and with an additional PDMS coating were measured. For comparison with the constant SIR measurements from Chapter 5, PDMS coatings were also evaluated with GPS. To verify reproducibility, each measurement was repeated four times, with the SIR value collected five hours before the transition to the next humidity level or before failure. The mean values were then plotted against the corresponding humidity levels (see Figure 6-1).

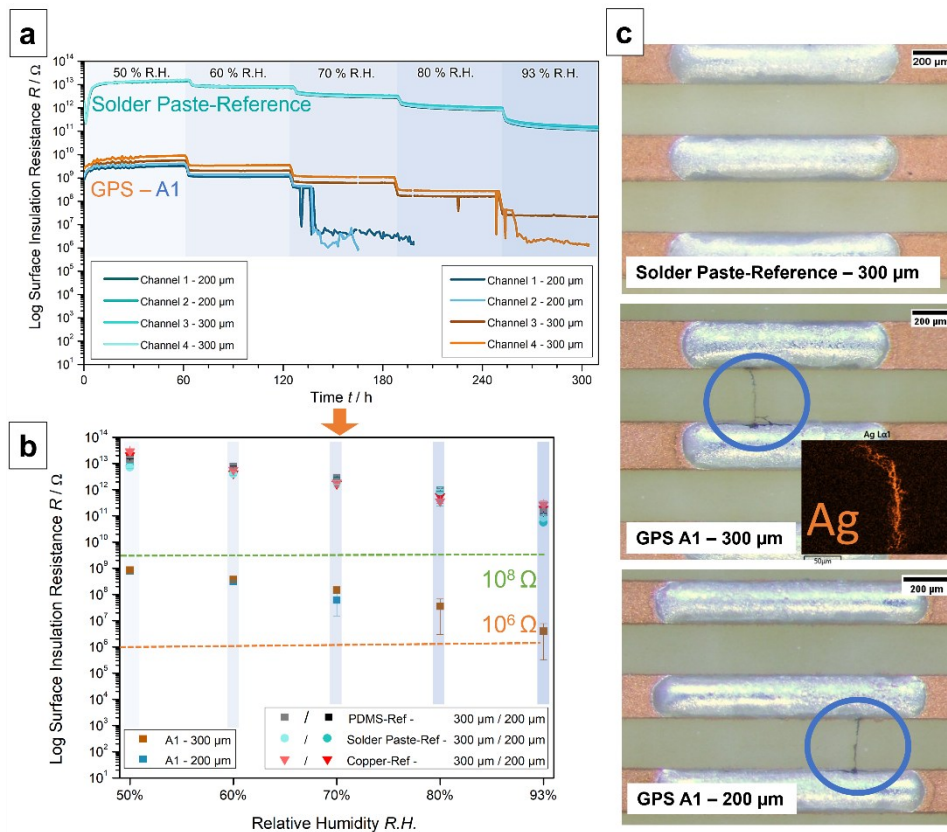


Figure 6-1: SIR values from dynamic SIR tests on PCBs with 200 μm and 300 μm Cu-Cu spacing a exemplarily plotted versus time and b their mean values plotted versus humidity level. c Light micrographs of PCBs after dynamic SIR tests reveal no

corrosion on soldered PCBs. In contrast, the formation of continuous Ag dendrites is clearly evident when coated with a GPS-containing PDMS layer.

Figure 6-1 a illustrates that the SIR values of the reference measurements, exemplified by the soldered PCB, stabilize at high resistance levels around $10^{13} \Omega$ after a short initiation phase. With increasing humidity, the SIR values decrease slightly, but remain consistently high for both types of comb structures at all humidity levels. Figure 6-1 b, which shows the mean resistance values, confirms that soldering and applying an additional PDMS layer results in stable SIR values as seen for bare Cu-Cu conducting tracks. These samples respond as expected to changes in relative humidity and maintain their insulating properties with a high degree of reproducibility. Furthermore, the electrochemical robustness of the soldered and PDMS-coated PCBs within the selected humid conditions is demonstrated by the light microscopic analysis in Figure 6-1 c, which shows no evidence of corrosion.

In contrast, the incorporation of the short-chain silane GPS with a molecular weight of $236 \text{ g} \cdot \text{mol}^{-1}$ ^[19] into the PDMS formulation initially results in lower SIR values, ranging between $10^9 \Omega$ and $10^{10} \Omega$ (see Figure 6-1). However, at 50 % *R.H.* and 60 % *R.H.*, these values remain above the critical insulation threshold of $10^8 \Omega$, indicating adequate insulation properties. As humidity rises above 70 % *R.H.*, a significant drop in resistance is observed particularly for 200 μm Cu-Cu comb structures, which ultimately fail. The electrochemical migration (ECM) of silver, caused by the dissolution from the solder paste, was confirmed by the formation of silver dendrites evidenced by light microscopy images and EDX analysis. The 200 μm Cu comb structures exhibit insulation failure as early as 70 % *R.H.* to 80 % *R.H.*, a phenomenon not observed at 93 % *R.H.* constant SIR measurements (see Figure 5-7 a.1 in Chapter 5). The 300 μm comb structures dropped below the critical insulation value of $10^8 \Omega$ at 80 % *R.H.*, and in some cases failed completely at 93 % *R.H.* Once again, GPS has been shown to significantly promote corrosion.

In a second step, the resistance of glycidyl-functionalized polymers with higher molecular weights was investigated.

6.3.1 Accelerated Electrochemical Reliability Assessment of functionalized Polymer Ligands

Based on the previous dynamic SIR measurements of GPS with a molecular weight of $236 \text{ g} \cdot \text{mol}^{-1}$ ^[19], further dynamic SIR measurements were performed under the same conditions for PDMS mono with $M_n = 5000 \text{ g} \cdot \text{mol}^{-1}$ ^[18] (see Figure 6-2 a) and PDMS di with $M_n = 800 \text{ g} \cdot \text{mol}^{-1}$ ^[17] (see Figure 6-2 b). In addition, hydrophobic modified fumed silica with a residual silanol content of 50 % (see Figure 6-2 B2 and C2) and highly hydrophobic fumed silica with a residual silanol content of 25 % (see Figure 6-2 B3 and C3) were added.

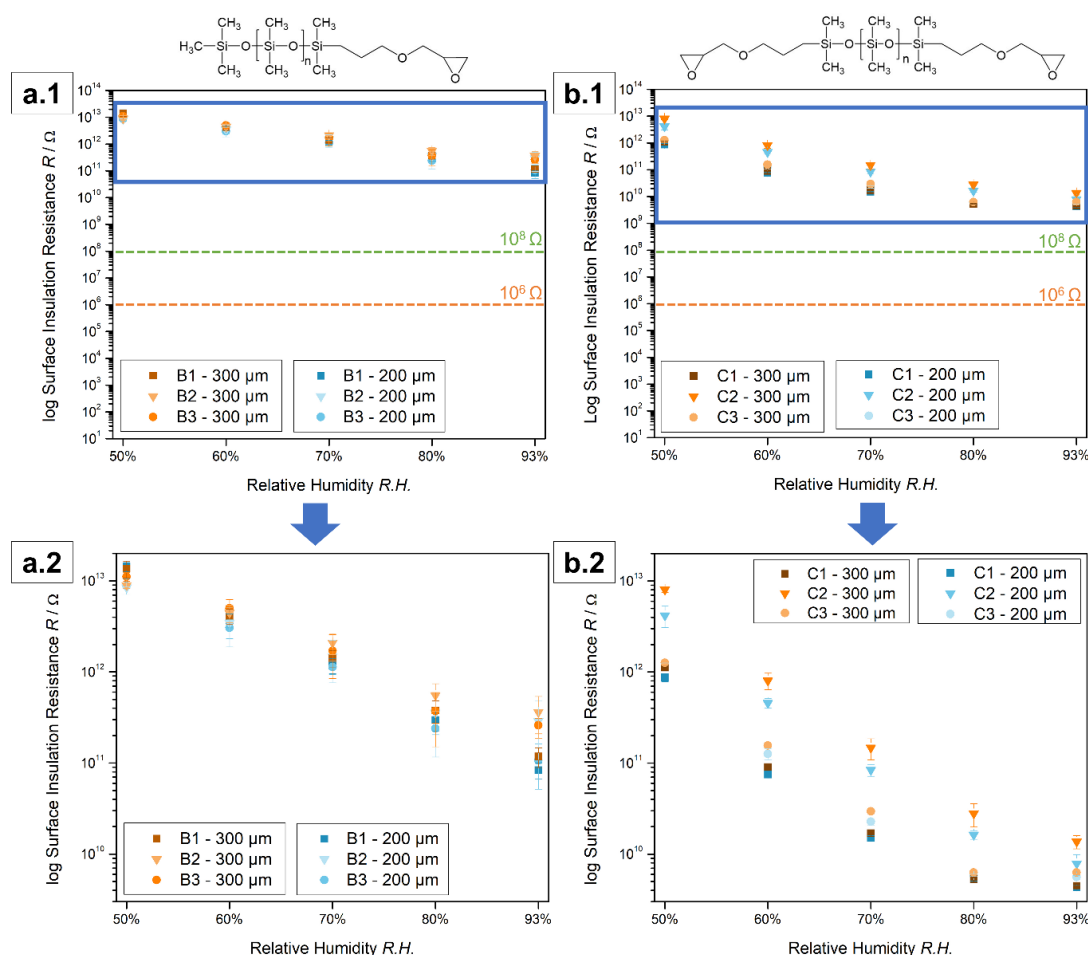


Figure 6-2: Plot of the mean values from the dynamic SIR measurements for the 200 μm and 300 μm comb structures of a.1 monoglycidyl ether-functionalized and b.1 diglycidyl ether-functionalized PDMS in PDMS formulations as a function of the individual humidity levels. Their corresponding magnifications are shown in a.2 and b.2.

As demonstrated in Figure 6-2, the dynamic SIR measurements clearly indicate elevated resistance values for both types of functionalized PDMS agents, well above the critical threshold of $10^8 \Omega$ across all humidity levels. Both types of comb structures respond to changes in humidity. As expected, their resistance decreases with increasing exposure to moisture. The 200 μm and 300 μm comb structures initially possess resistivity values exceeding $10^{13} \Omega$, undergo a moderate decline at 60 % *R.H.*, and ultimately attain values within the range of $10^9 \Omega$ und $10^{12} \Omega$. Light microscopy after SIR measurements shows no corrosion for both PDMS mono and PDMS di at both 200 μm and 300 μm Cu-Cu distances (see Figure 6-3 and Figure 6-4). In comparison to the resistance values of a GPS-containing PDMS coating, it is evident, that the increase in molecular weight of the functionalizing agents has a significant effect on the electrochemical robustness of PDMS-based coatings.

In addition to the molecular weight, the nature of the functional group, as illustrated by the magnifications of the SIR measurements (see Figure 6-2 a.2 and b.2), influence electrochemical reliability. The monoglycidyl ether functionality of PDMS with a higher molecular weight tends to exhibit higher resistance values comparable to those of a pure PDMS coating, as previously described. Moreover, it shows little impact from the addition of H_2 or H_3 , as well as from the reduction of Cu-Cu distances from 300 μm to 200 μm . At relative humidity levels above 70 % *R.H.*, a potentially higher resistance is observed for larger Cu-Cu distances and upon the addition of H_2 . A similar effect emerges in the case of diglycidyl ether-terminated PDMS. Both comb structure types exhibit the highest resistance values upon the addition of H_2 across all humidity levels, suggesting an interaction between fumed silica and the functionalizing agent, as previously observed in Chapter 5. Subsequently, the addition of H_3 results in slightly higher SIR values compared to PDMS formulations without fumed silica.

Consequently, the choice of functionality and molecular weight of functionalizing agents plays a crucial role in polymer protective coatings. Although the individual influence of these two factors cannot be clearly distinguished in this study, the overall findings indicate that their associated interactions with other components, such as silica, as well as potential reactions of the functional groups with moisture, can improve insulation resistance by adjusting these parameters.

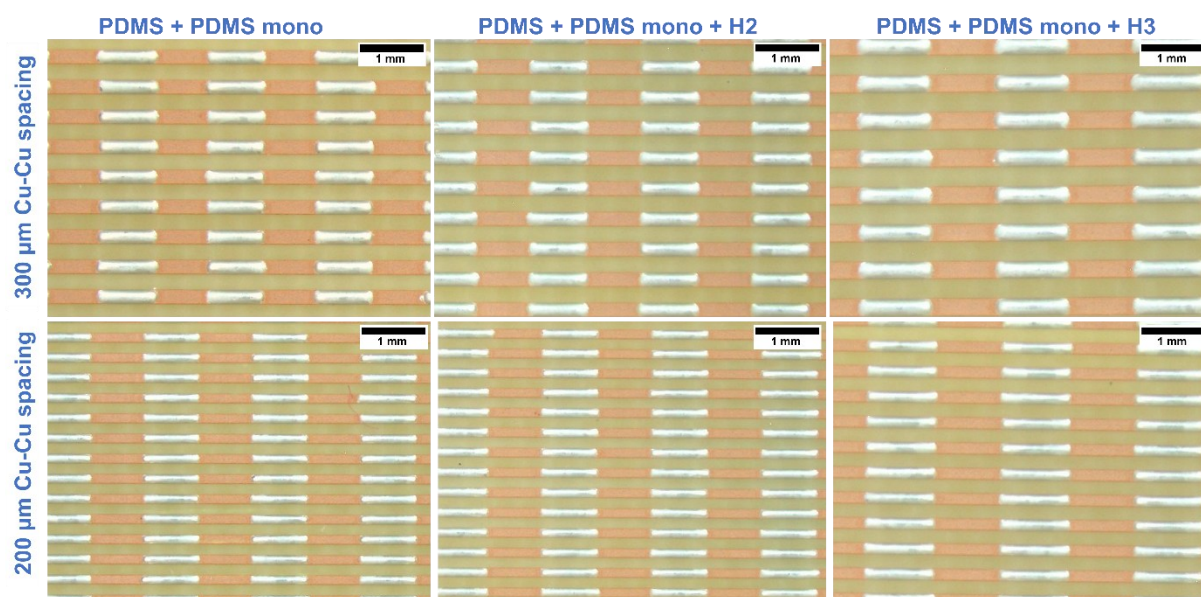


Figure 6-3: Light microscope images demonstrate the presence of 200 μm and 300 μm comb structures coated with PDMS formulations containing PDMS mono, H2, and H3. After dynamic SIR testing, no corrosion is observed.

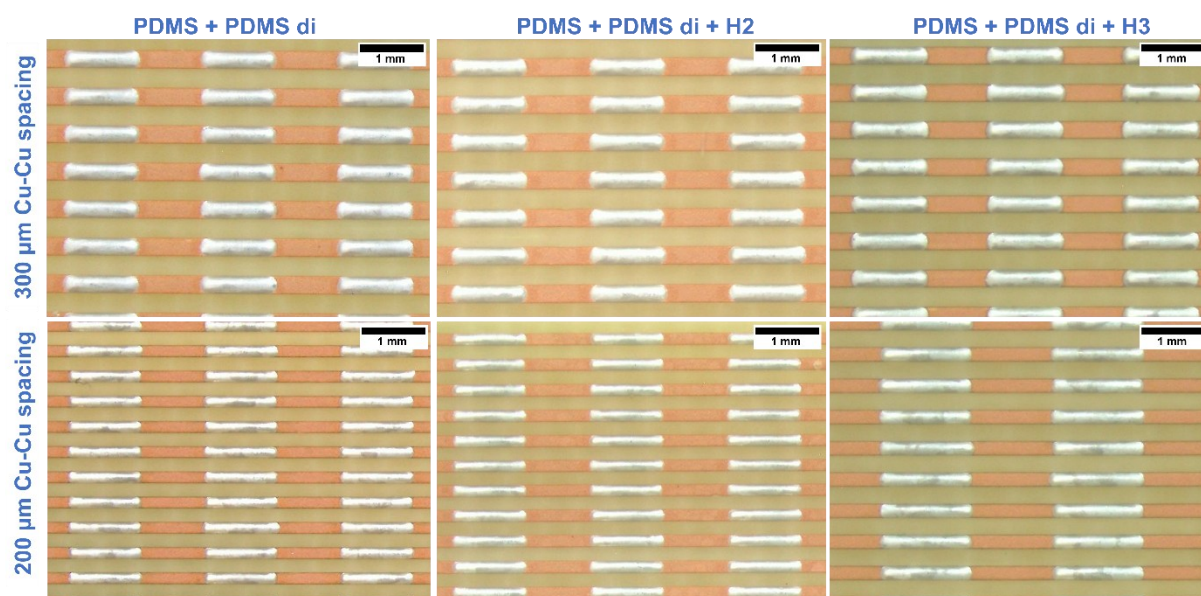


Figure 6-4: Microscopic analysis reveals that 200 μm and 300 μm comb structures, coated with PDMS layers containing PDMS di, H2, and H3, remain free from corrosion after dynamic SIR tests.

As a proof of concept, dynamic SIR measurements were performed on PCBAs under identical climatic conditions using PDMS coatings with monoglycidyl and diglycidyl ether-terminated polymer ligands (see Figure 6-5 b). The PCBs were made from FR-4 laminate, soldered, and coated with a solder mask, typically acrylic- or epoxy-based.^[24] The test PCBs were assembled with QFP0.4 components, where “0.4” denotes the 0.4 mm pitch between adjacent pin centers. Optical microscopy was used to examine soldered QFPs before and after SIR measurements, with exemplary images shown for PDMS coatings containing diglycidyl ether-terminated PDMS in Figure 6-5 a.

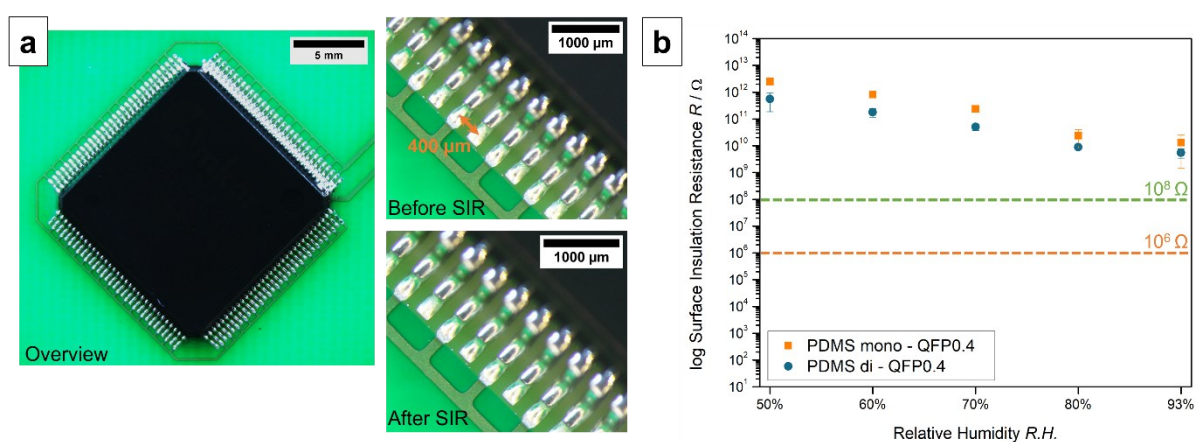


Figure 6-5: a Images of QFP0.4 assemblies coated with PDMS including PDMS-di, providing an overview and comparison before and after SIR testing. b SIR values of QFPs coated with PDMS including PDMS mono and PDMS di.

Light microscopic examination of the QFPs in Figure 6-5 a reveals no indications of corrosion or other abnormalities. These finding is further confirmed by the SIR measurements in Figure 6-5 b. It is evident that both of the selected functional groups initially achieve high resistivity values in the range of $10^{11} \Omega$ and $10^{13} \Omega$ and, as expected, decrease with increasing humidity content, but remain well above the critical value of $10^8 \Omega$ at each level. It is once more apparent that the choice of functional group has an influence on the insulating behavior of the coating system. Here, the resistance values of diglycidyl ether-terminated PDMS are lower than those of monoglycidyl ether-terminated PDMS, but they remain well above the $10^8 \Omega$ limit even at the maximum humidity level applied.

The findings indicate that polymer functionalizing agents are suitable for PDMS-based coatings due to their resistance to high temperatures, humidity, and applied voltage.

6.3.2 Investigation of the Humidity Robustness of functionalized PDMS

In order to study the changes in the coating material due to exposure to high temperature and humidity levels, ATR-FTIR measurements were performed locally in the area of the solder paste of the coated circuit boards before and after the dynamic SIR measurements (see Figure 6-6).

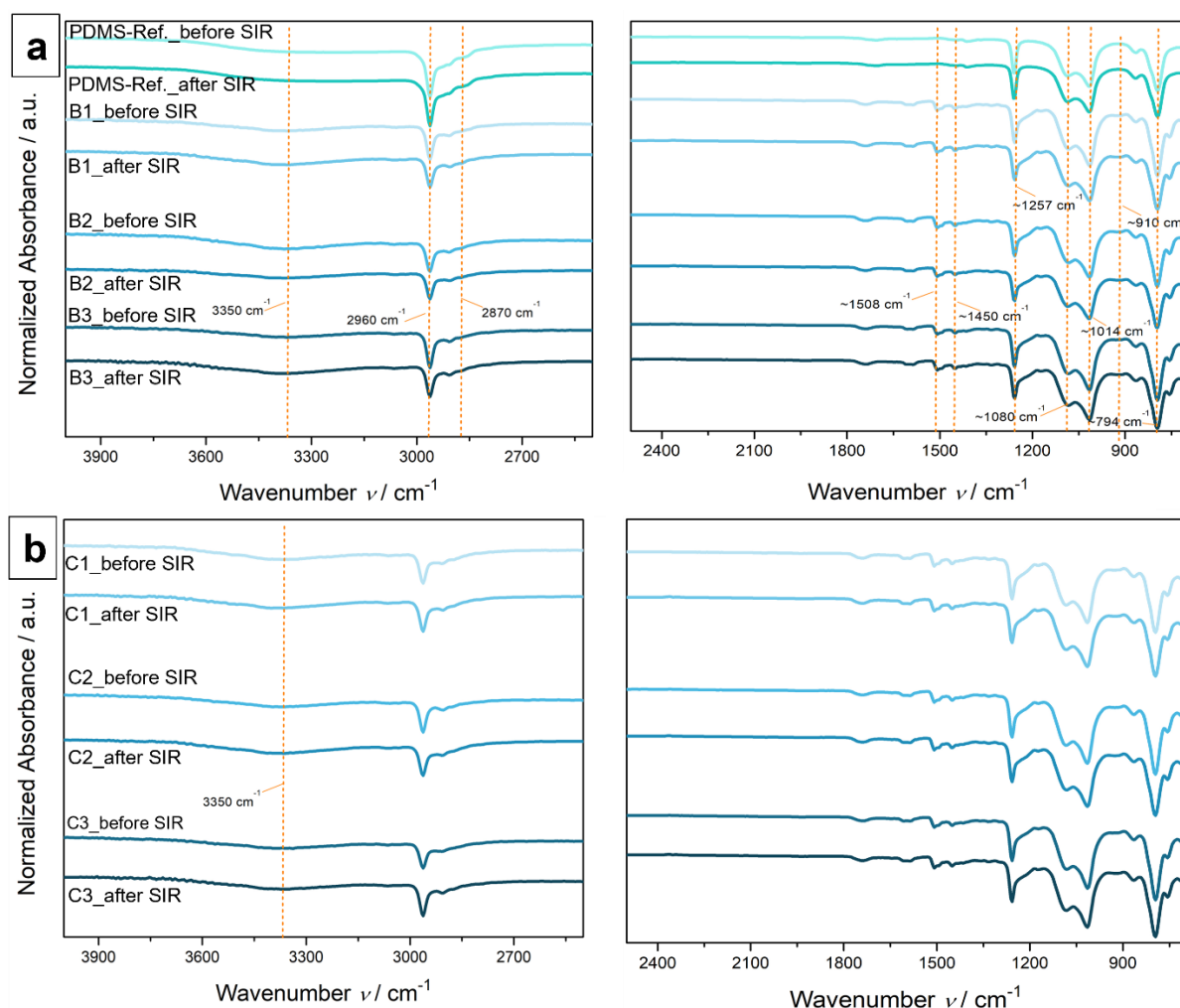


Figure 6-6: ATR-FTIR spectra of soldered PCBs coated with polymer coatings including fumed silica as well as a PDMS mono and b PDMS di before and after dynamic SIR measurements. A pure PDMS coated PCB was additionally measured as a reference measurement.

The ATR-FTIR spectra presented in Figure 6-6 a and b show the characteristic vibrations of PDMS. The asymmetric and symmetric C-H stretching vibrations of the methyl groups in PDMS are observed at 2960 cm^{-1} and 2870 cm^{-1} , confirming the aliphatic nature of the siloxane backbone. The bands at approx. 1257 cm^{-1} , 794 cm^{-1} , 1080 cm^{-1} and 1014 cm^{-1} are attributed to Si-CH₃ stretching vibrations and Si-O-Si vibrations of the siloxane backbone.^[25] In comparison to pure PDMS coatings, additional weak bands at 1508 cm^{-1} , 1450 cm^{-1} and 910 cm^{-1} are present. These peaks suggest additional deformation vibrations of methylene and methyl groups, as well as epoxy groups introduced by the functionalizing agent, confirming the incorporation of glycidyl-terminated PDMS.^[26] The peak at 3350 cm^{-1} , associated with O-H stretching vibrations, may indicate the hydrophilic nature of the epoxy functionality. This peak is slightly more pronounced in the case of diglycidyl-terminated PDMS, as observed in Figure 6-6 b, but is overall weak, indicating low moisture uptake.

For all formulations, only minor spectral changes are observed before and after SIR tests, suggesting that the incorporation of functionalized polymers into the PDMS matrix improves moisture resistance compared to short-chain silanes (see Chapter 5). To further evaluate the effects of climatic exposure, WCA and mass changes of different PDMS formulations were analyzed (see Figure 6-7).

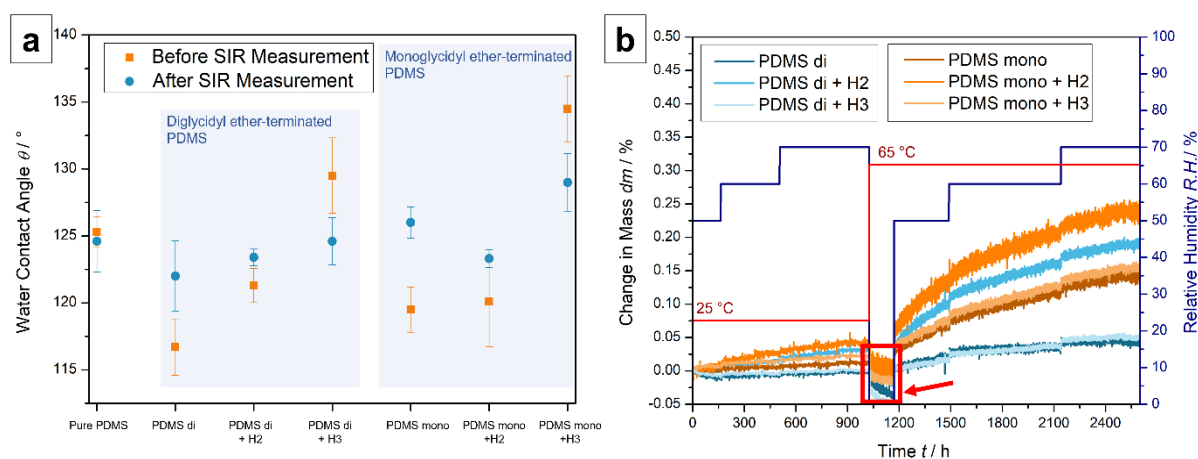


Figure 6-7: a) WCA measurements before and after dynamic SIR measurements and b) mass change as a function of temperature and relative humidity. The mass variation is mainly influenced by temperature, but also by humidity, type of functionalized polymer agent and fumed SiO₂.

The WCA measurements in Figure 6-7 a show an initial hydrophobic contact angle of $\Theta = 125.3^\circ \pm 1.2^\circ$ for the PDMS coating, which remains basically unchanged after SIR tests. This confirms the inherently high humidity resistance of PDMS due to its repeating units of methyl groups which form a non-polar surface.^[27] However, the addition of monoglycidyl ether- and diglycidyl ether-terminated PDMS reduces the initial contact angle $\Theta = 119.5^\circ \pm 1.7^\circ$ and $\Theta = 116.7^\circ \pm 2.1^\circ$, respectively. After the SIR test, the WCA value increases, indicating the desorption of the polymer ligand.

Furthermore, the addition of hydrophobic fumed silica results in more hydrophobic coatings. After SIR testing at 65 °C and elevated humidity levels, a decrease in WCA is observed in case of highly hydrophobic SiO₂ addition, showing its interaction with humidity, although the overall hydrophobic properties remain high at $\Theta = 124.6^\circ \pm 1.8^\circ$ and $\Theta = 129.0^\circ \pm 2.2^\circ$ for PDMS mono and PDMS di containing coatings, respectively. Notably, the addition of hydrophobic SiO₂ also leads to an increase in WCA after SIR testing, in contrast to the short-chain silane GPS investigated in Chapter 5, where a reduction in WCA was observed. This suggests an improved attachment of the polymer ligand to fumed silica. Unlike short-chain organosilane GPS, the functionalized polymer ligand remains within the polymer matrix due to its higher molecular weight rather than desorbing, thereby functionalizing the fumed silica surface.

The results from the WCA measurements are further supported by gravimetric analysis of the formulations (see Figure 6-7 b). Except for diglycidyl-terminated PDMS and the combination with H3, overall, a slight increase in mass is observed, although moisture uptake remains minimal and approaches the resolution limit of the instrument, as previously observed in ATR-FTIR measurements. Since mass changes occur in response to the climate profile already at 25 °C and humidity levels of 50 % *R.H.*, 60 % *R.H.*, and 70 % *R.H.*, the same humidity profile was applied at 65 °C, similar to the conditions used in dynamic SIR measurements. In gravimetric investigations, a short drying step is typically introduced between different climate settings to reset the moisture uptake of the samples to the initial value before applying a new climate profile. However, the drying step at 65 °C reveals a negative mass change, suggesting that, in addition to the desorption of previously absorbed and adsorbed moisture, desorption of the

functionalizing agent also occurs (Figure 6-7 b). This observation suggests that a combination of sorption and desorption processes occurs, allowing for a relative comparison of the data. The evaluation of the data was performed according to a first-order kinetic process:

$$m(t) = m_0 \cdot e^{-k_s t} \quad (6.1)$$

with

$m(t)$	= mass at time t
m_0	= initial mass
k_s	= sorption rate constant

The sorption rate constants were plotted against the relative humidity levels for both temperature settings (see Figure 6-8).

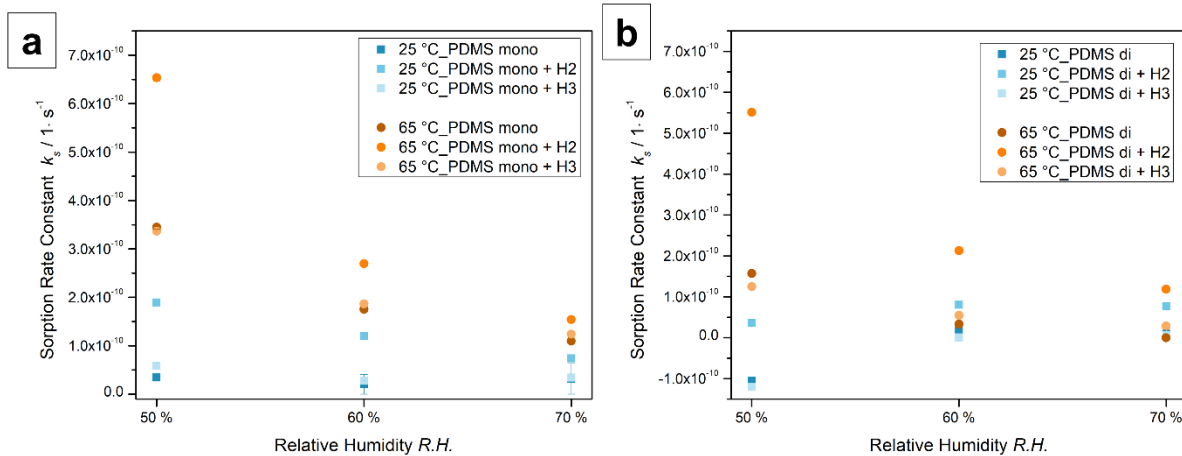


Figure 6-8: Sorption rate constant k_s as a function of relative humidity for PDMS with a monoglycidyl ether-terminated PDMS and b diglycidyl ether-terminated PDMS measured at 25 °C and 65 °C including H2 and H3.

Both plots in Figure 6-8 exhibit a general increase in the sorption rate constant k_s with a temperature rise from 25 °C to 60 °C, with few exceptions. This increase can be attributed to enhanced humidity diffusion at elevated temperatures. The highest moisture uptake of the PDMS-based formulation occurs at 50 % *R.H.* Differences in the gravimetric measurements can be attributed to the functional groups and the initial surface modification of the fumed silica within the PDMS matrix, as previously

suggested in the literature.^[28] Overall, the monoglycidyl ether-terminated PDMS exhibits its higher moisture sorption compared to diglycidyl ether-terminated PDMS. This difference can be explained by the molecular weight, as the monoglycidyl ether-terminated PDMS has a higher molecular weight of $M_{n \text{ PDMS mono}} = 5000 \text{ g} \cdot \text{mol}^{-1}$ leading to reduced migration and, consequently, an increased moisture sorption capacity. In contrast, the lower moisture uptake observed for diglycidyl ether-terminated PDMS in Figure 6-7 may suggest a reduced sorption capability. However, the initially negative sorption rate constants for PDMS di addition, as well as for the further addition of H3, and the desorption which occurs after the drying phase at 65 °C without the application of humidity, suggests that the lower molecular weight of PDMS di $M_{n \text{ PDMS di}} = 800 \text{ g} \cdot \text{mol}^{-1}$ leads to migration and subsequent desorption, resulting in a combined effect of desorption and sorption.

Additionally, the remaining silanol content and the initial dimethylsiloxyl modification, compared to the trimethylsiloxyl surface modification of SiO_2 , contribute to the highest moisture sorption for both polymer ligands and at both temperature settings. Interestingly, the observed increase in moisture sorption does not necessarily lead to a reduction in the performance of the polymer coating as can be seen from dynamic SIR measurements. On the contrary, as discussed in Chapter 5, the functionalizing agent's improved attachment to the fumed silica leads to more robust and reliable polymer coatings, despite the slightly higher moisture sorption.

The investigations of the humidity load demonstrate that the moisture uptake capacity of the PDMS-based coatings is not the predominant factor in determining their electrochemical reliability. Instead, the migration behavior and sufficient attachment of the functionalizing agents play a crucial role, highlighting the importance of careful selection of the individual components within polymer coatings.

6.3.3 Approach for Visual Analysis of Coating Defects by Neutron Imaging

In addition to adverse migration effects and suboptimal component combinations within silicon coatings, mechanical damage—such as delamination and crack formation in silicone-based coatings on PCBAs—is also critical as it facilitates moisture and

contaminant ingress. These defects can be amplified by thermal, mechanical, humidity, and electrical stressors.^[29]

Direct visual analysis of defects within polymer layers is challenging. While many modern polymers incorporate UV tracers to facilitate visual inspection, detecting defects or incomplete coverage in small or geometrically complex areas remains difficult.^[4] X-ray imaging, which primarily detects variations in electron density, is effective for identifying defects in metallic components like solder joints, but is less suitable for the investigation of light elements and soft matter.^[30] Neutron imaging offers high sensitivity to light elements and can penetrate heavy elements such as metals, making it a complementary tool for polymer coated PCBAs.^[31] Given that PCBAs contain both polymer- and metal-based components, two test PCBAs with polymer coatings were examined using neutron imaging. The test PCBs featured SOP, QFP, and BGA integrated circuit packages (see Figure 6-9).

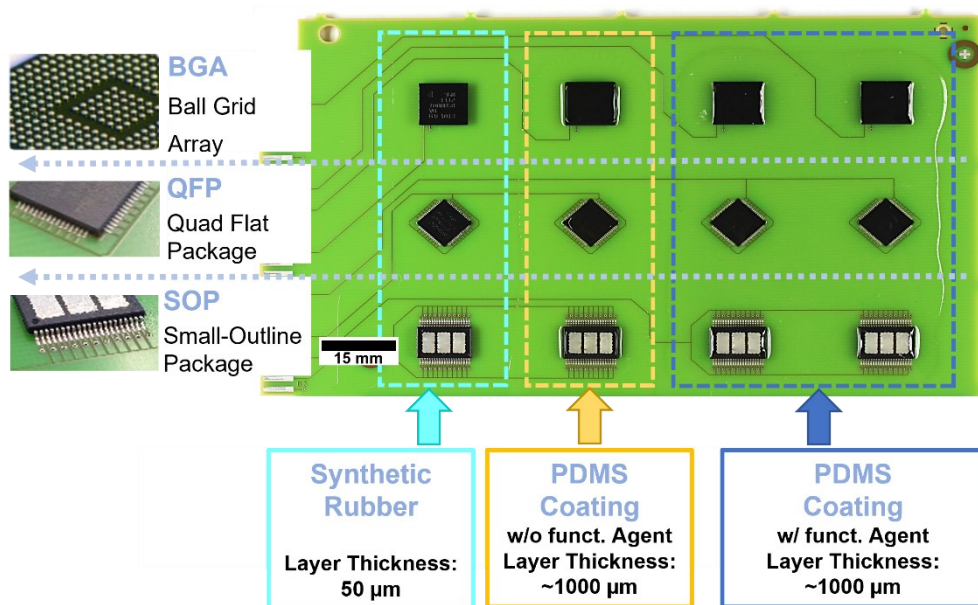


Figure 6-9: Photographic image of the thermal-shocked PCBA including solder paste, solder mask as well as coating with PDMS and synthetic rubber.

The coatings consisted of a 1000 μm-thick layer of PDMS in combination with fumed silica as well as the addition of functionalizing agents GPS and MPS. Moreover, a 50 μm-thick synthetic rubber layer was applied. To induce defects, one test assembly

underwent 50 thermal shock cycles between - 60 °C and + 150 °C, while the other served as a reference. Both PCBAs were then immersed in a 4.0 wt.% GdCl_3 aqueous solution within a vacuum chamber. After rinsing and drying, the samples were analyzed using the ANTARES neutron imaging facility. Afterwards, quantitative analysis of the Gd-load was performed using ImageJ, with the corresponding values displayed as percentages and highlighted in red (see Figure 6-10).

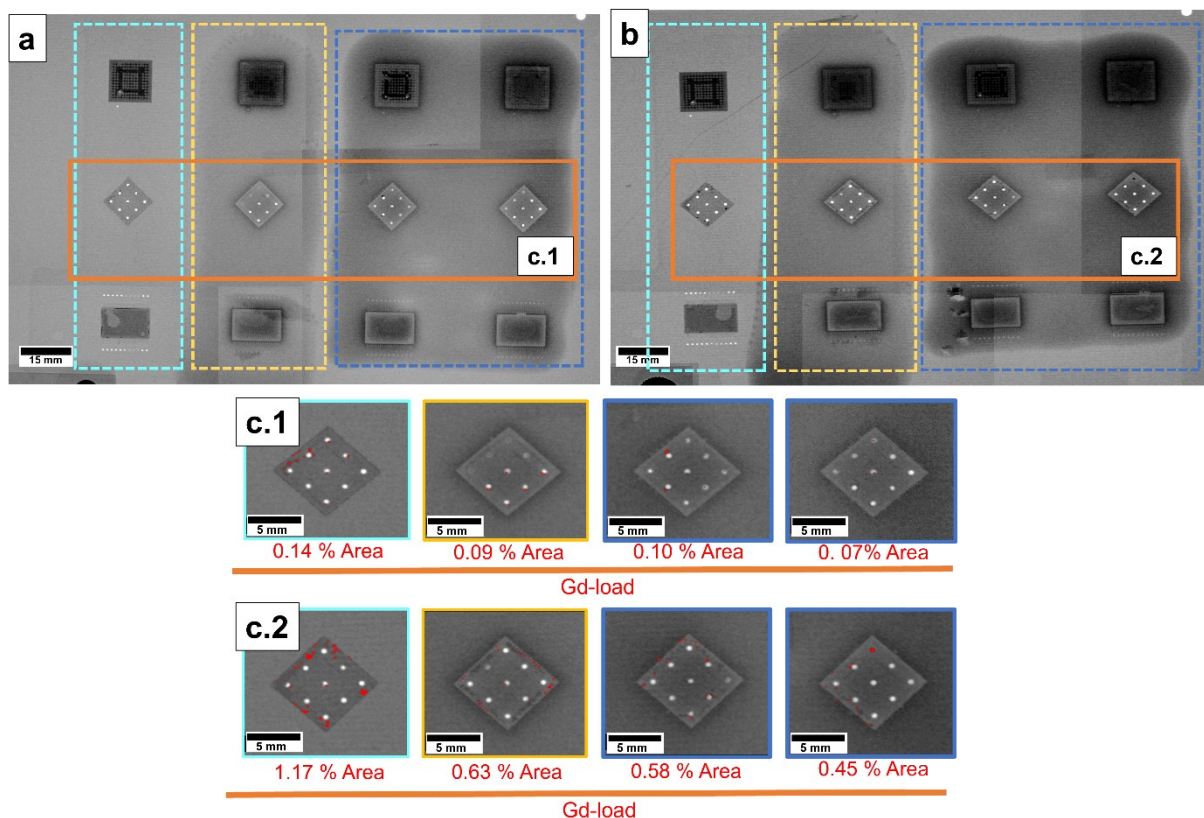


Figure 6-10: Assembled neutron image of polymer-coated a untreated and b thermo-shocked PCBAs. The sectional views show the focus on the QFP package and the Gd contrast agent of the c.1 untreated and c.2 treated PCBAs. The Gd-load is apparent in all QFPs, with the highest amount observed for the thinnest synthetic rubber layers.

The neutron images in Figure 6-10 clearly distinguish the polymer coatings from the conventional epoxy resin-based mold compounds of the integrated circuit packages and the PCB substrate, with the PDMS-based layers exhibiting the highest contrast.

Due to manual application, these PDMS layers are thicker and more inhomogeneous compared to the synthetic rubber coatings, which were applied using controlled jet dispensing. This inhomogeneity prevents a direct comparison between the two coating types. However, Gd-load is evident at the edges and beneath the QFPs. Furthermore, the percentage of contrast agent relative to the total coated area in the individual image sections (Figure 6-10 c.1 and c.2) increases significantly after thermal shock treatment. This suggests that thermal cycling may induce microstructural changes or defects, leading to enhanced permeability to the contrast agent solution. These findings mainly highlight that neutron imaging enables visualization of the most critical coating areas, which in this case include the outgoing leads and edges of the QFPs and the PCB surface, areas that were previously unobservable by visual inspection.

6.3 Conclusion

In conclusion, dynamic SIR measurements have proven to be particularly suitable for the evaluation of insulation performance and the moisture sensitive analysis of different compositions in PDMS-based coatings. The results show that conventional organosilane GPS leads to the failure of 200 μm comb structures already at 70 % *R.H.* due to ECM of silver from the SAC no-clean solder paste. In contrast, polymer ligands with comparable functional groups but higher molecular weight significantly improve insulation resistance, showing reduced migration. The degree of hydrophobic properties of micrometer-sized fumed silica also plays a critical role with regard to electrochemical reliability. While highly hydrophobic silica surfaces increase WCAs, the degree of water repellency alone does not determine insulation performance. Instead, the reduction in functionalizing agent migration achieved by improved attachment to fumed silica with higher residual silanol group content and dimethylsiloxo surface modification was identified to be crucial in terms of robust insulation properties. Finally, neutron imaging, due to its high sensitivity to light elements, was shown to have great potential as a future inspection method for detecting defects and ineffectively coated areas on PCB assemblies.

6.4 Outlook

Currently, electronic devices are inspected using visual and X-ray methods, while neutron imaging is used primarily in research and specialized laboratories. The infrastructure required to generate neutron beams is complex and costly, hindering their integration into industrial processes. However, advances in compact neutron sources, such as accelerator-driven low-energy neutron generators, are underway to make neutron imaging more accessible.^[32] These developments could lead to the adoption of neutron imaging in industrial applications, including electronics industry. In addition, the investigation of polymer coatings *via* neutron imaging can be improved both at the material level and through improvements in measurement setup. Automated application of polymer coatings facilitates a more homogeneous distribution and thicknesses, enabling better comparisons across different types and components of the coatings. Furthermore, *in-situ* neutron imaging studies could be conducted on actively SIR-measured and climate-treated test PCBs. To achieve this, the measurement setup developed at the Paul Scherrer Institute (PSI) can be utilized, comprising a climate chamber with neutron-transparent windows, a moisture generator, and connecting tubes.^[33] Integrating this setup with a potentiostat would allow for precise control and measurement of applied biases during the experiments. For improved contrast in neutron imaging, Low Temperature Co-fired Ceramic (LTCC) substrates can be employed instead of FR-4 laminates. This approach would enable *in-situ* observation of the effects of temperature, humidity levels, and applied biases on the polymer coatings, providing insights into their performance under varying environmental conditions.

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7 SUMMARY

In this thesis, it was demonstrated at both the micrometer and nanometer scales that functionalized polymers are crucial components in nanometer- and micrometer-sized composite materials. Due to their higher molecular weight and functional groups, these polymers offer significant advantages in addressing miniaturization challenges in nanotechnology and microelectronics. These challenges mainly include the tendency of anisotropic nanoparticles to aggregate and lose anisotropic shape, and the decreasing spacing between conductors in increasingly compact electronic devices.

First, the focus of the thesis was on nanocomposites. The attachment of polymer shells to AuNPs by ligand exchange was demonstrated by replacing citrate and CTAB by PEHA- and SH-terminated PS. By systematically adjusting the molecular weight of PS-PEHA, interparticle spacing in both spherical and rod-like nanoparticles was precisely controlled, reaching plateau values at higher molecular weights. UV-Vis-NIR spectroscopy and TEM analyses confirmed significant red shifts in surface plasmon resonances and preferential binding of PS-PEHA to the lateral surfaces of AuNRs. The moderate binding and lateral attachment were identified as crucial for maintaining the anisotropy of the nanoparticles. These findings provide valuable insights into optimizing ligand exchange processes by promoting moderate and flexible polymer attachment, contrasting with the commonly assumed necessity of strong affinity from *e.g.* thiol-functional groups.

Moreover, the successful synthesis of gold nanoparticles using a polymer-assisted seed-mediated growth approach, replacing conventional low molecular weight ligands with polymer ligands was shown. Spherical seeds grew to approximately 6 nm in diameter with amino-terminated PS, and both spherical and ellipsoidal morphologies were observed after silver-assisted growth. Comparable interparticle distances between ligand-exchanged and directly polymer-stabilized gold nanoparticles suggest similar polymer attachment in both methods, validating direct polymer attachment as an alternative to ligand exchange. Fully grown anisotropic gold nanoparticles could not be obtained through direct polymer stabilization, likely due to steric hindrance from long polymer chains limiting further gold ion deposition. However, optimization suggestions and an approach for understanding polymer-assisted gold nanoparticle synthesis were provided to enable reliable synthesis of polymer-stabilized nanoparticles.

After the fundamental study of nanocomposites, the focus shifted to PDMS coating model formulations with micrometer-scale microcomposites, although the model can also be extended to potting and sealing materials. It is described that the insulating properties of PDMS-based coatings on test PCBs are strongly influenced by their composition and interactions. While coatings with hydrophobic fumed silica initially maintained stable insulation resistance, the incorporation of short-chain silanes, particularly GPS led to rapid failure due to silver dendrite formation bridging copper paths. GPS migration and desorption behavior and its highly reactive epoxy functionality were identified as key factors contributing to degradation. Functionalizing hydrophobic SiO₂ with GPS reduced PCB failures, but slow methoxy group hydrolysis in GPS- and MPS containing coatings increased hydrophilicity, leading to failure in 200 μm comb structures. While GPS and MPS are already discussed in the literature to migrate during curing, this study shows that they continue to migrate and desorb after curing, which affect electrochemical reliability. Though this was observed using a model system, some commercial formulations with higher SiO₂ content may not initially show this phenomenon. However, the continuing miniaturization of electronics with reduced distances between conductive paths increases the importance of considering migration effects. Dynamic SIR measurements effectively evaluate the insulation performance and moisture sensitivity of PDMS-based coatings. Inclusion of GPS led to ECM and failure of 200 μm comb structures already at 70 % *R.H.* Conversely, polymer ligands with similar functional groups but higher molecular weights maintained high insulation resistance, attributed to reduced migration properties. While highly hydrophobic fumed silica increased water contact angles, improved attachment of functionalizing agents to silica with higher residual silanol content and dimethylsiloxy modification primarily influenced insulation performance. This suggests that both higher molecular weight and strong interactions between SiO₂ and functionalizing agents are crucial for moisture robustness and electrochemical reliability. In addition to surface isolation considerations, neutron imaging proved to be a promising future technique for detecting defects and inadequately coated areas on printed circuit board assemblies.

This work emphasizes the necessity of precisely adjusting individual components within nano- and microcomposite materials and applying concepts from both domains to create the best possible materials for future technologies.

8 OUTLOOK

In addition to the next steps already discussed in the respective chapters, the promising use of functionalized polymers at the micrometer and nanometer scale should in general be further explored in future research.

In the field of nanocomposites, direct functionalized polymer-assisted synthesis of primarily anisotropic nanoparticles offers significant advantages, particularly by eliminating the need for post-synthesis modifications such as ligand exchange processes. Beyond synthesis optimization and *in-situ* characterization of polymer-assisted nanoparticle growth, the possibility to control interparticle spacing of PS-PEHA stabilized nanoparticles shall be investigated, in accordance with molecular weight variation of the polymer ligand. Interparticle spacing in supracolloidal assemblies critically influences emerging effects: Small spacings enhance plasmon coupling, relevant for surface-enhanced Raman spectroscopy (SERS) applications, while larger spacings may be beneficial for luminescence enhancement. Precise plasmonic control *via* polymer ligands enables advances in nanotechnology and materials science.

In the area of microcomposites, functionalized polymers are expected to play an increasingly crucial role. PDMS-based materials, valued for their e.g. high thermal stability, insulation properties and flexibility, are expected to become more widely used, especially in the (micro-)electronics sector. This trend is further driven by the search for alternatives to per- and polyfluorinated alkyl substances (PFAS), which have come under increasing criticism for their environmental persistence and potential health risks. Consequently, understanding the interactions between the PDMS polymer matrix, fillers and interfaces will be essential. In this context, polymer functionalization agents that have proven themselves with one functional group can be further developed into copolymers with two functionalities. These copolymers can include functional groups such as glycidoxymoiety to interact with substrate surfaces and filler particles, while also containing C=C and C–H functional groups to ensure network connectivity during PDMS curing. This approach would reduce migration and improve the strength of adhesion and in general of the network. Beyond SIR measurements, additional mechanical tests—including tensile shear strength and tear resistance in addition to examining adhesion and cohesion behavior—should be performed to comprehensively evaluate bond development and overall material performance.

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APPENDIX

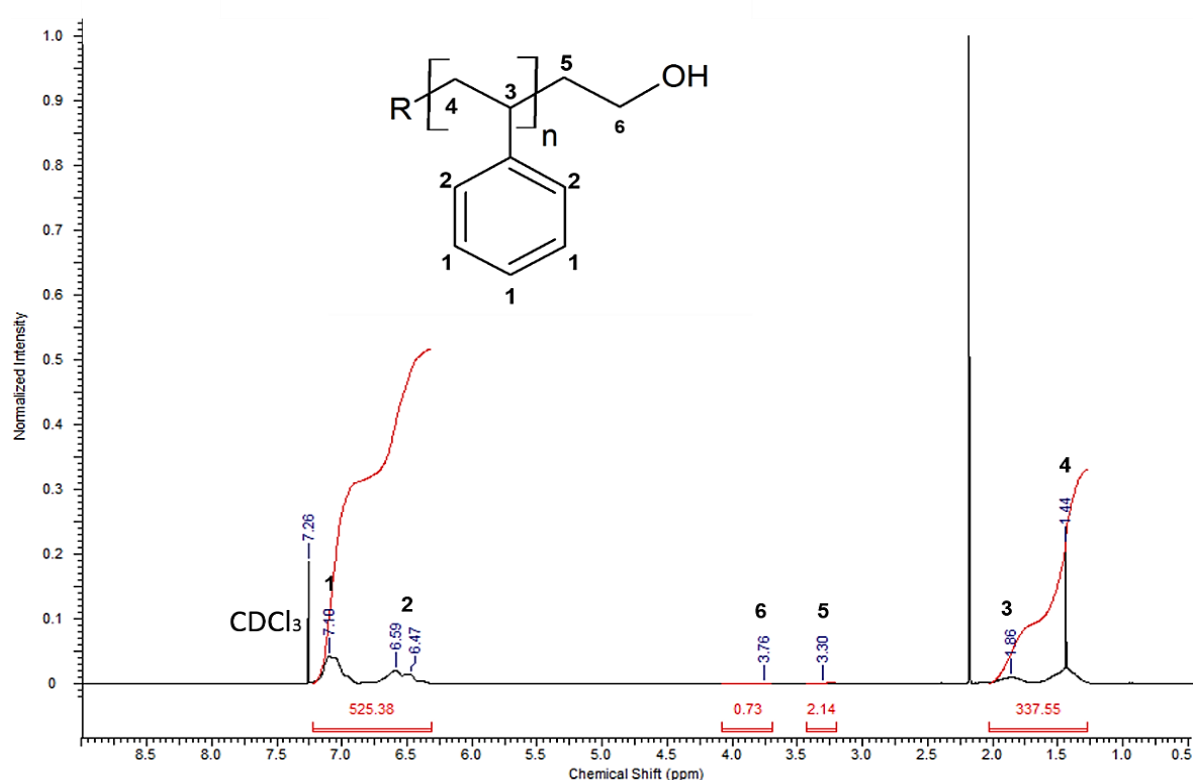


Figure A-1: Proton NMR spectrum of OH-terminated PS with $M_n = 11.5 \text{ kg} \cdot \text{mol}^{-1}$ at 300 Hz.

The assignments of the peak positions from the NMR spectrum are listed in Table A-1.

Table A-2: Peak positions and their assignments corresponding to Figure A-1.

Chemical Shift δ / ppm	Assignment
7.3	Peak caused by CDCl_3
7.1	Peak 1: Proton characteristic of benzene ring
6.6; 6.5	Peak 2: Protons representing the benzene ring
1.86; 1.44	Peak 3 and 4: Aliphatic protons from the backbone
3.8; 3.3	Peak 5 and 6: Weaker signals from protons adjacent to the hydroxyl group
2.2	Signal attributed to residual acetone from NMR tube cleaning

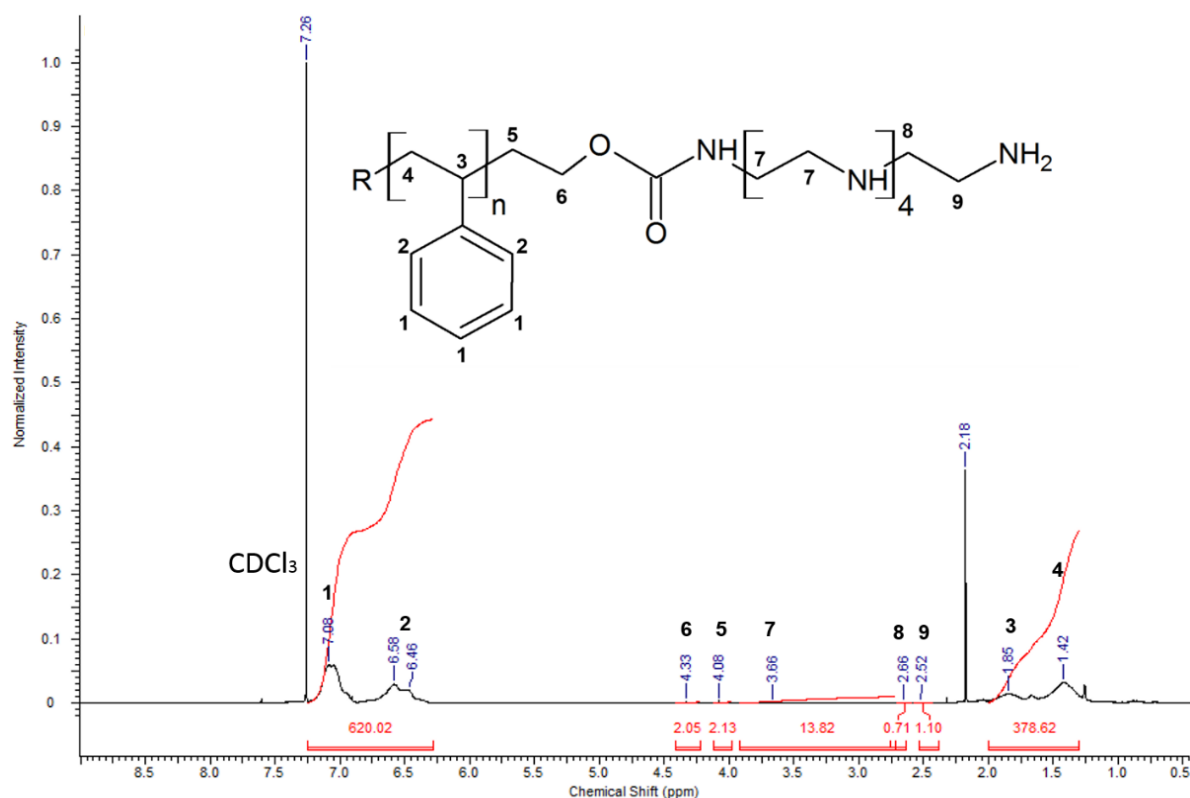


Figure A-2: Proton NMR spectrum of PEHA-terminated PS at 300 Hz.

The additional assignments of the peak positions from the PEHA-terminated PS NMR spectrum are listed in Table A-3.

Table A-2: Peak positions and their assignments corresponding to Figure A-2.

Chemical Shift δ / ppm	Assignment
4.33; 4.08	Peak 5 and 6: Remaining protons of methylene groups post CDI-activation
3.7	Peak 7: Broad peak in the proton NMR spectrum attributed to protons within the PEHA end group
2.66; 2.52	Peak 8 and 9: Peaks caused by methylene groups adjacent to the PEHA end group

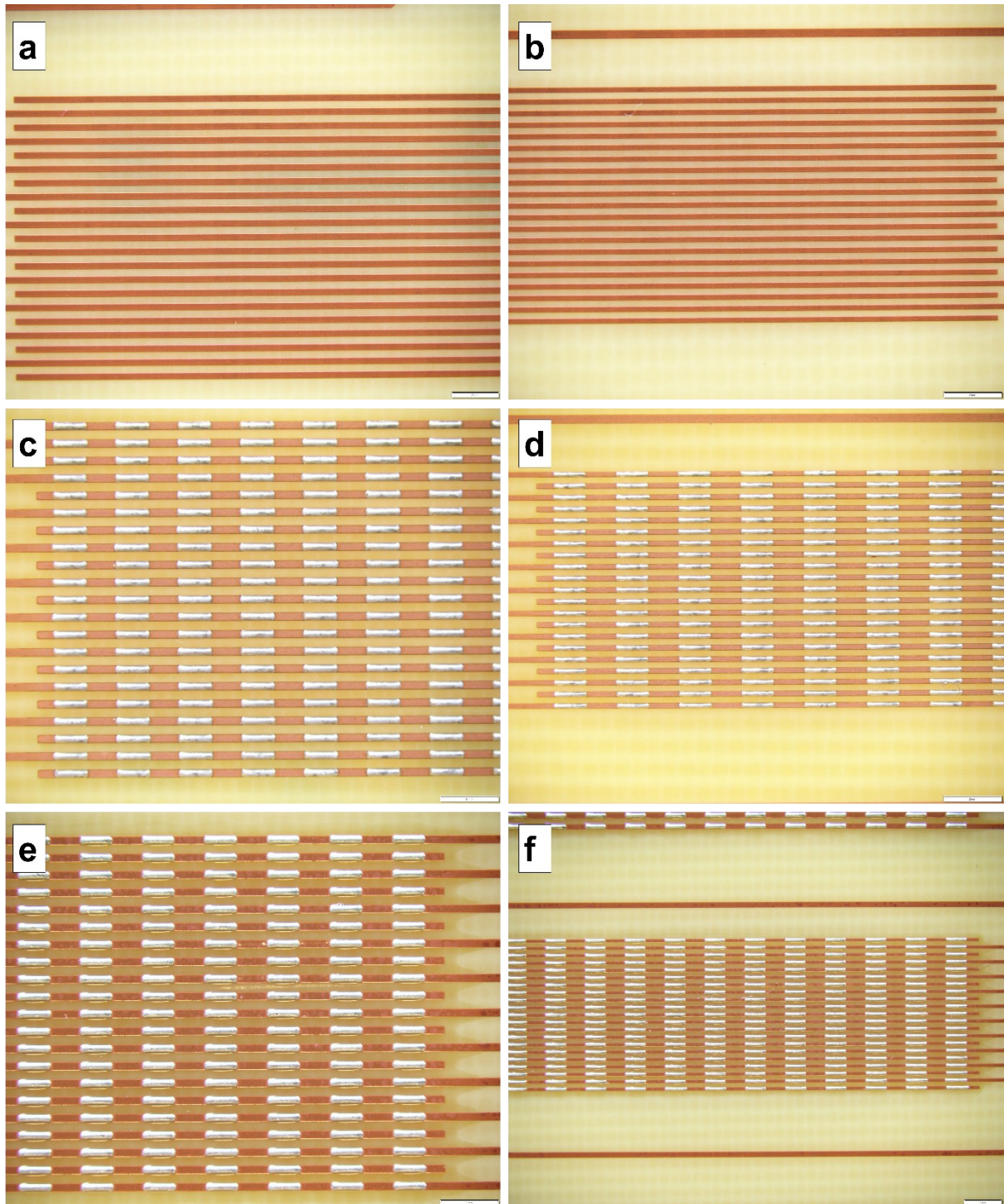


Figure A-3: Overview light micrographs of 300 μm Cu-Cu distances of a unsoldered, b soldered and c soldered and PDMS coated test boards after SIR measurements. The light micrographs of 200 μm comb structures are shown in b, d and f. The scale bars correspond to 2 mm.

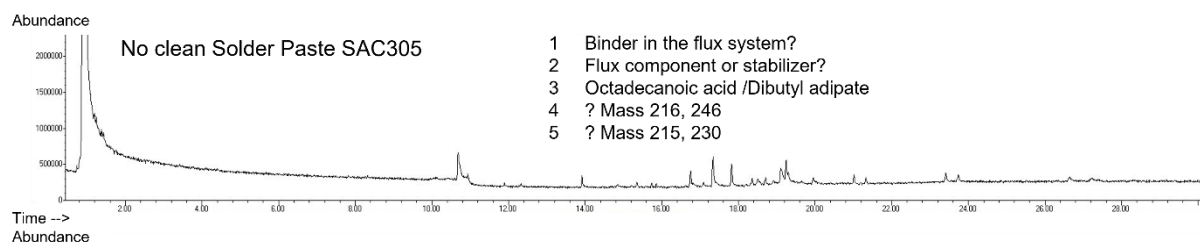


Figure A-4: Gas chromatogram of no-clean solder paste SAC305 after reflow soldering. Question marks indicate a missing or incomplete match with the database.

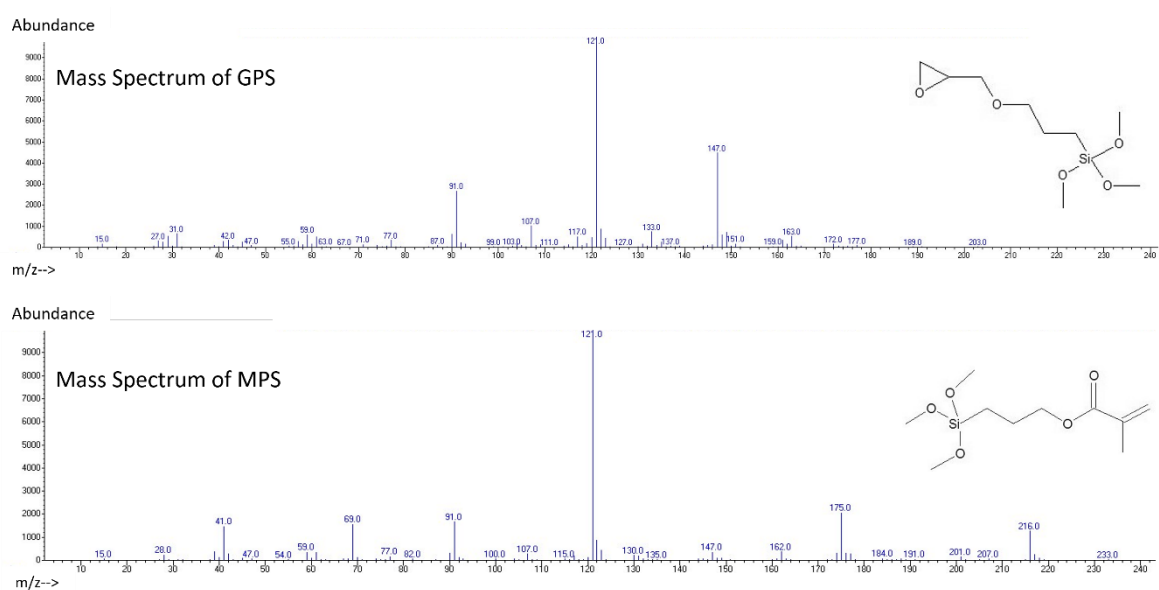


Figure A-5: Mass spectra of the PDMS coating containing GPS and MPS. The presence of trimethoxysilane is confirmed by the identification of the characteristic mass of 121.

EIDESSTATTLICHE ERKLÄRUNG

Ich, Alexandra Leluk, erkläre hiermit, dass diese Dissertation und die darin dargelegten Inhalte die eigenen sind und selbstständig, als Ergebnis der eigenen originären Forschung, generiert wurden.

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