© © 2015 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

Systematic Comparison of Metal Contacts on CVD Graphene

A. Gahoi, V. Passi, S. Kataria, S. Wagner, A. Bablich and M. C. Lemme

University of Siegen, School of Science and Technology, Hölderlinstr.3, 57076 Siegen, Germany

Corresponding author: max.lemme@uni-siegen.de

***Abstract*— An experimental study was conducted for forming high quality ohmic contacts to graphene. Metal contacts of platinum/gold (Pt/Au), nickel/gold (Ni/Au), palladium (Pd), Ni, and Au to monolayer chemical vapor deposited graphene were studied. The experimental data reveal that pure Au and Ni/Au provide highly reproducible low resistance ohmic contacts. The results presented in this work indicate potential contact metals suitable for high frequency electronic devices.**

Keywords— contact resistance; graphene; graphene transfer; rapid thermal annealing; TLM

I. INTRODUCTION

Graphene has triggered substantial scientific and technological interest due to its extremely high intrinsic mobility [1], which can reach values of up to 2 x 10^5 cm^2/Vs at a carrier density of n = 1 x 10^{12} cm^{-2} on SiO_2 substrates [2]. Graphene is a zero-bandgap semimetal with both electrons and holes as the charge carriers with very high electrical conductivity and can conduct electricity better than copper [1]. Chemical vapor deposition (CVD) is a technique that enables wafer scale synthesis of graphene [3][4] which still shows impressive charge carrier mobility [5]. Presently, graphene is investigated for a range of potential applications in radio frequency (RF) analog transistors [6], [7], [8] terahertz modulators [9], photodetectors [10], [11] and nanoelectromechanical systems [12][13]. It is evident that all of these diverse applications can only hope to fully exploit the exceptional properties of graphene if the electrical contact resistance (R_C) associated with the metal-graphene junction is low. In fact, a high value of R_C is identified as the major limiting factor for the maximum frequency of oscillation (F_{max}) in graphene field effect transistors (GFETs) [14]. The contact resistivity requirement for state-of-the-art silicon metal oxide field effect transistors (MOSFETs) is 80 Ω µm per contact [15]. Reported values for typical metal-graphene contacts, in contrst, demonstrate higher R_C values, varying greatly from a few hundred to a thousands of Ω µm [14]. This large variation in the values is attributed to the difference in the specific fabrication processes, gate bias and measurement conditions.

High R_C arises due to current injection from a 3D material (metal) to a 2D material (graphene), which typically leads to a line contact instead of an areal contact. Furthermore, the limited density of states (DOS) available in the graphene under the contact and metal-graphene coupling play a significant role in increasing R_C [16], [17], [18]. A unique physical interaction takes place at the metal-graphene interface/junction, which is illustrated in Figure 1. At the interface, a charge transfer region exists in the graphene, which gradually decreases away from the metal-graphene contact junction. The charge transfer leads to dipole formation at the interface which has a potential difference expressed as ΔV [17]. ΔV depends on the chemical bonding of metal and graphene and it is differs from the work function difference between graphene and metal $\Delta\Phi_{MG} = \Phi_M - \Phi_G$ where Φ_M is the work function of metal, Φ_G is the work function of graphene [17]. This dipole formation at the interface due to the charge transfer region increases the contact resistance. The low DOS around Fermi level (E_F) of graphene increases the screening length (λ) given by equation (1)

$$\lambda = [4\pi\, N(E_F)]^{-1/2} \qquad (1)$$

where $N(E_F)$ denotes the DOS at E_F [17]. Depending on the geometry and the carrier density and type in the graphene, the long charge transfer region (or large screening length) gives rise to a p-n junction in the graphene which results in an additional resistive component [17].

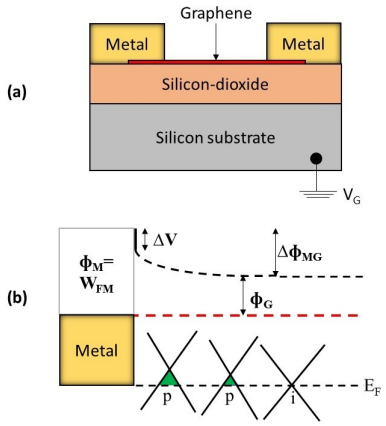


Figure 1: (a) Schematic of a back gated GFET (b) Energy band diagram of the metal-graphene contact (after [17]). The green area indicates charge transfer, which gradually decreases away from the metal-graphene interface.

The possible factors that influence R_C at the metal-graphene junction include dipole formation due to the charge transfer at the interface, the low DOS available in the graphene under the contact and the metal-graphene coupling strength. Undesired contamination introduced during device fabrication also affects R_C. Therefore, an empirical study is performed in a methodological manner to understand the factors influencing R_C.

A. Gahoi, V. Passi, S. Kataria, S. Wagner, A. Bablich, and M. C. Lemme, 'Systematic comparison of metal contacts on CVD graphene', in *2015 45th European Solid State Device Research Conference (ESSDERC)*, Sep. 2015, pp. 184–187. doi: 10.1109/ESSDERC.2015.7324744.

© © 2015 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

II. EXPERIMENT

Boron doped silicon wafers with a resistivity between 1-20 Ω cm were used as starting substrates. The silicon wafers were thermally oxidized to an oxide thickness of 85 nm, confirmed by spectral ellipsometry. The wafers were further diced into samples of 1.3 cm x 1.3 cm. The samples were cleaned in acetone for 5 min in an ultrasonic bath, followed by isopropyl alcohol (IPA) for 5 min and rinsing in deionized water (DI water). A Moorfield rapid thermal processing chemical vapour deposition tool was used to grow graphene on copper foils [4]. Graphene growth was performed in a three step process where (i) copper is first annealed at 950°C in a hydrogen (20%) atmosphere, then, (ii) argon (80%), methane (5%) and hydrogen (15%) gas is passed into through the heated chamber (at 950°C) where the methane dissociates leading to graphene growth, and finally (iii) the copper foil is cooled to room temperature [19]. The graphene films were transferred onto the SiO_2/Si samples using an electrochemical delamination technique [4][20]. Figure 2 shows an optical micrograph of graphene on an SiO_2/Si substrate after the transfer. The inset shows large area homogenous graphene. Optical lithography and oxygen (O_2) plasma etching were used to define graphene channels. Metal contact pads (Pt/Au, Ni/Au, Pd, Ni and Au) were deposited (on different samples) by an evaporation tool, followed by a lift-off process. A schematic of the entire fabrication process flow is shown in Figure 3.

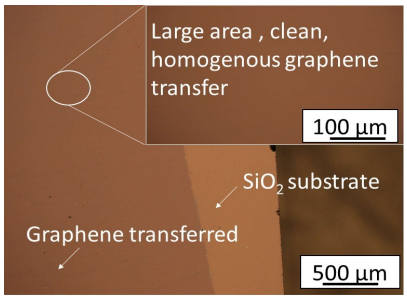


Figure 2: Large area, clean and homogenous graphene on a SiO_2/Si substrate.

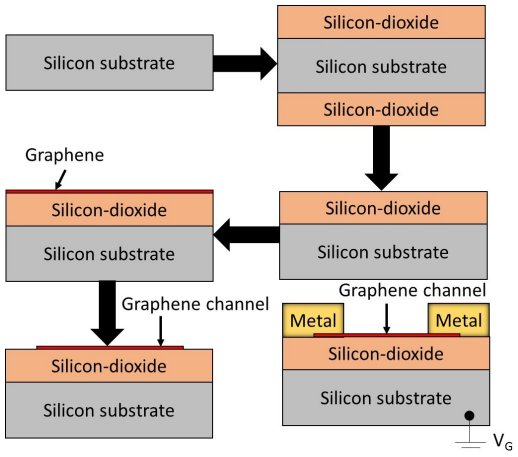


Figure 3: Fabrication process for graphene FET.

Transmission line method (TLM) structures [21] with contact spacings between 5 and 80 µm were fabricated as shown in the optical micrograph in Figure 4. TLMs with contact separation as small as 5 µm were designed to accurately estimate the contact resistance, whereas contact separations as large as 80 µm were designed to ensure that the measured resistance is dominated by the graphene channel resistance in order to extract the exact sheet resistance [22].

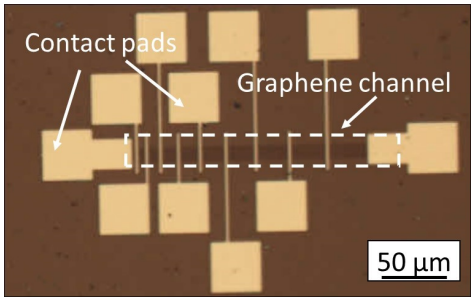


Figure 4: Optical micrograph of a TLM structure

III. RESULTS & DISCUSSION

Electrical characterization commenced by measuring the fabricated devices in ambient air using a Keithley parameter analyzer. Twenty TLM structures with channel widths of 4 µm, 5 µm, 8 µm, 10 µm, 16 µm, 20 µm, 30 µm and 40 µm were measured. For each contact separation (a variation of 10% between values was measured), four devices were measured. Rapid thermal annealing (RTA) was carried out for 1 hour in an argon (95%)/hydrogen (5%) atmosphere at 450ºC for Pd and Au contact. The extracted contact resistance for various metals to graphene is plotted in Figure 5 (Pd) and Figure 6 (Pt/Au, Ni/Au, Ni and Au). A device with a channel width of 4 µm was measured when Pd was used as the contact metal, and devices with a channel width of 40 µm was measured for other metal combination. The correlation coefficients (R^2) of the linear fits lie in the range between 0.9941~1. Low contact resistance is achieved with pure Au contacts and a stack of Ni/Au contacts..The results are summarized in Table 1.

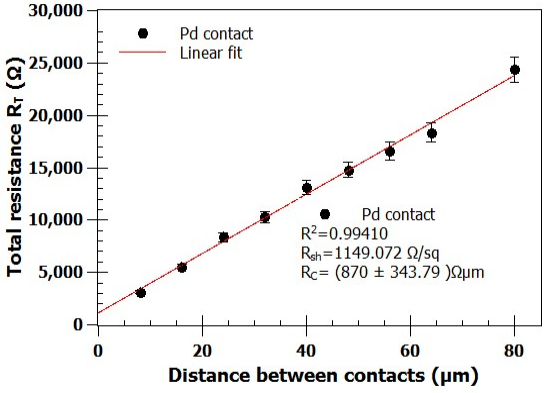


Figure 5: Total resistance (R_T) as a function of contact separation. The contact metal used was Pd, thickness 75 nm and the device measured had a channel width of 4 µm.The red line is the linear fitting curve.

A. Gahoi, V. Passi, S. Kataria, S. Wagner, A. Bablich, and M. C. Lemme, 'Systematic comparison of metal contacts on CVD graphene', in *2015 45th European Solid State Device Research Conference (ESSDERC)*, Sep. 2015, pp. 184–187.
doi: 10.1109/ESSDERC.2015.7324744.

© © 2015 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

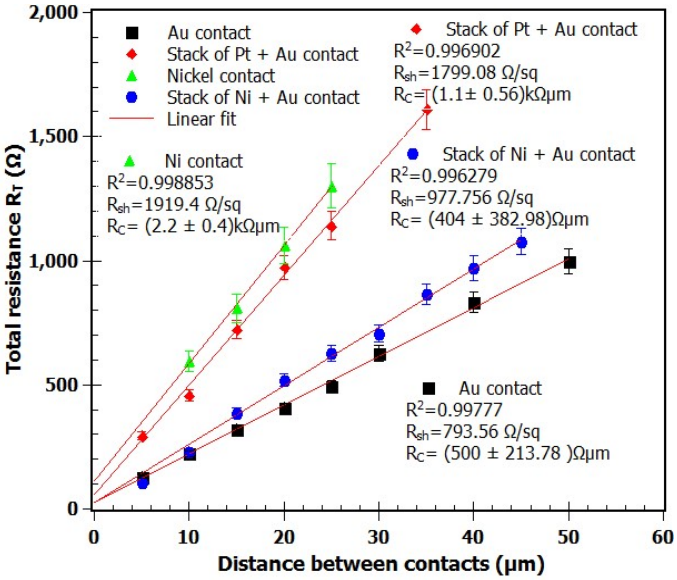


Figure 6: Total resistance (R_T) as a function of contact separation. The contact metal used was Pt/Au, Ni/Au, Ni and Au. The channel width is 40 μm. The red line is the linear fitting curve.

Further measurements were performed with a drain bias of 50 mV on the devices with a contact stack of Ni/Au for a lengths (L_g) of 5 μm, 10 μm, 15 μm, 20 μm and 25 μm and a channel width (W) of 40 μm. Transfer characteristics of the devices are presented in Figure 7. A constant drain bias of 50 mV was applied and the gate-source bias was swept from +80 V to -40 V. Minimum conductance (i.e. the "Dirac point") occurs at a gate bias of ~ 10.3 V for L_g = 5 μm. The contact resistance exhibits a gate voltage dependence, is highest at the Dirac point and decreases as the channel is electrostatically doped by the back gate.

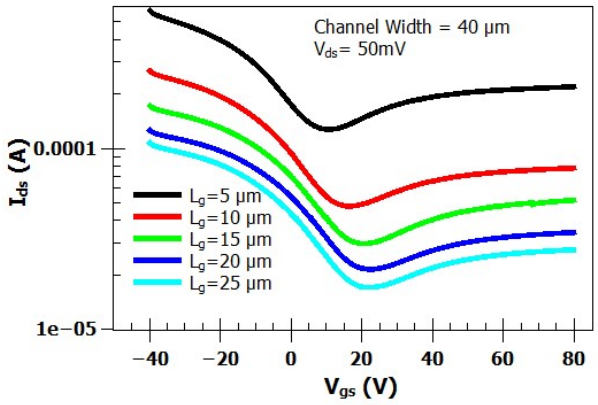


Figure 7: Transfer characteristics ($I_{ds} - V_{gs}$) for Ni/Au contact.

The TLM measurements were used to extract the R_C at the Dirac point (~10.3V, Figure 8). R_C was 3800 (± 592) Ω μm with a correlation coefficient of R^2= 0.9981. A smaller contact resistance was observed when the channel is heavily p-doped, e.g. at V_{bg} = -20 V. Here, the R_C value was found to be 172 (± 140) Ω μm with a correlation coefficient of R^2= 0.99751.

Table 1: Contact resistance and sheet resistivity of measured devices with various metal contacts

Contact Metal	Thickness (nm)	Channel width (W) (μm)	R_{sh} (kΩ/□)	R_CW (Ω μm)
Ni	75	40	1.919	(2248 ± 417)
Au	81	40	0.793	(500 ± 213)
Pd	75	4	1.149	(870 ± 343)
Stack of Ni/Au	Ni – 25 Au - 50	40	0.977	(404 ± 382.9)
Stack of Pt/Au	Pt – 25 Au - 50	40	1.799	(1068± 514.6)

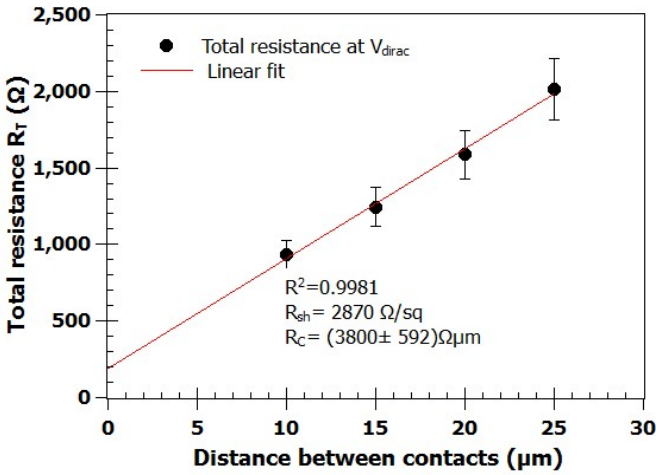


Figure 8: Total resistance (R_T) as a function of contact separation in a graphene FET with Ni/Au contact at ~ 10.3 V The red line is a linear fitting curve.

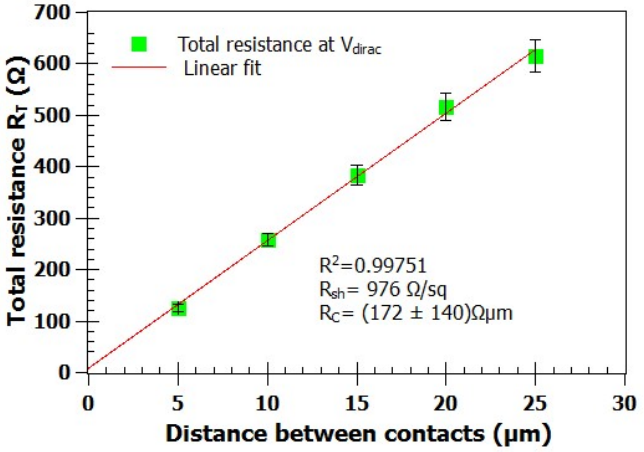


Figure 9: Total resistance (R_T) as a function of contact separation in a graphene FET with a Ni/Au contact at ~ [- 20 V] (p-doped). The red line is a linear fitting curve.

A. Gahoi, V. Passi, S. Kataria, S. Wagner, A. Bablich, and M. C. Lemme, 'Systematic comparison of metal contacts on CVD graphene', in *2015 45th European Solid State Device Research Conference (ESSDERC)*, Sep. 2015, pp. 184–187.
doi: 10.1109/ESSDERC.2015.7324744.

© © 2015 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

Devices with Pd and Au metal contacts were subjected to rapid thermal annealing (RTA). This resulted in a reduction in contact resistivity $R_C W$ (shown in Figure 10 and Figure 11), which is attributed to an improvement in the adhesion of the metal-graphene contacts. A possible explanation could be that carbon dissolves into the metal during RTA, which leads to defects in the atomic structure of graphene. This leads to so-called "end-contacts", i.e. covalent bonds between the metal and the graphene, reducing the contact resistance [23].

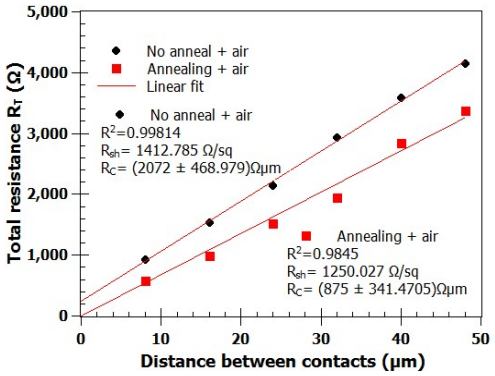


Figure 10: Influence of annealing for total resistance of the device for back gated transistors with Pd contact. The channel width is 17 μm.

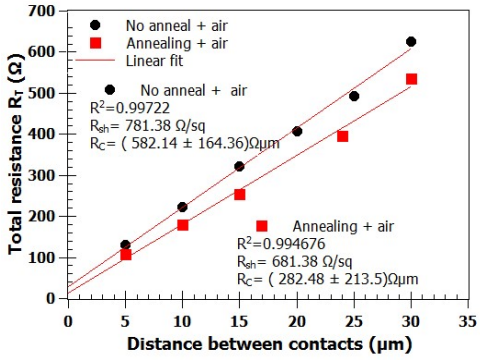


Figure 11: Influence of annealing for total resistance of the device for back gated transistors with Au contact. The channel width is 40 μm.

IV. CONCLUSION

Five different metal contacts (Au, Ni, Pd, Ni/Au, and Pt/Au) to CVD graphene have been studied experimentally and compared. The fabricated devices were characterized using a TLM structures to extract R_C. The lowest R_C is observed for devices with Au contacts. The R_C for the Ni/Au contacts (404±383) Ω μm is similar to that of pure Au, but with higher sheet resistance (977.8) Ω/□. Using pure Au contacts, low contact resistance (500±213) Ω μm and sheet resistance (793.56) Ω/□ are achieved.

REFERENCES

[1] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Mater.*, vol. 6, no. 3, pp. 183–191, 2007.

[2] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, "Intrinsic and extrinsic performance limits of graphene devices on SiO2," *Nat. Nanotechnol.*, vol. 3, no. 4, pp. 206–209, 2008.

[3] S. Rahimi, L. Tao, S. F. Chowdhury, S. Park, A. Jouvray, S. Buttress, N. Rupesinghe, K. Teo, and D. Akinwande, "Towards 300mm Wafer-Scalable High-Performance Polycrystalline Chemical Vapor Deposited Graphene Transistors," *ACS Nano*, Sep. 2014.

[4] S. Kataria, S. Wagner, J. Ruhkopf, A. Gahoi, H. Pandey, R. Bornemann, S. Vaziri, A. D. Smith, M. Ostling, and M. C. Lemme, "Chemical vapor deposited graphene: From synthesis to applications," *Phys. Status Solidi A*, vol. 211, no. 11, Nov. 2014.

[5] H. Zhou, W. J. Yu, L. Liu, R. Cheng, Y. Chen, X. Huang, Y. Liu, Y. Wang, Y. Huang, and X. Duan, "Chemical vapour deposition growth of large single crystals of monolayer and bilayer graphene," *Nat. Commun.*, vol. 4, 2013.

[6] J. S. Moon, D. Curtis, M. Hu, D. Wong, C. McGuire, P. M. Campbell, G. Jernigan, J. L. Tedesco, B. VanMil, and R. Myers-Ward, "Epitaxial-graphene RF field-effect transistors on Si-face 6H-SiC substrates," *Electron Device Lett. IEEE*, vol. 30, no. 6, pp. 650–652, 2009.

[7] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and P. Avouris, "100-GHz transistors from wafer-scale epitaxial graphene," *Science*, vol. 327, no. 5966, pp. 662–662, 2010.

[8] M. C. Lemme, L.-J. Li, T. Palacios, and F. Schwierz, "Two-dimensional materials for electronic applications," *MRS Bull.*, vol. 39, no. 08, pp. 711–718, 2014.

[9] B. Sensale-Rodriguez, R. Yan, M. M. Kelly, T. Fang, K. Tahy, W. S. Hwang, D. Jena, L. Liu, and H. G. Xing, "Broadband graphene terahertz modulators enabled by intraband transitions," *Nat. Commun.*, vol. 3, p. 780, 2012.

[10] F. Xia, T. Mueller, Y. Lin, A. Valdes-Garcia, and P. Avouris, "Ultrafast graphene photodetector," *Nat. Nanotechnol.*, vol. 4, no. 12, pp. 839–843, 2009.

[11] M. C. Lemme, F. H. Koppens, A. L. Falk, M. S. Rudner, H. Park, L. S. Levitov, and C. M. Marcus, "Gate-activated photoresponse in a graphene p–n junction," *Nano Lett.*, vol. 11, no. 10, pp. 4134–4137, 2011.

[12] A. D. Smith, F. Niklaus, A. Paussa, S. Vaziri, A. C. Fischer, M. Sterner, F. Forsberg, A. Delin, D. Esseni, P. Palestri, and others, "Electromechanical piezoresistive sensing in suspended graphene membranes," *Nano Lett.*, vol. 13, no. 7, pp. 3237–3242, 2013.

[13] C. Chen and J. Hone, "Graphene nanoelectromechanical systems," *Proc. IEEE*, vol. 101, no. 7, pp. 1766–1779, Jul. 2013.

[14] K. Nagashio, T. Nishimura, K. Kita, and A. Toriumi, "Metal/graphene contact as a performance killer of ultra-high mobility graphene analysis of intrinsic mobility and contact resistance," in *Electron Devices Meeting (IEDM), 2009 IEEE International*, 2009, pp. 1–4.

[15] L. Wilson, "International Technology Roadmap for Semiconductors (ITRS)," *Semicond. Ind. Assoc.*, 2013.

[16] F. Xia, V. Perebeinos, Y. Lin, Y. Wu, and P. Avouris, "The origins and limits of metal-graphene junction resistance," *Nat. Nanotechnol.*, vol. 6, no. 3, pp. 179–184, 2011.

[17] K. Nagashio and A. Toriumi, "Density-of-states limited contact resistance in graphene field-effect transistors," *Jpn. J. Appl. Phys.*, vol. 50, no. 7, p. 0108, 2011.

[18] B. Huard, N. Stander, J. A. Sulpizio, and D. Goldhaber-Gordon, "Evidence of the role of contacts on the observed electron-hole asymmetry in graphene," *Phys. Rev. B*, vol. 78, no. 12, p. 121402, 2008.

[19] S. Kataria, S. Wagner, J. Ruhkopf, A. Gahoi, H. Pandey, R. Bornemann, S. Vaziri, A. D. Smith, M. Ostling, and M. C. Lemme, "Chemical vapor deposited graphene: From synthesis to applications," *Phys. Status Solidi A*, p. n/a–n/a, Sep. 2014.

[20] Y. Wang, Y. Zheng, X. Xu, E. Dubuisson, Q. Bao, J. Lu, and K. P. Loh, "Electrochemical delamination of CVD-grown graphene film: toward the recyclable use of copper catalyst," *ACS Nano*, vol. 5, no. 12, pp. 9927–9933, 2011.

[21] D. K. Schroder, *Semiconductor Material and Device Characterization*. John Wiley & Sons, 2006.

[22] J. S. Moon, M. Antcliffe, H. C. Seo, D. Curtis, S. Lin, A. Schmitz, I. Milosavljevic, A. A. Kiselev, R. S. Ross, and D. K. Gaskill, "Ultra-low resistance ohmic contacts in graphene field effect transistors," *Appl. Phys. Lett.*, vol. 100, no. 20, pp. 203512–203512, 2012.

[23] W. S. Leong, C. T. Nai, and J. T. Thong, "What Does Annealing Do to Metal–Graphene Contacts?," *Nano Lett.*, vol. 14, no. 7, pp. 3840–3847, 2014.

Support from the European Commission through an ERC starting grant (InteGraDe, 307311) and an FP7 project (GRADE, 317839) as well as the German Research Foundation (DFG, LE 2440/1-1 and LE 2440/2-1) is gratefully acknowledged.

A. Gahoi, V. Passi, S. Kataria, S. Wagner, A. Bablich, and M. C. Lemme, 'Systematic comparison of metal contacts on CVD graphene', in *2015 45th European Solid State Device Research Conference (ESSDERC)*, Sep. 2015, pp. 184–187.
doi: 10.1109/ESSDERC.2015.7324744.