Graphene / a-Si:H Multispectral Photodetectors

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***Abstract*— We demonstrate the integration of large area graphene transparent conductive electrodes in flexible amorphous silicon multispectral (MS) photodetectors (PD). These MS diodes show a bias dependent maximum of their spectral response between the ultraviolet (UV) and visual wavelength range. This ability to shift the response maximum by external bias without the use of filter-structures and the possibility to deposit the device structure directly onto flexible polyimide substrates gives these sensors wide applicability as one-pixel color detectors. Graphene MS PDs show an extended detection range well into the UV when compared to rigid devices with aluminum doped zinc oxide electrodes. The integration of bi-layer graphene contacts boosts the maximum spectral response up to 185 mAW^{-1}, which is an improvement of 150 % compared to sensors with just one atom thick graphene contacts.**

Keywords*— *graphene, transparent electrode, amorphous silicon, photodetector, thin film solar cells, multispectral imaging, flexible electronics

I. INTRODUCTION

Multispectral photodetectors (MS-PD) are required when standard CCD or CMOS sensors with color filters (Bayer filters) are insufficient for the detection of specific spectral bands. In this work we present MS sensors based the integration of graphene with hydrogenated amorphous silicon (a-Si:H) which allow detecting different spectral bands with just one PD without implementing filter structures. The fabrication process enables deposition of the device structures directly on flexible polyimide (PI) due to low temperature plasma enhanced chemical vapor deposition (PECVD) This makes the device concept suitable for potential applications in flexible and wearable electronics.

A. Amorphous silicon based multispectral photodetectors

Filter-less MS sensors have to be built vertically in order to detect a large amount of photons (see schematic in Fig. 1a). In such a structure, high energy photons are absorbed close to the top of the sensor, while low energy photons will penetrate deep into the sensor structure. The information about the penetration depth of photons can be used to distinguish the incoming wavelengths and is used, e.g. in the crystalline silicon (c-Si) Foveon X3 sensor, which detects three colors in different depths of the sensor stack [1]. Instead of stacking several photodiodes to use each for a specific spectral band detection, our amorphous silicon (a-Si:H) MS devices are based on one unipolar pin structures [2], [3]. In these devices, band gap engineering is carried out to broaden the detectable spectrum. During PECVD growth, germane is added to the gas mixture of silane and hydrogen, resulting in a germanium-rich film and narrowing of the bandgap of the diode close to the back contact. Towards the end of the diode growth process, methane is added to the PECVD process that results in carbon-rich films with a wider band gap. Thus, higher energy photons can be detected close to the top contact. When the diodes are exposed to multispectral light, the location of maximum charge collection can be controlled with an electric field (E). This modulates the charge carrier drift length (l_{drift}) according to equation 1.

$$l_{drift} = \mu\tau \cdot E \qquad (1)$$

where μτ describes the product of the charge carrier mobility and lifetime. Increasing a negative bias voltage (V) across the sensor structure increases the electrical field and therefore additional photo-generated charge carriers will be accelerated towards the contact regions. Due to the low absorption coefficient of a-Si:H at higher wavelengths, high quantum efficiencies of vertical sensor structures are limited to the detection from the ultraviolet (UV) to the visual (VIS) region.

B. Graphene transparent conductive electrodes

Previous work on a-Si:H MS PDs with aluminum doped zinc oxide (ZnO:Al) transparent electrodes (TCEs) revealed fundamental limitations in detecting high energetic photons [4]. This can be attributed to the low transmittance (T) of the ZnO:Al electrode of about 20% at $\lambda = 350$ nm and vanishing transmittance below this wave length [5]. The single-atom thick material graphene is a perfect candidate for TCEs in broadband photodetectors due to its very high T of 97.7% over nearly the entire electromagnetic spectrum [6]. Several examples of graphene TCEs have been shown in [7], [8]. Here, we demonstrate graphene's superior suitability as a UV TCE for flexible multispectral photodetectors.

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II. Device Fabrication

Graphene-/a-Si:H photodetectors were realized on 5 cm x 5 cm large and 1 mm thick AF 32 eco (Schott) glass substrates. First, a 220 nm ZnO:Al electrode was sputter deposited at 100°C. Then, the band gap engineered a-Si:H thin film was deposited on top of the bottom electrode in a plasma-enhanced chemical vapor deposition (PEVCD) system. For the deposition of the 4 nm n- and p-doped layer, a forward RF power of 8 W (13.56 MHz) and a low temperature of 200°C were chosen. The chamber pressure was 500 mTorr for the doped layers and 1 Torr for the ~500 nm intrinsic layer. CVD single-layer graphene (SLG) grown on copper foil [9] was transferred onto the a-Si:H stack via poly-methyl methacrylate (PMMA) assisted wet transfer [10]. This transfer was repeated to fabricate bilayer graphene electrodes. A 220 nm ZnO:Al top electrode was sputtered onto the p-doped layer of a different device as a reference. All devices were structured by standard contact lithography. ZnO:Al was etched in 0.2 % hydrochloride acid (HCL) and graphene was reactive ion etched (RIE) in O2 plasma (80 sccm) at 50 W and a chamber pressure of 57 mTorr. The a-Si:H layers were structured into 1 mm x 1 mm diodes by SF_6/Ar (100/50 sccm) RIE at 100 W and a chamber pressure of 100 mTorr. ZnO:Al anodes dimensions were kept same as the a-Si:H stack, while graphene anodes were etched to a reduced size of 900 µm x 900 µm to avoid overlapping graphene parts after the a-Si:H structuring process. Fig. 1b shows an optical microscope image of a diode with a 900 µm x 900 µm SLG anode on a-Si:H. Flexible MS PDs were fabricated identically except for the use of a 125 µm thick polyimide (PI) substrate and a 180 nm sputtered Au bottom electrode, replacing ZnO:Al to achieve flexible PDs. Fig. 1c schematically shows the band diagram of our MS PDs.

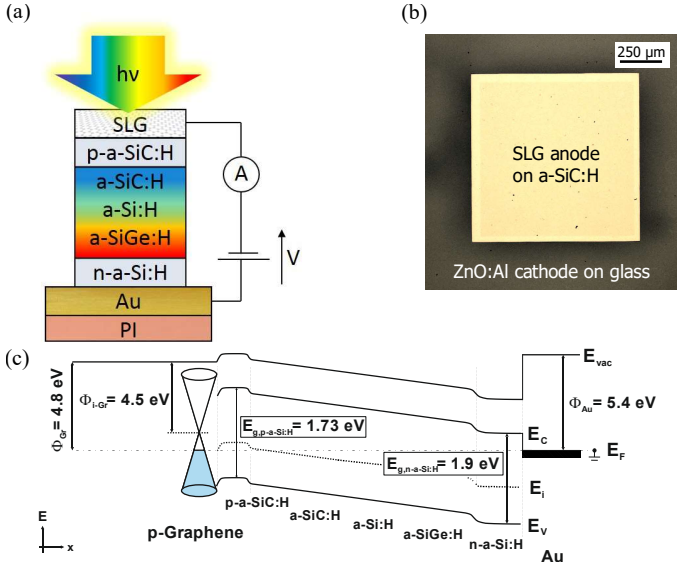


Fig. 1: (a) Cross-section of a a-Si:H MS-PD on a flexible PI substrate. (b) Optical microscope image of a structured 900 µm x 900 µm SLG anode on a-SiC:H. (c) Related band diagram of a MS-PD with SLG anode and Au cathode.

III. Results

A. Electrical characterization

Electrical measurements were carried out with a Keithley 4200-SCS semiconductor analyzer to record bias-dependent photo-generated currents. The MS PDs were illuminated by a tungsten halogen lamp (3300 K) with a white light illuminance of 8400 lux. The devices were further measured in the dark to calculate the dynamic range (DR), given by equation 2:

$$DR = 20 \cdot \log(j_{8400lux}/j_{dark}) \qquad (2)$$

Fig. 2 shows the electrical performance of MS PDs with different TCEs. A dynamic range of 49 dB at -8.5 V was extracted for devices with single layer graphene anodes (Fig. 2a), compared to the 96 dB at -1.5 V of the reference detector (Fig. 2c). While the dark currents of both devices are similar, the difference can be explained by the lower current densities in the SLG devices under illumination. The limiting factors for the lower current densities are the contact and sheet resistances: We have measured a sheet resistance of 1.3 kΩ / □ for the SLG electrode. This is lower than the 6 kΩ / □ fundamental limit of intrinsic graphene [11], and attributed to ambient doping during the graphene transfer [12], but still much higher when compared to the sheet resistance range of conventional TCOs. In our case, the ZnO:Al reference electrode has a sheet resistance on the order of 20 Ω / □, which results in a much higher electric field across the absorption layer at the same external bias voltage. The larger electric field accelerates more photo-generated charge carriers towards the contacts and thus creates higher photocurrents.

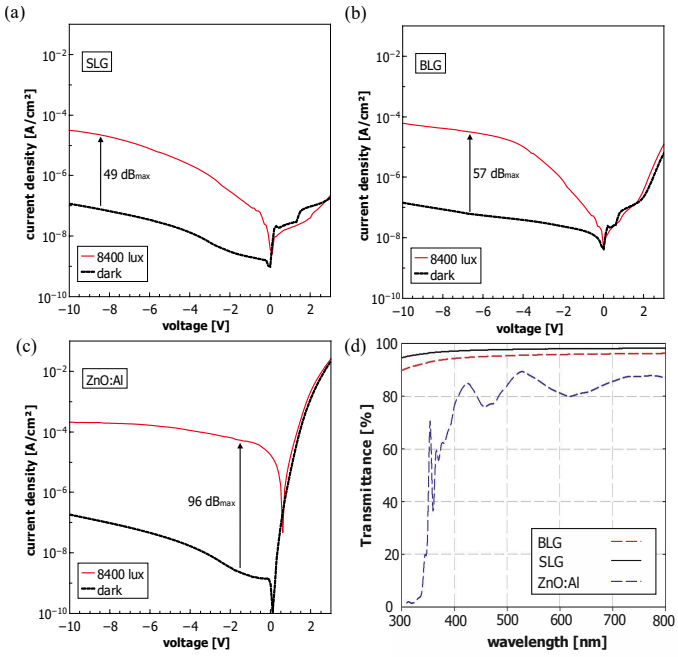


Fig. 2: Electrical characterization of a-Si:H multispectral photodetectors with (a) SLG, (b) BLG and (c) ZnO:Al electrode under illumination and in dark. (d) Shows a wavelength dependent transmittance of the different electrodes.

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A second graphene layer clearly improved the device performance by reducing the anode sheet resistance to 600 Ω / □. An enhanced maximum DR of 57 dB was measured at -6.3 V for the BLG device (Fig. 2c).

The wavelength dependent transmittance of the investigated electrode materials is shown in Fig. 2d. The edge filtering behavior of the ZnO:Al electrode below $\lambda \approx 350$ nm is apparent. In the graphene electrodes, in contrast, the broadband transmittance only decreases slightly at such wavelengths. The addition of the second graphene layer reduced T from 98.4 % to 96.5 % in the visible range. Stacking of graphene to reduce the sheet resistance, along with chemical doping [13], is thus demonstrated as a feasible method to improve graphene TCEs in comparison with conventional TCOs.

B. Optical characterization

The optical device performance was measured in a LabVIEW-controlled spectral response (SR) measurement setup. We illuminated the MS PDs with monochromatic light. The setup is calibrated with a commercial reference silicon detector in the wavelength range of 300 nm up to 800 nm. The corrected absolute SR curves are plotted in Fig. 3. The MS-PD with an single layer graphene electrode shows a peak spectral response of 127 mAW^{-1} at -10 V bias (Fig. 3a). The device with a bilayer graphene electrode shows a peak SR of 185 mAW^{-1}, about 150 % higher than the SLG device. The reference device with the 220 nm thick ZnO:Al electrode shows the highest peak SR of 327 mAW^{-1}. Nevertheless, the true advantage of graphene-based TCEs is demonstrated in their responsivities in the UV range. At 300 nm (-10 V bias) the SLG device has a strong SR of 64 mAW^{-1} which is 2 x higher compared to the ZnO:Al diode. The improved tenability to lower wavelength is shown in the normalized spectral response curves in Fig 3 d. Furthermore, graphene-based devices are less affected by interference fringes. This can be explained by the implementation of <1 nm thin anodes with nearly no reflectance in contrast to thick conducting oxide layers. This becomes particularly apparent in the response curves at 400 nm, where a second maximum in the SR is observed in the ZnO:Al diode. In addition to artefact-free spectral signals, graphene offers advantages in the tunability. The SLG electrode device allows shifting the SR maximum from 400 nm to 500 nm by applying a negative bias from -1 V to -10 V. The ZnO:Al device, in contrast, is limited in its shift from 520 nm to 560 nm at the same applied voltages.

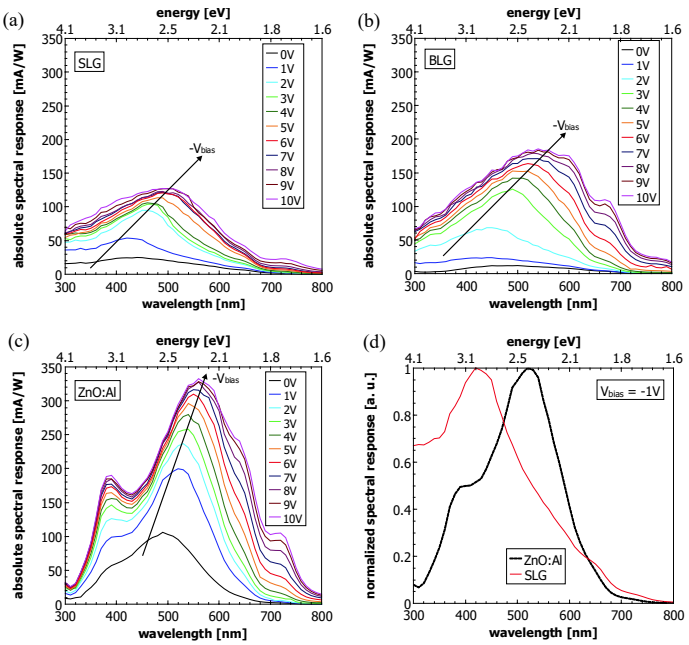


Fig. 3: Spectral response curves of multispectral PD with (a)SLG, (b) BLG and (c) ZnO:Al electrodes. (d) Comparison of the normalized spectral responses at -1 V bias for the devices with SLG and ZnO:Al electrodes.

C. Flexible multispectral sensors

A great benefit of graphene TCEs is the option to use single-atomic thick material on top of a-Si:H based MS PDs on temperature stable, flexible polyimide substrates (Fig. 4a). Obviously, a reference device with a ZnO:Al electrode could not be fabricated due to the brittleness of the material. The maximum dynamic range of the SLG flexible device is about 48 dB at -3.4 V (Fig. 4b)) and therefore in the same range as the rigid PD with a SLG electrode. The optical performance of this PD is shown in Fig. 4c where the SLG MS device shows a max. SR of 105 mAW^{-1} at -10 V bias, which is almost equal to the rigid SLG devices fabricated on glass. The device performance is thus independent of the substrate. We further observe that Au as the back contact material does not create more interference fringes than ZnO:Al cathodes. Fig. 4d shows the normalized SR of the flexible diode, demonstrating the ability to shift the SR maximum by applying suitable bias voltages. Here, the maximum responsivity can be tuned from UV (300 nm) to VIS (490 nm) by increasing the negative bias voltage up to -10 V.

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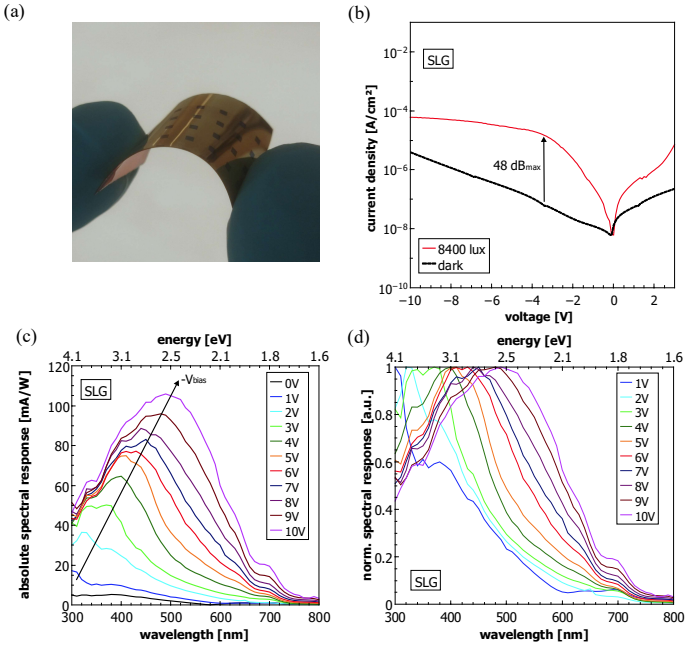


Fig. 4: (a) Photograph of a flexible a-Si:H multispectral PD on PI. (b) Electrical characteristics of a flexible SLG PD. (c) Absolute and (d) normalized spectral responses of a-Si:H based multispectral photodetector with SLG electrode fabricated on flexible PI sheet.

CONCLUSION

We have presented the implementation of large-area graphene TCEs on rigid (glass substrate) and flexible (polyimide substrate) a-Si:H photodetectors. The successful process integration yields electrical and optical characterizations of multispectral devices at wavelengths between 300 nm and 800 nm. The rigid a-Si:H/SLG PD shows a maximum SR of 127 mAW^{-1} which is weaker compared to a devices with state-of-the-art ZnO:Al TCEs. However, due to its high transmittance in UV, the response of 64 mAW^{-1} at 300 nm is twice as high for devices with graphene anodes. The high sheet resistance of SLG compared to state-of-the-art ZnO:Al TCEs was alleviated by using bilayer graphene. As a result, both the maximum spectral response and dynamic range were improved. Flexible multispectral photodiodes on PI show a maximum SR of 105 mAW^{-1} (-10 V bias) at 490 nm with just on atomic-thick graphene layer. The maximum responsivity of the fully flexible multispectral devices can be tuned from UV (300 nm) to VIS (490 nm) wavelengths by increasing the bias voltage. This work demonstrates the prospects of integrating graphene with silicon technology for low cost color-tunable detectors for UV/VIS spectroscopy. It further indicates the potential for flexible and wearable electronics enabled by graphene technology.

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