JVST A
Journal of Vacuum Science & Technology A

Enhancing the photo-response characteristics of graphene/n-Si based Schottky barrier photodiodes by increasing the number of graphene layers

Cite as: J. Vac. Sci. Technol. A **40**, 032203 (2022); https://doi.org/10.1116/6.0001758
Submitted: 19 January 2022 • Accepted: 31 March 2022 • Published Online: 19 April 2022

Mehmet Fidan, Özhan Ünverdi and Cem Çelebi

JVST A
Journal of Vacuum Science & Technology A

ARTICLE

avs.scitation.org/journal/jva

Enhancing the photo-response characteristics of graphene/n-Si based Schottky barrier photodiodes by increasing the number of graphene layers

Cite as: J. Vac. Sci. Technol. A 40, 032203 (2022); doi: 10.1116/6.0001758
Submitted: 19 January 2022 · Accepted: 31 March 2022 ·
Published Online: 19 April 2022

Mehmet Fidan,[1,2,a)] Özhan Ünverdi,[3] and Cem Çelebi[1]

AFFILIATIONS

[1]Department of Physics, Quantum Device Laboratory, İzmir Institute of Technology, 35430 İzmir, Turkey
[2]Department of Opticianry, İzmir Kavram Vocational School, 35230 İzmir, Turkey
[3]Department of Electrical and Electronic Engineering, Faculty of Engineering, Yaşar University, 35100 İzmir, Turkey

Note: This paper is a part of the Special Topic Collection: Celebrating the Early Career Professionals Contributing to the Advancement of Thin Films, Surfaces, Interfaces, and Plasmas.
[a)]**Electronic mail:** mehmet.fidan@kavram.edu.tr

ABSTRACT

The impact of the number of graphene layers on the spectral responsivity and response speed of graphene/n-type Si (Gr/n-Si)-based Schottky barrier photodiodes is investigated. Gr/n-Si photodiode devices are fabricated by transferring chemical vapor deposition-grown graphene layers one by one on n-Si substrates, reaching up to three graphene layers. The devices show a clear rectifying Schottky character and have a maximum responsivity at a peak wavelength of 905 nm. Wavelength-resolved and time-dependent photocurrent measurements demonstrated that both spectral responsivity and response speed are enhanced as the number of graphene layers is increased from 1 to 3 on n-Si substrates. For example, the spectral responsivity and the response speed of the fabricated device were found to be improved by about 15% (e.g., from 0.65 to 0.75 AW^{-1}) and 50% (e.g., 14 to 7 μs), respectively, when three graphene layers are used as the hole-collecting cathode electrode. The experimentally obtained results showed that the device parameters, such as spectral responsivity and response speed of Gr/n-Si Schottky barrier photodiodes, can be boosted simply by increasing the number of graphene layers on n-Si substrates.

I. INTRODUCTION

Owing to its high carrier mobility and inherently high optical transparency, graphene has become a preferred transparent conductive electrode material for the development of semiconductor-based optoelectronic devices such as photodetectors and phototransistors.[1–6] In the last decade, it has been shown that single-atom thick monolayer graphene films form a rectifying Schottky contact when it is placed on the unpassivated surface of bulk Si.[7–12] Such a rectifying contact enables graphene/Si heterojunctions to be used as Schottky barrier photodiodes that are sensitive to light in the visible and short wavelength infrared spectral ranges due to the bandgap of Si.[13] When graphene is employed as an electrode on Si, it not only acts as a transparent conductive layer, but it also functions as a photoactive material due to its ~2.3% optical absorption. Although a large amount of photons is converted into photogenerated charge carriers in Si, the optical absorbance in graphene contributes to photon sensing as well through internal photoemission over the Schottky barrier. The photogenerated charge carriers injected over the Schottky barrier are accelerated by the effective electric field in the depletion region even under a zero-bias regime. The accelerated charge carriers, multiplied in the Si lattice, enable an internal gain. A more detailed explanation for the photoresponse and gain mechanisms of Gr/Si Schottky barrier photodiodes can be found in Refs. 14 and 15.

Graphene/n-type Si (Gr/n-Si)-based photodiodes exhibit spectral responsivities in a range between 0.3–0.7 AW^{-1} and several AW^{-1} with a response time exceeding a few tens of microseconds.[4,7,16–20] Except for its response speed, the spectral responsivity of the Gr/n-Si heterojunction is comparable to those of commercial Si-based p-n and p-i-n type photodiodes. During the past few years, many interesting strategies have been proposed to enhance the spectral

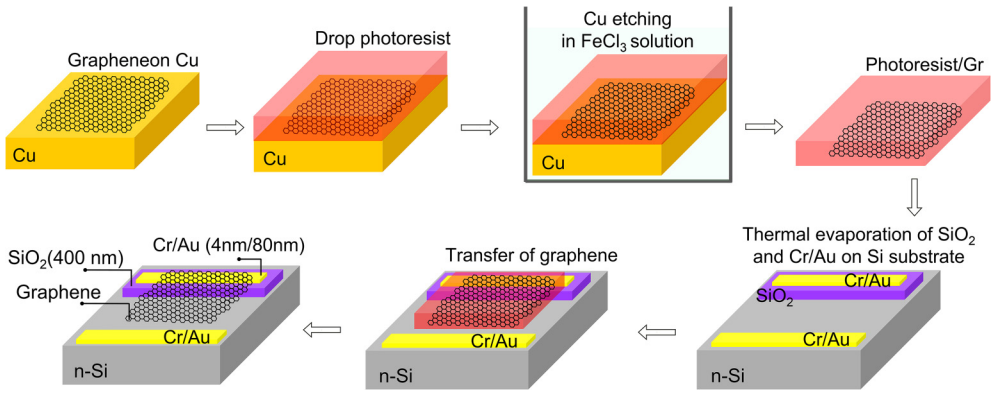

FIG. 1. Schematic illustration of graphene transfer and device fabrication processes.

responsivity of Gr/n-Si Schottky barrier photodiodes. These include the modification of the doping level of either the graphene electrode or the underlying Si substrate and/or placing a thin oxide layer in between them as well as nanotip patterning of the Si substrate underneath the graphene layer.[20] As an example, a self-powered Gr/n-Si photodiode fabricated out of chemical vapor deposition (CVD) graphene onto lightly doped unpassivated n-Si has been demonstrated.[8] When the diode was exposed to 850 nm wavelength light, the spectral responsivity and response time of the device were found to be 0.3 AW^{-1} and ~100 μs, respectively. It has also been shown that the maximum spectral responsivity of Gr/n-Si Schottky photodiodes at 850 nm peak wavelength can be boosted from 0.24 to 0.78 AW^{-1} when the Gr electrode is doped extrinsically with P3HT polymer molecules.[21] We recently showed that a spectral responsivity of around 0.76 AW^{-1} can be achieved simply by increasing the Gr/n-Si active junction area without the need of chemical modification of the graphene electrode.[13] Despite their enhanced spectral responsivities, Gr/n-Si Schottky barrier photodiodes exhibit lower response speeds due to relatively high response time.

In this work, we investigated the effect of the number of graphene layers on the spectral responsivity and response speed of Gr/n-Si Schottky barrier photodiodes. Wavelength-resolved photocurrent and time-dependent photocurrent measurements showed that the spectral responsivity and response speed of these types of photodiodes can be improved simultaneously as the number of graphene layers on n-Si is increased from 1 to 3.

II. EXPERIMENTAL DETAILS

The graphene layers were grown on 25 μm thick and 99.8% purity Cu foils by CVD technique. The growth and transfer processes for CVD graphene were done by means of the same procedure employed in our previous studies.[16] A schematic illustration of the experimental process to fabricate the Gr/n-Si photodiode that comprises graphene growth on the Cu foil and then transferring on the n-Si substrate is displayed in Fig. 1. As for the first step, Cu foils were cut into small pieces and then loaded in the tube furnace of the CVD system. Monolayer graphene was grown on

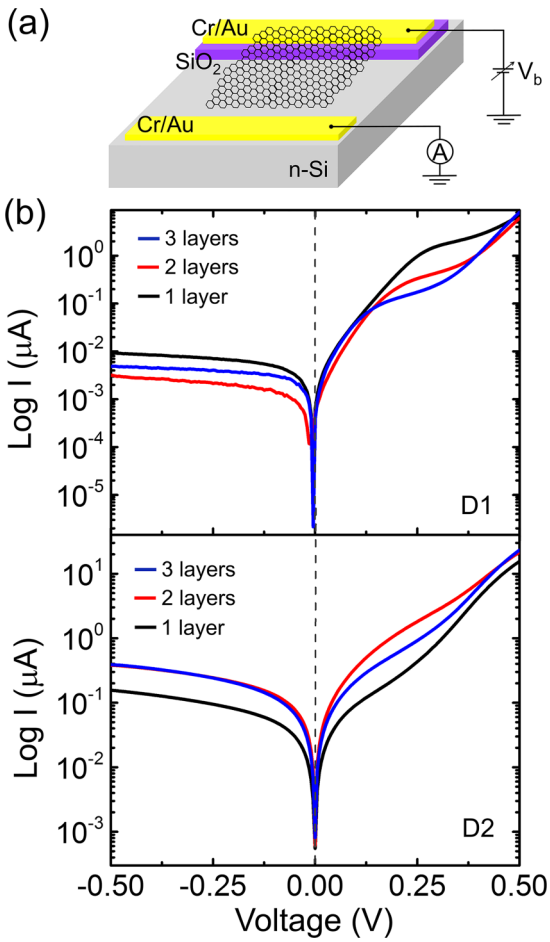

FIG. 2. (a) Schematic structure of the fabricated Gr/n-Si photodiode with electrical connections. (b) Dark I–V measurements of the samples D1 and D2 in the semilogarithmic scale.

these Cu foils under the flow of H_2, Ar, and CH_4 gases. The micro-posit S1318 photoresist (PR) was drop casted on the Gr/Cu structure as a supporting layer for the grown graphene and then annealed at a temperature of 70 °C overnight in an oven. After the Cu foil is etched in an iron chloride ($FeCl_3$) solution, the suspended PR/Gr bilayer is transferred on the n-Si substrate. The wafer used in this study was lightly doped n-Si with a resistivity of 1–5 Ω cm. Prior to the deposition of metallic contact pads, a 400 nm thick SiO_2 dielectric layer is evaporated to cover a portion of the surface of the n-type Si substrate. For I–V measurements, Cr (4 nm)/Au (80 nm) metallic contact pads were defined on the samples as shown in Fig. 1 using thermal evaporation technique. For the graphene transferring process, the PR/Gr was annealed at 110 °C for 4 min in order to provide good adhesion of the graphene layer on the n-Si substrate. The PR layer was removed by acetone and then rinsed with isopropanol and de-ionized water, respectively. Finally, Gr/n-Si photodiodes with active junction area of 4×5 mm^2 become ready for optoelectronic measurements.

The optoelectronic properties of the samples were measured at room temperature under ambient conditions using a probe station interfaced with a power tunable monochromator light source, Keithley 2400 Source-Meter, Keithley 6485 Picoammeter, and a calibrated Si photodetector. The spectral responsivity of the fabricated Gr/n-Si photodiodes was examined at the wavelength between 540 and 1050 nm. Time-resolved photocurrent measurements were performed using an LED driver with pulse modulation (DC2200, Thorlabs), a collimated LED source with 940 nm, a 905 nm laser line filter, and a transimpedance amplifier, and the signal was collected using a digital storage oscilloscope. Here, the irradiation wavelength

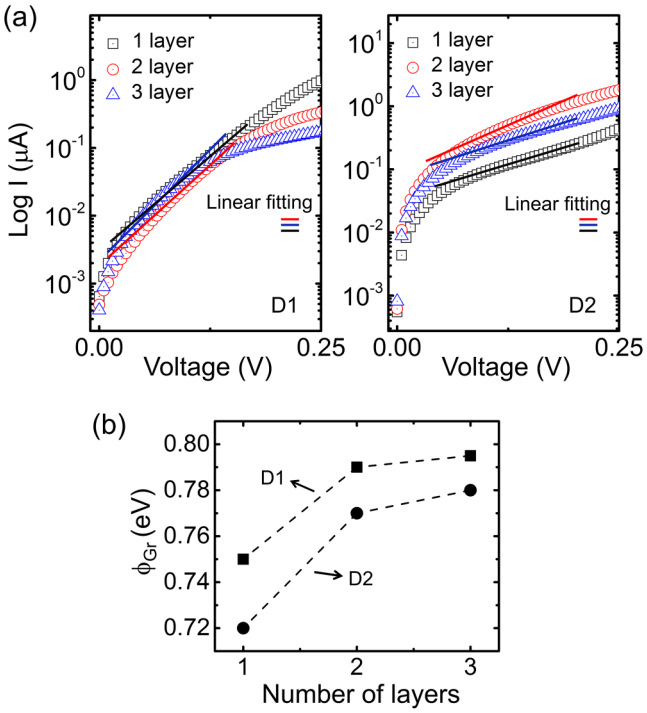

FIG. 3. (a) The forward-bias regions of the I–V plots shown in Fig. 2(b), which were linearly fitted to calculate the Φ_B values of the samples D1 and D2. (b) The extracted Φ_B values of the devices vs the number of graphene layers.

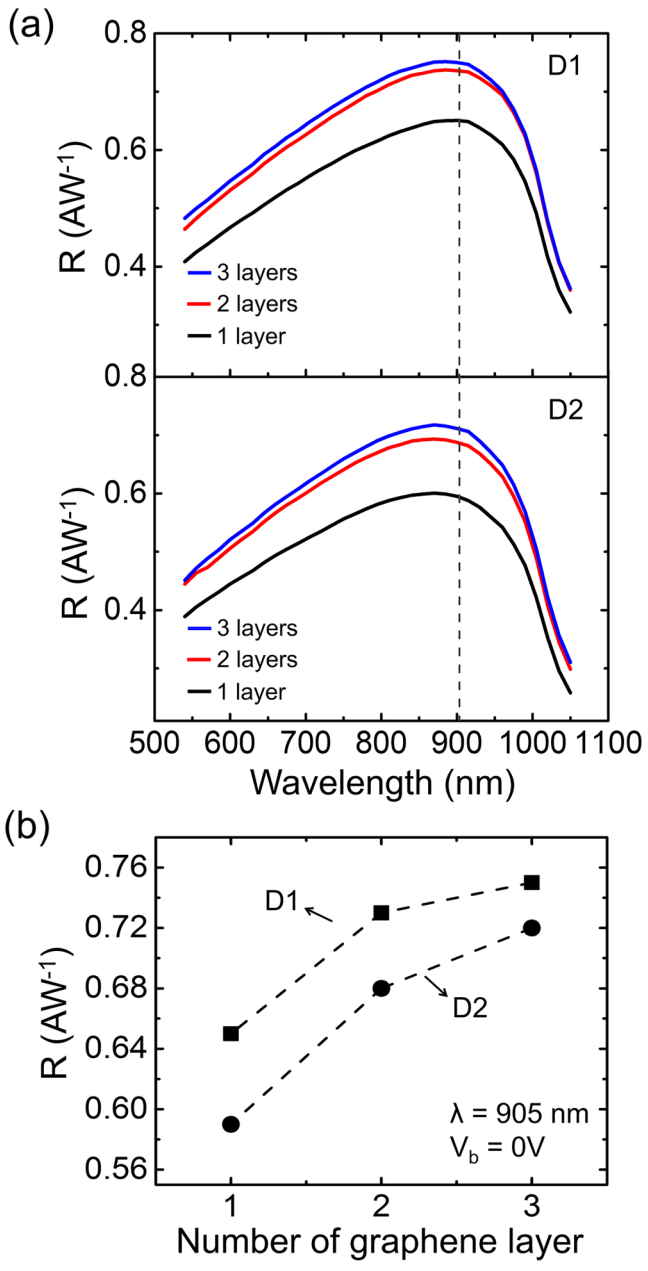

FIG. 4. (a) is the zero-bias spectral responsivity of the devices D1 and D2 measured in the wavelength range between 540 and 1050 nm at zero bias voltage. (b) Comparison of the zero-bias spectral responsivity of the two individual devices acquired at the peak wavelength of 905 nm.

is specifically selected to be 905 nm since it corresponds to the maximum spectral responsivity of our fabricated Gr/n-Si photodiode samples. Hall effect measurements were done with a lab-built four-point probe station having properly oriented Au-plated pins connected to the Keithley 6220 Precision Current Source and the Keithley 2000 Digital Multimeter. The measurements were done using a Neodymium-based permanent magnet providing an effective magnetic field of 350 mT.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A schematic illustration of the fabricated Gr/n-Si Schottky barrier photodiode with electrical contacts is displayed in Fig. 2(a). For comparison and verification, the electronic and optoelectronic characterizations were done on two individual samples, which were labeled as device-1 (D1) and device-2 (D2). Prior to photocurrent spectroscopy measurements, the I–V measurement of the samples was conducted under dark conditions with an applied bias voltage range between −0.5 and 0.5 V. The experiments were repeated for an increasing number of graphene layers transferred on the device structure as shown in Fig. 2(a). For both samples, all the obtained I–V curves exhibited typical rectifying Schottky contact behavior but with slightly different saturation current levels at the reverse bias region as seen in Fig. 2(b). This already suggest that the Schottky contact parameters (e.g., ideality factor, barrier height, etc.) and, hence, the rectification strength of the samples vary as a function of the number of graphene layers.

From the linear forward-bias region of the semilogarithmic scale I–V plots in Fig. 3(a), the Schottky barrier heights (Φ_B) of our devices were determined by using the method developed by Cheung *et al.*[22] The obtained Φ_B values were plotted as a function of the number of graphene layers in Fig. 3(b). As can be seen in Fig. 3(b), the Φ_B of both devices increases as a function of graphene layers. For both devices, the increment in Φ_B was found to be 5 meV in average as the number of graphene layers reach to three layers.

In order to determine the zero-bias ($V_b = 0$ V) spectral responsivity (R) of the samples, we conducted wavelength-resolved photocurrent spectroscopy measurements under illumination of light with different wavelengths tuned between 540 and 1050 nm. Here, R is defined as the ratio of output photocurrent and optical power incident to the sample surface. The measurements were repeated for an increased number of graphene layers on the device structure, and the results were plotted in Fig. 4(a). In all the measurements, the maximum R appeared at a peak wavelength of 905 nm, and the curves exhibited a downward trend toward a cut-off wavelength of 1050 nm. For a clear comparison, the maximum R values at 905 nm wavelength are plotted in Fig. 4(b) as a function of the number of graphene layers. The maximum R of the sample D1 rises from 0.65

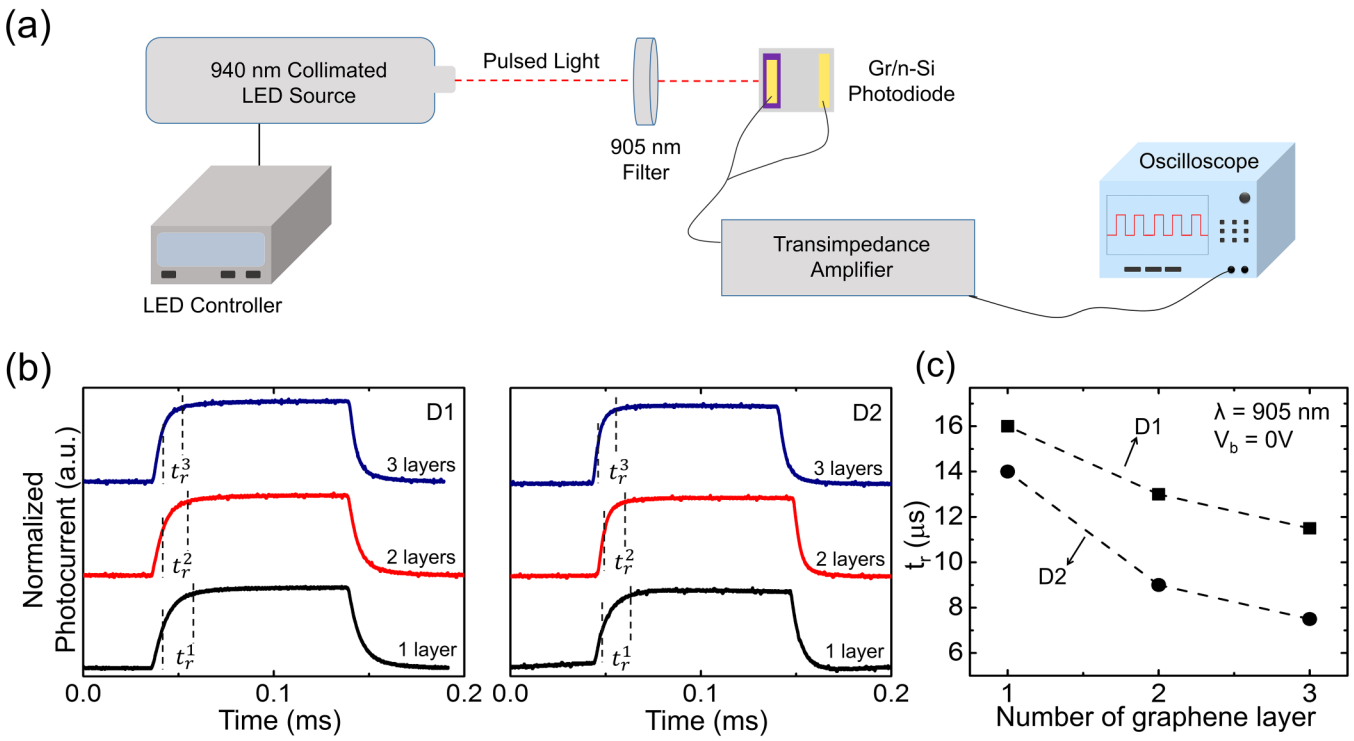

FIG. 5. (a) Schematic diagram of the time-resolved photocurrent measurement system. (b) The time-dependent photocurrent spectrum of the fabricated Gr/n-Si photodiodes D1 and D2. One cycle time-dependent photocurrent spectrum of the devices under fast varied 905 nm wavelength light with switching frequency of 5 kHz at zero-bias voltage. The measured photocurrents were normalized with the maximum values. (c) The rise time values of the devices as a function of the number of graphene layers.

to 0.75 AW^{-1} when the number of graphene layers is increased from 1 to 3. And for the sample D2, the maximum R was found to be rising from 0.59 to about 0.72 AW^{-1}. For both samples, the R values seemed to be converging to a saturation level in the case of three graphene layers used as the hole-collecting electrode.

Time-dependent photocurrent spectroscopy measurements were conducted using the experimental setup illustrated in Fig. 5(a) to determine the response speed of the fabricated devices as a function of the number of graphene layers. In the experiments, a collimated LED with the peak wavelength of 940 nm was used as the light source. The LED light is filtered with a laser line bandpass filter to get 905 nm wavelength light. The measurements were done at zero-bias voltage, and the output photocurrent was recorded under light pulses with a frequency of 5 kHz. Then, the obtained signals were converted to voltage with a transimpedance amplifier, and the data were collected by an oscilloscope.

Time-dependent photocurrent measurements were carried out with one-cycle switching on/off within 0.2 ms as seen in Fig. 5(b). All the samples with different number of graphene layers exhibited great capability to respond high-frequency pulsed light and on/off switching stability. To determine the response speed of the sample with different number of graphene layers, the rise time (t_r) values were extracted from single-pulse response measurements. Here, t_r corresponds to the time difference between the 10% point and the 90% point of the peak amplitude output on the leading edge of the pulse and describes the response speed of the detector. As seen in Fig. 5(c), the response speed of the samples increases with the number of graphene layers.

The variation in the spectral responsivity and response speed of Gr/n-Si photodiodes with the number of graphene layers can be explained in terms of the electronic transport characteristics of the graphene electrode and charge injection dynamics. The sheet resistance (R_s) and carrier density (n) of the graphene electrode were determined as a function of the number of graphene layers using four probe and Hall effect measurement techniques. For the transport experiments, the grown graphene layers were transferred on square-shaped quartz substrates having Cr/Au metallic contact pads at their corners. The measurements were carried out on two individual samples and repeated for an increased number of graphene layers. All the samples exhibited p-type conductivity with initial hole density ranging between 1.2×10^{13} and 3.2×10^{13} cm^{-2} in the case of one-layer graphene. As shown in Fig. 6(a), the hole density of the samples was identified to be increasing linearly as a function of the number of graphene layers. However, the sheet resistance of the samples first decreases sharply as the number of graphene layers is increased from 1 to 2 and then converges to a saturation level for three graphene layers.

It is known that a depletion region and a Schottky barrier are formed at the interface of the Gr/n-Si heterojunction due to the difference between the Fermi level of graphene (E_F^{Gr}) and of n-Si (E_F^{Si}).[14,15] To maintain thermodynamic equilibrium, the electrons in n-Si are injected to the graphene electrode until their Fermi levels are aligned across the junction. Under light illumination, the photons pass through the graphene electrode and penetrate into n-Si to create electron-hole pairs in the depletion region. A measurable photocurrent is generated as a result of the electrons moved to n-Si and holes transferred to the graphene electrode. As depicted in Fig. 6(b), the Fermi level is lowered relative to its initial stage when 2 and/or 3 graphene layers are used as the electrode due to

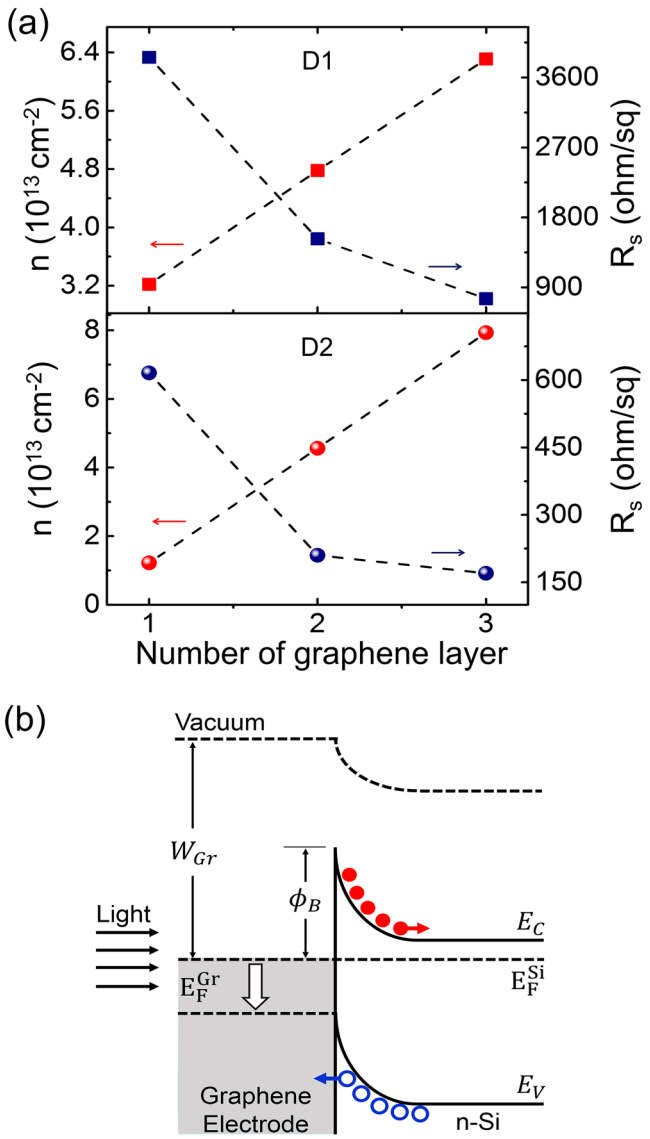

FIG. 6. (a) Charge carrier concentration and sheet resistance vs the number of graphene layers for the devices D1 and D2, respectively. (b) The schematic illustration of the energy band diagram for the Gr/n-Si Schottky junction photodiode under light illumination. W_{Gr} and Φ_B are the work functions of the graphene electrode and the Schottky barrier height at the Gr/n-Si heterojunction, respectively.

increased hole density. The shift of the Fermi level toward lower energy states increases the work function of the graphene electrode as well as the magnitude of the built-in potential and junction electric field at the Gr/n-Si interface. This promotes greatly the effective separation of the photogenerated charge carriers at the depletion region and enhances the photocurrent of the device. Therefore, the spectral responsivity and response speed of the samples are expected to rise as a function of the number of graphene layers in

agreement with increasing hole density shown in Fig. 6(a). The experimentally observed deviation of these two photodiode parameters from linearity can be correlated with the nonlinear decrease in the series resistance of the device.

IV. CONCLUSIONS

We have investigated the effect of the number of graphene layers on the spectral responsivity and response speed of Gr/n-Si Schottky barrier photodiodes. These two important photodiode device parameters were determined using wavelength-resolved and time-dependent photocurrent spectroscopy measurement techniques. All the fabricated devices exhibited a maximum spectral responsivity under 905 nm wavelength of light. The measurements showed that the spectral responsivity and response speed of Gr/n-Si Schottky barrier photodiodes can be improved to a large extent simply by increasing the number of graphene layers acting as the hole-collecting cathode electrode on the n-Si substrate. The deviation of spectral responsivity and response speed from linearity has been attributed to the nonlinear variation in the sheet resistance of the graphene layers. This study is expected to provide useful information for the realization of high-performance graphene/semiconductor-based Schottky barrier photodiodes with improved photodetection capability.

ACKNOWLEDGMENTS

The authors would like to thank Center for Materials Research at İzmir Institute of Technology and Sparks Electronics Ltd. in Turkey for their support in device fabrication processes. This work was supported within the scope of the scientific research project that was accepted by the Project Evaluation Commission of Yasar University under the project number and title of "BAP089_Grafen/Silisyum Heteroyapılı Fotodiyot Geliştirilmesi."

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the experimental findings of this study are available within the article and the references.

REFERENCES

[1]A. Bablich, S. Kataria, and M. Lemme, Electronics **5**, 13 (2016).
[2]X. Liu *et al.*, Org. Electron. **64**, 22 (2019).
[3]A. Hekmatikia and Y. Abdi, IEEE Electron Device Lett. **39**, 216 (2018).
[4]S. Riazimehr, A. Bablich, D. Schneider, S. Kataria, V. Passi, C. Yim, G. S. Duesberg, and M. C. Lemme, Solid State Electron. **115**, 207 (2016).
[5]X. Chen *et al.*, Nano Lett. **17**, 6391 (2017).
[6]A. Kim, G. Lee, and J. Kim, J. Vac. Sci. Technol. A **39**, 053412 (2021).
[7]X. Li *et al.*, Small **12**, 595 (2016).
[8]P. Lv, X. Zhang, X. Zhang, W. Deng, and J. Jie, IEEE Electron Device Lett. **34**, 1337 (2013).
[9]C. C. Chen, M. Aykol, C. C. Chang, A. F. J. Levi, and S. B. Cronin, Nano Lett. **11**, 1863 (2011).
[10]Y. Wang, S. Yang, D. R. Lambada, and S. Shafique, Sens. Actuators A **314**, 112232 (2020).
[11]D. Sinha and J. U. Lee, Nano Lett. **14**, 4660 (2014).
[12]D. Xiang, C. Han, Z. Hu, B. Lei, Y. Liu, L. Wang, W. P. Hu, and W. Chen, Small **11**, 4829 (2015).
[13]A. Pelella, A. Grillo, E. Faella, G. Luongo, M. B. Askari, and A. Di Bartolomeo, ACS Appl. Mater. Interfaces **13**, 47895 (2021).
[14]A. Di Bartolomeo, Phys. Rep. **606**, 1 (2016).
[15]A. Di Bartolomeo, G. Luongo, L. Iemmo, F. Urban, and F. Giubileo, IEEE Trans. Nanotechnol. **17**, 1133 (2018).
[16]M. Fidan, Ö. Ünverdi, and C. Çelebi, Sens. Actuators A **331**, 112829 (2021).
[17]N. Şahan, M. Fidan, and C. Çelebi, Appl. Phys. A **126**, 938 (2020).
[18]D. Periyanagounder, P. Gnanasekar, P. Varadhan, J. H. He, and J. Kulandaivel, J. Mater. Chem. C **6**, 9545 (2018).
[19]S. Riazimehr *et al.*, ACS Photonics **6**, 107 (2019).
[20]A. Di Bartolomeo *et al.*, 2D Mater. **4**, 015024 (2017).
[21]H. Aydin, S. B. Kalkan, C. Varlikli, and C. Celebi, Nanotechnology **29**, 145502 (2018).
[22]S. K. Cheung and N. W. Cheung, Appl. Phys. Lett. **49**, 85 (1986).

Mehmet Fidan received his B.Sc. and M.Sc. degrees in Physics Education from Yüzüncü Yıl University and in Physics from İzmir Institute of Technology (IZTECH), respectively. He is a Ph.D. candidate under the supervision of Professor Dr. Cem Çelebi at the Quantum Device Laboratory (https://qdl.iyte.edu.tr/) of the Physics department of IZTECH. Currently, he is writing up his Ph.D. thesis and expected to graduate in June 2022. His main research interests are in the fields of graphene synthesis, graphene/semiconductor-based devices, and their electronic/optoelectronic characterizations. He has contributed three research articles to date, one of which is the first author.