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Enhanced performance of photodetector and photovoltaic based on carrier reflector and back surface field generated by doped graphene

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We report the influence of carrier reflector and back surface field generated by doped graphene on n-ZnO nanoridges/p-silicon photodetectors and silicon solar cells. It is found that the p-type graphene not only acts as an electron blocking layer, but also helps the collection of photogenerated holes. Quite surprisingly, the on/off ratio of the photodetector with the insertion of doped graphene can be increased by up to 40 times. Moreover, we demonstrate that typical silicon solar cells with the doped graphene, the cell efficiency can be enhanced by about 20%. Our approach would expand numerous applications for graphene-based optoelectronic devices. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4746763]

Graphene, an atomically thin film composed of a single layer of carbon, has been a subject of intense research for promising nanoelectronic1 and optoelectronic devices2,3 due to its exceptionally electrical and optical properties.4–7 To realize the graphene-based devices such as diodes or logic gates, doping modulation, an intentional process to tailor the electrical properties of semiconductors, is of great technological importance.8,9 One of the excellent examples is that silicon photovoltaic devices fabricated with doped graphene have been demonstrated by using the advantage of graphene with a tunable work function.10 Previously, various approaches have been applied to control both carrier types and concentration in graphene by means of transverse electric-field,11 molecular adsorbrates,12 and electrical modification of the substrates.13 Nevertheless, each method has its own drawbacks. For example, doping graphene with a transverse electric-field was typically fabricated by e-beam lithography or photolithography processes, which is not efficient compared with direct patterning methods.14 Besides, the residue solvent from molecular adsorbrates is inevitable and affects the electrical characteristics of graphene.15 Quite interestingly, it has been found recently that the doping type of graphene can be easily controlled by the intercalation of metal atoms between graphene and its substrate,16–19 which offers an excellent opportunity for the creation of optoelectronic devices consisting of graphene.

Despite the intensive investigation in optoelectronic devices, including photodetectors and solar cells, there exists several challenges to reach higher efficiency. One of the important factors that causes the reduction of the conversion efficiency is the recombination loss. The major recombination loss arises from the back-surface recombination created by the poor interface quality between active layer and metal contact. Especially, it is known that the electron diffusion length in high quality semiconductors can be as large as several hundred micro-meters. For example, electron diffusion length in lightly doped p-Si can be greater than 300 μm.20 Therefore, a large fraction of photogenerated electrons can reach the back side of optoelectronic devices and recombine with interface defects. To this end, by taking the advantage of the feasible doping capability of graphene, we aim to solve the above difficulty. With the insertion of a heavily doped p-type graphene between semiconductor and back side metal contact, we anticipate that the p-type graphene not only can generate a back surface field (BSF) and accelerate the transport of holes, but it also can induce a conduction band barrier due to the band alignment between p-type graphene and semiconductor to serve as a blocking layer for photogenerated electrons. Thus the responsivity of optoelectronic devices can be significantly improved. To illustrate our working principle, n-ZnO nanoridges/p-silicon (n-ZnO NRs/p-Si) photodetectors have been investigated. It is found that the on/off ratio of the photodetector with the doped graphene can be increased by up to 40 times. Furthermore, we show that the efficiency of p-n junction silicon solar cells can be enhanced by 20% with the insertion of doped graphene at the back surface. Because specific doping of graphene is very important and timely, our study shown here should be able to expand numerous applications for graphene-based optoelectronic devices.

P-type, (100)-oriented silicon wafers with resistivity in the range 7–12 Ω-cm were used as substrates. Initially, the surface of p-Si was rinsed in acetone, isopropanol and DI water. We then assembled the graphene layer by spin-coating process at the backside of p-Si at 1000 rpm for 20 s. The aqueous graphene solution was prepared by exfoliation of graphite in surfactant-water solutions according to Ref. 21. The obtained thickness of the graphene layer is observed with large quantities of bilayers and trilayers. The addition of sodium dodecyl benzene sulfonate (SDBS) in aqueous graphene solution would degrade the electrical conductivity of graphene since SDBS is not as conductive as graphene. Rapid-thermal-annealing (RTA) in N2 at 700 °C

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for 3 min was applied in order to remove the SDBS and achieve higher DC conductivity. The as-deposited graphene layer corresponds to a DC conductivity of 35 S/m and increases to 1500 S/m after annealing. The Raman spectrum of our graphene is shown in Figure 1(a), which is similar to previous report. The observed D band intensity indicates the level of defects and disordered carbon atoms in our graphene. The transmission electron microscopy (TEM) image reveals the graphene layer as shown in the inset of Figure 1(a). The wafer-scale n-ZnO NRs were synthesized from n-ZnO quantum dots (QDs) colloidal solution followed by thermal annealing. The n-ZnO colloidal solution consists of 0.75 M zinc acetate dehydrate and 0.75 M monoethanol-amine in 2-methoxyethanol and was spun-coated on p-Si at 3000 rpm for 30 s. After dipping the n-ZnO QDs layer, p-Si substrate was immediately moved on the hot plate at 200 °C for 5 min to remove the residue organic material. Then the thermal annealing was performed in furnace for 30 min at 275 °C to form the self-assembled n-ZnO NRs. The scanning electron microscopy (SEM) image of the n-ZnO NRs is shown in Figure 1(b). The thickness of the n-ZnO NRs is about 200 nm and the pitch of the n-ZnO NRs is about 500 nm. Ohmic contact was made by depositing an Ag film on n-ZnO NRs and an Al electrode on graphene at the back side of p-Si via shadow mask, which generated the doped graphene. The active area of the device was about 2.25 cm².

To investigate the effect of doped graphene on silicon-based solar cells, the solar cells were fabricated by a conventional solar cell process. In brief, this process includes a standard RCA cleaning, phosphorous coating on the front side, thermal diffusion of phosphorous by RTA at 850 °C for 4 min, phosphosilicate glass (PSG) layers removing by dipping them in buffered oxide etch (BOE) solution for 2 min. After each fabrication step, the solar cell was cut into 2.25 cm² pieces for the measurements of electrical and optical characteristics.

Both of the back contact of photodetectors and solar cells were annealed at 500 °C for 4 min. It is worth noting that the metal would intercalate between graphene and its substrate at this temperature. It is believed that the metal atoms bond with the substrate and the carbon atoms through the atomic defects in the graphene layer under annealing. The intercalation of metal atoms would change the electronic structure of graphene and result in quasi-free standing graphene as shown in previous reports. The metal intercalation of Au, Ag, Pt leads to a upward shift of the Fermi-level (n-type doping) but Al leads to a downward shift of the Fermi-level (p-type doping).

The chemical composition of elements at the back side of p-Si was determined by electron energy dispersive spectroscopy (EDS). The carbon signal is uniformly distributed on the p-Si substrate, which indicates that graphene was uniformly spun-coated on p-Si. Moreover, it is found that the SDBS, a surfactant consists of 12-carbon tail connected to the sulfate group, was mostly vaporized during annealing process. The residue sulfate group exists only in a few regions which would not affect the electrical properties of graphene.

Figure 2(a) shows the schematics of Ag/n-ZnO NRs/p-Si/graphene/Al photodetector used for this study. The electrical properties of our Ag/n-ZnO NRs/p-Si/graphene/Al and Ag/n-ZnO NRs/p-Si/Al devices are characterized by I-V measurements at room temperature, as shown in Figure 2(b). The dark current of Ag/n-ZnO NRs/p-Si/Al device is larger than that of Ag/n-ZnO NRs/p-Si/graphene/Al device, indicating that the additional graphene layer leads to a lower leakage current of the photodetectors. Besides, as shown in Figure 2(c), it demonstrates that the Ag/n-ZnO NRs/p-Si/graphene/Al device has a significant photocurrent enhancement compared with that of the Ag/n-ZnO NRs/p-Si/Al structure under AM1.5 illumination with a reverse bias. Notably, it is worth noting that the on/off ratio of the photodetector with the doped graphene is enhanced by up to 40 times.

In order to understand the above interesting results, we believe the main underlying mechanism arising from the fact that the graphene on Ag/n-ZnO NRs/p-Si/graphene/Al device is a heavily p-type doped layer. The nonuniform carrier concentration between p-Si and heavily doped p-type graphene generates a strong BSF at the back side of Ag/n-ZnO NRs/p-Si/graphene/Al device similar to the direction of the built-in electric field in the p-n junction of n-ZnO NRs/p-Si, which is able to enhance the conduction of holes. It will reduce the recombination of photogenerated electron-hole pairs and increase the photocurrent.

In addition to the generation of BSF, due to the inherent nature of the band alignment between heavily doped p-type graphene and lightly doped p-Si, a conduction band barrier will be created across the interface. The formation of the conduction band barrier arising from the band offset between heavily doped graphene and lightly doped p-Si thus can be expected. Because the conduction band barrier can work as an electron reflector, it leads to the decrease of electron...

![Figure 1](image_url)

**Figure 1.** (a) Raman spectrum and TEM image (inset) of graphene layer. (b) SEM image of the n-ZnO NRs.
current at the p-Si/graphene interface,\textsuperscript{26} and the probability of the recombination loss of carriers due to the Al/Si interface defects is greatly reduced. Figure 2(d) shows the band alignment of our working device and illustrates the underlying mechanism of the enhanced performance of the photodetector.

Since the BSF and electron reflector generated by p-type graphene/Al film are much more efficient than pure Al thin film for the studied photodetectors, we examine further their application for photovoltaic devices. We have performed the devices by depositing an Al film at the back side of silicon solar cell with/without graphene as rear contact and front contact was made by depositing Au/Ti film, as shown in Figure 3(a). Figure 3(b) shows the I-V measurement at room temperature under AM1.5 illumination. In the absence of graphene layer, the device exhibits an open-circuit voltage ($V_{oc}$) of 0.54 V, a short-circuit current ($J_{sc}$) of 16.5 mA/cm$^2$, and a fill factor (FF) of 0.53. However, the device with the incorporation of graphene has a $V_{oc}$ of 0.56 V, a $J_{sc}$ of 17.9 mA/cm$^2$, and a FF of 0.58. The $V_{oc}$ difference for the cell with and without graphene is 20 mV, which is much larger than the uncertainty value of 0.06 mV in our experiment and has the same order of magnitude for the cells with and without BSF as shown in previous reports.\textsuperscript{27–29} It is clear that both of $V_{oc}$ and $J_{sc}$ were improved by the insertion of graphene layer. This behavior can be easily understood in terms of BSF and electron reflector generated by the heavily doped graphene layer, which is added to increase the output voltage as well as enhance the charge carrier collection. Consequently, the power conversion efficiency (PCE) can be improved from 4.72\% to 5.81\%. Moreover, the dark current of Au/Ti/silicon solar cell/Al device and Au/Ti/silicon solar cell/graphene/Al device as shown in the inset of Figure 3(b) indicates that the reduction of dark current is due to the p-type graphene interlayer. Therefore, our result provides a firm evidence that the BSF and electron reflector generated by p-type graphene/Al film is suitable for silicon solar cells application. It is worth noting here that a large number of graphene/Al cells have been fabricated and achieved 10\%–20\% efficiency enhancement in comparison with Al cells. These results show that the device yield and reproducibility of our experiment are quite well. However, the variation of efficiency enhancement has yet to be improved since the quality of graphene strongly depends on the fabrication of graphene solution and coating process.

To further demonstrate the doping capability of graphene by different metals, we have performed an additional experiment to modify the doping type of graphene to support the above proposed mechanism. Figure 4(a) shows the schematics of silicon solar cells, which is similar to the above devices, but Al rear contact was replaced by Au. I-V measurements of our devices with/without graphene at room temperature under AM1.5 illumination are shown in Figure 4(b). The photocurrent of graphene/Au device is kept in similar tendency as that of Au device, but it shifts to the third quadrant. The photovoltaic performance of graphene/Au devices is much poorer than that of Au devices. The most probable explanation for this phenomenon is that the graphene was n-doped by the intercalation of Au atom. In contrast to the intercalated Al atom, the intercalated Au atom acts as an

![FIG. 2. (a) Schematics of Ag/n-ZnO NRs/p-Si/graphene/Al photodetector. (b) J-V characteristics of n-ZnO NRs/p-Si photodetectors with/without graphene at room temperature under dark condition. (c) J-V characteristics of n-ZnO NRs/p-Si photodetectors with/without graphene at room temperature under AM1.5 illumination. (d) Schematics of band alignment of n-ZnO NRs/p-Si/p-type graphene for the illustration of the back surface field and the electron reflector generated by p-type graphene.](https://apl.aip.org/about/rights_and_permissions)
electron donor for graphene as pointed out by previous reports.\textsuperscript{16,17} The p-n junction formed by n-Si/p-Si and the p-n junction formed by p-Si/n-graphene could be regarded as a back-to-back double diode. When the current is only controlled by the p-n junction of n-Si/p-Si, a clear rectifying J-V characteristic is observed. However, when both of the p-n junctions of p-Si/n-graphene and n-Si/p-Si exist, the p-n junction of p-Si/n-graphene will largely depress the rectifying behavior of the p-n junction of n-Si/p-Si, resulting in the increase of leakage current under reverse bias, thereby compromising PCE. The J-V characteristic of a back-to-back double diode is clearly revealed in Figure 4(b) under AM1.5 illumination. Figure 4(c) shows the I-V measurements of our devices with graphene/Al back contact and Au back contact at room temperature under AM1.5 illumination. It had been reported that the $V_{oc}$ improvement of the cell with Al BSF ranges from 4 mV to 100 mV in comparison with the cell without Al BSF.\textsuperscript{27–29} This $V_{oc}$ difference is of the same magnitude of our work. Figure 4(c) clearly reflects in the major difference of $V_{oc}$ between Au back contact (without BSF) and graphene/Al back contact (with BSF) in silicon solar cell. From our study, we conclude summarily that the intercalated Al atoms act as electron acceptors and the intercalated Au atoms act as electron donors, leading to different doping type of graphene. However, this unknown and complicated doping mechanism remains a matter for debate, which is waiting for further investigation.

In summary, we have demonstrated a strategy for the application of graphene by taking the advantage of doping capability of graphene by metal intercalation. It is found that the BSF and carrier reflector due to band alignment generated by doped graphene not only acts as a blocking layer for minority carriers but also helps the collection of photogenerated majority carriers. This approach may open up a route for the application of graphene in numerous optoelectronic devices. In view of the importance of doping modulation in semiconductors, our finding shown here should be very useful and timely.

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\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) Schematics of Au/Ti/silicon solar cell/graphene/Al device. (b) J-V characteristics of silicon solar cells with Al rear contact and with/without graphene at room temperature under AM1.5 illumination. The inset shows the J-V characteristics of silicon solar cells with Al rear contact and graphene/Al rear contact under dark condition.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(a) Schematics of Au/Ti/silicon solar cell/graphene/Au device. (b) J-V characteristics of silicon solar cells with Au rear contact and with/without graphene at room temperature under AM1.5 illumination with higher bias. (c) J-V characteristics of silicon solar cells with Au rear contact and graphene/Al rear contact at room temperature under AM1.5 illumination.}
\end{figure}