Revised diode equation for Ideal Graphene-Semiconductor Schottky Junction

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Graphene-Semiconductor (G-S) Schottky diode is a building block of future graphene-based electronic and optoelectronic devices. Currently, there are debates in using the traditional bulk metal-semiconductor Schottky diode equation to describe the I-V characteristics of G-S Schottky junction [Nano Lett. 14, 4660-4664 (2014)]. In this work, we propose a revised diode equation for a Graphene-semiconductor (G-S) Schottky contact and it is able to explicitly include the properties of graphene (such as Fermi velocity and tunale Fermi energy level). It is found that the equation is able to reproduce the IV characteristics for different semiconductors that have been used experimentally in various G-S Schottky contact, and also able to explain the measured much lower Richardson constant as compared to the bulk metal-semiconductor Schottky contact. Excellent agreement of our model with various recent experimental data indicates that the established diode equation is better to describe the IV characteristic of G-S Schottky junction.

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When a metal comes into contact with a semiconductor, a barrier (known as Schottky barrier) is formed at the metal-semiconductor (MS) interface. The barrier height of a Schottky contact is one of important parameters affecting the performance of various modern electronic and optoelectronic devices. The net current density through a MS Schottky contact due to thermionic emission is normally described by the Schottky diode equation given by

\[ J = J_S \left[ \exp \left( \frac{qV}{\eta k_B T} \right) - 1 \right], \]

\[ J_S = A \times T^2 \exp \left( -\frac{\phi_{Bn}}{k_B T} \right). \]

Here, \( J_S \) is the reverse saturation current density, \( V \) is the applied forward voltage, \( q \) is the elementary charge, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \phi_{Bn} \) is the height of the Schottky barrier, \( A = 4\pi q m^* k_B^2 / h^3 \) is the effective Richardson constant, \( m^* \) is effective electron mass, and \( h \) is the Planck constant. The fitting parameter \( \eta \) is the diode ideality factor accounting for the deviation from the thermionic emission process and \( \eta = 1 \) refers to the pure thermionic emission process. Note \( J_S \) in Eq.(1) is based on the classical thermionic emission model (or Richardson’s law) for bulk materials, and Eq.(1) is valid for doped semiconductor (low to moderate level) operating around \( T = 300 \) K.

With the emerging two-dimensional (2D) materials such as graphene, much effort has been devoted to developing graphene-based post-CMOS devices and to exploring the unique properties of graphene for novel applications. Due to its finite density of state (DOS), monolayer graphene is considered as an atomically thin semimetal, and it can be used to fabricate graphene-semiconductor (GS) Schottky junction by depositing a graphene on top of a bulk semiconductor. The studies of GS Schottky junction are mainly focused on fabrication of possible electronic and optoelectronic devices, such as integrated MOSFET, Barristor, photodetector, sensor, solar cell, and so on. So far there has been only one recent paper to study if the traditional diode equation (see Eq. 1) is valid for GS Schottky junction. The other work simply makes the assumption that it is valid, and uses Eq. (1) to fit or explain experimental measurement and to estimate the barrier height.

Due to its importance both scientifically and applications, developing a consistent model to describe transport process through a non-traditional Schottky contact such as graphene-semiconductor (G-S) contact, is crucial for the performance of graphene-based devices. In this paper, we will propose a new equation which agrees well with experimental measurement...
without any fitting parameters. Note Eq. (1) is based on thermionic emission model (or Richardson’s law), and it contains a constant $A = 4 \pi q m^* k_B^2 / h^3$, which depends on electron effective mass $m^*$. This mass dependence is from the concept of effective mass for bulk materials having a parabolic energy dispersion, which may not be valid for graphene as its linear band structure will lead to a zero-effective electron mass. From Eq. (1), we can also see that it does not reflect the unique properties of graphene like its ultrafast Fermi velocity ($v_f = 10^8$ cm/s) and Fermi energy (which can be tunable externally).

These issues can also be seen in the recent experimental results\cite{16}, which demonstrated that Eq.(1) cannot account for a much lower Richardson constant $A$ obtained from the measurement. In order to resolve the controversy, a model is proposed by introducing a constant $\tau$ to account for the time scale for carrier injection. To agree with the experimental results, however, some numerical values of $\tau$ were used. Due to this limitation, we believe that a revised equation (see Eqs. 2 and 3 below) can be formulated so that the model is able to capture the fundamental parameters, such as Fermi energy level and Fermi velocity of graphene, and the barrier height (between the graphene and the semiconductor). Using this revised equation, we are also able to reproduce the lower values of $A$ without any arbitrary new constant like $\tau$ mentioned above. Excellent agreements with various experiments from different groups indicate the robustness of our proposed equation.

In Fig. 1, the band diagrams of a Graphene and n-type Semiconductor Schottky (GS) junction are illustrated (a) before and (b) after the contact is established with a barrier height of $\Phi_{Bn}$. The band diagram under applied forward bias or revised bias, is shown respectively, in Fig. 1(c) and 1(d). Consistent with the definition of Schottky junction, we have used the following assumptions: (a) thermal equilibrium is reached at the interface; (b) there is a net flow of electrical current from graphene to semiconductor; and (c) Fermi level is flat throughout the space charge region.

From Eq. (1), the reversed saturated current density $J_s$ is simply the Richardson-Dunshman (RD) law for electron thermionic emission over the Schottky barrier $\Phi_{Bn}$. For a single layer graphene, this may not be valid as the effect of the supply function of the electrons in the graphene behaving like massless fermion quasiparticles is not included, and a new model has been proposed recently\cite{17}, given by

$$J(E_F, T) = \frac{e k_B^3 T^3}{\pi \hbar^3 v_f^2} \exp\left[-\frac{\Phi_{Bn} - E_F}{k_B T}\right].$$

(2)
Here, $\hbar$ is the reduced Planck constant and $v_f$ (10^6 m/s) is the velocity of massless Dirac fermions in the graphene, $E_f$ is the Fermi energy level of the intrinsic graphene, which is located at the Dirac point. It is very important to note that Eq. (2) is independent of electron mass $m$, and the effects of $v_f$ and $E_F$ are explicitly included in additional to the temperature $T$ dependence. The details of the equation and its comparison with experimental results can be found in the paper, and will not be reproduced here.

Equation (2) can be considered as the reversed current density, namely $J_{GS} = J(E_F, T)$ for which the current density flowing from a n-type semiconductor to graphene must equal to the current density from graphene to n-type semiconductor. Thus for a graphene-semiconductor (GS) Schottky junction, the traditional Schottky diode equation for a metal-semiconductor contact [Eq. (1)] becomes

$$J = J_{GS}(\exp(\frac{eV}{\eta k_B T}) - 1),$$

$$J_{GS} = A^* \times T^2 \exp[-\frac{\phi_{Bn} - E_F}{k_B T}],$$

where the modified Richard constant $A^* = \frac{e k^3 T}{\pi \hbar v_f}$ is no longer a constant but a function of $T$ and $v_f$. Note that the exponential term in Eq. (4) also contains the Fermi energy level $E_F$, which is different from Eq. (1).

Some recent works have revealed that the Fermi level is not pinned when graphene is in contact with Silicon, which allows for modulating the Schottky barrier height to meet specific performance of devices. Without the pinning effect, the famous Schottky-Mott rule holds for ideal G-Silicon contact. Considering the work function is around 4.5 eV for intrinsic graphene from recent works and silicon’s electron affinity of 4.05 eV and band gap of 1.1 eV, we estimate that the Schottky barrier height is, respectively, about 0.45 eV and 0.65 eV, respectively for the ideal G/n-type Silicon contact and G/p-type Silicon contact.

It is well known that the Fermi level in the graphene can be tuned by gate voltage, which will induce a change in the Schottky barrier height, $\Delta E_F = \Delta \phi_{Bn}$, as shown in many experiments. The gate-voltage induced shift in the Fermi level is given by

$$\Delta E_F = \operatorname{sgn}[V_g] \hbar v_f \sqrt{\frac{\pi \varepsilon_0 \varepsilon_r V_g}{e \times d}},$$

where $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of vacuum and oxide layer (e.g. SiO$_2$), respectively; $d$ is the thickness of the insulating oxide layer, and $V_g$ is the applied gate voltage. Using Eq.
the Fermi energy level in Eq. (2) becomes $E_F = E_{Fo} + \Delta E_F$, where $E_{Fo}$ is the intrinsic Fermi energy level for graphene.

Recently Sinha and Lee\textsuperscript{16} have extracted the effective Richardson constant via measuring the activation energy for Graphene/n-type Silicon Schottky junction. Compared with the traditionally measured Richardson constant (112 Acm$^{-2}$K$^{-2}$), this experiment reported a very low value 1.47 Acm$^{-2}$K$^{-2}$, indicating that the traditional Schottky diode equation Eq. (1) is not valid. A quantum Landauer transport model was developed by them to interpret the unusual low value of Richardson constant. However, an arbitrary value of $\tau$ is required to have good agreements. In comparison, Eq. (2) proposed here is not only successful in manifesting the unique properties of G-S junction but also is able to reproduce the much lower value of measured Richardson constant. For example, at $T = 300$ K as used in the experiment, we have a $A^*$ of about 3.47 Acm$^{-2}$K$^{-2}$ using our model, which is quite closed to the measured value. In Fig. 2, our model developed in this paper is able to reproduce the measured curves\textsuperscript{21,22} of $\ln(J_{GS}/T^3)$ vs 1/$T$ without using any adjusted parameters. The comparison shows excellent agreement between the calculated results (solid lines) and experimental data (symbols). We also make a comparison in the fitting to our model and Richardson's law. It is found that the extracted Schottky barrier heights for all Schottky junctions are less than ones by Richardson's law and that the fitting errors for our model are comparable to Richardson's law: 5 % vs 5.1% for graphene/Si\textsuperscript{23}, 1.7% vs 1.72 % for graphene/MoS\textsubscript{2}\textsuperscript{24}, 1.9% vs 1.99% for graphene/GaAs\textsuperscript{21} and 4.45% vs 4.49% for graphene/GaN\textsuperscript{22}. These evidences strongly support the argument that Eqs (3) and (4) describe the fundamental transport mechanisms across graphene/semiconductor Schottky junctions, instead of Eqs (1) and (2).

In Fig. 3a, we plot the calculated current density $J$ (in semilogarithmic scale) for a graphene/n-type-Silicon Schottky junction\textsuperscript{21} as a function of biased voltage for different diode ideality factor $\eta = 1, 2, 3, 4, 5$ and 6. With increasing reverse voltage, the Fermi level in the graphene is tuned up, and the Schottky barrier height is reduced. Thus the reverse current density across the Graphene-Silicon junction is saturated as the reversed biased voltage ($V < 0$) increases. This is consistent with the band diagram shown in Fig.1d and it has been confirmed by recent work\textsuperscript{6,16,21}. It is this unique characteristic of Graphene/Semiconductor Schottky junction that makes it different from the traditional metal-semiconductor junction. The variation in the $\eta$ does not greatly affect the reversed
current density. However the deviation from pure thermionic injection \( (\eta = 1) \) enables the reduction in the forward current density for \( \eta > 1 \), as other transport mechanisms, such as quantum tunneling, diffusion, and others will become important. In addition, we find that the turn-on voltage for current across Graphene-Silicon Schottky junction is around 0.9 V as shown in the insert in Fig. 3a, which is in good agreement with the recent experiment result\(^2\).

In Fig. 3b, we show the effect of temperature \( (T = 260 \text{ to } 360 \text{ K}) \) on the current-voltage (IV) characteristics at \( \eta = 1 \). Note that the reverse current density increases with increasing temperature over the whole range of applied reverse voltage. For the forward current density, the increment of current due to higher temperature is only up to about \( V = 0.5 \) volts. Note the calculated results shown in Fig. 3b (in the range of \(-4 < V < 0.5\)) is comparable to the experimental results\(^\text{21}\) [see Fig. 6 in the paper].

In summary, unlike the traditional metal-semiconductor Schottky diode, G-S diode exhibits some novel and unique I-V characteristics. The new diode equation developed in this paper perfectly accounts for these unique properties and explains experiment results perfectly, and offers a deep insight of understanding charge carrier transport across the G-S Schottky junction. An excellent agreement of our model with the recent experiment results indicates that our equation describes the fundamental physics mechanism of carrier transport across G-S Schottky junction. These findings may pave the wave for the exploration and design of novel and more efficient electronic and optoelectronic device based on G-S Schottky junctions, such as photodetector, solar cell, sensors, etc.

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A. Captions

**Fig. 1** Schematic band diagrams of Graphene/n-type Semiconductor Schottky diode junction. (a) Before contact. (b) After contact, Fermi level is aligned and there is no net current flow in the thermal equilibrium. (c) With forward voltage $V_f$, more holes created in the graphene leads to the increase in the work function of graphene. The Schottky barrier height $\phi_{Bn}$ is also increased for electrons in the graphene, resulting in decreasing reverse current. However, electrons in the semiconductor are easier to flow into graphene. (d) With reverse biased voltage $V_R$, the Fermi level is upshifted to reduce the barrier height for electron in the graphene. Electrons in the semiconductor are harder to climb up the barrier due to the lowered Fermi level. Here, $\Phi_G$ is the work function of intrinsic graphene, $\chi_{semi}$ is the affinity of semiconductor, $V_{bi}$ is the built-in potential, $E_g$ is the band gap of semiconductor. Orange line represents the Fermi level.

**Fig. 2** $\ln(J_{GS}/T^3)$ as a function of $1/T$. Theoretical results based on Eq. (4) of our model (solid lines) are in an excellent agreement with various experiment results (symbols) with different semiconductors: (a) Graphene/Si$^{23}$, (b) Graphene/MoS$_2^{24}$, (c) Graphene/GaAs$^{21}$, (d) Graphene/GaN$^{22}$.

**Fig. 3** Room-temperature current density-voltage (J-V) characteristics of Graphene/n-type Silicon Schottky junction at $\eta = 1$. The J-V curve clearly demonstrates the rectifying property as shown in the inset. (a) semilogarithmic plots ln(J)-V with different diode ideality factor $\eta = 1, 2, 3, 4, 5$ and 6. (b) Temperature dependence of the current density ln(J) as a function of biased voltage (V) across graphene/silicon Schottky junction from 260 K to 360 K. The arrows point towards direction of increasing temperature.
Before contact

(a) Forward voltage

(b) After contact

(c) Forward voltage

(d) Reverse voltage

FIG. 1.
Experiment data
Fitting to Eq. (4)

\[ \ln \left( \frac{J_{GS}}{T^3} \right) = \frac{1}{T} (1/K) \]

(a) Graphene/Si
\[ \phi_m = 0.437 \text{ eV} \]

(b) Graphene/MoS\(_2\)
\[ \phi_m = 0.276 \text{ eV} \]

(c) Graphene/GaAs
\[ \phi_m = 0.447 \text{ eV} \]

(d) Graphene/GaN
\[ \phi_m = 0.69 \text{ eV} \]

FIG. 2.
FIG. 3.