Quantitative analysis of the Schottky interface of reduced graphene oxide Schottky diodes

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Abstract
A Schottky contact is greatly vital for electronic devices; therefore, a quantitative analysis of the Schottky interface is important in realizing a high-performance Schottky diode. In this study, we fabricate an r-GO-based Schottky diode and elucidate the charge traps in r-GO by analyzing the current–voltage characteristics. The conduction becomes space charge limited (at high voltage) because of these traps. The trap energy and concentration were calculated as ∼0.20 ± 0.02 eV and 2.11 × 1015 cm−3, respectively. Quantitative information about charge traps will help in the fabrication of high-quality r-GO-based electronic devices. The trap density is the core challenge for the material community; therefore, controlling the traps is essential in improving the performance of r-GO-based electronic devices. We believe that the quantitative analysis of the Schottky interface could be beneficial for the improvement of the charge transport in r-GO-based electronic devices.

1. Introduction
Graphene oxide (GO), a chemically modified graphene derivative enriched with oxygen functionalities, is considered as a marvel material because of its extraordinary physical, thermal, mechanical, and electrical properties [1]. Considering its amazing properties, GO has received special attention from researchers in the recent years and facilitated the development of advanced functional devices. GO comprises sp2 and sp3 hybridized carbon atoms, which characterize its electronic properties. The reduction process of chemical, thermal, and electro deposition (ED) can tune the electrical and mechanical properties of GO. ED is an effective technique for manipulating graphene layers in liquid suspensions to produce graphene derivatives and graphene-based composite [2]. In the recent years, ED approaches have gained much interest in r-GO synthesis because of its simplicity and time efficacy [1, 3]. The r-GO has been increasingly used in fabricating electronic devices that exhibit extremely superior performances. The large bandgap of r-GO is considered as advantageous for optoelectronic devices furthermore the r-GO can be well dispersed in different solvents and the electrical properties are dependent on the reduction methods and degree of reduction. Although large-area r-GO-based organic solar cells, field effect transistors, chemical sensors, and ultra-capacitors have been reported, a stable and good-quality Schottky contact on r-GO is a crucial vehicle for these electronic applications [4–7]. To realize r-GO-based electronic devices, an efficient analysis of the current transport in the Schottky diode and the extraction of diode parameters are very important because of their significant impact on the device performance. Schottky diodes based on r-GO have been implemented in the recent years [8, 9]. The rapid progress of r-GO-based electronics has led to a growing need of understanding the role of interface traps on the electrical characterization of r-GO. Thus, the quality of Schottky contacts is the most critical for the performance of r-GO-based electronics because the electrical parameters of devices could be contaminated by many extrinsic factors, such as interface traps and technology-dependent defects. The quality of the Schottky interface may be helpful in the fabrication of r-GO-based electronic devices.

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We demonstrate herein the r-GO-based Schottky diodes fabricated by the ED method and analyze the charge transport kinetics in the r-GO-based Schottky diodes. A resourceful analysis was accomplished to extract evidence on surface states. The current transport mechanism demonstrates different regimes. At a low bias, the conduction is Ohmic, while at a high bias, the conduction becomes a space charge limited current (SCLC) because of the exponential distribution of traps. The deep level parameters were calculated from the current–voltage measurements. In addition, we estimate the average trap density and energy of the traps. The quantitative study of the charge traps presented in this work will help improve the carrier transport by passivating the defects to fabricate high-quality r-GO devices, which help r-GO replace conventional materials in many practical applications.

2. Experimental details

The GO used in this study was purchased from Angstrom Materials (Dayton, USA). The ITO substrates were cleaned in an ultrasonic cleaner in acetone, isopropyl alcohol, and deionized water sequentially. We used 5 ml GO aqueous solution with 10 ml phosphate buffer solution (0.2 M molar concentration). A conventional three-electrode electrochemical cell was used, in which the ITO-coated glass substrate was used as the working electrode; a platinum coil was used as the counter electrode; and a Ag/AgCl electrode was used as the reference electrode. Cyclic voltammetry (CV) was performed by scanning between 0 and −1.0 V at a rate of 10 mV s$^{-1}$ for a single voltammetric cycle. The r-GO thickness was 800 nm. The Al Schottky contact of 3.0 mm diameter and 500 nm thickness was evaporated on an r-GO thin film. The work function of r-GO is 4.4 eV therefore the metals with work function lower than r-GO such as Titanium (4.3 eV), Chromium (4.5 eV) and Aluminum (4.06–4.26 eV) can be used to make Schottky contact while metals with higher work function such as Au(5.1–5.4 eV) and ITO (4.8 eV) can be used to form ohmic contacts [10–14]. Figure 1 demonstrates the schematic process diagram.

The surface morphologies were investigated through JEOL JEM-2100 Plus transmission electron microscopy (TEM). Energy dispersive x-ray analysis (EDX) analyses were performed using a scanning electron microscope. Fourier-transform infrared (FTIR) spectroscopy was studied using a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies). The electrical current–voltage (I–V) measurements of the Schottky diodes were performed by using Keithley 2400.
3. Results and discussion

The TEM image represents a sheet with a variable thickness and folded r-GO nanosheets with many wrinkles (figure 2).

Figures 3 and 4 depict the EDX analysis of GO and r-GO, respectively. Table 1 presents the relative atomic/weight ratios, from where the degree of oxidation/reduction of the r-GO can be estimated from the C/O ratio. The GO exhibited a C/O atomic ratio of 1.19. The atomic weight ratio C/O of the r-GO increased to 3.24, which is an evidence of GO reduction. We found some impurities from the substrate. Furthermore, in the reduction process, the oxygen content was decreased by 21.42%.

Figure 5 shows the FTIR spectra of GO and r-GO. The broad peak between 3000 and 3700 cm$^{-1}$ was caused by the stretching and bending vibration of the C–OH groups [15]. The peak at 1718 cm$^{-1}$ can be assigned to the C=O carbonyl stretching from the carbonyl and carboxylic groups [16]. The peak located at 1626 cm$^{-1}$ can be assigned to the vibrations of the adsorbed water molecules and the contributions from the skeletal vibrations of the un-oxidized graphitic domains (aromatic C=C bonds) [16]. The peak at 1408 cm$^{-1}$ was related to the C–OH or C–O–C bond [17]. The characteristic absorption bands corresponding to the C–OH stretching at 1164 cm$^{-1}$ and the C–O stretching at 1058 cm$^{-1}$ were also observed [18].
The FTIR spectrum of r-GO (figure 5) demonstrated that the peaks corresponding to the oxygen-containing functional groups were successfully removed or weakened, which confirmed the successful oxidation–reduction of GO. The peak at 1640 cm$^{-1}$ corresponded to the C=C stretch, further verifying the high degree of GO reduction [16, 19].

The typical I–V characteristics for the Al/r-GO Schottky diode and ITO/r-GO ohmic contact are shown in figures 6(a) and (b) respectively. The resulting Al/r-GO Schottky diode I–V characteristics described by the
thermionic emission theory. The current in the device could be expressed as

\[
I = I_o \left[ \exp \left( \frac{eV}{nkT} \right) - 1 \right]
\]  

(1)

The saturation current \(I_o\) is given as

\[
I_o = AA^*T^2 \exp \left( -\frac{e\Phi_b}{kT} \right)
\]  

(2)

Using equations (1) and (2), the ideality factor \(n\) and the barrier height \(\Phi_b\) were calculated as 4.8 and 0.68 eV, respectively. Zhu et al reported that with different reduction methods, the value of \(\Phi_b\) for r-GO fluctuated between 0.64 and 0.69 eV [20].

The higher value of the ideality factor can be attributed to the barrier tunneling or generation recombination in the space charge region and series resistance [21]. The ideality factor ranging from 2 to 5.5 was reported for the r-GO-based Schottky diodes [22–24]. Diode resistance (R) defined as \(R = \frac{dV}{dl}\) is shown in figure 7. The R decreases with increasing the forward bias and diode resistance becomes constant after turn on voltage.

The double logarithmic plot of the I–V characteristic was investigated (figure 8) to obtain an insight of the charge transport properties of the Schottky diode. Figure 8 depicts three different current regions: Region I indicates that the current transport is dominated by tunneling and corresponds to the ohmic behavior (I–V); Region II shows that the current increases exponentially with the increasing voltage using \(I \sim \exp (cV)\) relation;
and Region III indicates that the current follows a power law ($I \sim V^m$), where $m$ is the slope, and the slope was 2, implying that the charge transport through the junction is influenced by the SCLC mechanism, which has been previously reported [25–27]. The SCLC mechanism occurs when the injected carriers from the metal electrode to the semiconductor are dominated over the background carriers. The injected carriers spread and create a space charge field [14, 28, 29]. The SCLC model is one of the experimental methods used for the detection of trap states in semiconductor materials. The trap density was probably greater at the Schottky interface because of the surface damage during the contact deposition and the non-uniformity of the r-GO film on the ITO substrate. The interface states play an important role in the electrical properties of the Schottky diodes. Lampert and Mark [30] developed a single carrier SCLC model with the presence of traps at a trap-filled limit voltage $V_{TFL}$, where all the traps are filled, and conduction would become an SCLC representing the Mott–Gurney law [31].

$$J = \left( \frac{9\varepsilon\varepsilon_0 \mu AV^2}{8d^3} \right)$$

(3)

The trap-filled limit voltage $V_{TFL}$ is given as follows [32, 33]:

$$V_{TFL} = \frac{N_t qd^2}{2\varepsilon\varepsilon_0}$$

(4)

where, $N_t$ is the trap density.
The effective carrier concentration \( n_e \) in the active region is given by the following expression:

\[
J(2V_{TFL}) \sim \frac{N_t}{n_0} \]

\[
n_e = N_t e^{(E_F - E_c)/kT} \]  
(6)

where, \( J(V_{TFL}) \) is the current density at \( V_{TFL} \), and \( J(2V_{TFL}) \) is the current density at a voltage twice the \( V_{TFL} \).

Deep level parameters were calculated from the experimental \( V_{TFL} \) at RT. The values of the trap density \( (N_t) \) and the energy of traps were \( 2.11 \times 10^{13} \text{ cm}^{-2} \) and \( -0.20 \pm 0.02 \text{ eV} \), respectively.

4. Conclusions

In summary, we report herein an investigation of the current transport mechanism in r-GO Schottky diodes that illustrates the following observation: at high bias, the conduction becomes an SCLC because of the exponential distribution of traps. The deep level parameters, average trap density, and trap energy were calculated. The quantitative study of the charge traps presented in this work will help improve the carrier transport by passivating the defects to fabricate high-quality r-GO devices. We believe that a quantitative analysis of the Schottky interface could be beneficial for the improvement of the charge transport in r-GO-based electronic devices; however, more research is needed to understand the formation of these traps.

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