Temperature-dependent properties of semimetal graphite-ZnO Schottky diodes

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Highly rectifying semimetal graphite/ZnO Schottky diodes with a low-ideality-factor (1.08 at 300 K) were investigated by temperature-dependent current-voltage measurements. The current transport was dominated by thermionic emission between 300 and 420 K and the extracted barrier height followed the Schottky-Mott relation. A Richardson constant ($A^{**} = 0.272$ A cm^{-2}K^{-2}) extracted from the Richardson plot shows nearly linear characteristics in the temperature range 300–420 K. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4761958]

Zinc oxide (ZnO) is a wide band-gap (3.37 eV at room temperature) semiconductor with many advantageous properties such as large exciton binding energy of about 60 meV, high optical gain (about three times higher than in GaN), radiation hardness, or the possibility of wet-chemical processing. ZnO is a promising material for ultraviolet light emitting devices, laser diodes, solar cells, and gas sensors.[1]

In recent years, increased interest in the application of ZnO in optoelectronic and microelectronic devices has emerged. One of the crucial tasks, which have come into play, is understanding and control of ZnO electrical contact properties. High quality ohmic and Schottky contacts are a prerequisite for the fabrication of high performance ZnO based devices. Moreover, high quality Schottky contacts are crucial vehicles to study electrically active defects in semiconductor materials by capacitance-based defect characterization techniques such as capacitance-voltage measurement (C-V), deep-level transient spectroscopy (DLTS), and admittance spectroscopy (AS). Schottky contacts to ZnO were reported in 1965 on vacuum cleaved n-type surfaces.[2] Since then, different transition metals, such as Pd, Pt, Au, Ag, and Ir, have been reported to form relatively high Schottky barriers of 0.6–0.9 eV.[3] The barrier height for a particular metal strongly varies depending on the crystal quality,[4,5] the polarity,[6,7] the surface preparation, and condition under which the contact was formed.[8–11] Recently, we have demonstrated the formation of a Schottky contact by printing colloidal graphite on an O- and Zn- face of the ZnO substrate.[12] The low-energy deposition of colloidal graphite resulted in high quality Schottky diodes (SD) on the O-face ZnO. The values of the barrier height and of the ideality factor extracted from I-V characteristics were 0.89 eV and 1.07, respectively). The graphite contact appears a promising candidate for replacing conventional metal contacts, which degrade easily at high temperatures by diffusing into semiconductor and irreversibly impair the rectifying properties of the contact.

Here, we report temperature dependence of I-V characteristics of semimetal graphite/ZnO Schottky diodes prepared by printing colloidal graphite at room temperature (RT). The current transport is dominated by thermionic emission between 300 and 420 K, and the extracted value of the barrier height follows the Schottky-Mott relation with deduced graphite work function agreeing well with literature values.

SDs were fabricated on the O-face of n-type ZnO substrates grown by hydrothermal method (supplied by MTI Corporation). The O-face was preferred because of the higher quality of graphite Schottky barriers achieved as compared to the Zn-face.[12] The free electron concentration of 1.8×10^{14} cm^{-3} and the Hall mobility of 140 cm^2/Vs were determined by Hall measurements at RT. Schottky contacts were created by printing colloidal graphite at RT. A drop of commercial colloidal graphite suspension (supplied by Agar Scientific) was deposited with a teflon rod and let dry. The contact area was checked by optical microscopy to maintain the diameter close to 1 mm. The influence of the graphite contact thickness on the I-V characteristics was negligible.[12] Prior to the graphite deposition, the ZnO surface was cleaned in boiling methanol for 5 min. An ohmic contact on the back side was formed by rubbing liquid gallium with a tin rod. The diodes were characterized by current-voltage measurements (I-V) at different temperatures using the 237 High-Voltage Source-Measure Unit (Keithley).

Figure 1 shows I-V characteristics of the graphite/ZnO SD measured at atmospheric conditions in a dark chamber. The temperature was varied from 300 K to 420 K. After cooling down to room temperature, the sample showed identical I-V characteristic. The current transport through the Schottky barrier can be described by thermionic emission model (TEM). According to TEM, the forward I-V relationship of a Schottky diode at $V > 3kT/q$ can be expressed as

$$J_s = J \exp(\mathrm{qV}/\eta kT), \qquad (1)$$

where

$$J_0 = A^{**}T^2 \exp(q\phi_B/kT). \qquad (2)$$

where A^{**} is the Richardson constant, which has theoretical value of 32 A cm^{-2}K^{-2}, T is the absolute temperature, k is the Boltzmann constant, ϕ_B is the barrier height, and η is the ideality factor. By fitting the forward I-V curves (voltage in the interval of 0.1 to 0.3 V), the barrier height and ideality factor were determined for each temperature, and the results

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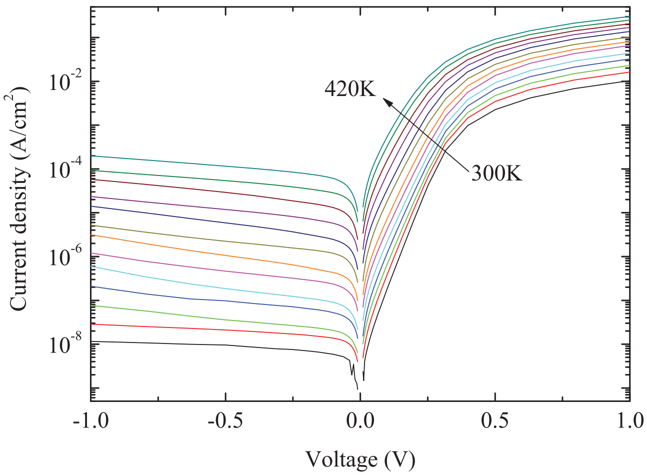

FIG. 1. Semi-logarithmic I-V characteristics of the graphite/ZnO(O-face) Schottky diode over the temperature range of 300–420 K.

are shown in Figure 2. ϕ_B and η showed small temperature dependence. The deviation from linearity above 0.3 V in the semi-logarithmic I-V characteristics is due to the series resistance of the structures.

The Richardson constant is a fundamental parameter that characterizes the TEM in Schottky barrier diodes. For ZnO SDs, the characteristics of Schottky contacts are frequently far from ideal, and the reported Richardson constant values 0.15 A $cm^{-2}K^{-2}$ by Shen *et al.*[13] and 0.248 A $cm^{-2}K^{-2}$ by Gur *et al.*[14] are significantly lower than the theoretical value. Most recently, an experimental A** value of 10 A $cm^{-2}K^{-2}$ for nearly ideal AgO_x/ZnO SD was reported by Allen *et al.*[15]

Equation (2) was used to construct a Richardson plot of $\ln(J_0/T^2)$ versus 1000/T (Figure 3). Based on the Eq. (2), A** = 0.272 A $cm^{-2}K^{-2}$ was obtained using linear fitting ($y = -1.30$–$8.77\,x$). The barrier height of the semimetal graphite/ZnO SD at room temperature was revaluated to be 0.75 eV using experimentally deduced Richardson constant in Eq. (2). Using the Schottky-Mott relation ($\phi_b = \phi_m - \chi$, where ϕ_m is a metal work function and χ is a semiconductor affinity), which relates Schottky barrier height to the metal work function and the semiconductor affinity (4.2 eV for ZnO[3]), together with the assumption that the Fermi level of the semiconductor is not pinned, we calculated the graphite contact work function ($\phi_{graphite}$) to be 4.95 eV. This value is

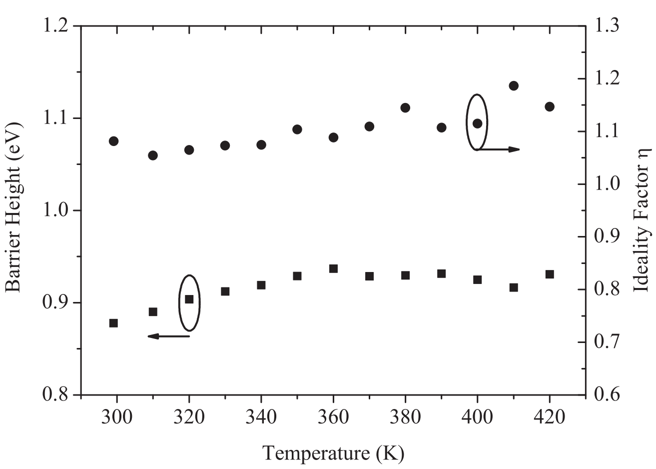

FIG. 2. Temperature dependence of the ideality factor (η) and barrier height (ϕ_b) for the graphite/ZnO(O-face) Schottky diodes.

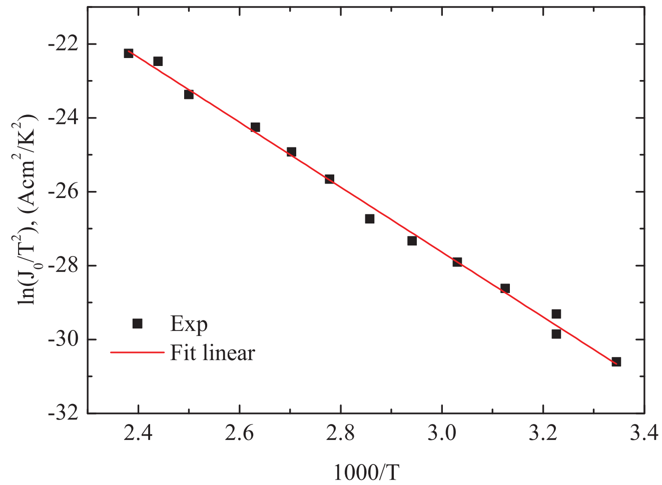

FIG. 3. Richardson plot of $\ln(J_0/T^2)$ versus 1000/T together with a linear fit to determine A*.

in good agreement with theoretical and experimental values (ranging from 4.4 eV to 5.2 eV) reported in the literature.[16,17] An attempt to conduct the measurements below RT was made. To avoid the water vapour condensation in a closed-cycle cryostat equipment, measurements had to be done in vacuum ambient. As shown in Figure 4, the ambient change from air to vacuum evokes substantial increase of the reverse leakage current. This increase can be explained by the activation of surface conductivity in vacuum. It is well known that the surface conductivity of ZnO strongly depends on the ambient condition.[18,19] Oxygen molecules absorbed on the surface extract electrons from the conduction band of ZnO to form O^-, O^{2-}anions. This process leads to the formation of a depletion region with reduced carrier concentration near the sample surface resulting in its higher resistivity. Under vacuum, oxygen molecules are easily desorbed and the surface conductivity strongly increases.

In conclusion, we demonstrated that the low-energy deposition of colloidal graphite on ZnO substrate is a viable option for replacing conventional metal contacts. Temperature dependent I-V measurements of the semimetal graphite/ZnO SDs showed that thermionic emission was dominant in current transport at room temperature and above. An experimental

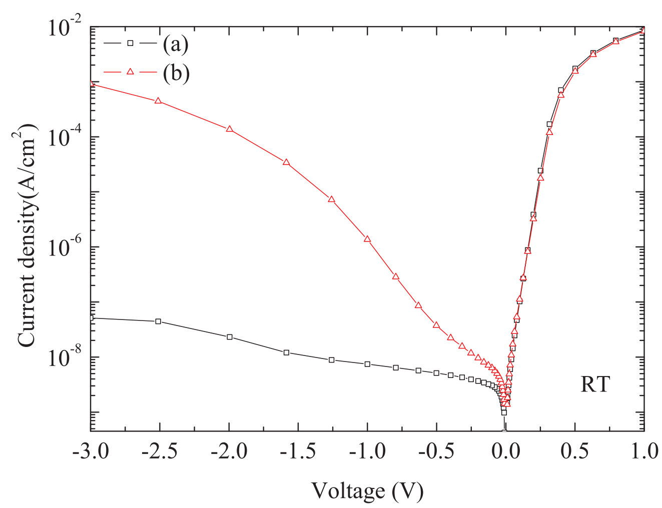

FIG. 4. I-V characteristics of the graphite/ZnO(O-face) SD measured in a different ambient. (a)-air and (b)-vacuum.

Richardson constant of 0.272 A $cm^{-2}K^{-2}$ was determined from I-V-T characteristics. The graphite contact work function of 4.95 eV, agreeing well with literature values, was deduced by using Schottky-Mott relation. When the SD was operated in vacuum, its performance was degraded by the activation of surface conduction paths.

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