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Investigation of significantly high barrier height in Cu/GaN Schottky diode

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Current-voltage (I-V) measurements combined with analytical calculations have been used to explain mechanisms for forward-bias current flow in Copper (Cu) Schottky diodes fabricated on Gallium Nitride (GaN) epitaxial films. An ideality factor of 1.7 was found at room temperature (RT), which indicated deviation from thermionic emission (TE) mechanism for current flow in the Schottky diode. Instead the current transport was better explained using the thermionic field-emission (TFE) mechanism. A high barrier height of 1.19 eV was obtained at room temperature. X-ray photoelectron spectroscopy (XPS) was used to investigate the plausible reason for observing Schottky barrier height (SBH) that is significantly higher than as predicted by the Schottky-Mott model for Cu/GaN diodes. XPS measurements revealed the presence of an ultrathin cuprous oxide (Cu_2O) layer at the interface between Cu and GaN. With Cu_2O acting as a degenerate p-type semiconductor with high work function of 5.36 eV, a high barrier height of 1.19 eV is obtained for the Cu/Cu_2O/GaN Schottky diode. Moreover, the ideality factor and barrier height were found to be temperature dependent, implying spatial inhomogeneity of barrier height at the metal semiconductor interface. [http://dx.doi.org/10.1063/1.4939936]

INTRODUCTION

Group III-Nitride based electronic devices have seen a strong growth in interest and application over the past two decades due to their unique properties. Gallium Nitride (GaN) is a promising semiconductor for high-temperature, high-frequency and high-power applications because of improved material parameters such as higher energy bandgap, higher breakdown field, higher electron saturation velocity, higher thermal conductivity, and direct bandgap.[1–4] GaN based opto-electronic devices such as light emitting diodes, avalanche photodiodes, and electronic devices such as high electron mobility transistors (HEMTs) require good quality Schottky contacts for a reliable performance.[5–8] For HEMT applications, a Schottky gate contact with large barrier height is always desirable to achieve improved transconductance, maximum drain current and high breakdown voltage of the device. It also results in small gate leakage current, thus reducing the noise level. From previous reports on GaN based Schottky diodes, it was seen that high barrier heights can be achieved using metals with high work functions. Schottky barrier contacts on GaN epitaxial films using high work function metals like Platinum (Pt), Nickel (Ni), Palladium (Pd) etc. covered by a high conductive top metallization (usually gold) have been reported.[9–12] Among them Ni is commonly used as a Schottky contact to study current transport mechanism at the metal/semiconductor interface.[13–16]

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Copper (Cu) with low metal work function (4.65 eV[17]) was introduced as a Schottky contact on n-type and p-type silicon by Aboelfotoh *et. al.* in 1990.[18] Variable temperature current-voltage study based on thermionic emission theory was reported. Ideality factor (IF) of 1.01 and Schottky barrier height (SBH) of 0.60 eV was found at the room temperature. In 2003, Jin-Ping Ao *et. al.* used copper as a gate material to n-GaN and AlGaN/GaN epitaxial films, and found low gate leakage current as compared to Ni/GaN.[19] In addition to this, IF of 1.04 and higher SBH of 1.15 eV were calculated from I-V measurements for Cu/n-GaN, as compared to the values for Ni/n-GaN where IF and SBH were found to be 1.05 and 0.97 eV, respectively. From the previous reports on Ni/n-GaN Schottky barrier diodes,[13–16] it has been observed that in this metal/semiconductor diode, the SBH lied in between the values predicted by the Schottky-Mott model[20,21] ($\phi_B = \phi_m - \chi$) and the Bardeen model[22] ($\phi_B = (E_g/q) - \phi_o$). Here, ϕ_B is the SBH, ϕ_m is the metal work function, χ is the electron affinity of the semiconductor, E_g is the bandgap of the semiconductor, q is the electronic charge and ϕ_o is the energy location of the charge neutrality level. In the present work related to Cu/GaN Schottky diode, the experimental SBH was found to be more than as predicted by the Schottky-Mott model. Hence, the possible reason for experimental SBH to be 1.19 eV instead of the theoretical BH of 0.55 eV (considering ϕ_{Cu}=4.65 eV[17] and χ_{GaN}=4.1 eV[23]) needs to be investigated. This interesting observation has not been explored in detail earlier. Furthermore, the analysis of current-voltage (I-V) characteristics of the Schottky barrier diode at room temperature only does not give detailed information about the current transport process or the nature of the barrier formed at the MS interface. The temperature dependence of the I-V characteristics allows us to understand different aspects of the current transport mechanisms.

In this paper, the analysis of current transport mechanisms in the forward bias at the Cu/GaN interface using temperature dependent current-voltage (I-V-T) characteristics has been reported. The investigation regarding significantly high barrier height for Cu/GaN Schottky diode has been carried out using X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

GaN epitaxial films used in this study were grown on sapphire substrate using metal organic vapor phase epitaxy (MOVPE) technique. The layers were n-type with thickness of about 3 μm, sheet resistance of about 285 Ω/□, carrier concentration of about 4.6×10^{17} cm^{-3} and Hall electron mobility of about 160 cm^2/V-s at room temperature, as measured by Ecopia Hall measurement set up (HMS 5000). Prior to metal deposition, the samples were ultrasonically cleaned in de-ionized (DI) water, then in acetone, followed by boiling iso-propanol for 5 min. each, to leave the surface free from organic contaminants. The surface was again rinsed off by DI-water and then mildly etched in a solution of hydrochloric acid: DI-water in the ratio of 1:2 for 30 s to remove native oxide layer formed on the surface. Then the samples were finally rinsed off with DI-water for a prolonged time, and thereafter dried in air. After this cleaning process, the samples were immediately loaded into the thermal evaporation deposition chamber. For ohmic contact, Indium (In) metal was evaporated on the corners of the samples with a thickness of about 100 nm. Then the samples were thermally annealed at 350°C for 60 s to form the ohmic contacts. Later Schottky contacts of Cu/Au (40 nm/100 nm) metals were deposited on the GaN samples as circular dots with diameter of 2 mm using a thermal evaporation system at the base pressure of 10^{-6} Torr. The deposition rate was about 1 Å/s. The current-voltage (I-V) characteristics were measured using Keithley Semiconductor Characterization System (SCS-4200), in the temperature range of 80-340 K with steps of 20 K. During each measurement, the temperature was controlled and stabilized with in ±1 K using Cryocon Temperature controller (Model 32).

RESULTS AND DISCUSSION

Temperature dependent current-voltage (I-V-T) characteristics on semi-log scale have been plotted in Fig. 1. From the figure, it can be seen that the current rectification at ±2V is of the order of 10^8 in the temperature range of 240-340 K, but the rectification decreases with the decrease in

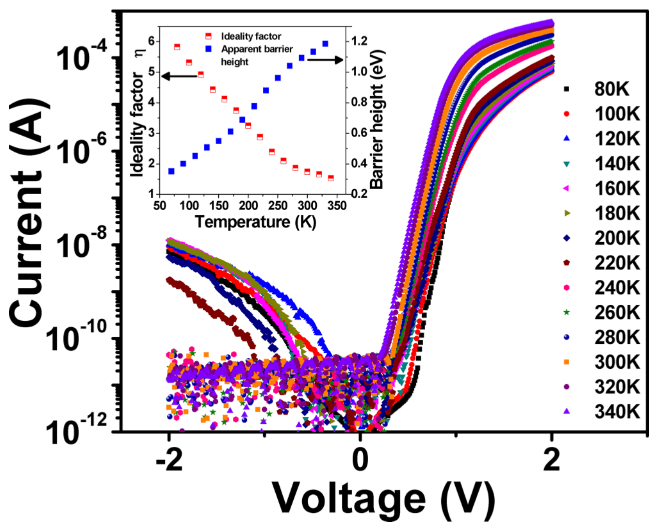

FIG. 1. Measured I-V curves of Cu/n-GaN Schottky diode as a function of temperature. The inset shows the variation of ideality factor and barrier height with temperature in the range of 80-340K.

temperature. For thermionic emission (TE) and V > 3kT/q the general diode equation is given by[24]

$$I_n = \left[AA^{*}T^{2}exp\left(-\frac{q\phi_{BnTE}}{kT}\right)\right]\left[exp\left(\frac{qV}{\eta kT}\right)-1\right] \tag{1}$$

where A is the area of the Schottky diode, A^{*} is the effective Richardson coefficient, T is the absolute temperature, q is the fundamental electronic charge, ϕ_{BnTE} is the barrier height, k is the Boltzmann's constant, V is the applied voltage and η is the ideality factor. From the forward logI vs V plot at room temperature (RT), an ideality factor of 1.7 and a barrier height, ϕ_{BoTE} of 1.09 eV were calculated from the slope and intercept of the linear region, respectively. The calculated ideality factor increased from 1.5 to 5.8 as the temperature was decreased from 340 to 80K. Since $\eta > 1$, the I-V behavior deviates from the TE model in the forward bias region. In order to explain the observed I-V-T behavior deviating from TE mechanism for the Cu/n-GaN Schottky diode, the tunneling transport mechanism based thermionic field-emission (TFE) model proposed by Padovani and Stratton[25] was taken into account. Under forward bias, the current due to TFE and for $V_F > kT/q$ is given by

$$I_{TFE} = \frac{AA^{*}T\sqrt{\pi E_{oo}q\left(\phi_{BnTFE}-\phi_n-V_F\right)}}{k\,cosh\left(E_{oo}/kT\right)}exp\left[\frac{-q\phi_n}{kT}-\frac{q\left(\phi_{BnTFE}-\phi_n\right)}{E_o}\right]exp\left(\frac{qV_F}{E_o}\right) \tag{2}$$

where, $E_{oo} = (q\hbar/2)(N/m^{*}\epsilon_s)^{1/2}$ is the characteristic energy related to the tunneling probability of a triangular potential barrier, $E_o = E_{oo}coth(E_{oo}/kT)$, V_F is the forward bias voltage, ϕ_n is equal to $E_C - E_F$, ϕ_{BnTFE} is the Schottky barrier height, h is the Planck's constant, N is the donor density, m^{*} is the effective mass and ϵ_s is the dielectric constant. E_o can also be written as ηkT. For N=4.6×10^{17} cm^{-3} in our sample, E_{oo} is calculated as 9.4 meV. A barrier height ϕ_{BoTFE} of 1.19 eV was obtained by applying the current equation as given by Eq. (2) due to TFE at RT.

It can be seen here that for Cu/GaN system with metal work function 4.65 eV[17] and semiconductor electron affinity 4.1 eV,[23] the Schottky barrier height should be ≤ 0.55 eV, as predicted by Schottky-Mott model. In order to understand the reason for having SBH higher than that predicted by the Schottky-Mott model, XPS was performed on Cu/Au Schottky contacts on GaN epitaxial layer using PH01BOS HSA3500 150 R6 [HW Type 30:14] MCD-9 model photoelectron spectrometer with a Mg Kα X-ray excitation (1253.6 eV) in ultra-high vacuum environment. Since the XPS system had capability of probing the depth of only 15-20nm, a separate sample was prepared for the measurement, with the thickness of Cu and Au on GaN layer as 10 nm each. Fig. 2 and 3 show the XPS spectra of Cu, Au, Ga and N elements before and after etching the sample using argon ion beam with different energy. First, a broad area scan of the sample was taken. Since the gold layer had a thickness of 10 nm,

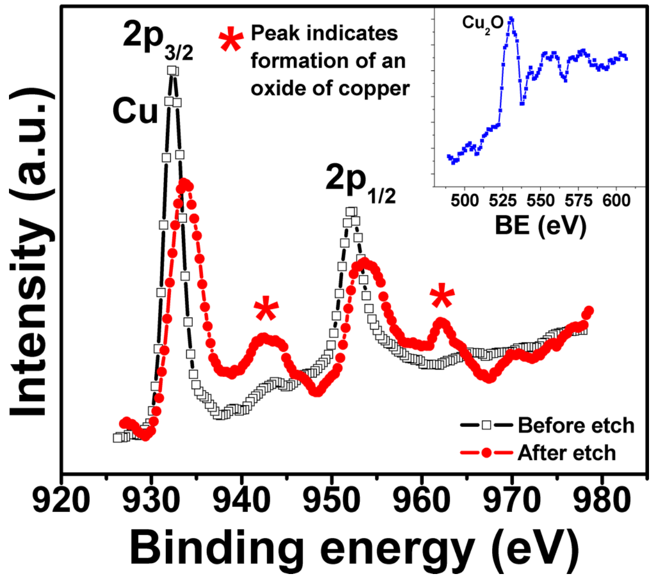

FIG. 2. XPS spectra showing Cu peaks before etching and CuO peaks after etching using argon ion sputtering at 2 keV energy for 3 min. The inset shows XPS peak arising due to Cu_2O formation at the interface between Cu and GaN.

very high Au 4d and 4f peaks were observed. Along with this, molybdenum (due to the sample holder), carbon and oxygen peaks were also observed. The observed carbon and oxygen peaks were shifted towards higher binding energy (BE) as compared to the standard value. This BE error considering carbon peak as a reference was subtracted from all the experimental data. Then the sample was etched using argon ion sputtering at 1 keV energy for 3 min. The wide sample scan showed Copper 4d peaks at approximately 932 eV and 952 eV and the intensity of the gold peak got reduced. The sample was further etched at 2 keV energy for 3 min. Two extra peaks along with copper peaks slightly shifted to higher binding energy were seen, as shown in Fig. 2. The two extra peaks and the peak shift imply the presence of an oxide of copper layer. In the same scan, an extra small peak was also observed at 530 eV as shown in inset of Fig. 2. This BE corresponds to the standard value of cuprous oxide (Cu_2O) peak. The sample was finally etched at 3 keV energy for 5 min. It was observed from the scan,

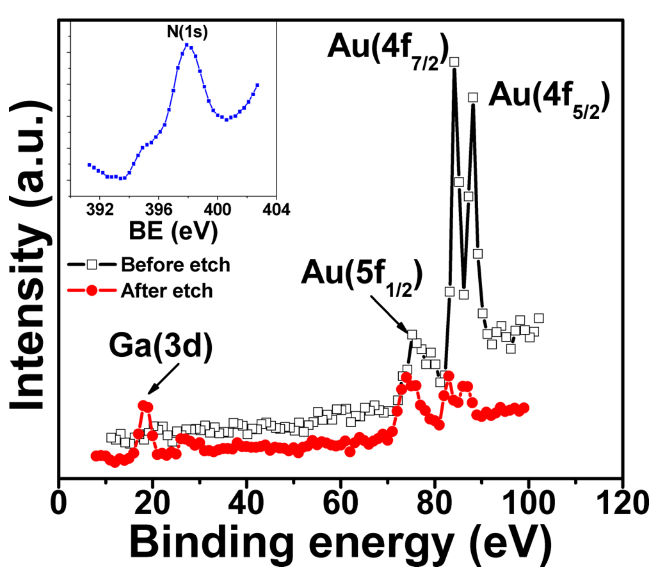

FIG. 3. XPS spectra showing Au peaks before etching and Ga peaks after etching using argon ion sputtering at 3 keV energy for 5 min. The XPS peak in the inset corresponds to N (1s).

and shown in Fig. 3, that the gold 4f peaks were drastically reduced and gallium 3d peak emerged at its standard position. Furthermore, a nitrogen 1s peak was also observed at 397 eV. This means that after sputtering for 5 min, Au and Cu layer got removed and we reached close to GaN surface.

The values of ideality factor η and barrier height ϕ_B calculated using TFE current equation (Eq. (2)) depending on temperature are plotted in inset of Fig. 1. The experimental value of η increased and ϕ_B decreased with decrease in temperature, as can be seen in the plot. Such variation with temperature implies that the Schottky barrier consists of laterally inhomogeneous patches of different barrier height. Spatial distribution of ϕ_B at the metal-semiconductor interfaces are explained by J. H. Werner and H. H. Güttler[26] in the form of Gaussian distribution of ϕ_B with standard deviation σ_s around mean barrier height of $\overline{\phi_B}$. One of the major reasons behind the origin of the interface inhomogeneities is that the metal-semiconductor interface is not atomically flat but rough.[26] This is because the metal was not epitaxially grown on n-GaN surface, which resulted into local variations of the electric field which in turn caused SBH to vary locally. This means that the electrons at low temperature are able to cross the interface through lower barriers. Accordingly, the current transport is dominated by carriers moving through patches of lower barrier height and larger ideality factor. As the temperature increases, more electrons have sufficient energy to overcome the higher local barriers. Consequently the apparent barrier height increased and ideality factor decreased with temperature. More detailed explanation is give elsewhere.[27,28]

From the I-V-T measurement results, it is believed that the effect of ideality factor greater than 1 for all temperatures can be modeled by considering current transport in the device to be explained by thermionic field-emission. The forward bias current transport mechanism is mostly determined by the value of the ideality factor. If η=1, the current flow is the TE current, while if η>1, the tunneling or recombination current should be taken into account. Tunneling probability is enhanced due to presence of high-density defect states at the interface. Its contribution can be judged by comparing the characteristic tunneling energy E_{oo} with kT. If $E_{oo} \approx kT$, the current flow is mainly due to tunneling, while if $E_{oo} \ll kT$ TE current dominates. For our sample, E_{oo}~9.4 meV at RT, which is not much smaller than kT. In addition to this, GaN is known to suffer from an unusual high dislocation density.[29,30] Therefore, tunneling through the barrier is expected, which can explain the forward bias characteristics of Cu/n-GaN metal/semiconductor interface.

From the XPS depth profiling measurement results it can be said that a cuprous oxide (Cu_2O) interlayer was formed in between the copper layer and the GaN epitaxial film. This may be due to the reaction of copper metal and the oxide layer of GaN, which could have been formed due to low vacuum pressure (10^{-6} Torr) thermal evaporation system. Generally, cuprous oxide is observed to be a p-type semiconductor in the as-deposited state. This is attributed to the fact that it has a bandgap of 2.1 eV[31] and an electron affinity of 2.9eV.[32] In addition, it may be considered as a degenerate semiconductor also because of its high work function of 5.36 eV, as experimentally proved by A. Soon *et. al.*[33] Hence, the Cu/n-GaN metal-semiconductor system actually became as Cu/p^+-Cu_2O/n-GaN system after the formation of the interface as shown in Fig. 4. Now, the degenerate semiconductor

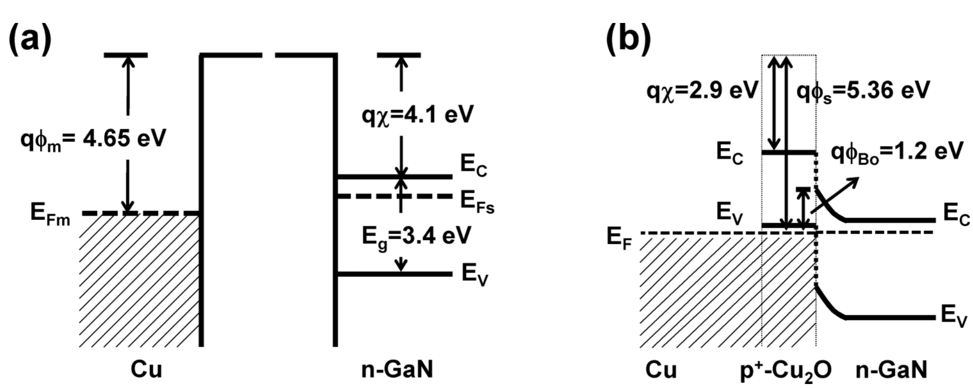

FIG. 4. Energy band diagram when (a) Cu and n-GaN are separated from each other, and (b) Cu is deposited over n-GaN. An ultrathin p-Cu2O layer is formed between Cu and GaN, leading to the enhancement of Schottky barrier height up to a value of 1.19 eV.

is heavily doped in such a manner that it acts like a metal. Thereby, a metal1-metal2-semiconductor system may be considered where the metal2 has a work function of 5.36 eV. Since GaN is in direct contact with a high work function material, its Fermi energy level would respond accordingly leading to a higher Schottky barrier height as compared to the Cu case. This metal1-metal2-semiconductor system clearly follows the Schottky Mott rule. The theoretical value according to the Schottky Mott rule is now approximately 1.26 eV, considering the metal work function as 5.36 eV and semiconductor electron affinity as 4.1 eV. This is the possible reason for the observation of significantly high value of Schottky barrier height i. e. 1.19 eV at RT for the fabricated Cu/GaN Schottky diodes.

CONCLUSION

The current-voltage (I-V) characteristics of Cu/n-GaN Schottky barriers was investigated and analyzed. Using thermionic emission current mechanism, ideality factor of 1.7 at RT was calculated, which implied deviation from TE theory in the forward bias. Thermionic field-emission governed the carrier transport across the metal-semiconductor interface. Schottky barrier height of 1.19 eV was calculated using TFE current equation at RT. Layer by layer XPS measurement was done. It was seen that cuprous oxide (Cu_2O) form of copper oxide layer was present as an interlayer between Cu and GaN. Cu_2O is generally a p-type semiconductor. But in this case, it is considered a degenerate semiconductor because of its high work function of 5.36 eV. Hence, the formation of metal-like Cu_2O in the vicinity of GaN can possibly be the reason for the high experimental Schottky barrier height, which is in agreement with the Schottky Mott model. The temperature dependence of η and ϕ_B implied spatial inhomogeneity of barrier height at the interface.

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