Electronic transport and Schottky barrier heights of p-type $CuAlO_2$ Schottky diodes

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A $CuAlO_2$ Schottky diode was fabricated and investigated using current density-voltage (J-V) and capacitance-voltage (C-V) methods. It is shown that the barrier height ($q\phi_B$) determined from J-V measurements is lower than that determined from C-V measurements and $q\phi_B$ determined from C-V measurements is close to the Schottky limit. This is due to a combined effect of the image-force lowering and tunneling. Time domain measurements provide evidence of the domination of electron trapping with long-second lifetime in $CuAlO_2$. Carrier capture and emission from charge traps may lead to the increased probability of tunneling, increasing the ideality factor. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4806970]

Transparent conducting oxides (TCOs) are very important for various kinds of devices and are commonly used in transparent electronics. The combination of low electrical resistivity and high transparency in the visible light range makes TCOs fascinating in various practical applications. Thereafter p-type TCO technology becomes a very important and emerging area of research and various research groups around the globe during last few years reported the syntheses and characterization of several delafossite and non-delafossite p-type TCO thin films. Among the many p-type TCOs, the beneficial properties of $CuAlO_2$ (CAO), such as wide direct band gap and high transparency, have attracted significant interest for application in semiconductor devices. p-type transparent CAO with a 3.5-eV direct energy gap (E_g) at room temperature has attracted much interest because of its application to optoelectronic and microelectronic devices such as light-emitting diodes, ultraviolet Schottky barrier photodetectors, solar-blind Schottky photodiodes, dilute magnetic semiconductors, and p–n heterojunction diodes.[1–7] In this letter, the fabrication and characterization of CAO Schottky diodes are presented. The metal–semiconductor (MS) contact is one of the most widely used rectifying contacts in the electronics industry. Due to the technological importance of Schottky diodes, which are the most simple of the MS contact devices, a full understanding of the nature of their electrical characteristics is of great interest. It is important to study the electrical characteristics if the current transport mechanism of the CAO Schottky diode is to be understood. However, the mechanism of current flow through the interface has not been established and the exact value of the barrier height ($q\phi_B$) has not yet been estimated using the current density–voltage (J-V) or capacitance-voltage (C-V) measurements.

The glass substrates were ultrasonically cleaned in acetone, methanol, and deionized water. The CAO films were prepared on glass substrates by rf magnetron sputtering. The target size is 2 in. and the target-substrate distance is 65 mm. A high-purity $CuAlO_2$ target (rf power was fixed at 60 W) and an Al target (rf power was fixed at 30 W) were used for deposition of CAO films. The sputtering pressure was fixed at 5×10^{-3} Torr. The substrate temperature was fixed at 500 °C. The target was used in conjunction with Ar/O_2 as an ambient gas for sputtering. The flow of Ar and O_2 was 70 and 5 SCCM (SCCM denotes standard cubic centimeter per minute), respectively. The film thickness was about 65 nm for CAO samples. Structural properties were investigated by x-ray diffraction (XRD). The carrier concentration, mobility, resistivity, and conduction type were obtained from the Hall measurements in the van der Pauw configuration for all samples. The electrodes were fabricated by depositing Au metal on the CAO layer through a shadow mask. According to the Hall measurement at room temperature, the hole concentration (N_h) and mobility were 8.21×10^{16} cm^{-3} and 0.1 cm^2/V s, respectively. Then, In Schottky contacts and Au ohmic contacts were, respectively, deposited onto the CAO surface by a sputter coater. The current-time (I-t), J-V, and C-V measurements were performed using a Keithley Model-4200 semiconductor characterization system. C-V measurements made in the reverse-bias mode are complementary to J-V measurements made in the forward-bias mode and provide useful information about the magnitude of the built-in potential and $q\phi_B$ at the In/CAO interfaces. The photoresponse was measured under 100 mW/cm^2 and illumination intensity from a 150 W solar simulator with an AM 1.5G filter (obtained from Newport Corporation). The photoresponse was measured by recording the current versus time while sunlight illumination was turned on and off by a shutter. The photoresponse measurements of CAO Schottky diodes provide a method to examine the charge trapping effect.

Figure 1 shows the X-ray spectra pertaining to materials that corresponded to various processing conditions. In the XRD spectra shown in Fig. 1, peaks of the CAO phases are, respectively, marked. Three peaks [corresponding to the CAO (006), CAO (101), and CAO (018) planes][8–11] were observed. The measured S^2/C^2 as a function of applied voltage V for CAO Schottky diodes in the dark is shown in

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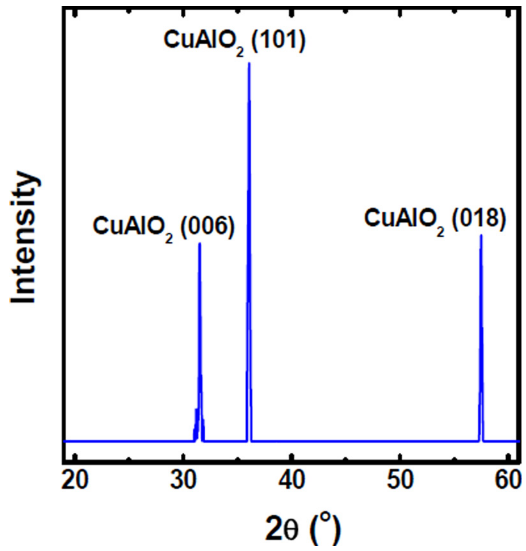

FIG. 1. XRD spectra of CAO films.

Fig. 2. S is the contact area. The inset of Fig. 2 shows a schematic cross-sectional view of CAO Schottky diodes. The C-V relationship between the metal and the semiconductor is given by[12]

$$S^2/C^2 = (2/\varepsilon_s q N_A)(V_i - V), \tag{1}$$

where $\varepsilon_s = 3.5\varepsilon_0$ for CAO,[13] ε_0 is the permittivity in vacuum, q is the electron charge, N_A is the acceptor concentration, and V_i is the x intercept at $S^2/C^2 = 0$. According to Eq. (1), N_A of $1.48 \times 10^{17}\,cm^{-3}$ and V_i of 0.9 V were calculated. N_A is slightly higher than N_h obtained from the Hall measurement. This is attributed to incomplete ionization for acceptors in CAO. $q\phi_B$ is related to V_i by the relationship[12]

$$q\phi_B = qV_i + kT + qV_n, \tag{2}$$

where T is the measurement temperature, k is the Boltzmann constant, V_n $[V_n = (kT/q)\ln(N_v/N_h)]$ is the potential difference between the energy of valance band edge (E_v) and the energy of Fermi level (E_F) of CAO.[14] N_v is the effective density of states in the valence band of CAO. Based on the well-known N_v, that is, $N_v = 2\,(2\pi m^* kT/h^2)^{3/2}$,[14] the N_v value was calculated to be $4.1 \times 10^{18}\,cm^{-3}$ for CAO samples, h is Planck's constant, m^* ($m^* = \sim 0.3\,m_o$)[15] is the hole effective mass, and m_o is the free electron mass. $q\phi_B$ was calculated to be 1.00 eV.

Figure 3 shows the J-V characteristics of CAO Schottky diodes in the dark and the fitting curve. From thermionic emission (TE) theory, the J-V characteristic of a Schottky diode is given by[12,14]

$$J = A^* T^2 \exp\left(-\frac{q\phi_B}{kT}\right)\left[\exp\left(\frac{qV}{\eta kT}\right) - 1\right], \tag{3}$$

where η is the ideality factor, and A^* is the effective Richardson constant ($36\,A\,cm^{-2}\,K^{-2}$ for CAO based on $m^* = \sim 0.3\,m_o$).[15] The $q\phi_B$ and η were obtained from the forward J-V characteristics according to Eq. (3). $q\phi_B$ and η were calculated to be 0.76 eV and 1.6. Note that $q\phi_B$ determined from C-V measurements is larger than that determined from J-V measurements, owing to the image-force lowering.[12,16] The reduction of barrier height ($\Delta q\phi$) was analyzed by taking into account the image force lowering effect.[16] For CAO Schottky diodes, $\Delta q\phi$ was calculated to be about 0.1 eV. The $\Delta q\phi$ value is lower than the difference in $q\phi_B$ determined from J-V and C-V measurements, implying that the lower $q\phi_B$ determined from J-V measurements than that determined from C-V measurements is due to a combined effect of the image-force lowering and the carrier transport with a tunnel component. In addition, the value of η falls within the reasonable range ($2 > \eta > 1$), indicating that the J-V characteristic is limited by the forward-bias current behavior of the conventional Schottky junction. Deviation of η from unity may be attributed to the domination of the current transport at the In/CAO interface by a defect band.[17–20] Carrier capture and emission from charge traps may lead to an increase in current flow under forward bias conditions, thus, increasing η. Kwak *et al.* have suggested that the current transport at the metal/p-type GaN interface was dominated by the deep level defect (DLD)

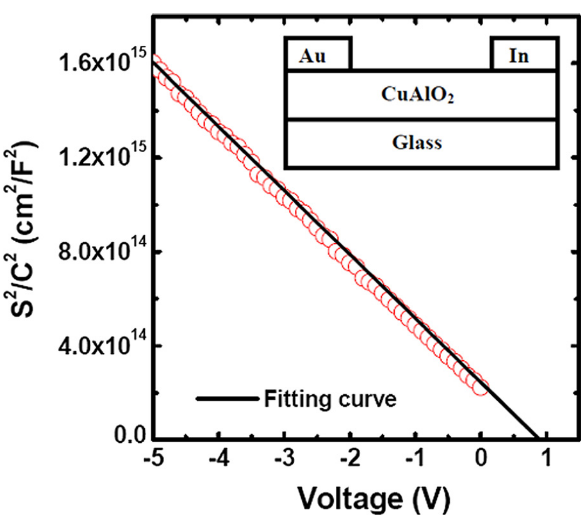

FIG. 2. S^2/C^2-V plot of CAO Schottky diodes in the dark. Inset: Schematic device structure.

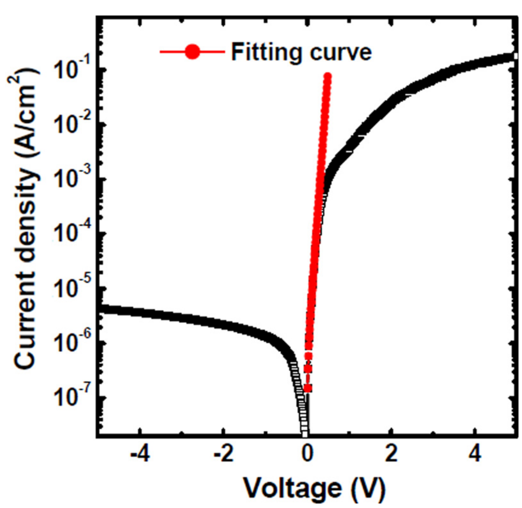

FIG. 3. J-V characteristics of CAO Schottky diodes in the dark and the fitting curve.

band.[19] Shiojima *et al*. have found carrier capture and emission from acceptor-like DLDs for Ni/p-type GaN Schottky diodes.[20]

To confirm this picture, time domain measurement was performed on the CAO Schottky diode. The photocurrent (I_P) values were measured for V varying from 0 to 1 μV for 100 s (illumination was turned on at t = 0 s). Figure 4 shows the normalized photocurrent decay for CAO Schottky diodes and the fitting curve. $|I_P|$ should slowly decay for CAO Schottky diodes, since the charge traps in CAO films influence the electronic conduction through the device. In this study, we consider two possible physical pictures to explain the observed I_P characteristic: It is mainly dominated by the long-lifetime or short-lifetime charge traps. To estimate the time constants for $|I_P|$ decay, we fit the data to exponential decay functions. The transient was fitted to second-order exponential decay $|I_P'| = A_1 e^{-(t/\tau 1)} + A_2 e^{-(t/\tau 2)}$ using the nonlinear least-squares method,[21–23] with four fitting parameters. $|I_P'|$ is the normalized $|I_P|$. This equation reflects two different charge trapping mechanisms with time constants τ_1 and τ_2 ($\tau_1 > \tau_2$). The values of A_1 and A_2, where $A_1 + A_2 = 1$, represent weighing factors that quantify the contribution of each mechanism to the decay process. The first (second) term, which can be attributed to long-lifetime (short-lifetime) charge trapping, dominates the decay process. τ_1, τ_2, A_1, and A_2 were calculated to be 10.54 s, 1.21 s, 0.67, and 0.33. The data show that $|I_P|$ slowly decayed, owing to the domination of long-lifetime charge trapping ($A_1 > A_2$). Incident photon illumination in the ultraviolet light range can create electron-hole pairs in the space charge region at the In/CAO interfaces that will be swept out producing the photocurrent. Holes originating from the photogenerated electron-hole pairs were swept out of the space charge region by the built-in electric field into the CAO layer and electrons originating from the photogenerated electron-hole pairs were swept out of the space charge region by the built-in electric field into the In layer. The photoresponse result confirms that the photocurrent decay is due to the domination of electron trapping with long-second lifetime in CAO.[23,24] The detrapped electrons and holes may recombine in pairs in the CAO film, resulting in a decaying hole population.

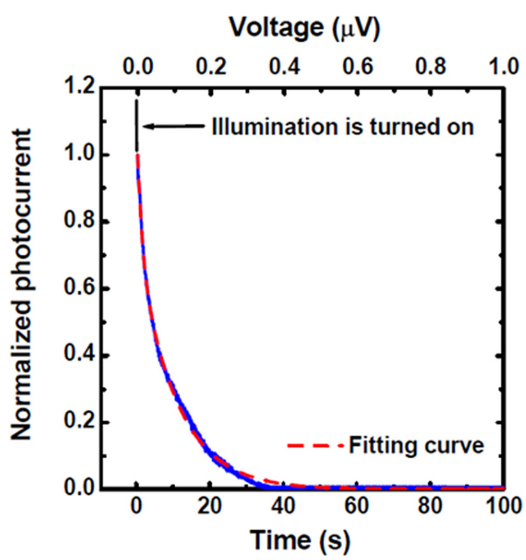

FIG. 4. The normalized photocurrent decay for CAO Schottky diodes and the fitting curve.

For In/CAO Schottky diodes, the ideal Schottky barrier height ($q\phi_I$) is given by[12,14,25]

$$q\phi_I = (\chi + E_g) - W_{In} = 5.2 - W_{In}, \tag{4}$$

where W_{In} is the work function of In ($W_{In} = 4.12$ eV) and χ is the electron affinity of CAO. Benko and Koffyberg suggested that the valence band lies 5.2 eV below the vacuum level.[26] According to Eq. (4), the Schottky limit could be calculated to be 1.08 eV. For CAO Schottky diodes, $q\phi_B$ evaluated from C-V measurements is close to the Schottky limit.

A detailed analysis of the electrical characteristics of the CAO Schottky diode was carried out to determine the nature of the conduction behavior. This behavior was clarified through an electrical characterization of CAO Schottky diodes, demonstrating the presence of charge traps. The photoresponse result confirms that the photocurrent decay is due to the domination of electron trapping with long-second lifetime in CAO. Consequently, $\eta > 1$ is attributed to carrier capture and emission from charge traps leading to the increased current flow under forward bias conditions. In addition, we found that $q\phi_B$ determined from J-V measurements is lower than that determined from C-V measurements and $q\phi_B$ determined from C-V measurements is close to the Schottky limit. This is due to a combined effect of the image-force lowering and the carrier transport with a tunnel component. The knowledge of trap-induced effects can be a useful tool for understanding and interpreting the diode measurements.

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