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Defects in Cu₂O studied by deep level transient spectroscopy

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Hole traps in *p*-type Cu₂O were studied by means of deep level transient spectroscopy in the heterostructure of *p*-Cu₂O/*i*-ZnO/*n*-ZnO. In addition to the trap level at about 0.45 eV from the valance band edge, which is already reported as being due to Cu vacancy, we found a new trap level at about 0.25 eV. The new trap is tentatively assigned as Cu-di-vacancy from the trap concentration dependence on oxygen flow rate and substrate temperature. © 2006 American Institute of Physics. [DOI: 10.1063/1.2175492]

Cuprous oxide (Cu₂O), a direct band gap semiconductor with a band gap energy of 2.0 eV, has been regarded as one of the most promising materials for application to photovoltaic cells,^{1,2} especially for the top cell in a tandem structure. The attractiveness of Cu₂O as a photovoltaic material lies in the fact that the constituent materials are nontoxic, low cost and abundantly available. Cu₂O/ZnO heterojunction has been fabricated by radio frequency (rf) magnetron sputtering and showed the photovoltaic effects, but did not demonstrate good performance.³ Knowledge of defect energies as well as their densities is an important input for further improvement of the performance of Cu₂O thin film polycrystalline solar cells. There are several reports on the deep trap in Cu₂O by measuring deep level transient spectroscopy (DLTS).⁴⁻⁶ A hole trap with the activation energy of about 0.45 eV from the valance band edge has been observed and assigned as Cu vacancy using Schottky diodes. However, the temperature range in the DLTS measurements was too narrow. It is necessary to measure the DLTS in the expanded temperature range in order to understand the origin of the defect in Cu₂O. In this work, the DLTS spectra of Cu₂O with the junction of *n*-ZnO/*i*-ZnO/*p*-Cu₂O structure in the temperature range between 100 and 350 K is reported. We observed a new trap with the activation energy of 0.25 eV from the valance band edge in addition to the 0.45 eV trap, and the origin of the 0.25 eV trap is discussed based on the sample preparation conditions.

Polycrystalline *p*-Cu₂O/*n*-ZnO heterostructure was grown by means of rf magnetron sputtering on Corning 7059 glass substrate using a Cu target of 99.99% purity, ZnO target and Ar as sputtering gas. Oxygen was introduced during the growth of Cu₂O through a nozzle whose end was placed near the substrate. We prepared two sets of samples for Cu₂O, with various oxygen flow rates (Sample 1: 140 ml/min, Sample 2: 155 ml/min, Sample 3: 163 ml/min, Sample 4: 173 ml/min) and another set with various substrate temperatures (Sample I: 570 K, Sample II: 670 K, Sample III: 720 K, Sample IV: 770 K). At the interface between *n*-ZnO and *p*-Cu₂O, intrinsic ZnO(*i*-ZnO) layer was deposited. The *i*-ZnO and *n*-ZnO were deposited using undoped and 1 wt% Al₂O₃ doped ZnO target, respectively. The thickness of each layer was 800, 100, and 1700 nm for *n*-ZnO, *i*-ZnO and *p*-Cu₂O, respectively. The hole concentration of Cu₂O was in the range between 1 × 10¹⁶ and

4 × 10¹⁷ cm⁻³, and the electron concentration of *n*-ZnO was kept constant at 1 × 10²⁰ cm⁻³. Ohmic contacts were performed on Cu₂O by thermal evaporation of gold (Au) with the diameter of 0.3 mm. The schematic heterostructure is shown in Fig. 1.

The structural properties were studied by x-ray diffraction (XRD) in the θ -2 θ mode using Cu *K* α radiation. The capacitance-voltage (*C*-*V*) measurements were performed on these samples with the modulation frequency of 1 MHz. DLTS measurements were performed with the reverse bias voltage between 0 and -0.5 V, with the pulse width and duration of 0.1 and 50 ms, respectively. By scanning the transient capacitance change over a wide range of temperatures under various rate windows, the hole emission rate e_p as a function of inverse temperature (T^{-1}) can be obtained. From the Arrhenius plot (i.e., $\ln(T^2\tau)$ vs T^{-1} , where $\tau=1/e_p$), the activation energy E_a of the defect level was extracted.⁷ The hole emission rate is related to the capture cross section and activation energy of the trap level expressed as

$$e_p = s_p \nu_{th} N_v \exp(-E_a/kT), \quad (1)$$

where, s_p is the capture cross section, ν_{th} is the hole thermal velocity, N_v is the effective density of state of the valance band and k is the Boltzmann's constant. The value of N_v was calculated to be 1.7 × 10¹⁹ cm⁻³ using the effective hole mass of 0.8 m_0 .⁸ The hole trap density, N_T , can be calculated by using the expression

$$N_T = (2\Delta C/C_0)N_a. \quad (2)$$

The acceptor concentration, N_a , is determined by *C*-*V* measurements, which give the average acceptor concentration in the Cu₂O layer. C_0 is the zero bias capacitance that is ob-

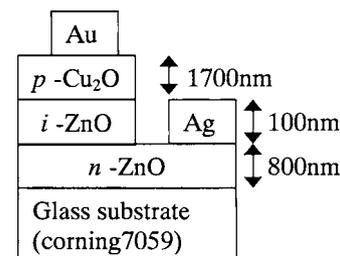


FIG. 1. Schematic structure of *n*-ZnO/*i*-ZnO/*p*-Cu₂O for DLTS measurements.

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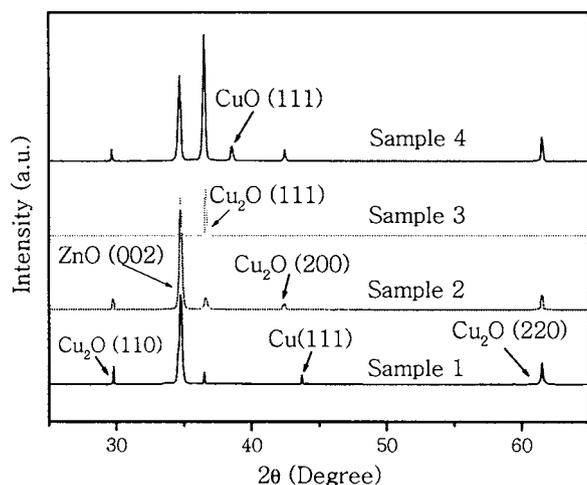


FIG. 2. XRD profiles of *n*-ZnO/*i*-ZnO/*p*-Cu₂O heterostructure with the oxygen flow rate of 140, 155, 163, and 173 ml/min.

tained from the *C*-*T* data at the corresponding DLTS peak temperature.

The XRD profiles in θ - 2θ mode using Cu *K* α radiation of the heterostructures from Sample 1 to Sample 4 are shown in Fig. 2. Diffraction peaks of (110), (111), (200) and (220) planes of Cu₂O are observed. We found a small intensity of Cu(111) diffraction peak for low O₂ flow sample (Sample 1) and CuO(111) for high O₂ flow sample (Sample 4). It is clear that the samples prepared in this study contain oxygen deficient Cu₂O and oxygen excess Cu₂O.

The *C*-*V* measurements on the heterostructure of Cu₂O/ZnO were carried out at room temperature. The relation between $1/C^2$ and *V* was basically expressed by a straight line. These results indicate that the depletion region increases with increasing the applied voltage and the value of the capacitance is not so affected by the existence of the heterointerface of ZnO/Cu₂O. This means that the signal of the capacitance only comes from Cu₂O layer.

A typical DLTS spectrum of Sample 4 is shown in the inset of Fig. 3. Two clear hole traps were observed for all samples. Only one trap has been reported in Cu₂O by DLTS measurements in the temperature range between 200 and 300 K. We expanded the temperature range of the DLTS measurements between 100 and 350 K and a new hole trap at around 140 K denoted as trap A in the inset of Fig. 3 was observed. The trap B in the inset of Fig. 3 was observed in

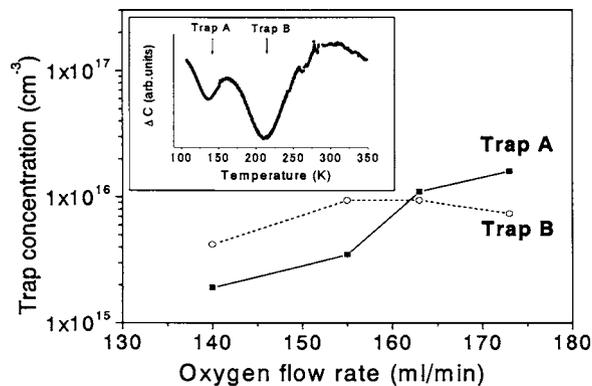


FIG. 3. Relationship between trap concentration and oxygen flow rate. A typical DLTS spectrum of Sample 4 is shown in the inset. The reverse bias, filling pulse and the pulse width were -0.5 V, 0 V and 0.1 ms, respectively.

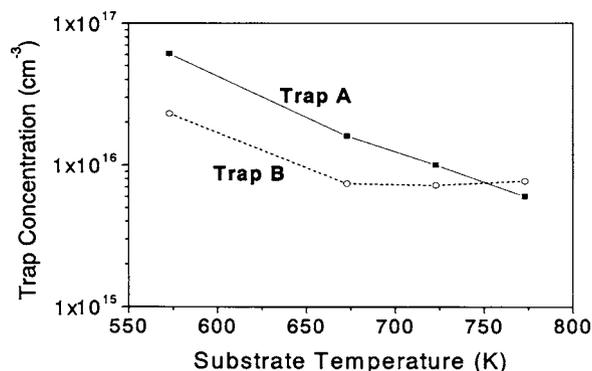


FIG. 4. Relationship between trap concentration and substrate temperature.

the same temperature range as reported. The average activation energy of the trap B was calculated to be 0.45 eV from the Arrhenius plots. Judging from the activation energy and the pre-exponential factor in the Arrhenius plots, trap B is the same as that reported, which is assigned as Cu vacancy.⁹⁻¹³ The assignment is completely consistent with that obtained theoretically.¹⁴

The average activation energy of trap A was calculated to be 0.25 eV. To consider the origin of trap A, the relationship between the trap concentration and oxygen flow rate during growth was studied, and the results are shown in Fig. 3. The concentration of trap A increased with increasing oxygen flow rate, on the other hand the concentration of trap B slightly increased and then slightly decreased. The dominant trap changed from trap B to trap A with increasing oxygen flow rate. We can expect that the concentration of Cu vacancy and interstitial oxygen increased with increasing oxygen flow rate. Therefore, oxygen interstitial may be one of the candidates for trap A, although it is not clear that the interstitial oxygen can act as an acceptor. A more plausible candidate for the trap A may be Cu vacancy complex like Cu-di-vacancy, since the concentration of trap B tends to decrease even in the strong condition of Cu deficiency which is confirmed by x-ray diffraction as shown in Fig. 2. It may be reasonable to consider that the formation of Cu-di-vacancy is enhanced with increasing the concentration of Cu-mono-vacancy and dominant defect changes from mono-vacancy to di-vacancy with increasing vacancy concentration. The trap level of the di-vacancy may be shallower than that of the mono-vacancy because of the vacancy-vacancy interaction as discussed theoretically.¹⁴ The activation energy of trap A (0.25 eV) is shallower than that of trap B (0.45 eV), so the Cu-di-vacancy is a strong candidate for the trap A.

We also studied the deep trap in the Cu₂O with the effect of substrate temperature. The samples also showed trap A and trap B in DLTS spectra. The relationship between the trap concentration and the substrate temperature is shown in Fig. 4. The concentration of both trap A and B decreased with increasing substrate temperature, and dominant trap was trap A for relatively lower substrate temperature and it changed to trap B at higher temperature, as shown in Fig. 4. As reported earlier, the crystal quality of Cu₂O was improved by increasing substrate temperature.¹⁵ For example, carrier concentration of undoped Cu₂O and the value of the full width at half maximum of x-ray diffraction peaks decreased, and the hole mobility increased with increasing substrate temperature. These results indicate that the defect den-

sity in Cu_2O decreased with increasing substrate temperature. The results shown in Fig. 4 are consistent with the previously reported results.

When the trap concentration is relatively high, trap A is dominant, and when the trap concentration is relatively low, trap B is dominant. This tendency was also observed in Fig. 3. As discussed on Fig. 3, we consider that the Cu-mono-vacancy is mainly generated when the vacancy concentration is relatively low and when the vacancy concentration exceeds a threshold value, Cu-di-vacancy becomes dominant. If this process is true, the variation of the trap concentration with substrate temperature shown in Fig. 4 is reasonably well understood. That is, when the defect density is high due to lower substrate temperature, trap A (Cu-di-vacancy) is dominant. When the defect density is low due to higher substrate temperature, trap B (Cu-mono-vacancy) is dominant. The variation of the defect density with the growth condition seems to be consistent with the proposed defect model.

In conclusion, DLTS measurements were performed for Cu_2O with the $\text{Cu}_2\text{O}/\text{ZnO}$ heterostructure and two kinds of hole traps were detected. One of the traps (trap A) whose activation energy is 0.25 eV was observed. The density of trap A increased with increasing O_2 flow rate during the

growth. Trap A is tentatively assigned as Cu-di-vacancy. The origin of the other trap whose activation energy is 0.45 eV may be Cu-mono-vacancy consistent with the results reported earlier.

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