Photoconductivity Study of Sputter-Deposited Cu₂O Films

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Cuprous oxide (Cu₂O) thin films were deposited by radio frequency sputtering technique on fused silica substrates. The X-ray diffraction study of the Cu₂O samples showed reflections from (111) and (200) planes of cubic Cu₂O. The samples were then annealed at 1008 K in nitrogen (N₂) atmosphere. Annealed samples indicated strain relaxation. The samples were then characterized optically by measuring the transmittance using an ultraviolet-visible-near infrared photospectrometer. The band gap of the as-deposited samples were found to be ≈ 2.1 eV, whereas the annealed samples had a band gap of ≈ 2.6 eV. The transient photocurrent decay measurements of the annealed films indicated slow non-exponential power law decays in several time windows, indicating multiple trapping of the carriers in the deep defects within the band gap. The steady-state photo and dark current measurement and persistent photocurrent (PPC) was carried out on the annealed samples. In general, the photocurrent was found to be much smaller than the dark current. The steady-state and transient photocurrent measurements were utilized to determine the carrier lifetime-mobility product, $\langle\mu\tau\rangle$ of the samples and to determine the carrier mobility, $\langle\mu\rangle$.

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1. Introduction

In the context of photovoltaics, Cu₂O has a very important role to play as the *p*-type heterojunction and absorber layer, with the theoretical Cu₂O based solar cell efficiency being predicted to be about 18% [1]. Cu₂O (band gap $E_g \approx 2.1$ eV) is abundantly available, nontoxic in nature, with low cost of production. The *p*-type conductivity arises due to copper vacancy (V_{Cu}), which is reported to form acceptor levels at 0.12–0.70 eV above valency band [2]. But, presence of deep donor levels (oxygen vacancy V_O induced) in Cu₂O is also accepted and has been discussed in literature [3]. It has a large absorption coefficient [4], higher than single crystalline silicon [5], which justifies its importance for application in solar panels. Apart from photovoltaics, Cu₂O thin films might also find application in resistive random access memories, spintronics, gas sensors and photocatalysis [6–9]. But, in order to put the material into device applications, especially for photovoltaics, clear idea about its optical and transport property holds the key in terms of performance.

In this communication we report on the optical and transport property of Cu₂O thin films deposited by rf sputtering technique. Crystallite growth and orienta-

tion was inferred from X-ray diffraction (XRD) study. Microstructural characteristics were obtained by scanning electron microscopy (SEM). The optical band gap of the samples was determined by measuring the transmittance. The dark and photoconductivity of the samples were compared with their transient photocurrent (TPC) characteristics. The slow photocurrent decay was explained by multiple trapping (MT) model (due to deep defects). PPC effect was studied. The carrier mobility within the samples was also determined using the data obtained from transient and steady state measurements.

2. Experimental details

The thin Cu₂O films were deposited onto fused silica substrates by rf sputtering technique for 30 min time, using Cu₂O target (99.9% pure, 10 cm diameter). Prior to deposition, the system was evacuated to a base pressure of 10^{-6} mbar. During deposition, a constant 5.0 sccm of Ar gas flow was maintained with an additional steady oxygen flow rate of 0.4 and 0.6 sccm, for the films named Min001 and Min002, respectively. The depositions were carried out at 300 K. All the depositions were performed with 200 W rf power at 13.56 MHz frequency. The distance between the target and substrate was kept at 5 cm. The last film Min003 was deposited with all the parameters kept unchanged except for the use of copper (Cu) target (purity 4N) and oxygen flow rate which was set at 2.0 sccm. All the films were then annealed at 1008 K (2/3 of melting point temperature) under nitrogen flow

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for 2 h and used for further microstructural, optical and transport property characterizations.

The films were tested by XRD measurements (using Cu K_α line ≈ 0.154 nm) to determine the crystal phase and orientation. SEM revealed the microstructural details of the films. The band gap of the films were determined by measuring the transmittance at room temperature using a UV-VIS-NIR photospectrometer. The transport properties of the annealed films were investigated by steady-state and transient dark and photocurrent measurements. The steady-state conductivity of the films was measured at 300 K using a Keithley picoammeter and a 30 V dc power supply. The measurements were carried out with coplanar aluminum contacts deposited on the films. The photoconductivity measurement was carried out at room temperature (300 K) using a 10 mW, 325 nm HeCd laser. The sample was attached to a preamplifier, where the chopped signal (chopper speed ≈ 18 Hz) was fed directly into a dual phase SR830 lockin amplifier. PPC measurements were also carried out at 30 V using the 325 nm He-Cd laser line. As for the transient photoresponse, a 532 nm UV line of Q-switched Nd:YAG laser, shooting 5 ns pulses at ≈ 2 mJ/cm², with a repetition rate of 5 pulses/s and a spot size of 5 mm diameter was used. The decay signal was recorded with a Tektronix 200 MHz bandwidth digital oscilloscope. The photocurrent decay was measured in several time windows ranging from 100 μ s to 500 ns, at 15 V bias voltage. The p -type nature of the films was verified by thermoelectric measurements previously.

3. Results and discussions

Figure 1 shows a representative plot for the transmittance for Min002 as-deposited and annealed film. Absorption coefficient of the films was derived from the transmittance spectra (using Lambert-Beer's law), thereby, the band gaps were calculated from Tauc's plot [10]. The measured band gap of the annealed samples was around 2.6 eV which is near the first allowed direct transition of Cu₂O. The absorption coefficient for the annealed films had values of about 10^5 cm⁻¹, near the band edge. For comparison, the as-deposited samples had band gaps of around 2.2 eV, which is near the first direct but forbidden transition of Cu₂O (2.17 eV). The thickness of the films, calculated from the interference fringes [11] of the transmittance spectra, was around 470 nm for Min001 and Min002, whereas the Min003 film was around 900 nm thick.

The representative SEM micrograph of an annealed sample (Min002) is shown in Fig. 2. The SEM images revealed compact surface, with excellent coverage. The same feature was observed for the rest of the annealed samples. As for the as-deposited ones, good substrate coverage was observed, but the annealed ones showed better grain aggregation and growth. The XRD spectra (not shown here) showed reflections from (111) and (200) planes of cubic phase Cu₂O for as-deposited films, the

Fig. 1. Representative transmittance spectra of Min002 as-deposited and annealed films.

reflex being shifted to a smaller angular indicating tensile strain in the layers. After annealing the films in a N₂-flow at 1008 K (2/3 of the melting point temperature) the (200) reflex was found to be near the literature value of 42.39° 2θ (ICDD card no. 65-3288), indicating stress relaxation. The (111) peak was also present. But, both the peaks were more intense, and the (200) peak was much sharper.

Fig. 2. Representative SEM micrograph for sample (Min002) annealed at 1008 K.

Representative photocurrent characteristic for the annealed Min002 film is shown in Fig. 3 (inset 1 showing the corresponding dark current). As is evident from the figure, the photocurrent (I_p) is much smaller than the dark current (I_d). For the sample Min001 and Min002, the ratio I_p/I_d was $\approx 10^{-3}$, whereas I_p/I_d for Min003 was $\approx 10^{-4}$, measured at 300 K at 20 V applied voltage. This might be due to the high degree of carrier depletion at the surface, owing to the Fermi level pinning at the surface by large density of defect states. PPC was observed in the Cu₂O samples. The inset 2 of Fig. 3 shows a representative PPC measurement for annealed Min002 sample. It could be observed that the current increased to a maximum value over the dark level, upon exposure to the 325 nm laser He-Cd line (10 mW), and once the illumination is cut off after that, the current

falls exponentially and then stabilizes to a value higher than the baseline, approaching it asymptotically. The decay time in the samples was typically several hours. This current would probably approach the dark current level after several hours or days. This PPC phenomenon has also been observed in p -type chalcopyrites; however it is known that compared to them (e.g. $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) with decay time of about 1 h) the decay time of Cu_2O is extremely large [12]. PPC in Cu_2O is interpreted in terms of simple electronic model [13] where deep donors can capture and re-emit electrons but possess a tiny capture cross-section for holes. Here, the illumination induces a transfer of electrons into the compensating donor states, reducing the compensation ratio leading to an increase of conductivity. This increase in conductivity persists even after the illumination is removed; and if the donor level is deep enough, the trapped electrons are emitted after a very long time. The metastable conductivity increase is therefore explained by the donor filling by photogenerated electrons and its decay to the emission of electrons.

Fig. 3. Representative photo and dark current characteristics of Min002 annealed sample. Inset shows the PPC characteristics of the same sample.

The TPC characteristic of a representative film (Min002 annealed) is shown in Fig. 4. The TPC characteristics reveal slow non-exponential decay in several time scales, which was also the case for the rest of the samples. This is typical for disordered or high resistive materials with large band tailing, wherein the defects capture and re-emit the photocarriers, thereby attributing a slow time dependence to their mobility and in turn the photocurrent exhibits a slow power law decay with time, given by the equation, $I = I_0 t^{-\alpha}$. This is the MT model for TPC decay [14].

Table shows the various characteristics of the films obtained from the transient measurements [15]. The sample Min003 had the slowest decay with $\alpha = 0.42$, followed by Min002 with $\alpha = 0.52$ and Min003 with $\alpha = 0.61$. From these values, Min003 sample had the

Fig. 4. Log-log plot of transient photocurrent decay with time for annealed Min002 sample.

TABLE
Cu₂O transient photocurrent characteristics.

Sample (annealed)	α	$\langle \mu \tau \rangle \times 10^{-10}$ [cm ² V ⁻¹ s]	τ [ns]	$\langle \mu \rangle \times 10^{-3}$ [cm ² V ⁻¹ s ⁻¹]
Min001	0.61	1.9	226.3	0.84
Min002	0.52	6.8	240.6	2.81
Min003	0.42	45	289.1	15.52

largest amount of deep defects (which could contain surface states), followed by Min002 and Min001, respectively, whereas Min002 and Min003 had higher contribution to loss of carriers by recombination, and the amount of charge trapping was smaller. This is also reflected from the photocurrent decay time (τ), which was largest for Min003 sample (measured in the 500 ns time window). Interestingly, the carrier lifetime-mobility product ($\langle \mu \tau \rangle$) was highest for sample Min003, followed by Min002 and then Min001, also the same trend was followed in case of the mobility ($\langle \mu \rangle$), determined from $\langle \mu \rangle = \langle \mu \tau \rangle / \tau$. Min003 had the mobility of $15.52 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, followed by Min002 with $2.81 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and lastly Min001 with $0.84 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These results suggest that in the case of our Cu_2O samples, the carriers were not lost in the deep defects, rather, the traps acted as sinks to keep the carriers from being lost due to recombination, which resulted in higher density of free carriers in the samples which had relatively higher density of deep defects, upon application of voltage and/or light. In other words, the defects were not acting as recombination centers, and so, more free carriers were available for Min003, followed by Min002 and Min001, respectively. Since the (macroscopic) mobility is a function of the ratio of free to trapped carrier density, hence, we got a higher mobility for Min003, than Min002 or Min001, as calculated from the dark and photocurrent measurement. This was also reflected in the photocurrent measurement where at 20 V, sample Min003 had a photocurrent of $\approx 10.8 \text{ nA}$, Min002 had photocurrent of only 0.86 nA and Min001 had 0.24 nA . Correspondingly, the TPC decay was slowest in sample Min003 (low recombination, but high trapping rate), followed by Min002 and, finally, by Min001 showing the fastest decay.

4. Conclusion

Cu₂O samples were deposited by rf sputtering technique. The microstructure of the samples was compact with good grain coverage. The XRD spectra of the annealed samples showed strain relaxation, with the 42.39° peak showing appreciable shift from the literature value in the as deposited sample. Steady-state dark and photocurrent measurement in the annealed samples showed a small photo-to-dark current ratio, which could be due to the high degree of carrier depletion at the surface, owing to surface Fermi level pinning. A strong PPC effect was observed in our samples, and discussed within the model of trapping of electrons by deep donor levels, which have a small hole capture cross-section. The transient photoresponse can be well explained in terms of MT model. The sample Min003 had the slowest TPC decay, followed by Min002 and Min001, respectively; with Min002 and Min001 showing higher contribution of recombination, leading to faster photocurrent decay.

We conclude that sample Min003 had the highest amount of deep defects followed by Min002 and Min001, respectively. But, interestingly Min003 had also the highest $\langle\mu\tau\rangle$ (estimated from steady-state photocurrent measurements) and macroscopic carrier mobility $\langle\mu\rangle$ (calculated from transient and from dc measurements), as compared to Min002 and Min001, which is in accordance with the model assumption that the trap states impeded carrier loss by recombination.

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