

## Photocurrent enhancement of d.c. sputtered copper oxide thin films

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**Abstract.** Copper oxide (CuO) thin films with photocurrent as high as  $25 \mu\text{A}/\text{cm}^2$  were deposited on conductive glass substrates using d.c. reactive sputtering. This was the highest reported photocurrent for sputtered *p*-type copper oxide measured in the electrolyte KI. The photocurrent drastically increased up to  $25 \mu\text{A}/\text{cm}^2$  as the sputtering pressure and the substrate temperature were increased up to 8.5 mbar and  $192^\circ\text{C}$ , respectively. All the synthesized films contained single phase of CuO in this range of pressure and substrate temperature. Variation of the photocurrent, photovoltage, structure and absorbance with deposition conditions were studied in detail.

**Keywords.** Sputtering; photocurrent; photovoltage; XRD pattern; absorption spectra.

### 1. Introduction

CuO is an interesting candidate in the applications of solar energy converting devices, gas sensors (Jiao *et al* 2002; Chowdhuri *et al* 2003; Liu *et al* 2003; Wang *et al* 2003) and superconducting devices. Thin films of CuO have been synthesized using molecular-beam-epitaxy method (Catana *et al* 1992), sol–gel technique (Armelaio *et al* 2003) earlier. It is difficult to crystallize the single phase of CuO (Wang *et al* 2003). The contamination can be completely avoided by using the deposition methods in high vacuum such as sputtering. But it is difficult to find any early report related to the deposition of copper oxide thin films using sputtering methods for photovoltaic applications. The photovoltage and the absorbance of thin films of *n*-type zinc oxide, which were deposited using d.c. sputtering, depend on the deposition pressure and deposition time according to our earlier studies (Samarasekara *et al* 2002). But the properties of sputtered copper oxide films mainly depend on the deposition temperature and sputtering pressure. According to some of our earlier studies related to the deposition of magnetic materials, the films could be crystallized only above some minimum crystallization temperature and the crystallization improved with deposition temperature (Samarasekara and Cadieu 2001a,b).

### 2. Experimental

All these films were deposited in a vacuum chamber with a base pressure of 4.2 mbar by means of the Edwards

S150B sputter coater. The films were deposited on the conductive surface of cleaned conductive glass substrates with an area of  $2 \times 2 \text{ cm}$  in Ar/O<sub>2</sub> gas combination using a circular copper target with diameter, 6 cm for 6 h. The separation between the target and the substrate was approximately 1.5 cm. Argon and oxygen gases served as sputtering and reactive gases, respectively in this reactive sputtering process. The argon gas entered into the chamber through a flow controller with fine adjustments. The oxygen content in the residual amount of air in the chamber was sufficient to form the oxide phase in thin films. The total pressure of Ar/O<sub>2</sub> mixture was increased from 6–8.5 mbar by raising the rate of argon flow entering into the chamber in this dynamic sputtering process. The substrate was heated using a heater coil attached to an external power supply, and substrate temperature which varied from 70– $192^\circ\text{C}$  was measured by means of a thermocouple attached to a digital thermometer. The substrate temperature and the sputtering pressure could not be raised above  $150^\circ\text{C}$  and 8 mbar, respectively, due to the over heating of the vacuum chamber. The d.c. current and d.c. voltage of the d.c. sputter coater varied from 5–35 mA and 0.4–1.9 kV, respectively depending on the deposition pressure. When the argon gas pressure of the chamber was raised, the d.c. current gradually increased and d.c. voltage gradually decreased.

Both photocurrent and photovoltage of sputtered films were measured with respect to a platinum plate (counter electrode) of area,  $2.5 \times 2.5 \text{ cm}$ , immersed in the electrolyte solution, KI, with a concentration 0.01 M. The film was illuminated with a normal 60 W white light bulb placed 2 cm away from the sputtered film in order to measure the photocurrent and photovoltage. The photocurrent of the synthesized films was measured using

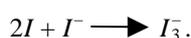
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Hakuto Denko Potentiostat/Galvanostat HA-301 attached to a calomel reference electrode. First, the dark current was set to zero by applying an internal voltage. Then the current indicated on the scale of this equipment after illuminating with 60 W bulb gave the photocurrent directly. The open circuit photovoltage between the platinum plate and the sputtered films was measured by means of a digital multimeter. The difference between the voltages after illuminating with 60 W bulb and before illuminating was taken as the photovoltage. In both cases, the bulb was placed so that the substrate (conducting glass) was facing the bulb. The structure of the synthesized films was determined using X-ray diffraction patterns (XRD). The absorption spectra of the fabricated films were measured by means of Shimadzu UV-1601 visible Spectrophotometer.

### 3. Results and discussion

According to figure 1, the photocurrent drastically increases from 6.25–25  $\mu\text{A}/\text{cm}^2$  as the deposition temperature is increased from 70–192°C at the constant total pressure of 8.5 mbar. The photocurrent also increases from 7.5–25  $\mu\text{A}/\text{cm}^2$ , when sputtering pressure is increased from 6–8.5 mbar at the constant deposition temperature of 192°C as shown in figure 2. The open circuit photovoltage also varies with the substrate temperature and the sputtering pressure in a similar manner as shown in figures 3 and 4.

Redox couple,  $I_3^-/I^-$ , forms in KI electrolyte according to the following reaction:

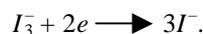


Following reactions take place at the *p*-type semiconductor sample and the counter electrode.

At the illuminated *p*-type semiconductor,

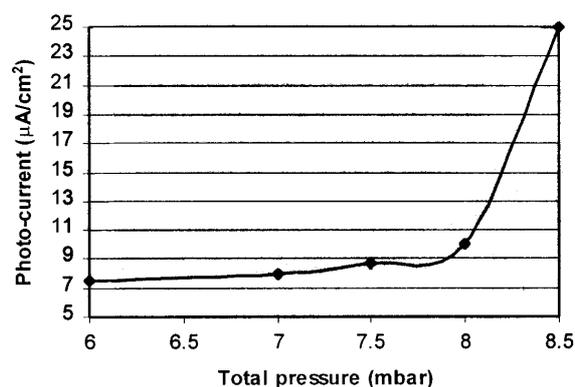


At the counter electrode (platinum plate),

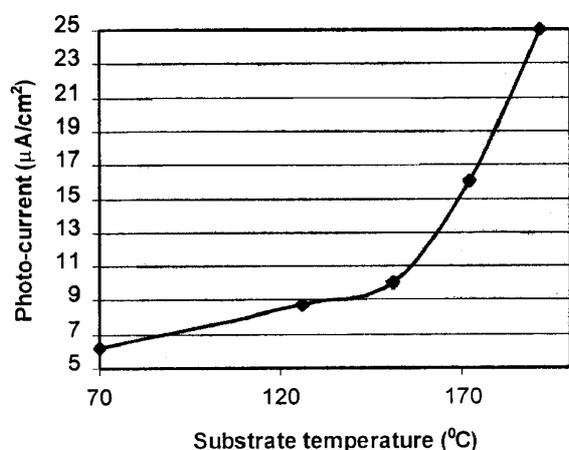


These conduction electrons flowing from *p*-type semiconductor to the counter electrode contribute to the photocurrent and photovoltage.

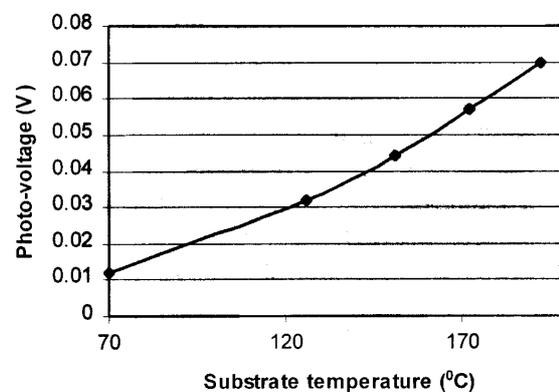
The absorption spectroscopy of the film deposited at 192°C and 8.5 mbar for 6 h is shown in figure 5. Films with higher absorbance always provide a higher photocurrent. Because the peak value of the absorbance of the sputtered film is higher than the maximum measurable absorption of the spectrophotometer, the peak value of this graph is not observable. The extrapolation of tangent line drawn to the part of the absorption curve with maximum slope intercepts the X-axis at the wavelength of 590 nm. The energy gap calculated using this wavelength was found to be 2.1 eV. Because the maximum intensity of the solar spectrum is observable at the wavelength of 570 nm, these sputtered films can be potentially used in solar energy applications.



**Figure 2.** The graph between the photocurrent and the sputtering pressure at the constant deposition temperature of 192°C.



**Figure 1.** The graph between the photocurrent and the deposition temperature at the constant total pressure of 8.5 mbar.



**Figure 3.** The graph between the photovoltage and the deposition temperature at the constant total pressure of 8.5 mbar.

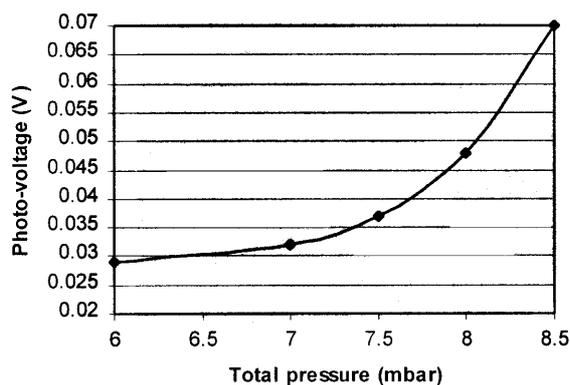
The XRD pattern of a film deposited at 6 mbar total pressure and substrate temperature of 151°C is given in figure 6. All the peaks observed in this XRD pattern belong to the powder diffraction pattern of CuO implying that film contains the single phase of CuO. The XRD pattern of a film deposited at 8.5 mbar total pressure and substrate temperature of 192°C is shown in figure 7. All the peaks in this XRD pattern also belong to the phase of CuO, indicating that only the single phase of CuO is crystallized in this range of pressure and substrate temperature. Amorphous glass substrates do not contribute to the XRD patterns. When the substrate temperature is raised, the intensity of each XRD peak increases according to these XRD patterns. This implies that the crystallization of film sample improves with the substrate temperature and total pressure.

Because the mobility of target atoms reaching the substrate is higher at higher substrate temperatures, the crystallization improves with the substrate temperature according to our earlier studies too (Samarasekara and Cadieu 2001a,b). As long as the base pressure of the sputtering

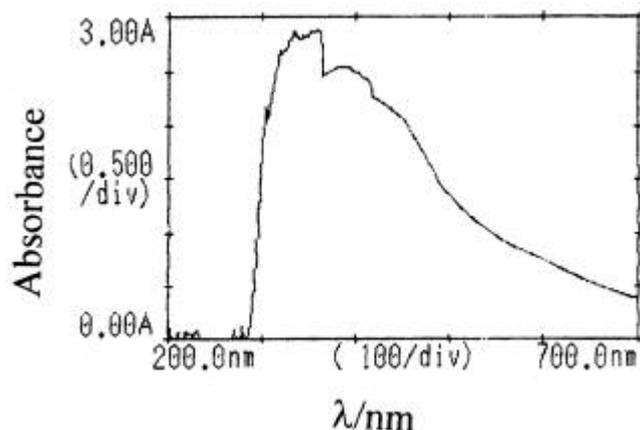
chamber remains the same, increasing the argon partial pressure inside the chamber raises the total pressure. The deposition rate and hence the substrate temperature increases with the argon partial pressure in sputtering methods. Therefore, the crystallization improves with the total pressure inside the sputtering chamber. The mobility of electrons reduces mainly at the grain boundaries, and this factor solely governs the electrical conductivity of the sample. The size of grain boundaries reduces with the improvement of crystallization. Therefore, the photocurrent and the photovoltage of the films increase with pressure and substrate temperature due to this higher crystallization.

#### 4. Conclusions

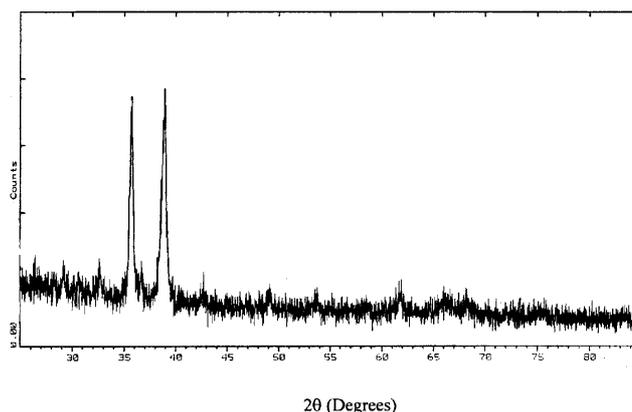
Photocurrent and photovoltage as high as 25  $\mu\text{A}/\text{cm}^2$  and 0.07 V, respectively could be obtained for sputtered CuO films. So far this is the highest reported photocurrent obtained for sputtered CuO. As the sputtering pressure and deposition temperature were varied in the ranges of



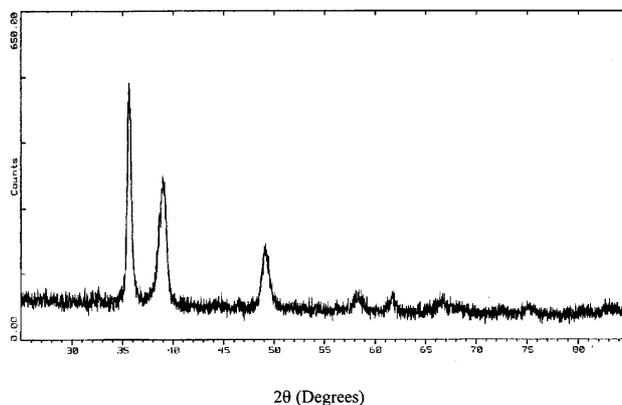
**Figure 4.** The graph between the photovoltage and the sputtering pressure at the constant deposition temperature of 192°C.



**Figure 5.** The absorption spectroscopy of the film deposited at 192°C and 8.5 mbar.



**Figure 6.** The XRD pattern of the film deposited at 6 mbar and 151°C.



**Figure 7.** The XRD pattern of the film deposited at 8.5 mbar and 192°C.

6–8.5 mbar and 70–192°C, respectively the single phase of CuO remained unchanged. The absorbance of these sputtered CuO films was found to be remarkably high according to UV absorption spectroscopy measurements.

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