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The Effect of Sputtering Conditions on the Optical Transmission and Wettability of Amorphous Copper Oxide Thin Films Prepared by Magnetron Sputtering

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Introduction

Cuprous oxide (Cu_2O) is a semi-conductor which shows a varying optical behavior because of stoichiometric deviations arising from it's preparation methods and parameters [1]. It has been reported that many of the growth methods for cuprous oxide result in a combined growth of copper (I) oxide Cu_2O and copper(II) oxide CuO[1]. Cu_2O and CuO are both semi-conductors with band-gap energies of 2.1eV and 1.3eV respectively [2]. Cu_2O oxide films are reported to have high transparency, with a slightly yellowish appearance and absorb usually at wavelengths below 600nm, while CuO absorbs strongly throughout the visible spectrum and is black in appearance .The current application areas of copper oxide thin films include solar cells and electro-chromic devices [1,2] and it has a potential for application as a transparent conducting oxide (TCO), if it's electronic conduction and electron mobility can be improved by a suitable choice of substitutional dopant such as has been conducted for ZnO:F. We report the result of our investigation into how the deposition conditions selected during the magnetron sputtering process affects two properties that are essential for copper oxide to perform optimally in the application areas identified above, i.e. it's optical transmission (transparency) in the visible spectrum and it's wettability by moisture from the atmosphere i.e. water vapor.

Deposition Conditions

A cryo-pumped vacuum chamber (CVC) magnetron sputtering unit was used for the thin film deposition. The starting materials were a solid copper target and two gases namely, Oxygen and Argon. The deposition conditions are as indicated below:

- Argon (Ar) flow rate used in the chamber: 50 sccm (standard cubic centimeter)
- Chamber pressure was 2.50 mTorr ± 0.20 mTorr
- Deposition time was kept the same for every deposition: 30 seconds
- Depositions were done at room temperature
- Reflected power was less than 5 W
- Substrate : Glass

The investigated deposition parameters are as follows:

Forward Power: 200 W, 400 W, 600 W and 800 W.

Oxygen Flow Rate: 4 sccm, 6 sccm, 7 sccm, 8 sccm, 9 sccm and 10 sccm.

Film Characterization

Chemical and structural characterization was conducted on the films using X-ray diffraction and the EDAX facility on the scanning electron microscope. The X-ray diffraction investigation revealed an amorphous structure for all the samples. The EDAX analysis also revealed the presence of copper and oxygen.

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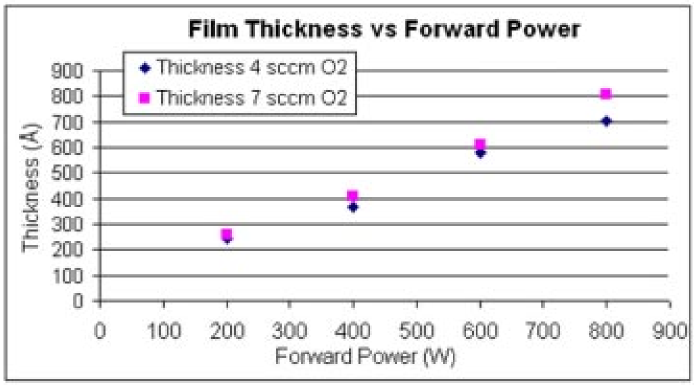

Figure 1: Film thickness against the forward power

Thickness Measurement

The thickness measurement on the prepared films was carried out with a Dektak profilometer and checked for accuracy by Atomic force microscopy (AFM) step-height analysis using a Digital instruments Nanoscope 3 Atomic force microscope. Figure 1 shows how the thickness of the copper oxide deposited varies with the input (forward) power during the sputtering process for the same deposition time.

The thickness of the film was found to be proportional to the applied forward power during deposition as shown in figure 1.

An increasing flow rate of oxygen in the deposition chamber as shown in figure 2 is also found to lead to an increase in film thickness for the same deposition time.

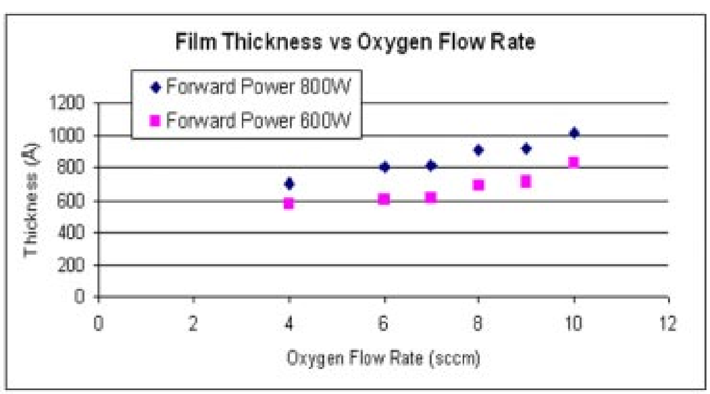

Figure 2: Film thickness against the oxygen flow rate

Optical Transmission Measurements

The optical transmittance of the copper oxide films was studied in the green (550 nm wavelength) using a Hitachi U-3501 model spectrophotometer. Figure 3 shows the observed percentage optical transmission at 550nm wavelength against the oxygen flow rate at an input power of 800W. The optical transmission is found to be quite low, with slight increases observed as the flow rate of oxygen increases.

However as shown in figure 4 a decrease in the forward power results in a corresponding improvement in optical transparency, and this was typical for all oxygen flow rates investigated.

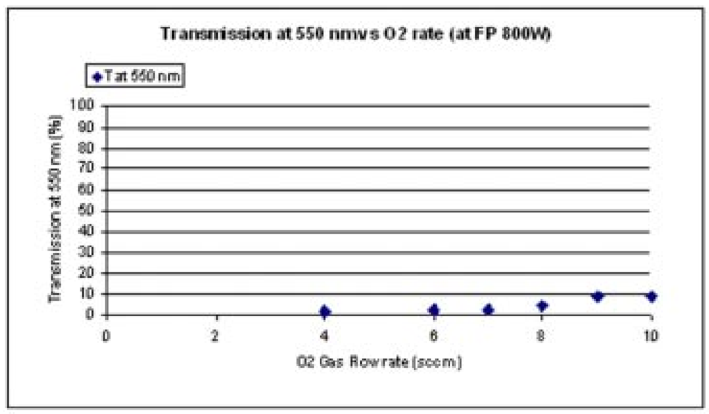

Figure 3: Transmission against oxygen flow rate

As shown for the thickness measurements in figure 1, the film thickness and therefore the deposition rate increases with the input power during deposition for the same oxygen flow rate, implying that the improvement in optical transparency with reduced power may be associated with a reduction in the absorption of the incident light with a decrease in film thickness.

Figure 5 summarizes the inter-relationship between the input power, oxygen flow rate and the optical transmission at 550nm wavelength in the amorphous copper oxide films. The predominant factor controlling the optical transmission seems to be the input or forward power. However, for films deposited at 400 and 600W power, there are clear indications of variations in the optical transmission due to changes in

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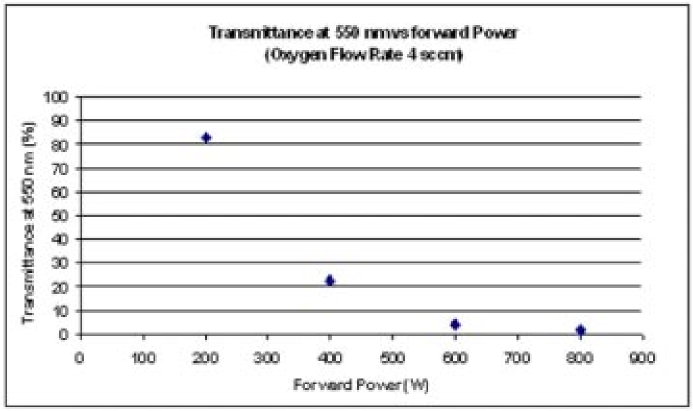

Figure 4 Transmittance against the forward power

the oxygen flow rate during deposition. We have also observed a gradual color change from transparent slightly yellowish appearance for films deposited at 200W power to a more yellowish less transparent film at 400W and dark absorbing non-transparent films at 800W power for all oxygen flow rates investigated. It is apparent that apart from the observed increase in film thickness created by increasing the input or forward power during film deposition, changes in the color of the films with input power is associated with the production of Cu_2O with a transparent yellowish appearance at a low input power of 200W and black absorbing CuO at a forward power of 800W. It also appears that a co-deposition of Cu_2O and CuO is produced for forward powers of between 400 and 600W as already reported in the literature for other deposition methods[1] based on the observed color changes. Also contrary to reports in the literature that Cu_2O is strongly absorbing for wavelengths below 600nm [2], we have observed transmissions of between 80% and 90% for our films at a low forward power of 200W for all oxygen flow rates investigated. This indicates a likely dependence of the optical transmission, structure as well as stoichiometry of the deposited films on the input or forward power during deposition.

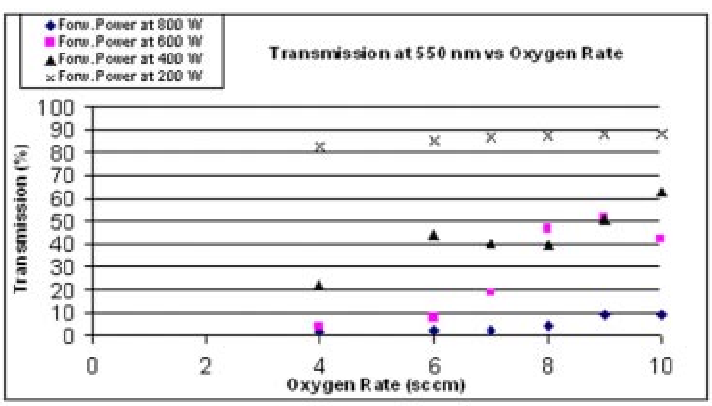

Figure 5: Transmittance against the oxygen flow rate (for each forward power) for the amorphous copper oxide thin films.

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Contact Angle Measurements

The contact angle measurement was carried out with the KSV CAM 200 computer controlled video based instrument, using distilled water in a syringe. Drops of water deposited on the sample were captured on the video camera and analyzed on the computer. Figure 6 shows the contact angle measurements against the forward power during the deposition process. The films are hydrophobic ($\theta > 90°$) in most of the cases. The hydrophobic nature of the surface of the copper oxide films is a good indicator of the potential to use the films for the earlier identified functional applications and other applications in a high humidity environment.

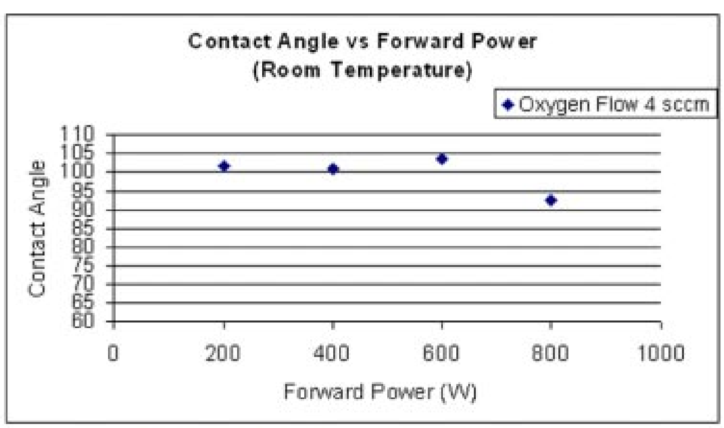

Figure 6: Contact Angle against forward power