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Electroless chemical deposition technique for Cu_2O thin films

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Abstract

An electroless, solution growth deposition technique for Cu_2O thin films, suitable for large-area depositions at relatively low temperatures ($\leqslant 70°C$) has been developed. Uniform and electroconductive Cu_2O films were deposited on glass or clear polyester film substrates, pre-coated with an ultrathin layer of Cu_xS. Post-deposition treatment of the chemically deposited Cu_2O films in diluted solutions of Na_2S resulted in further increase of conductivity and absorbance. Rutherford backscattering analyses confirmed sulfur implantation into the Cu_2O films.

1. Introduction

There has been a growing interest in preparation and study of the optical and electrical properties of various metal oxides, particularly those suitable for application as energy converters for solar energy. Cuprous oxide (Cu_2O), which is known to be p-type semiconductor due to copper vacancies, has been receiving continued attention and is considered a promising and inexpensive metal oxide semiconductor for use in thin film solar cells [1]. The interest in this material began with the invention of the Cu_2O rectifier by Grondahl [2]. Photosensitive devices based on Cu_2O followed, and this application has been well reviewed by Lange [3]. During the past decade, research on Cu_2O has only intensified. A number of techniques have been developed to deposit Cu_2O films on copper and other metal substrates. Among these are thermal oxidation of copper [4–6], anodic oxidation [7], reactive sputtering [8] and recently, pulsed excimer laser ablation [9]. However, the resistivities of the films obtained by these methods are high and were reported to be between 10^2 and 10^6 Ω cm. Application of Cu_2O in thin film solar cells and other devices requires low resistivity. Additionally, a development of a low-cost technique for deposition of Cu_2O films on substrates other than metals would be welcome, in order to make the best use of Cu_2O thin films as a semiconductor.

The aim of this work was to come up with a simple electroless (or solution growth) technique for deposition of Cu_2O films suitable for both small and large area depositions, and at low temperatures, so that glass and even plastics can be used as substrates. Additionally, obtaining Cu_2O films of higher conductivity was also part of the goal of this work.

This work reports, possibly for the first time, a solution growth technique for Cu_2O films. It also presents the basic optical and electrical properties of the as-deposited and post-deposition treated Cu_2O thin films. The technique presented here is in fact a modification of a previously reported successive immersion technique for deposition of Cu_2O films [10], in which the glass substrates were first immersed in a cold copper–thiosulfate complex solution and then in

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a hot sodium hydroxide solution. The technique was good for examining the properties of the Cu_2O films, but inconvenient for large-scale applications and the obtained films were of low conductivity. The solution growth technique described here offers an inexpensive fabrication process for conductive Cu_2O films and it is also convenient for large-area depositions.

2. Experimental procedure

2.1. Deposition of the films

Standard microscope glass slides, 75 mm×26 mm×1.0 mm and clear polyester films commonly used as overhead transparencies were used as substrates in this work. However, in order to produce uniform and conductive films, the substrates were pre-coated with ultrathin ($\leqslant 20$ nm) Cu_xS films, as follows. Clean glass or polyester substrates were immersed in a chemical bath containing Cu^{2+} and thiosulfate ions, $(S_2O_3)^{2-}$, in a molar ratio 1 : 1 and ultrathin Cu_xS ($x \approx 2$) films were deposited at 40°C in about 5 min after precipitation in the bath began. More details on chemical deposition of Cu_xS films are reported elsewhere [11]. The pre-coated substrates were then preserved for further use in the deposition of Cu_2O films.

A typical chemical bath for growth of Cu_2O films was composed as follows. 20 cm^3 of 1 M aqueous solution of $Cu(NO_3)_2$ were placed in a 250 cm^3 beaker. 80 cm^3 1 M aqueous solution of $Na_2S_2O_3$ were added to reduce and complex the copper ions. A colorless clear solution was obtained. The beaker was placed on a hot plate and magnetic stirring was applied. Then, 3 M aqueous solution of NaOH was slowly introduced into the bath until the solution turned orange-yellow. At this point, the pre-coated substrates were vertically mounted into the bath, and the temperature was raised and kept at about 60–70°C. Precipitation starts in a few minutes and Cu_2O films grow on both sides of the substrates. The substrates can be kept in the bath for up to 1 h, depending on the desired thickness. A terminal thickness of about 0.3 μm was obtained from a single bath in 1 h, under the experimental conditions described. Thicker films can be obtained, if needed, by re-introducing the initially grown films into a fresh bath, with a risk of peeling off with some of the films. The substrates with the deposited films on both sides were washed with distilled water, dried in air and preserved for investigation of their properties.

2.2. Post-deposition investigations

Identification of the deposited material was done by X-ray diffractometry (XRD) on film samples deposited on glass. The thickness of the films was estimated by weighing of the material removed from one of the sides of the substrate, assuming the same density as that of a bulk Cu_2O (6.0 g cm^{-3}).

Optical transmission studies were carried out in the spectral range 0.3–2.5 μm wavelength. The sheet resistance of the films was measured between two gold-pasted electrodes, 1 cm in length and 1 cm apart. Resistivity can be calculated taking into consideration the film thickness.

The optical and electrical properties of the deposited films were also studied after treatment in diluted Na_2S aqueous solution (0.5 g dm^{-3}) and/or annealing at 150 and 250°C in air.

Rutherford backscattering spectrography (RBS) was used to determine sulfur implantation into Cu_2O films.

3. Results and discussion

The chemical processes that eventually led to the formation of Cu_2O films in alkaline copper–thiosulfate baths are yet to be studied. However, the deposited material was positively identified as Cu_2O by X-ray diffractometry. The XRD pattern of a 0.26 μm thick Cu_2O film deposited by the described technique is shown in Fig. 1. The reflexions were compared against the standard JCPDS-ICDD from PDF-2 Sets 1-43 Database, and were found to match those of the synthetic cubic Cu_2O, file 5-667. The diffusion background is due to the glass substrate.

The optical transmission spectrum of an as-deposited Cu_2O film in the VIS–NIR spectral region is presented in Fig. 2, curve 1. A sharp absorption edge can be observed at about 0.5 μm wavelength. No changes in the spectrum were observed with the annealed samples for up to 24 h at 150 or 200°C, in air. However, notable changes in transmission took place after

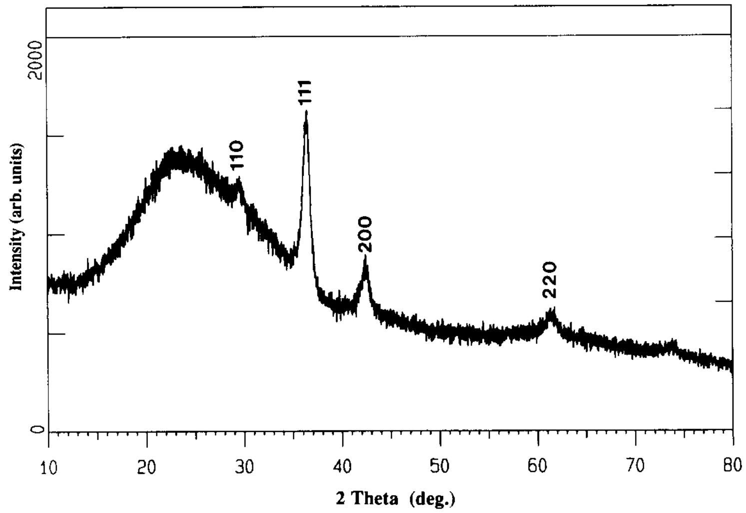

Fig. 1. X-ray diffraction pattern of a 0.26 μm thick Cu_2O film on glass substrate.

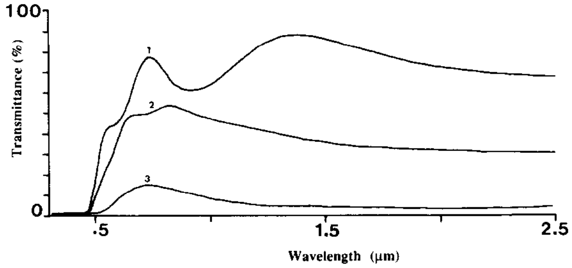

Fig. 2. Optical transmission spectra of Cu_2O films: (1) as-deposited film; (2) 1.2% S content and (3) 5.1% S content.

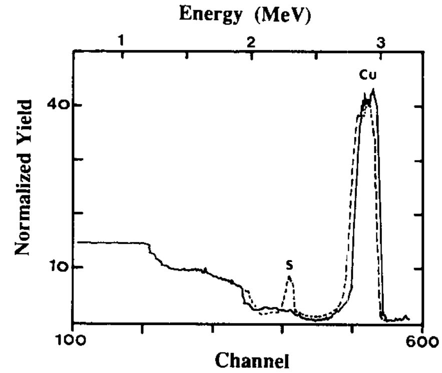

Fig. 3. RBS spectra of as-deposited (solid line) and 5.1% S-doped (dashed lines) Cu_2O films.

treating the as-deposited Cu_2O films for 5 min (Fig. 2, curve 2) and 15 min (Fig. 2, curve 3) in Na_2S solution, at room temperature. As doping with sulfur proceeds, the absorption of the material over the entire spectral range increases dramatically and the absorption edge becomes less defined and shifts towards higher wavelengths. RBS analyses showed that sulfur was indeed implanted into the material, during the treatment of the as-deposited films in a Na_2S solution. Fig. 3 shows the RBS spectra of an as-deposited Cu_2O film (optical spectrum 1 in Fig. 2) and a sulfur-doped (5.1% S) Cu_2O film (optical spectrum 3 in Fig. 2).

The electrical properties of the as-deposited, annealed and sulfur-doped films were also studied. The electrical resistances of the films are summarized in Table 1. The thermo-EMF polarity showed that all films had p-type conductivity. The results in Table 1 show that heat treatment of the Cu_2O films results in increase of sheet resistance values, a phenomenon observed with Cu_2O films in an earlier report [10]. Additionally, the conductivity of the as-deposited films with the technique described in this work is surprisingly high, probably due to sulfur implantation in the Cu_2O films during the deposition process (either from the Cu_xS pre-coating on the substrate surface, or from the sulfide ions generated during the hydrolytic decomposition of the thiosulfate ions in the bath). Indeed, RBS analysis has shown traces of sulfur atoms even in the as-deposited films, before they were treated with Na_2S. Additional support for such

Table 1
Electrical resistances of as-deposited and treated CuO_2 films

Sample	Thickness (μm)	Treatment	Electrical resistance [a] (Ω)
A	0.10	as-deposited	2400
		annealed, 24 h at 150°C	26000
		annealed, 20 min at 250°C	60000
B	0.28	as-deposited	3000
		10 min in Na_2S	45
		annealed, 24 h at 150°C	120
C	0.25	as-deposited	2700
		15 min in Na_2S	27
		annealed, 24 h at 150°C	55
		annealed, 20 min at 250°C	160

[a] Measured between two gold-pasted electrodes, 1 cm long and 1 cm apart.

a consideration is the further decrease in resistance values observed with the samples treated in Na_2S solutions.

The band-gap energy for the as-deposited films was found to be 2.28 eV which is higher than the value of 2.0 eV, reported in Refs. [10,12] and 1.7 eV in Ref. [9]. The graphical determination of the optical band-gap energy for the chemically deposited films in this work is shown in Fig. 4.

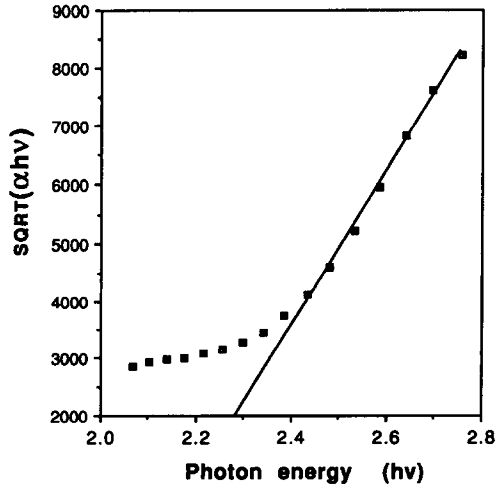

Fig. 4. Graphical determination of the optical band-gap energy for Cu_2O films.

4. Conclusion

A simple electroless, solution growth deposition technique for Cu_2O thin films on glass or polyester films has been described. The technique offers a possibility for large-area deposition at relatively low temperature ($\leqslant 70°C$). The use of pre-coated substrates with Cu_xS ($x \approx 2$) ultrathin films results in fabrication of conductive and uniform Cu_2O films. A further dramatic improvement of conductivity for the Cu_2O films has also been demonstrated by post-deposition treatment of the films in diluted Na_2S solutions. The latter results also in increased absorption of the sulfur-doped Cu_2O films throughout the entire VIS–NIR spectrum, which can be of significance in the application for solar energy conversion devices.

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