Mat. Res. Bull., Vol. 24, pp. 753-760, 1989. Printed in the USA.
0025-5408/89 $3.00 + .00

PREPARATION AND CHARACTERIZATION OF COPPER(II) OXIDE THIN FILMS GROWN BY A NOVEL SPRAY PYROLYSIS METHOD

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(Received April 6, 1989; Refereed)

ABSTRACT

A novel spray pyrolysis reactor was used to prepare thin films of CuO on silica substrates. The resulting films were characterized by x-ray diffraction, electron microscopy, optical and electrical measurements. The films were single phase, homogeneous, and uniform.
MATERIALS INDEX: copper, oxides

Introduction

Copper(II) oxide thin films have been grown by reactive-ion sputtering (1), oxidation of evaporated copper metal (2), and metal-organic chemical vapor deposition (3,4). Spray pyrolysis has been shown to be an effective method for the preparation of thin films of oxides including SnO_2, In_2O_3, Fe_2O_3, Cr_2O_3, PbO, and ZnO (5,6); however, this technique has not been applied to the preparation of CuO thin films. It was the purpose of this study to investigate the preparation of CuO thin films by decomposing ultrasonically nebulized aqueous copper(II) salts on silica substrates using a novel two-zone horizontal reactor. The CuO thin films were characterized by electron microscopy, x-ray diffraction, and optical and electrical measurements.

Experimental

The spray pyrolysis reactor used in this investigation is shown in Fig. 1. A Holmes commercial ultrasonic nebulizer (Fig. 1, No. 14) was used to nebulize the copper(II) acetate solution. An oxygen sweep flow carried the mist to the substrate and an additional constant oxygen purge flow was passed through the reactor as labeled in Fig. 1. The reactor was heated by a two-zone mirror furnace (Transtemp Co., Chelsea, MA). Temperature was maintained using two Theall TC-1000 temperature controllers. Layers of thin film were deposited on the rotating substrate in the lower temperature zone and were translated to the higher temperature zone which densified the film onto the substrate. This cycle was then repeated many times to produce the final film. Electronic

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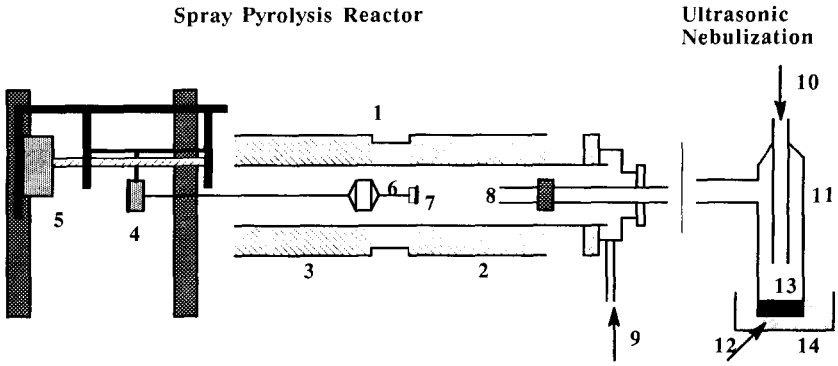
timers controlled substrate travel between zones, substrate rotation, nebulization time, and oxygen sweep time.

A typical set of reaction parameters involved in the growth of CuO films are given in Table I. Each layer of the film was deposited at 375°C and fired at 700°C. The substrate-to-nozzle distance and the oxygen sweep flow rate were critical for obtaining uniform films.

The aqueous copper(II) acetate solution was prepared by dissolving copper metal in a 1:1 mixture of nitric acid:distilled water. The resulting solution was evaporated to near dryness and a 1:3 mixture of acetic acid:distilled water was added. The resulting solution was again evaporated to near dryness and redissolved in the acetic acid:distilled water solution. This solution was evaporated to approximately 25 ml and was brought to the final desired volume with the acetic acid:distilled water solution.

The silica substrates used in this study were 0.5 in. squares cleaned thoroughly in boiling sulfuric acid. Just prior to deposition, the substrates were soaked in concentrated sulfuric acid for 5 min., followed by a thorough rinse in distilled water. The substrates were then immersed in methanol for 1 min. and allowed to dry.

The cleaned substrate was secured on the substrate holder and placed in the reactor. Fifteen ml of 0.1M Cu(II) solution was placed in the solution chamber and deposition started when the furnace attained equilibrium.



Spray Pyrolysis Reactor

1. Two zone furnace
2. Low temperature zone
3. High temperature zone
4. Substrate rotating motor (Synchron 4 rpm)
5. Reversible motor
6. Substrate holder (Hurst 120 rpm)
7. Substrate
8. Injection tube
9. Oxygen purge flow

Ultrasonic Nebulization

10. Oxygen sweep flow
11. Solution chamber
12. Polyethylene film
13. Solution
14. Commercial ultrasonic humidifier

Fig. 1. Apparatus for spray pyrolysis of CuO films.

Table I

Reaction Parameters

Firing zone temperature	700 °C
Deposition zone temperature	375 °C
Furnace diameter	38 mm
Purge flow O_2	200 cc/min
Sweep flow O_2	3 l/min
Nebulization time	5 sec
Oxygen sweep time	20 sec
Complete cycle time	160 sec
Solution concentration	0.1 M
Substrate to nozzle distance	60 mm
Nozzle diameter	9.3 mm

Film Characterization

Film thickness was measured using a Sloan Dektak surface profile measuring system (Part number 900050). Cu/Si ratios determined by EDAX analysis using an AMR 1000A scanning electron microscope gave the uniformity of film thickness. The SEM operated at 20 kV accelerating voltage, 16.5 kX magnification, and a 3x3 cm window.

Photomicrographs of the film surface were taken on an AMRAY 1830I scanning electron microscope.

X-ray diffraction patterns of thin film and powder samples were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$, radiation (λ = 1.5405Å). The diffraction patterns were taken in the range 12° < 2θ < 72° with a scan rate of 1° 2θ/min and a chart speed of 30 in/hr.

Optical transmission spectra of the films on silica substrates were obtained using a Cary model 17 dual beam ratio recording spectrophotometer in the range of 500 nm to 1500 nm. The optical band gap was deduced from the transmittance near the absorption edge.

Resistivity at room temperature was measured in the center portion of the film on the substrate using the van der Pauw technique (7). Contacts to the film were made by painting a colloidal mixture of graphite and isopropanol (Electrodag 154, Port Huron, MI) to the edge of the film. Ohmic behavior was established by measuring current-voltage characteristics. A qualitative Seebeck voltage measurement was made to determine the carrier type.

Results and Discussion

In spray pyrolysis a solution is atomized, sprayed onto a hot substrate, and decomposed, resulting in thin film growth. The solution can be nebulized ultrasonically, and sprayed continuously or in pulses. Viguie and Spitz (8) suggested four possible growth mechanisms for the spray pyrolysis process as a

function of substrate temperature. These are shown in Fig. 2 and can be related to the growth of CuO films in this study. In the first process, the spray droplet impinges directly on the substrate, followed by evaporation of the solvent, and decomposition of the metal salt to the oxide. In the second process, the solvent is evaporated just prior to contacting the substrate, followed by decomposition of the oxide. The third mechanism involves volatilization of the dried metal salt, diffusion of the vapor to the substrate, followed by decomposition to the oxide. This process is referred to as low temperature chemical vapor deposition (LTCVD). The fourth process is a homogeneous nucleation of the vapor phase forming the oxide particle which then deposits on the substrate.

The formation of CuO films in this study probably proceeds by the third mechanism since the deposited films are smooth, homogeneous, and have a mirror-like appearance. Albin et al. (5), have suggested the deposited film obtained by the last process would have a powdery appearance. Viguie and Spitz (6) have shown that films grown by processes A and B have a rougher microstructure than films grown by process C.

EDAX ratios of copper-to-silicon determined the relative uniformity of the CuO films and a Sloan Dektak surface profile measuring system determined the absolute thickness. The thickness and EDAX ratios of the films varied with the number of cycles involved in film preparation, and this is shown in

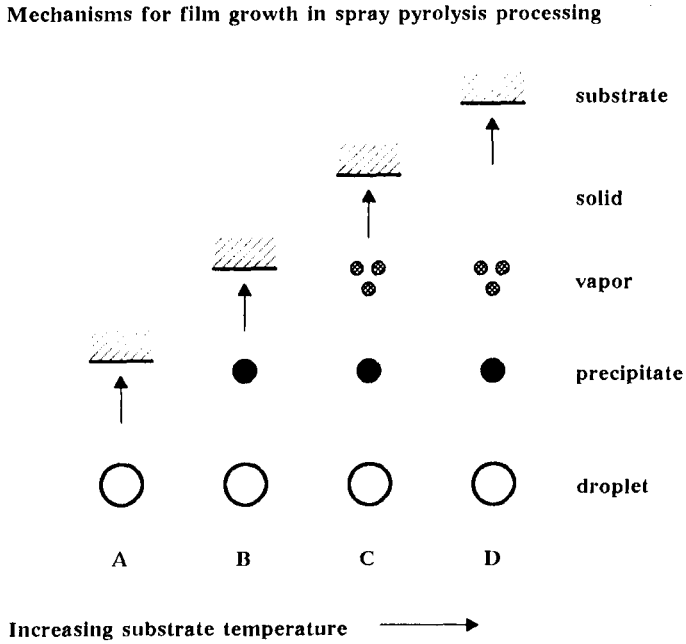


Fig. 2. Mechanisms of film growth.

Table II. After preparation, film thickness was determined from a calibration of EDAX Cu/Si ratio vs. thickness obtained from the data in Table II. The desired thickness could be approximated by the number of cycles in the preparation. EDAX ratios were taken at five points from edge to edge on the films and these ratios clearly show that CuO films prepared by this method are uniform.

Table II

EDAX Cu/Si Ratios vs Thickness and Number of Cycles

Position #	Film A	B	C	D
1	0.38(1)	0.08(1)	0.18(1)	0.16(1)
2	0.39	0.08	0.18	0.16
3	0.39	0.08	0.17	0.16
4	0.39	0.08	0.18	0.17
5	0.38	0.08	0.17	0.17
Thickness (Å)	2700	1200	1900	1850
Number Cycles	150	75	110	110

An SEM photomicrograph taken at low magnification of a 2000A CuO film prepared in this study is shown in Fig. 3. The nature of the particles in these CuO films are very different from CuO films prepared using MOCVD by Laurie and Norton (4), where the films are comprised of needle-like particles.

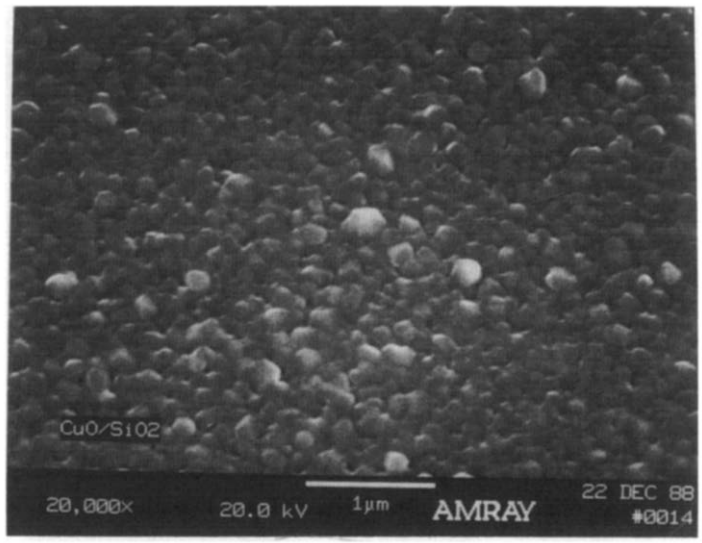


Fig. 3. Photomicrograph of a typical CuO film prepared from an acetate solution.

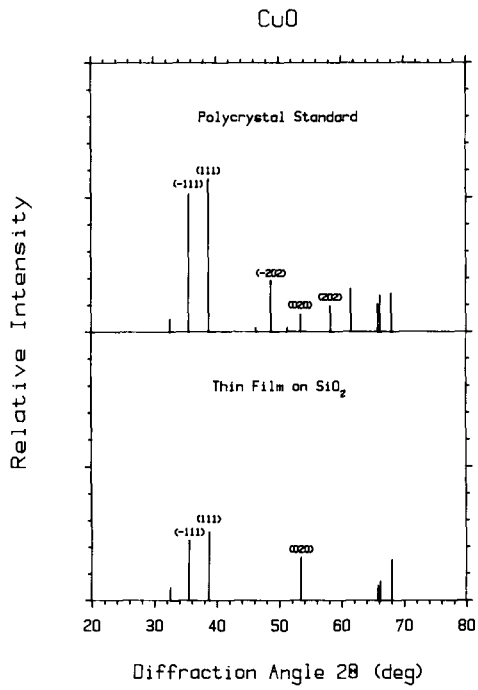


Fig. 4. X-ray diffraction pattern of a CuO film on a silica substrate as compared with that of a polycrystalline CuO standard. The differences in relative peak intensities demonstrate the existence of a preferred orientation in the film.

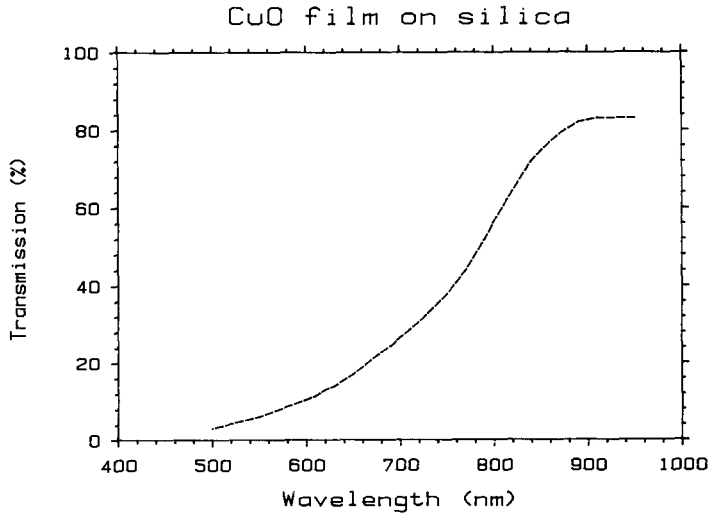


Fig. 5. Optical transmission spectrum of a CuO film on a silica substrate.

X-ray diffraction data is shown in Fig. 4. A CuO standard was prepared by heating Cu metal (JM 50250A) in air at 600°C. By comparing the x-ray of the film to the standard, it can be seen that the intensity of the (020) peak of the film is increased and the (-202) and (202) peaks are absent. This can be attributed to preferred orientation of the particles making up the film, growing with the b-axis perpendicular to the substrate.

The transmission spectra for a copper(II) oxide film prepared from copper(II) acetate is shown in Fig. 5, and is in agreement with copper(II) oxide films prepared by Ajayi et al. (3). The optical transmission was used to generate plots of $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$. It was found that the indirect band gap of the prepared copper(II) oxide films was 1.36(1) eV.

All CuO thin films prepared in this study were p-type semiconductors with room temperature resistivity of 10^2 ohm-cm. Beensh-Marchwicka et al. (1) have reported resistivities of 1 ohm-cm at room temperature for CuO films grown by reactive-ion sputtering; however, carrier type was not measured. The low resistivity is consistent with the presence of mixed formal valence of copper. If Cu(II) and Cu(III) were present in the film, then annealing the film in argon would increase the resistivity by reducing the Cu(III) to Cu(II). In contrast, if the low resistivity of the film was due to the presence of Cu(I) and Cu(II), then an argon anneal would further decrease the resistivity by increasing the amount of Cu(I) in the sample. Typical films of CuO were annealed in argon at 650°C for 15 hrs and the resulting resistivity and carrier type were measured. The resistivity of the films increased to 10^3 ohm-cm and remained p-type. Reannealing these films in oxygen at 650°C for 15 hrs resulted in resistivity decreasing to 10^2 ohm-cm. The resistivity of the films annealed in argon is higher than the resistivity of the films prepared in oxygen with no change in carrier type. This higher resistivity of films annealed in argon is consistent with a decrease in Cu(III) as a result of the annealing process.

Conclusion

Uniform, homogeneous copper(II) oxide thin films can be prepared in a novel two-zone horizontal spray pyrolysis reactor by decomposing aqueous copper(II) salts. The spray in the form of an aerosol was produced by a commercial ultrasonic humidifier. The film was grown by spraying pulses of the aerosol and heating the deposited thin layer at a higher temperature after each spray pulse. The films grew with preferred orientation as indicated by x-ray diffraction. In addition, the films were p-type semiconductors with room temperature resistivity of 10^2 ohm-cm. The p-type nature of the films was determined to be due to the presence of Cu(III).

Acknowledgements

This research was partially supported by the National Science Foundation under Grant No. DMR-8803184 and by the Eastman Kodak Company of Rochester, NY.

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