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GROWTH AND CHARACTERIZATION OF THIN FILLMS OF Y_2O_3, La_2O_3 AND La_2CuO_4

by

Y-M. Gao, P. Wu, K. Dwight and W. Wold

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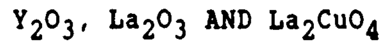

Y_2O_3, La_2O_3 AND La_2CuO_4

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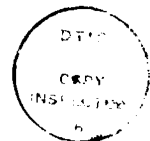

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Abstract

Y_2O_3, La_2O_3 and La_2CuO_4 films were prepared by an ultrasonic nebulization and pyrolysis method using acetylacetonates of the corresponding metals in alcohol solvents as source materials. Homogeneous, uniform films with good adherence have been obtained using this simple technique. As-deposited yttrium and lanthanum oxide films were poorly crystallized. After post-annealing in oxygen at higher temperature, they crystallized into cubic and hexagonal phases, respectively. Transparent yttrium and lanthanum oxide films have high electric breakdown voltages. Single phase polycrystalline La_2CuO_4 thin films were obtained from a source solution with a La:Cu ratio of 2:1.

Introduction

Yttrium oxide and lanthanum oxide films are mechanically and chemically stable and have high electrical breakdown field strengths (1-3) as well as high dielectric constants (4-5). They are also optically transparent over large ranges from ultraviolet to infrared (6-7). These films have attracted particular attention for application in gate insulators of metal oxide semiconductor field effect transistors (MOSFET) (4), optical antireflection coatings (7), and protective coatings (8-9). Various fabrication techniques have been employed for the preparation of Y_2O_3 films (1,4,8,10) and La_2O_3 films (2,5) such as electron beam evaporation (4-5), sputtering and subsequent oxidation (1), spray pyrolysis (8) and chemical vapor deposition (CVD) (10).

Recently a novel ultrasonic nebulization and pyrolysis technique has been developed in this laboratory for the preparation of thin oxide films of high quality (11-12). This paper reports on the preparation of yttrium and lanthanum oxide thin films as well as lanthanum copper oxide thin films by this simple method. The structural, optical and electrical properties of the films are investigated.

Experimental

Precursor preparation. Yttrium acetylacetonate was chosen as precursor for the preparation of yttrium oxide films. To 4.6 g of Y_2O_3 (Johnson Matthey 99.99%) was added 34 ml of 6 M hydrochloric acid and 53 ml of distilled water. The solution was heated on a steam bath in a fume hood until the solution was

clear. Then, 6 M ammonium hydroxide was added to the solution dropwise until a precipitate appeared. At this point, 6 M hydrochloric acid was added to the solution dropwise until the precipitate dissolved. This solution was then immersed in an ice bath with constant stirring and 16 ml acetylacetone (Aldrich) and 16 ml of propylene oxide (Aldrich) were added. To the solution, 10 ml of concentrated ammonium hydroxide were added and a fluffy white precipitate was formed. The precipitate and solution were refrigerated overnight and filtered. The precipitate was rinsed with cold distilled water and hexane and air-dried. The crude product was vacuum-dried at room temperature at 0.05 mm Hg or lower. The content of Y(III) was determined by a back-titration method using Cu-EDTA in an acetate buffer with PAN (Fisher) as the indicator (13-14).

Lanthanum acetylacetonate was the precursor for the preparation of lanthanum oxide and lanthanum copper oxide films. A solution was prepared by dissolving 4.04 g of La_2O_3 (Aesar 99.99%) in 14 ml of 6 M hydrochloric acid. This solution was immersed in an ice bath with constant stirring and 10 ml acetylacetone (Aldrich) and 10 ml of propylene oxide (Aldrich) were added. To this solution, 6 ml of concentrated ammonium hydroxide were added and a fluffy white precipitate was formed. The precipitate and solution were refrigerated overnight and filtered. Lanthanum acetylacetonate was recovered as described above for yttrium acetylacetonate.

Copper acetylacetonate was the precursor for the preparation of lanthanum copper oxide films. A solution was prepared by dissolving 3.41 g of $CuCl_2 \cdot 2H_2O$ (Baker and Adamson) in 10 ml of methanol. This solution was immersed in an ice bath with constant stirring and 5 ml acetylacetone

(Aldrich) and 5 ml of propylene oxide (Aldrich) were added. The solution was kept in the ice bath for 10 minutes and a blue-violet precipitate was formed. Sufficient distilled water was added to the precipitate and solution to give a total volume of 200 ml and then refrigerated overnight and filtered. Then a similar procedure as described for the preparation of yttrium acetylacetonate was followed to obtain copper acetylacetonate.

Thin Film Preparation. Thin films of yttrium oxide, lanthanum oxide and lanthanum copper oxide have been prepared by an ultrasonic nebulization and pyrolysis technique developed in this laboratory (12). The acetylacetonates of the corresponding metals were used as precursors for the thin film preparation. The reactor used in this investigation is shown in Fig. 1 and was heated by means of a two-zone mirror furnace (Trans-Temp Co., Chelsea, MA). An alcohol solution of the precursor was nebulized by a commercial ultrasonic humidifier (Holmes Air) and was carried into the horizontal reactor by argon. The substrate was held perpendicular to the gas flow in the furnace by a silica holder which was rotated by a low speed motor to achieve best uniformity. Both the efficiency of the deposition and the uniformity of the films were affected by the deposition parameters used. For the best uniformity, 1 inch of the tip of the nozzle was bent upward at an angle of about 15°. Typical reaction conditions used in the film preparation are listed in Table 1. Both silicon and silica wafers were used as substrates. Cleaning of the silicon substrates was carried out just prior to the deposition according to the procedure described by Fournier et al. (15). Silica substrates were cleaned with hydrochloric acid, distilled water and semiconductor grade acetone prior to the deposition. All films were post annealed in flowing oxygen for 30 minutes.

Film Characterization. The thickness of the films on silicon substrates was determined by ellipsometry using a Rudolph Research Auto EL-II ellipsometer (16). The wavelength of the laser beam was 632.8 nm. Values of the two ellipsometric angles, delta and psi, were recorded and input to a Hewlett-Packard 9825A computer to calculate the thickness. Additional input parameters for this calculation were the real (n_s = 3.877) and complex (k_s = 0.019) values for the index of refraction of the silicon substrate, and a trial value (n_p = 1.91) for the index of refraction of the La_2O_3 and Y_2O_3 films. The thickness of films deposited on silica substrates was obtained from the interference fringes in their optical spectra.

X-ray diffraction patterns of these films were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405 A). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range $10° < 2\theta < 80°$. In order to detect the presence of trace impurity phases in La_2CuO_4 films, a step counting technique was used (17). Counts for 200 seconds were made over the ranges $29.5° < 2\theta < 30.5°$ and $38.5° < 2\theta < 39.5°$. These are the positions of the major (101) and (111,200) diffraction peaks of La_2O_3 and CuO, respectively. Five measurements were made at each angle.

The surface topography of the films was studied by scanning electron microscopy. Pictures were taken with a JEOL 840F Scanning Electron Microscope. Optical measurements of the films on silica substrates were performed using a Cary model 17 dual beam ratio recording spectrophotometer in

the range of 190 nm to 2500 nm. Measurements were made in the transmission mode.

Current-voltage measurements were performed to determine the DC breakdown voltage of yttrium oxide and lanthanum oxide thin films. The measurements were carried out with samples in an Au/oxide/Si configuration (12). Gold was evaporated through a mask to obtain an array of circular electrodes of area 1 mm^2 on the surface of the film. Contact to a gold dot electrode was obtained by touching a gold-tipped micromanipulator to the surface. Contacts to the silicon substrate (p-type with a resistivity of 1 Ω-cm) consisted of indium alloy (Indalloy 9, Indium Corporation of America) ultrasonically bonded to the back surface. The indium alloy contacts were checked for ohmic behavior before measurement of the current-voltage characteristic. The reported current-voltage behavior is that for the gold dot electrode made negative with respect to the substrate. The area measured ignores a 1 mm boundary along the substrate edge.

Results and Discussion

Smooth and homogeneous thin films of yttrium oxide, lanthanum oxide and lanthanum copper oxide have been grown on both silicon and silica substrates using ultrasonic nebulization of acetylacetonate solutions, followed by pyrolysis. The films had good adherence to both substrates. They appeared uniform and shiny. Both yttrium and lanthanum oxide thin films had bright colors varying with the thickness. Such interference colors were also visible with thin lanthanum copper oxide films, although these films usually appeared darker due to the nature of the compound. For yttrium and lanthanum oxide

thin films on silicon substrates, the thickness was measured at different positions on the film with an ellipsometer. It was found that the thickness variation on a substrate of 1 x 1 cm was within 1% except near the very edge. The bright and uniform color of the films on both silicon and silica substrates also revealed that they were uniform.

The films which were prepared by the above method were analyzed by x-ray diffraction. In the diffraction pattern of an as-deposited yttrium oxide film of 0.5 μm in thickness on (100) silicon, only a broad peak at 29° could be identified. This indicated that the as-deposited yttrium oxide film was poorly crystallized. After the film was annealed in oxygen at 600°C for 6 hours, all of the diffraction peaks could be indexed on the basis of a cubic yttrium oxide phase with (111) preferred orientation (18). No impurity phase could be found. Heitmann (7) has reported that as-deposited yttrium oxide films prepared by vacuum evaporation were amorphous but that a certain crystallization was detected in annealed films (2 hrs at 400°C in air). Frank et al. (8) have reported crystalline yttrium oxide films prepared by spray pyrolysis.

Singh (2) has reported the preparation of amorphous lanthanum oxide films by vacuum deposition. In this study, the diffraction pattern of an as-deposited lanthanum oxide film of 0.5 μm on (100) silicon, only a weak broad peak at 29-31.5° could be identified. This indicated that the as-deposited lanthanum oxide film was poorly crystallized. After the film was annealed in oxygen at 800°C for 6 hrs, all the diffraction peaks corresponded to the reflections of a hexagonal lanthanum oxide phase (19). No impurity phase could be found.

In the preparation of lanthanum copper oxide films, reaction parameters influenced their composition. For a fixed deposition temperature, carrier gas flow rate and distance between substrate and nozzle, different La:Cu ratios in a mixed-source solution of lanthanum acetylacetonate and copper acetylacetonate were tested. X-ray diffraction patterns were taken from lanthanum copper oxide films of 0.5 μm in thickness which had been annealed in air at 800°C for 6 hrs. Fig. 2 shows the x-ray diffraction pattern of a lanthanum copper oxide film prepared on (100) silicon from a source solution with a La:Cu ratio of 2:1. The diffraction pattern of a standard sample of polycrystalline La_2CuO_4 is also shown in Fig. 2. All the peaks in this pattern can be indexed on the basis of the face-centered orthorhombic unit cell of La_2CuO_4 with cell parameters a = 5.400(2) A, b = 13.14(1) A, and c = 5.356(2) A, in good agreement with the literature (17). Because the 0.5 μm film was less well crystallized, its x-ray peaks were broader and some of the distinct peaks of La_2CuO_4 remained unresolved.

Furthermore, a small amount of unreacted constituents might not appear as additional phases in the diffraction pattern of a thin film. Therefore, step counting was performed on these films over the range where lanthanum oxide and copper oxide have their strongest diffraction peaks. Films prepared from source solutions containing different lanthanum to copper ratios were analyzed. For the film prepared from a source solution with La:Cu = 2:1, there was no evidence of the presence of any detectable impurity phase. However, a trace amount of CuO appeared in the film prepared from a source solution with La:Cu = 1.8:1. A trace amount of La_2O_3 appeared in the film prepared from a solution with La:Cu = 2.2:1. Hence, it was possible to

control the stoichiometry of such ternary oxide films by varying the ratio of the precursor concentrations in the source solution.

The prepared films were examined with scanning electron microscopy. They showed uniform grain textures. Fig. 3 shows a photomicrograph of an as-deposited lanthanum copper oxide film of 0.3 μm thickness on silicon. The surface of the film showed a submicron grain texture with an average particle size of 0.1 - 0.2 μm.

The UV, visible, and near-IR transmission spectra of as-prepared yttrium and lanthanum oxide films on silica are shown in Figs. 4 and 5, respectively. It can be observed in the spectra that the prepared yttrium and lanthanum oxide films are highly transparent over a large range from UV to near-IR.

Current-voltage measurements were made on as-deposited yttrium and lanthanum oxide films approximately 0.2 μm thick in $Au/Y_2O_3/Si$ and $Au/La_2O_3/Si$ configurations, respectively. There was no observed voltage breakdown up to 18 V applied DC potential. These results demonstrate the formation of high-density films and are in agreement with those reported in the literature (1-2).

Acknowledgments

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Figure Caption Sheet

Fig. 1. Schematic diagram of the deposition apparatus.

Fig. 2. X-ray diffraction patterns of a) a 0.5 μm film of La_2CuO_4 and b) a polycrystalline standard sample of La_2CuO_4.

Fig. 3. Photomicrograph of a typical lanthanum copper oxide film of 0.3 μm thickness.

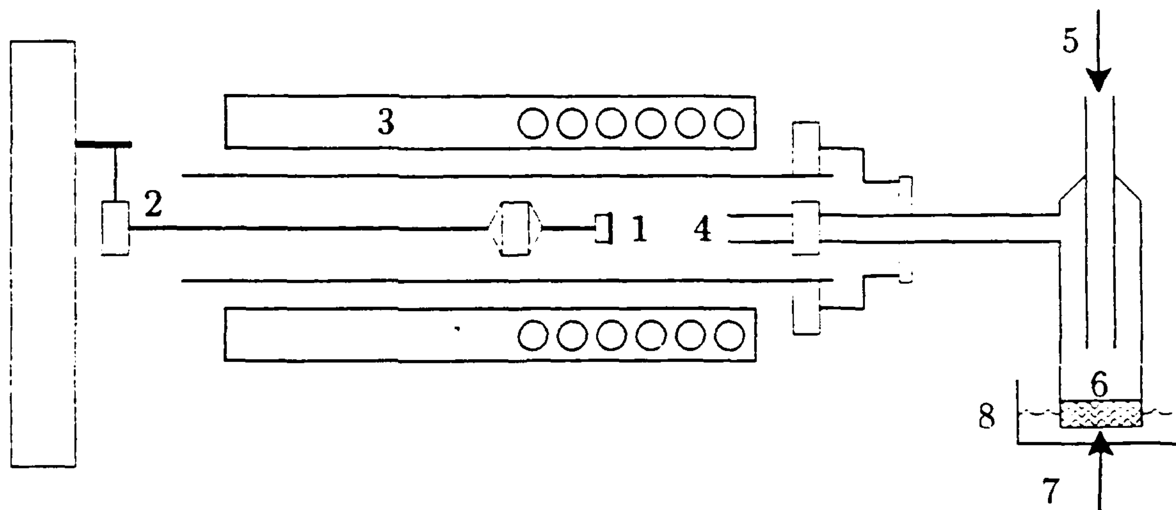
Fig. 4. Transmission spectrum of a typical Y_2O_3 film on silica.

Fig. 5. Transmission spectrum of a typical La_2O_3 film on silica.

Table 1

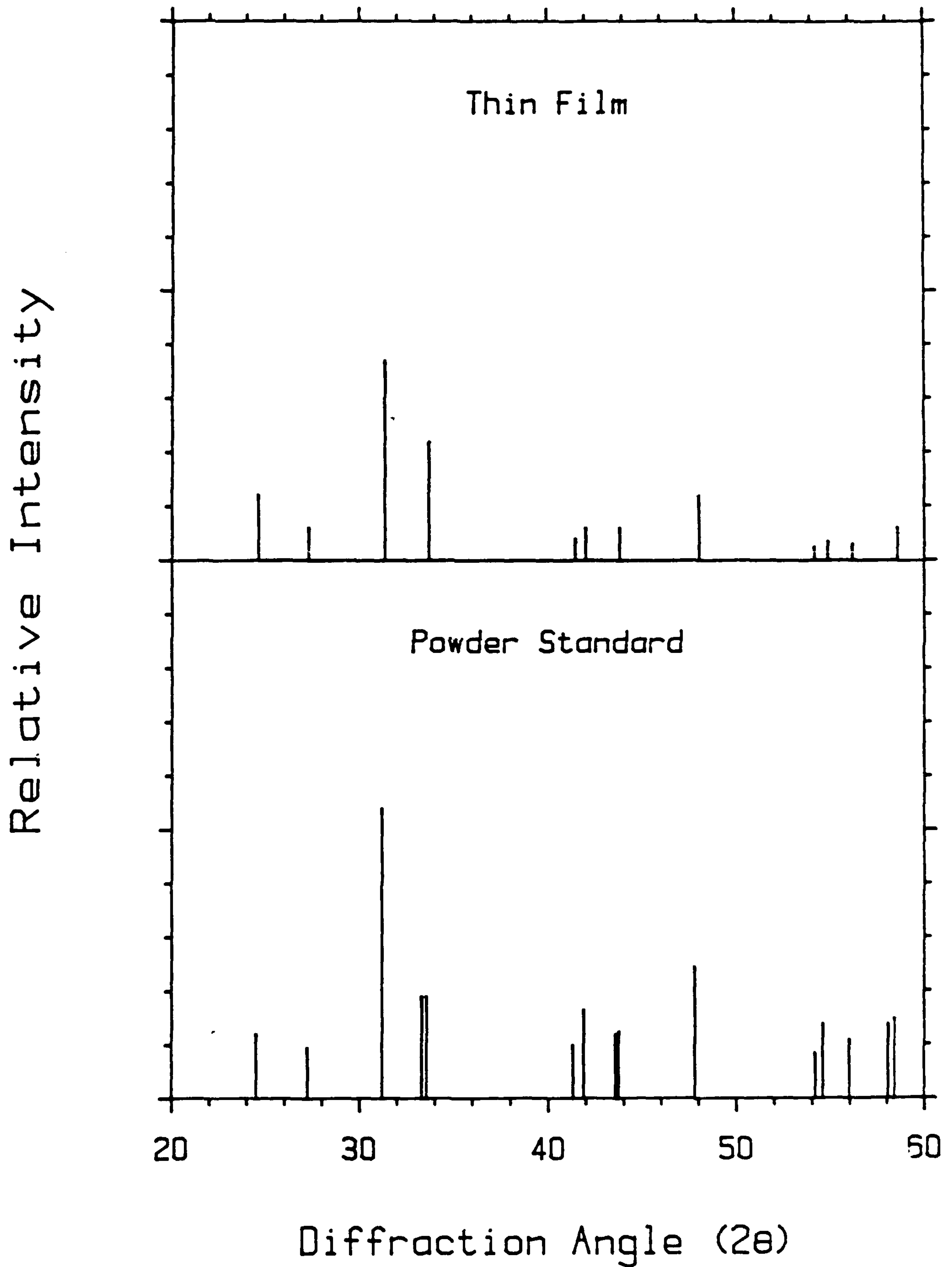
Reaction Parameters

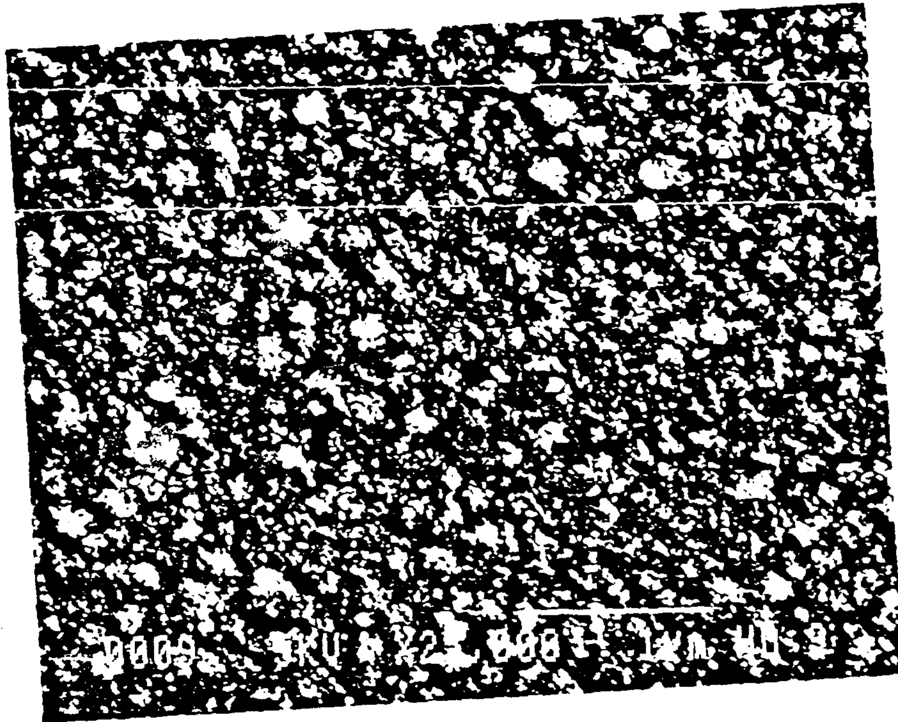
Thin Films	Y_2O_3	La_2O_3	La_2CuO_4
Precursor Concentration	$Y(acac)_3$ 0.01 M	$La(acac)_3$ 0.01M	$La(acac)_3$ 0.01 M $Cu(acac)_2$ 0.005 M
Solvent	Ethanol	Ethanol	Methanol
Deposition temperature	400°C	400°C	550°C
Substrate to nozzle distance	9 cm	9 cm	10.2 cm
Argon flow rate	3.7 l/min	3.7 l/min	4.1 l/min
Post anneal temperature	500°C	500°C	600°C

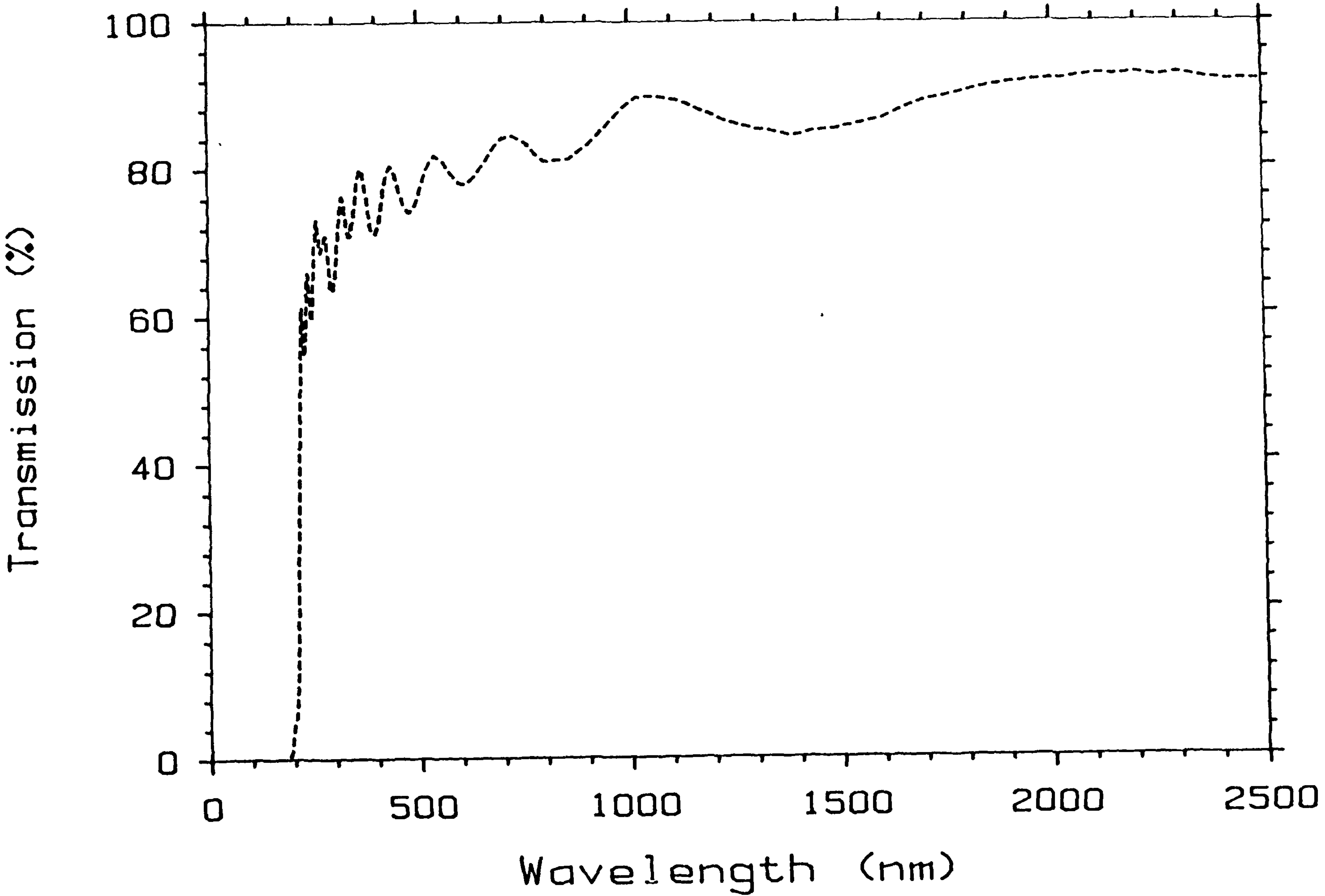


1	Substrate	5	Carrier gas
2	Substrate rotation motor	6	Solution
3	Furnace	7	Membrane
4	Spray nozzle	8	Ultrasonic Humidifier

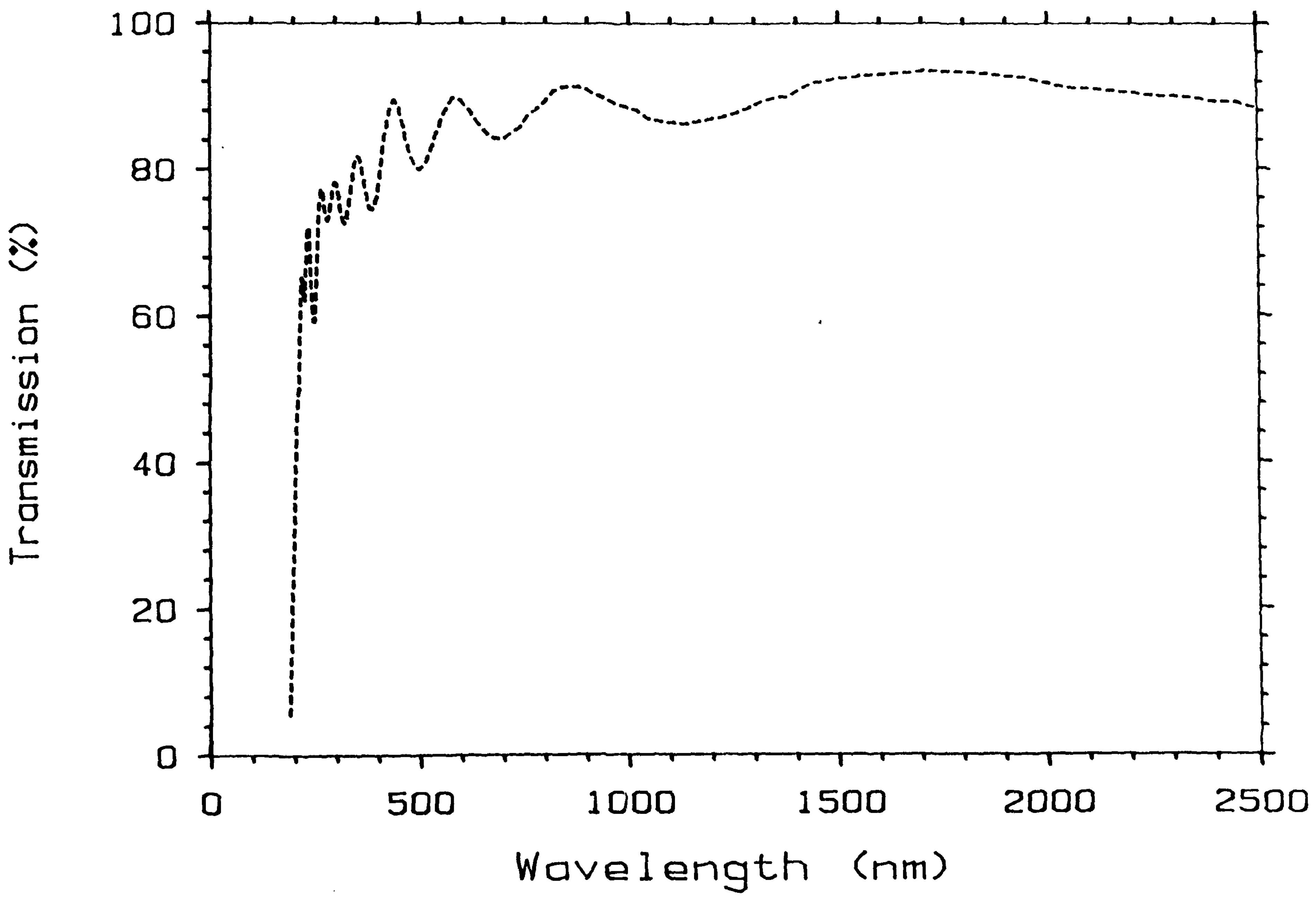
X-ray Analysis of La_2CuO_4







Spectrum of Y_2O_3 on SiO_2
100
80
60
40
20
0
Transmission (%)
0
500
1000
1500
2000
2500
Wavelength (nm)


Spectrum of La2O3 on SiO2
Transmission (%)
100
80
60
40
20
0
0
500
1000
1500
2000
2500
Wavelength (nm)