JOURNAL OF SOLID STATE CHEMISTRY 92, 208–212 (1991)

Preparation and Characterization of Iron(III) Oxide Films by a Novel Spray Pyrolysis Method

Y-T. QIAN, C-M. NIU, C. HANNIGAN, S. YANG, K. DWIGHT, AND A. WOLD

Department of Chemistry, Brown University, Providence, Rhode Island 02912

Received October 8, 1990

α-Fe_2O_3 thin films were deposited on silicon substrates by nebulization of a 0.01 *M* solution of iron acetylacetonate in a 50% methanol/water mixture followed by pyrolysis and annealing in flowing oxygen. The resulting films were characterized by X-ray diffraction, scanning electron microscopy, and their electrical transport behavior. The IR transmission spectrum of α-Fe_2O_3 recorded from such films agreed with published theoretical analysis based on the crystal structure. © 1991 Academic Press, Inc.

Introduction

Various techniques have been employed for the preparation of iron oxide films such as pulsed laser evaporation (*1*), sputtering (*2*), sol-gel processes (*3*), chemical vapor deposition (*4*), and spray pyrolysis (*5, 6*). Films of iron oxide deposited using a spray pyrolysis technique have been identified as α-Fe_2O_3 (*6*) by conversion electron Mossbauer spectroscopy and X-ray analysis.

IR spectra of polycrystalline α-Fe_2O_3 have been studied extensively (*7–9*). However, the position, width, and relative intensity of the observed absorption bands lack consistency, and depart from theoretical expectations. This discrepancy is caused by the diversity in the size and shape of the sample particles (*7–9*). Diverse preparative conditions as well as the nature of the matrix in which the powder is embedded play important roles in determining the nature of the product. Most of the spectral measurements described in the literature were made on powder samples using KBr as a matrix. Because of the difficulty in controlling the parameters involved in preparing such pellets, this technique generally does not yield reproducible spectra.

Recently, a novel spray pyrolysis process has been developed for the preparation of thin oxide films of high quality (*10–12*). Uniform, mirror-like oxide films with submicron texture can be easily deposited on silicon substrates. Such films afford a unique opportunity to obtain IR spectra of oxides directly without the use of KBr as a matrix.

This study concerns the preparation and properties of α-Fe_2O_3 thin films deposited on silicon substrates by this simple method. An iron acetylacetonate solution was ultrasonically nebulized, sprayed onto substrates, and thermally decomposed. The resulting films were characterized by X-ray diffraction, IR transmission spectra, scanning electron microscopy, and their electrical transport.

0022-4596/91 $3.00

TABLE I

REACTION PARAMETERS

Substrate temperature	500°C
Carrier gas	Oxygen
Flow rate	3.5 liters/min
Nozzle–substrate distance	8.5 cm
Cycle time	35 sec
Nebulization time	5 sec
Number of cycles	200

Experimental

Preparation of films. Iron acetylacetonate was prepared following the method described in the literature (*13*). A solution of 0.01 *M* iron acetylacetonate in a 50% methanol/water mixture was ultrasonically nebulized, sprayed onto substrates, and thermally decomposed at 500°C in the reactor described previously (*10–12*). The reactor was heated by a two-zone mirror furnace (Trans-Temp, Chelsea, MA). The solution was nebulized by a commercial ultrasonic humidifier (Holmes Air) and the resulting mist was swept into the reactor by a stream of oxygen. The nebulized solution was delivered to the substrate in 5-sec pulses with 30-sec intervals between pulses. The substrates consisted of 1-cm squares of *n*-type (100) silicon (Brookville Electronics) with 0.01 Ω-cm resistivity. They were cleaned and etched immediately prior to the deposition according to the procedure described by Fournier *et al.* (*14*). For measurement of the optical band gap, silica substrates were used. These were cleaned with hydrochloric acid, distilled water, and semiconductor grade acetone prior to the deposition. Typical sets of reaction parameters for obtaining films of 2500-Å thickness are given in Table I. Following deposition, an additional heat treatment at 500°C in flowing oxygen was carried out for 1 hr in the same reactor in order to ensure complete conversion of the film to α-Fe_2O_3.

Characterization of films. X-ray diffraction patterns of the films were obtained using a Philips diffractometer with monochromated high intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range $12° < 2\theta < 72°$. The thickness of the films was determined using a Sloan Dectac machine with a diamond stylus which has a tip radius of 0.0001 in and bears on the specimen being measured with a force of about 0.1*g*. The vertical motion of the stylus over a step relative to the reference plane is recorded as the thickness of the film. The steps on the film were made by partially masking the film with wax and etching with hydrochloric acid, followed by soaking the film in benzene to remove the wax. The surface morphology of the films was examined by means of a JEOL-840F Scanning Electron Microscope (SEM) operating at 4.5 kV.

The IR spectra were obtained using a Bruker IR 98 FTIR Spectrometer with a deuterated triglycine sulfate detector equipped with a polyethylene window. The light source was a Hg arc; 12-, 6-, and 3.5-μm mylar beamsplitters were used. The spectra of films were obtained by subtracting the spectra of the uncoated substrates, measured prior to the film deposition, from the corresponding spectra of the coated substrates measured after deposition. Optical measurements of the films on silica substrates were performed using a Cary Model 17 dual beam ratio recording spectrophotometer in the range of 350 to 100 nm. Measurements were made in the transmission mode. The optical band gap was deduced from the transmittance near the absorption edge.

Electrodes for measuring the electrical transport properties of the films were prepared as follows: gold was evaporated through a mask to obtain an array of circular electrodes of area 1.1 mm^2 each on the surface of the films; an indium alloy (Indalloy No. 9, Indium Corp. of America) was ultrasonically bonded to the back of the silicon substrate. Contact to a gold electrode was made by touching a gold-tipped micromanipulator to the desired spot. The dc current–voltage behavior was measured with the gold positively biased with respect to the substrate and with the reversed polarity.

Results and Discussion

Films of iron oxide of approximately 2500-Å thickness have been deposited on both silicon and silica substrates by an ultrasonic nebulization and pyrolysis technique using the conditions given in Table I. The films had good adherence to both substrates. They appeared uniform and shiny. The thickness of films on silicon substrates was measured at different positions on the film by a dectac technique and was found to be uniform to within 1% on a substrate of 1 × 1 cm^2. The bright and uniform color also revealed that the films were of uniform thickness.

Both as prepared and annealed films were analyzed by X-ray diffraction and characterized by scanning electron microscopy. The X-ray diffraction pattern of a film of 2500-Å thickness on (100) silicon showed only reflections from the silicon substrate. Hence, films of about 5000 Å were similarly prepared. The X-ray diffraction patterns of these thicker films could be indexed as belonging to a α-Fe_2O_3 (hematite), which has the corundum structure with lattice parame-

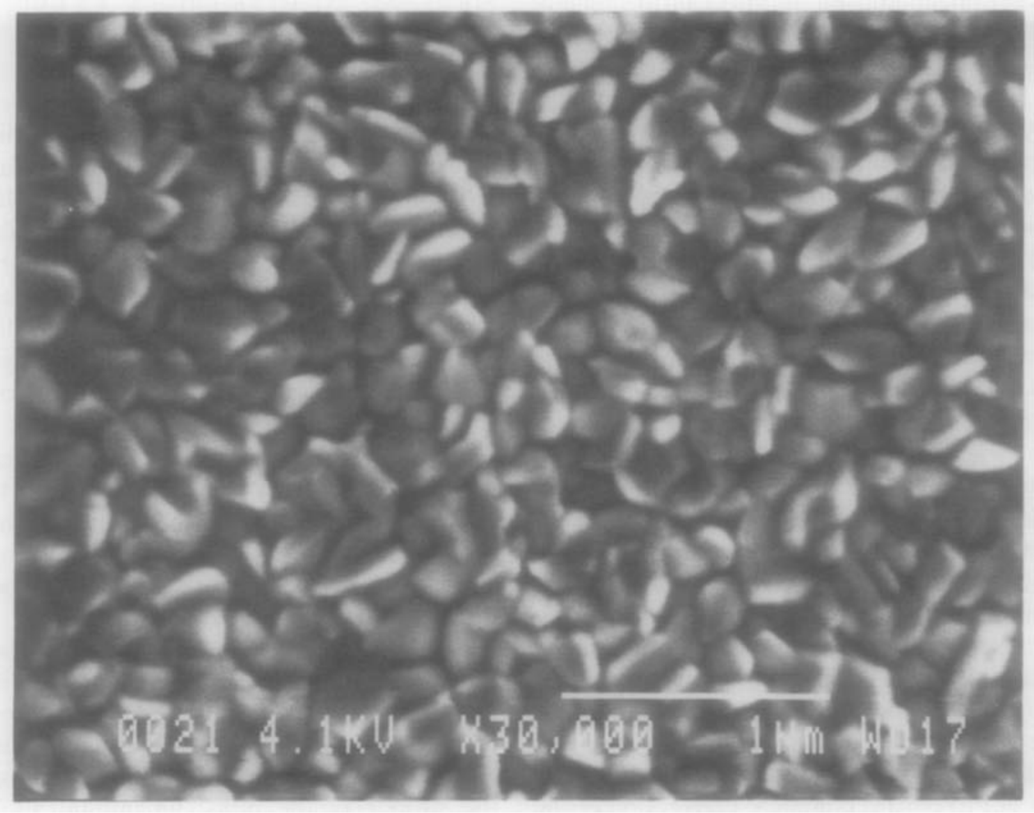

FIG. 1. Electron photomicrograph of an α-Fe_2O_3 film of 5000-Å thickness.

TABLE II

COMPARISON OF THEORETICAL IR MODES[a] WITH EXPERIMENTAL ABSORPTIONS FOR α-Fe_2O_3

Symmetry	ν_{exp} (cm^{-1})	ν_T (cm^{-1})	ν_L (cm^{-1})
E_u ($E \perp c$)	517	524	662
	432	437	494
	291	286	368
	231	227	230
A_{2u} ($E \parallel c$)	517	526	662
	291	299	414

[a] From Ref. (*7*).

ters a = 5.0345 Å and c = 13.739 Å. A photomicrograph of films of 5000-Å thickness is shown in Fig. 1. Uniform grain texture can be observed in the picture, with a typical grain size of about 0.2 μm.

α-Fe_2O_3 crystallizes with the corundum structure which has a symmetry of $R\bar{3}c$ (D_{3d}^6). The factor group theoretical analysis of the normal modes of the corundum structure was made by Bhagavantam and Venkatarayudu (*15*). The two one-dimensional A_{2u} modes with polarization parallel to the crystalline c axis and four two-dimensional E_u modes with polarization perpendicular to the c axis are IR active. The validity of this analysis for α-Fe_2O_3 has been confirmed by IR reflectance spectra of single crystals (*16*). The theoretical phonon frequencies of α-Fe_2O_3 given by Serna *et al.* (*7*) in comparison with those obtained from thin films on silicon substrates are tabulated in Table II. It can be seen from Table II that the frequencies of absorption bands are at $\nu_{exp} = \nu_T$, in which ν_T is the frequency of the long wavelength transverse optical modes. This indicates (*17*) that the polarization charge induced on the surface of such films by electromagnetic fields is small. Moreover, the relative intensity of the absorption bands for α-Fe_2O_3 is consistent with that calculated from crystal structure data (*7*). The IR spectrum of α-Fe_2O_3 obtained by subtracting the spectra of the bare substrates from the spectra of the coated substrates is shown in Fig. 2. Similarly, IR data of α-Cr_2O_3 obtained from thin films prepared by this simple method (*12*) are also consistent with those of theoretical calculations based on the crystal structure of α-Cr_2O_3 (*7, 18*).

The results of X-ray diffraction, IR, and SEM showed that the composition of the annealed films was α-Fe_2O_3. Moreover, annealing improves the optical band gap and current–voltage characteristics of films. The transmission spectra of iron oxide films on silica were recorded from 350 to 1000 nm. The optical absorption derived from such data was used to generate plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$, which gave a band gap energy of 1.97 eV for the as deposited film and a band gap energy of 2.2 eV for the annealed film. The reported band gap for pure α-Fe_2O_3 is 2.2 eV (*19*) which is in agreement with the value obtained for annealed films. The dc current–voltage measurements were made on several films approximately 2500-Å thick. A significant change of current was observed at 3.5 and 5.5 V of applied potential for the as deposited and annealed films,

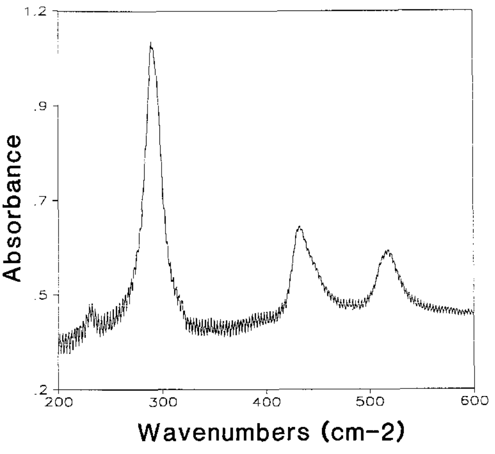

FIG. 2. IR spectrum of α-Fe_2O_3 film of 2500-Å thickness.

respectively. Differences in the band gap and the current–voltage behavior can be related to the existence of Fe(II) in the films as prepared. In a previous study (*19*), it was shown that pure α-Fe_2O_3 is not a photoconductor and a necessary condition for the observation of any appreciable conductivity is the existence of Fe(II). Post annealing of the films in oxygen is essential for the production of high quality films.

Conclusions

α-Fe_2O_3 thin films were prepared by an ultrasonic nebulization and pyrolysis method using a methanol/water solution of iron acetylacetonate as the source material. Homogeneous, uniform films with good adherence have been obtained using this simple technique. Post annealing of the films in oxygen was essential for the formation of high-quality α-Fe_2O_3. These films have submicron grain texture with a band gap value of 2.2 eV and are of comparable quality to films prepared by more elaborate methods. The IR transmission spectrum of α-Fe_2O_3 recorded from such films is consistent with published results of theoretical calculations based on crystal structure data, in both position and relative intensity of absorption bands.

Acknowledgments

This research has received partial support from the Office of Naval Research, NSF Contract No. DMR 880 3184, Eastman Kodak Company and the GTE Laboratories, Incorporated.

References

1. S. Joshi, R. Nawathey, V. N. Koinkar, V. P. Godbole, S. M. Chaudhari, and S. B. Ogale, *J. Appl. Phys.* **64**(10), 5647 (1988).
2. J. K. Lin, J. M. Sivertsen, and J. H. Judy, *IEEE Trans. Magn. MAG22,* 50 (1986).
3. G. Kordas and R. A. Weeks, *J. Appl. Phys.* **57**(1), 3812 (1985).
4. M. Langlet, M. Labeau, and J. C. Joubert, *IEEE Trans. Magn. MAG22,* 600 (1986).
5. J. A. Cusido, X. Obradors, J. Fontcuberta, A. Isalgue, F. Canal, J. Cortadellas, M. Langlet, and J. C. Joubert, *IEEE Trans Magn. MAG23,* 74 (1987).
6. K. Nomura and Y. Ujihira, *Thin Solid Films* **128,** 225 (1985).
7. C. J. Serna, J. L. Rendon, and J. E. Iglesias, *Spectrochim. Acta, Part A* **38**(7), 797 (1982).
8. C. J. Serna, M. Ocana, and J. E. Iglesias, *J. Phys.* **20,** 473 (1987).
9. J. E. Iglesias, M. Ocana, and C. J. Serna, *Appl. Spectroscopy* **44**(3), 418 (1990).
10. W. DeSisto, M. Sosnowski, F. Smith, J. DeLuca, R. Kershaw, K. Dwight, and A. Wold, *Mat. Res. Bull.* **24,** 753 (1989).
11. P Wu, Y-M. Gao, J. Baglio, K. Dwight, and A. Wold, *Mat. Res. Bull.* **24,** 905 (1989).
12. Y-T. Qian, R. Kershaw, K. Dwight, and A. Wold, *Mater. Res. Bull.,* in press.
13. J. D. Reedy, U.S. Patent No. 3,946,057, March 23, 1976.
14. J. Fournier, W. DeSisto, R. Brusasco, M. Sosnowski, R. Kershaw, J. Baglio, K. Dwight, and A. Wold, *Mater. Res. Bull.* **23,** 31 (1988).
15. S. Bhagavantam and T. Venkatarayudu, *Proc. Indian Acad. Sci.* **A9,** 224 (1939).
16. S. Onari, T. Arai, and K. Kudo, *Phys. Rev. B* **16**(4), 1717 (1977).
17. R. Ruppin and R. Englman, *Rep. Prog. Phys.* **33,** 149 (1970).
18. G. Lucovsky, R. J. Sladek, and J. W. Allen, *Phys. Rev. B,* **16**(10), 4717 (1977).
19. P. Merchant, R. Collins, R. Kershaw, K. Dwight, and A. Wold, *J. Solid State Chem.* **27,** 307 (1979).