

THERMAL CHARACTERIZATION OF IRON OXIDE FILMS*

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ABSTRACT

Films of iron oxide were prepared by chemical vapor deposition techniques (CVD) and by sputtering in an oxygen atmosphere. These films were examined by thermogravimetry, differential thermal analysis, evolved gas analysis, infrared spectroscopy, Mössbauer spectroscopy, and X-ray diffraction analysis. CVD films were found to contain 5-10% divalent iron and large amounts of chemisorbed and chemically bonded CO_2 . The carbonate ion was decomposed by heating to 500°C and the film converted to well crystallized $\alpha\text{-Fe}_2\text{O}_3$. The chemisorbed CO_2 was released on further heating to 1000°C . The films sputtered in O_2 are already largely $\alpha\text{-Fe}_2\text{O}_3$ when prepared and become well crystallized by 500°C with much smaller quantities of chemisorbed gases.

INTRODUCTION

It has recently been shown that Fe_2O_3 films made by low temperature reaction of $\text{Fe}(\text{CO})_5$ and O_2 ¹ can be made insoluble in 6 M HCl by treatment with either an electron beam² or with focussed light from an argon ion laser³. The Fe_2O_3 film prepared in this way can, therefore, be viewed as either an electron resist or a photo-resist. As a result of these procedures one can anticipate simplification and improvements in making see-through photomasks.

It has been noted that an initially amorphous Fe_2O_3 film is crystallized as a result of either the electron beam or laser treatment. Bagley⁴ has recently discussed the kinetics of such amorphous to crystalline transitions. In order to gain greater insight into the process involved in thermal treatments of Fe_2O_3 films, we have made measurements on chemical vapor deposition techniques (CVD) and sputtered films by evolved gas analysis (EGA), differential thermal analysis (DTA), thermogravimetry (TG), infrared spectroscopy, Mössbauer spectroscopy, and X-ray diffraction. These measurements and discussion of the results are the subject matter of this report.

EXPERIMENTAL PROCEDURES

Preparation of films

In general, CVD films were prepared using techniques outlined by Sullivan⁵. CO_2 was bubbled through $\text{Fe}(\text{CO})_5$ and the resulting gaseous mixture was merged

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with flowing O_2 near the heated substrate. Deposition temperatures as a function of heater voltage were determined by calibration runs using a thermocouple attached to the substrate surface. For EGA determinations some Fe_2O_3 films on soda lime glass substrates were used. These samples were obtained from Towne Laboratories, Somerville, N. J. For most runs Coors alumina (AD995) thin film substrates were used to minimize the possibility of CO_2 evolution from the substrate material. No important substrate effects were noted. CVD Fe_2O_3 was deposited onto single crystal NaCl discs for the DTA and TG determinations. These were usually thick films and were detached by scraping lightly with a razor blade.

Some films for DTA and TG studies were prepared by sputtering in O_2 . The experimental apparatus and conditions have been described elsewhere⁶ with one important deviation from these conditions. The NaCl substrate used was attached to a liquid N_2 -cooled holder to minimize crystallite growth.

Thermogravimetry

A Perkin-Elmer thermobalance was used which had been modified to provide digital output on punched paper tape⁷. Temperature calibration was based upon the use of magnetic standards as previously described⁷. The heating rate was nominally $2.5^\circ C \text{ min}^{-1}$. Air was passed over the sample through the approximately 15 mm in diameter tube at a rate of 30 ml min^{-1} .

The samples were in the form of small, very light flakes of film and it was necessary to use a platinum mesh cover for the platinum sample pan. Samples weighed in the range of 3–10 mg depending upon the availability and packing of the material.

Differential thermal analysis

A Dupont thermolyser was used with a heating rate of $10^\circ C \text{ min}^{-1}$ and an air atmosphere at a flow rate of 20 ml min^{-1} . Samples of 5–15 mg were placed in platinum cups and an empty cup served as the reference.

Evolved gas analysis

Approximately 50 cm^2 samples of the CVD films on alumina or glass were broken into small pieces and placed in a platinum tube which had been previously baked at $1000^\circ C$ and $1 \times 10^{-6} \text{ mm Hg}$. The sample chamber was evacuated to about $1 \times 10^{-6} \text{ mm Hg}$ and then heated at approximately $5^\circ C \text{ min}^{-1}$ with continued pumping. A Veeco SPI-10 residual gas analyzer in the system was repeatedly scanned over the range of 10–55 amu. The output from the analyzer and a Pt/Pt-10% Rh thermocouple in contact with the sample were recorded on a two pen recorder.

Mössbauer spectroscopy

A constant acceleration spectrometer similar to that described by Wertheim and Herber⁸ was used. The source was ^{57}Co in Pd. Calibration was based upon the ground state splitting of ^{57}Fe . A value of 3.92 mm sec^{-1} obtained from NMR and

Mössbauer measurements was used^{9,10}. Isomer shifts of magnetically split spectra were determined from the centroid of the lines.

Infrared spectroscopy

Both sputtered and CVD films were deposited on single crystal NaCl. Samples were removed from the NaCl prior to heating to 1000 °C for 10 min and KBr pellets were prepared from both the heated and unheated powders. The infrared spectra of both the KBr pellets and supported films were measured using a Perkin-Elmer Model 421 grating instrument.

X-ray diffraction

A G.E. Model XRD-3 diffractometer and CrK_α radiation was employed. Samples of both CVD and sputtered films were deposited on glass slides and their diffraction patterns determined.

RESULTS AND DISCUSSION

Precise correlation of temperature between the various experimental techniques are impossible due to differences in heating rates. Fig. 1 shows TG traces for a CVD

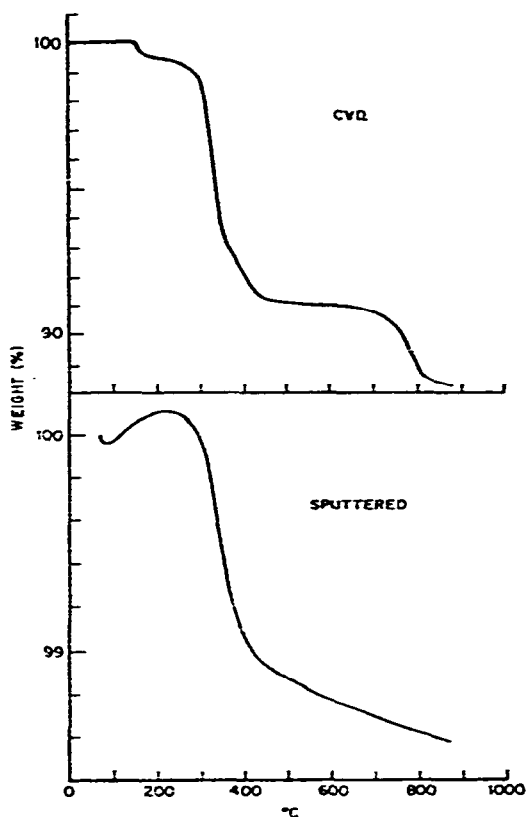


Fig. 1. Thermogravimetric curves of films which convert to $\alpha\text{-Fe}_2\text{O}_3$.

film prepared at 100°C and for a sample of sputtered film. The DTA patterns for the same samples are shown in Fig. 2. The sputtered film shows relatively little weight loss while the CVD film loses about 9 wt. % below 450°C and a clear exothermic peak for the CVD film in the region of 390–440°C. There is a much weaker exotherm for the sputtered film in the same temperature region. There are no other peaks for either material from room temperature to 900°C.

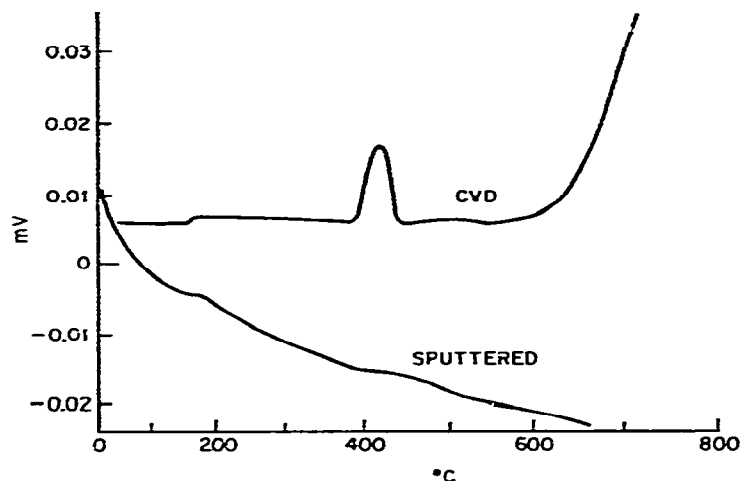


Fig. 2. Differential thermogravimetric curves of films which convert to $\alpha\text{-Fe}_2\text{O}_3$.

X-ray diffraction patterns obtained from both types of film heated to 500°C indicate a sharp pattern of $\alpha\text{-Fe}_2\text{O}_3$. At room temperature the sputtered film gives a diffuse weak pattern corresponding to $\alpha\text{-Fe}_2\text{O}_3$ while the CVD film yields no discernible peaks.

It appears then that the sputtered film is basically small crystalline $\alpha\text{-Fe}_2\text{O}_3$ at room temperature and upon heating undergoes only a slight weight loss which is probably associated with adsorbed gases on the large surface area. These gases are desorbed due to both the elevated temperatures and reduction in surface area. The CVD film on the other hand appears to be an amorphous or microcrystalline material with chemically bonded as well as physically adsorbed gaseous species.

Inspection of the EGA data indicates that some water and large amounts of CO_2 are evolved as the temperature is raised. Figure 3 shows a plot of the relative intensity of the mass (CO_2) peak as a function of temperature. The peak around 400°C correlates well with the weight loss and DTA peak. There is also a high temperature peak correlating with the onset of a second weight loss at 700°C and the change in slope of the DTA curve.

Selected infrared spectra are presented in Fig. 4. The spectrum of the sputtered film (4a) is nearly free of absorptions as would be expected. The weak absorption at 3400 cm^{-1} is associated with hydroxide ion, which is always present at about this strength in KBr pellets. Since the absorption coefficient of hydroxide ion is very

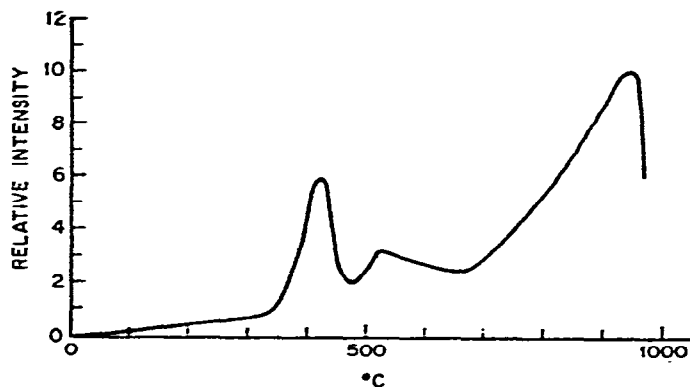


Fig. 3. Relative intensity of the mass 44 peak evolved as a function of temperature.

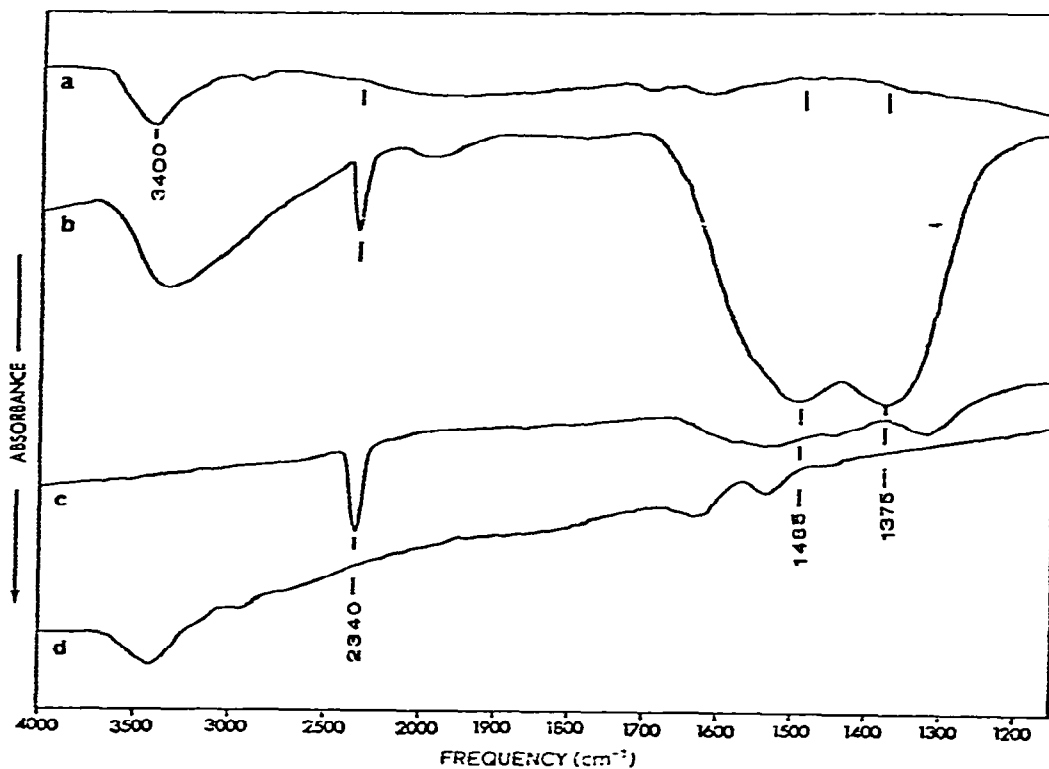


Fig. 4. Infrared spectra of some films which convert to α - Fe_2O_3 . a, sputtered in O_2 , unheated, KBr pellet; b, CVD, unheated, on NaCl; c, CVD, heated to 500°C , on NaCl; d, CVD, heated to 1000°C , KBr pellet.

strong, it is assumed that the amount of hydroxide ion introduced with the sample is small.

The CVD film at room temperature (4b) shows (1) two strong absorptions at 1485 and 1375 cm^{-1} which are indicative of carbonate ion, (2) an absorption around

2340 cm^{-1} where molecular carbon dioxide absorbs, and (3) a band at 3400 cm^{-1} attributable to hydroxide ions. When heated to 500–700 $^{\circ}\text{C}$ (4c) the absorptions due to carbonate (1485 and 1375 cm^{-1}) ions virtually disappear while that attributed to carbon dioxide (2340 cm^{-1}) persists. After the sample is heated to 1000 $^{\circ}\text{C}$ (4d) these absorptions are no longer present. It was necessary to remove the CVD film from the NaCl substrate prior to heating it to 1000 $^{\circ}\text{C}$ since this is above the melting point of NaCl and then to run the film as a KBr pellet after heating. Consequently, the absorption at 3400 cm^{-1} is again typical of hydroxide ion in KBr.

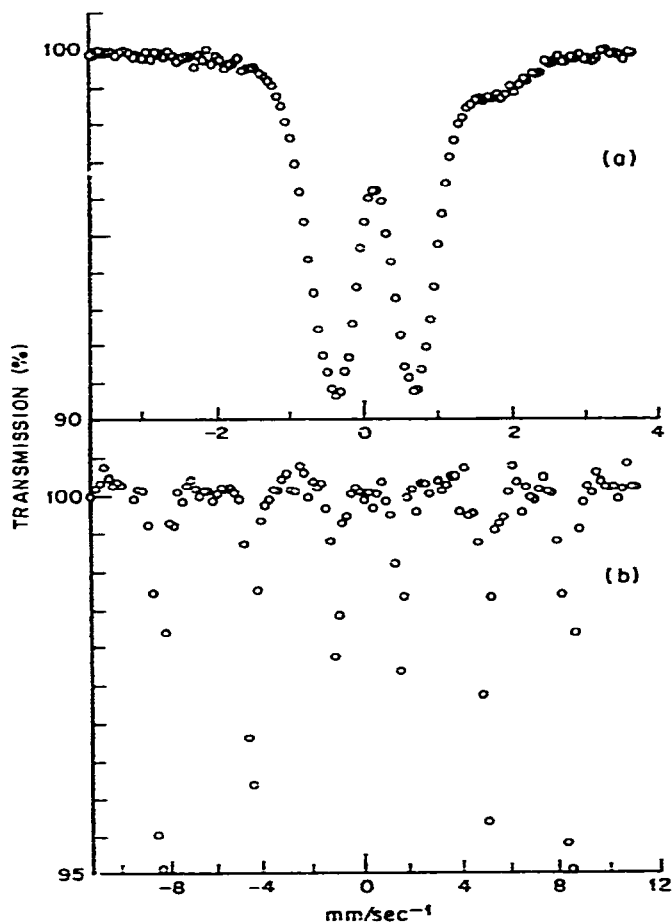


Fig. 5. Mössbauer spectra of CVD films. a, as prepared, RT; b, heated to 5000 $^{\circ}\text{C}$, RT.

Mössbauer spectra of the CVD films are shown in Fig. 5. The as deposited film consists primarily of a quadrupole doublet having an isomer shift of +0.19 mm sec^{-1} and a splitting of 1.07 mm sec^{-1} . The isomer shift is typical of trivalent iron. The quadrupole splitting is very large and indicative that the iron sites in this amorphous or microcrystalline film are highly asymmetric with respect to the electrical charge distribution surrounding the iron nucleus. There is also some divalent iron present

as indicated by the small shoulder at about $+2.0 \text{ mm sec}^{-1}$. This is undoubtedly one half of quadrupole split doublet whose other half is concealed within the much larger trivalent absorption.

When the film has been heated to 500°C the resulting Mössbauer spectrum is that of well crystallized $\alpha\text{-Fe}_2\text{O}_3$.

Figure 6 shows Mössbauer spectra of the unheated sputtered film. The spectrum at room temperature clearly shows two separate patterns each exhibiting the six-line pattern associated with magnetic hyperfine interaction. The narrow line pattern has an isomer shift of $+0.17 \text{ mm sec}^{-1}$ and a hyperfine splitting of 509 koe and is ascribed

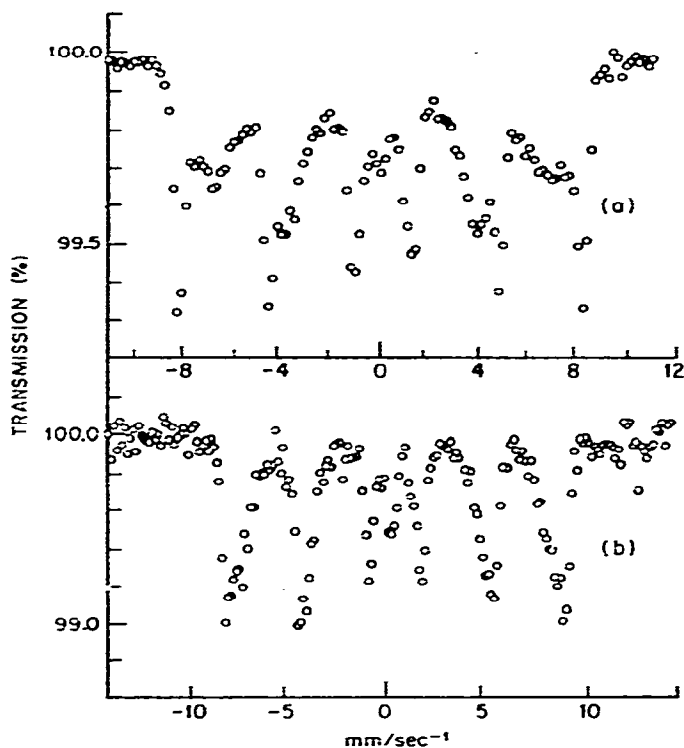


Fig. 6. Mössbauer spectra of sputtered films. a, as prepared, RT; b, as prepared, 78 K.

to the crystallized $\alpha\text{-Fe}_2\text{O}_3$ evident in the X-ray pattern of this sample. The much broader pattern has an isomer shift of $+0.19 \text{ mm sec}^{-1}$ and a hyperfine splitting of 423 koe. The isomer shift value clearly establishes it to be trivalent iron. This material is either a more finely divided $\alpha\text{-Fe}_2\text{O}_3$ which is approaching superparamagnetism or a second phase of trivalent iron.

The spectrum at 78 K shows that the broad spectrum at room temperature has sharpened up considerably and the magnetic hyperfine splitting has increased to almost match the well crystallized $\alpha\text{-Fe}_2\text{O}_3$ portion. This suggests that the material is a more finely divided $\alpha\text{-Fe}_2\text{O}_3$.

CONCLUSIONS

Based on the body of experimental data the conclusion is that films sputtered in oxygen are to a large degree crystallized iron oxide. Upon heating to 1000°C there is a small weight loss, about 1.5 wt %, due to the decrease in adsorbed gases resulting from the reducing in surface area of the oxide. By 500°C the film is completely crystallized α -Fe₂O₃.

The CVD films are originally an amorphous or micro-crystalline film which contains predominantly trivalent iron but has approximately 5–10% of divalent iron. There are large amounts of carbon dioxide and some water present corresponding to an approximate formula of Fe₂O₃ · ½CO₂ assuming that the weight loss is exclusively CO₂. The CO₂ is present both as carbonate ion and apparently also as chemisorbed CO₂. The amount of divalent iron and carbonate ion may be related.

Upon heating CVD films to 500°C the carbonate ion is decomposed and CO₂ is evolved along with the water. The film is converted to crystalline α -Fe₂O₃ although the bulk of the chemisorbed CO₂ is retained. This CO₂ is then evolved as the temperature is raised and the surface area of the oxide decreases due to sintering. Several investigations^{2,5,11} have previously shown that the crystallization of CVD films occurs in this temperature range accompanied by a reduction of solubility in 6 M HCl. These measurements now show that there is a concomitant loss of significant amounts of CO₂ from the film.

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