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Characterization of iron oxide thin films

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Iron oxide thin films were grown with gas-phase deposition on a glass substrate in order to study the effects of the deposition temperature and time on the film properties. Characterization of the samples was performed using x-ray photoelectron spectroscopy, x-ray diffraction, and atomic force microscopy. It was observed that the film deposited at 350 °C consisted of γ -Fe₂O₃ whereas films produced at temperatures between 400 °C and 500 °C could be identified as α -Fe₂O₃. Increasing the deposition temperature resulted in an increase of the grain size at temperatures between 350 °C and 450 °C. When the deposition time was decreased, a part of the iron ions were observed to be in the divalent state. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: iron oxide; thin film; XPS; AFM; XRD

INTRODUCTION

Iron oxides are interesting due to their catalytic, magnetic, and semiconducting properties, and because they are produced during corrosion. Their applications include, e.g., usage as pigments, catalysts in styrene synthesis,¹ and as a material for high-density magnetic storage. At room temperature, the normal stoichiometric forms of iron oxides are magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃); in addition, they form hydroxides. In maghemite and hematite the iron cations are in the Fe³⁺ state but magnetite contains both Fe²⁺ and Fe³⁺ ions. Magnetite is particularly important in magnetic applications whereas several oxide forms are involved in corrosion and catalysis. The basic properties of the various iron oxide forms are summarized, e.g., in Ref. 2.

In this work, we studied iron oxide thin films deposited from the gas phase on a glass substrate. Our purpose was to find out the effects of the growth temperature and deposition time on the chemical state and morphology of the film. The chemical analysis was performed with XPS, the surface morphology was analysed with AFM (atomic force microscopy), and the crystal structure was characterized with XRD (x-ray diffraction).

EXPERIMENTAL

The studied samples were produced by gas-phase deposition on a glass substrate. Samples A–D were grown at different temperatures between 350 °C and 500 °C. For samples E and F the deposition temperature was 500 °C and the growth time was decreased by one and two orders of magnitude in order to study the initial stage of the film growth.

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After deposition, the film thickness was measured with a Tencor Alpha-Step 300 profilometer. Table 1 summarizes the sample parameters.

XPS measurements were performed with a Surface Science Instruments SSX-100 spectrometer using monochromatic Al K_α radiation. The spectra were recorded with a pass energy of 50 eV, an x-ray spot size of 300 μm, and a step size of 0.1 eV. To compensate the surface charging, the binding energy scale of each spectrum was shifted to set the oxide O 1s peak at 530.3 eV. This binding energy is found to be highly independent of the iron oxide type and can thus be used as a reference.³ The samples were transported in air into the XPS system, which caused some carbon contamination on the surface. In spite of this, the samples were not sputtered because, owing to the higher sputtering yield of oxygen compared to iron, sputtering would have changed the Fe/O ratio of the surface resulting in a decrease of the measured oxidation state of iron. AFM images were recorded in ambient conditions with a Digital Instruments Nanoscope III microscope operated in the non-contact mode. XRD measurements were performed with a Philips PW1830 spectrometer using Cu K_α radiation. All measurements were made at room temperature.

Table 1. Deposition parameters of the studied samples. The thickness of sample F was below the measurement range of the profilometer used

Sample	Temperature (°C)	Relative deposition time	Thickness (nm)
A	350	100	37
B	400	100	70
C	450	100	37
D	500	100	75
E	500	10	40
F	500	1	<10

RESULTS AND DISCUSSION

Figure 1 shows the Fe 2p XP spectra of the samples grown at 350–500 °C (samples A–D) and the corresponding XRD spectra are presented in Fig. 2. The 2p_{3/2} photoelectron peak is observed around 711 eV and there is a distinctive shake-up satellite around 719 eV. These features indicate that the films consist of Fe₂O₃.^{3–7}

From the XRD spectra it is observed that the crystal structure changes between 350 °C and 400 °C. The main peaks in the spectrum of sample A (350 °C) can be identified as those of γ -Fe₂O₃ whereas the spectra of samples B–D (400–500 °C)

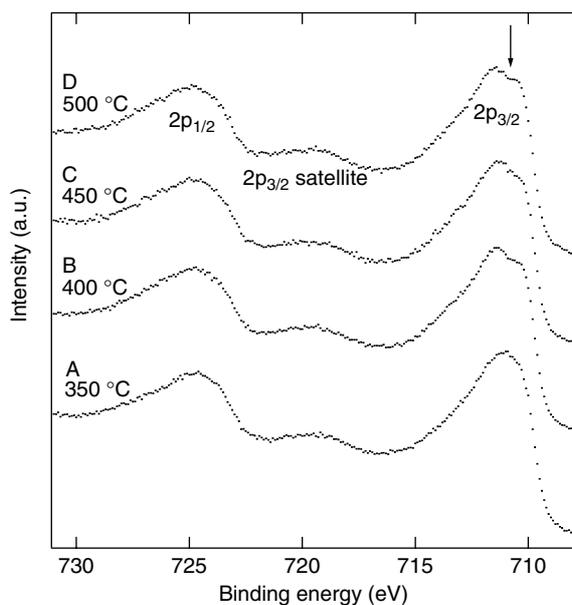


Figure 1. Fe 2p XP spectra of the samples grown at 350–500 °C (A–D). The arrow indicates a small step, characteristic to α -Fe₂O₃,⁶ in the low binding energy edge of the 2p_{3/2} peak of the samples grown at 400–500 °C. The sample deposited at 350 °C is interpreted as γ -Fe₂O₃.

correspond to α -Fe₂O₃.⁸ In addition to γ -Fe₂O₃ peaks, the XRD spectrum of sample A contains peaks that could result from a small amount of γ -FeOOH. This is reasonable because at the deposition temperature of 350 °C –OH groups can remain within the film. The change from γ -Fe₂O₃ to α -Fe₂O₃ is also supported by the photoelectron spectra: in the low binding energy side of the 2p_{3/2} peak a small step, shown by the arrow in Fig. 1, is observed in the spectra of samples B–D but not in the spectrum of sample A. According to Ref. 6, the step is characteristic for α -Fe₂O₃ and results from larger multiplet splitting of the 2p_{3/2} peak of α -Fe₂O₃ compared to γ -Fe₂O₃. A prominent difference was observed also in the valence band spectra (not shown) between samples A and B supporting the change from γ -Fe₂O₃ to α -Fe₂O₃.

The O 1s spectra (not shown) of samples A–D were similar and in accordance with the Fe₂O₃ O 1s spectra presented in the literature. The main peak corresponding to oxidic O²⁻ (530.3 eV) was accompanied with a weak shoulder at about 1.5 eV higher binding energy. This component is usually related to a small amount of OH⁻ caused by moisture in the air or non-stoichiometric surface oxygen.^{3–6} Distinction between Fe₂O₃ and FeOOH was confirmed using valence band spectra as outlined in Ref. 9.

Figure 3 presents the AFM images of samples A–C and F. The grain size is observed to increase from samples A (350 °C) to C (450 °C): the grain diameter in sample A is 80–180 nm, whereas the largest grains in sample C have a diameter of about 500 nm. A further increase in the deposition temperature (sample D) was not observed to produce larger grains.

The effect of the deposition time on the oxidation state of iron is seen by comparing the Fe 2p XP spectra of samples D, E, and F, presented in Fig. 4. As shown, e.g., in Refs 6, 7, 10 and 11, the 2p peaks of iron oxide cannot be deconvoluted with a single symmetric Gaussian/Lorentzian peak because strong multiplet splitting results in an asymmetric peak shape. Instead, a set of several closely spaced peaks should

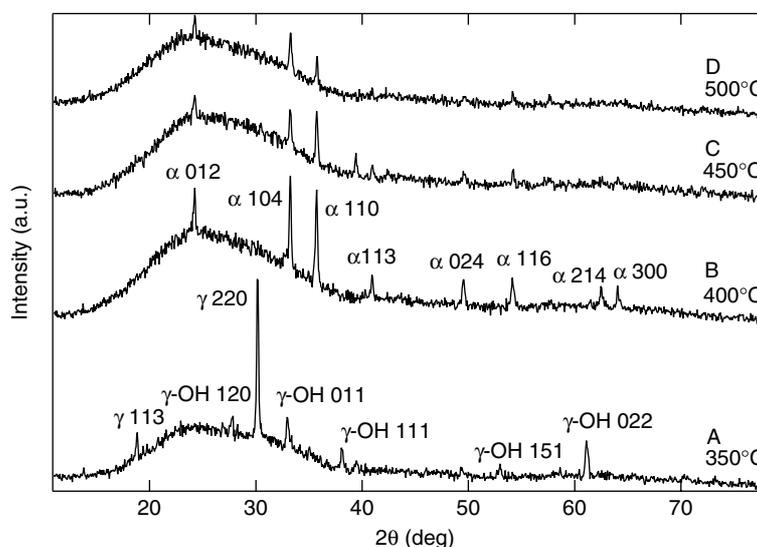


Figure 2. XRD spectra of the samples grown at 350–500 °C (A–D). The change from γ -Fe₂O₃ to α -Fe₂O₃ is observed to take place between 350 °C and 400 °C. The sample grown at 350 °C consists of γ -Fe₂O₃ and a small amount of γ -FeOOH. The peaks are identified according to Ref. 8.

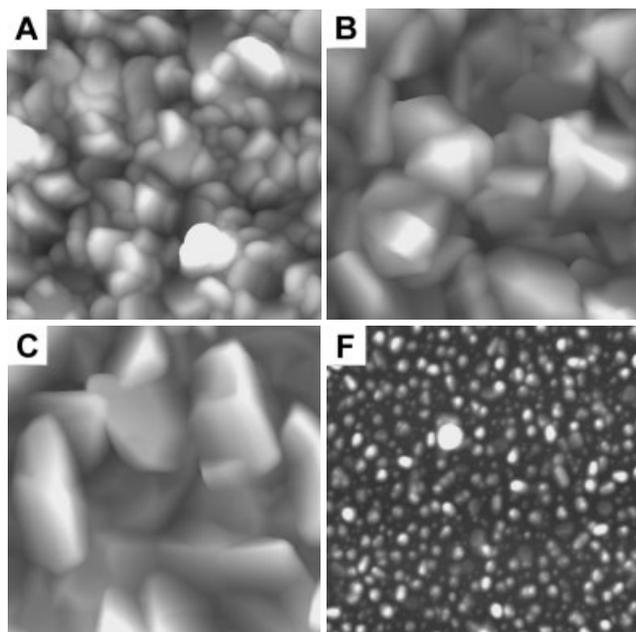


Figure 3. AFM images of samples A–C and F. The size of each image is $1 \times 1 \mu\text{m}^2$.

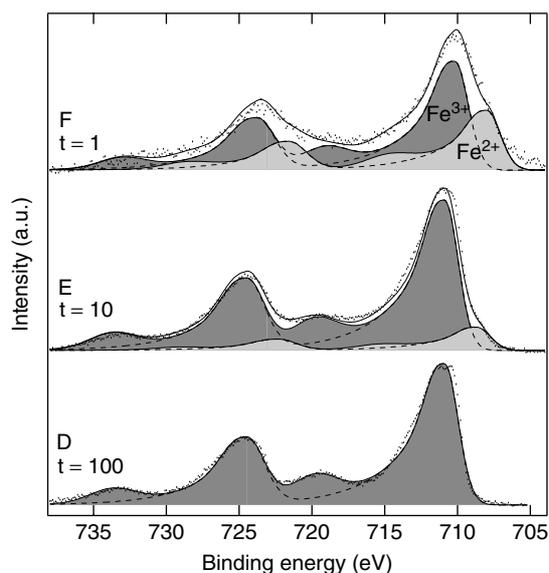


Figure 4. Fe 2p XP spectra of the samples D–F grown using different relative deposition times (t). The growth temperature is 500°C in all cases. A Shirley background is subtracted before the deconvolution. With decreasing deposition time, the relative amount of Fe^{2+} increases.

be used to represent the multiple final states of both $2p_{3/2}$ and $2p_{1/2}$ states. In this work, we used a simplified approach and presented the $2p_{3/2}$ and $2p_{1/2}$ peaks with one Gaussian peak accompanied with an exponential tail representing the sum of the multiple final states. A symmetric Gaussian peak was used for the shake-up satellites. A Shirley background¹² was subtracted from the spectra before the deconvolution although its physical model is considered somewhat incorrect.

Taking into account the XRD results and the spectral features, the 2p spectrum of sample D can be assumed to correspond to pure Fe^{3+} .^{3–7} This was used to find out the values for the peak parameters for the Fe^{3+} state, and the Fe^{2+} spectrum was constructed by changing only the peak position and the separation between the main and satellite peaks according to Refs 3–7. After the decomposition it is observed that sample E contains a small amount, and sample F a larger amount, of divalent iron. However, owing to the use of a simplified peak structure and background model, the deconvolution results have to be considered qualitatively. Probably a more accurate way to do the analysis would be that of Graat and Somers^{13,14} in which reference spectra of Fe^{2+} and Fe^{3+} are measured and a Tougaard background¹⁵ is subtracted to remove the contribution of inelastically scattered electrons.

AFM measurements showed that the grain size of sample E is about the same size as for sample D, but in sample F, shown in Fig. 3, the grains are significantly smaller (40–90 nm) and the substrate is seen between the grains.

CONCLUSIONS

Iron oxide thin films were grown by gas-phase deposition on a glass substrate in order to study the effects of deposition temperature and time on the film properties. The film grown at 350°C was observed to consist mainly of $\gamma\text{-Fe}_2\text{O}_3$ whereas higher temperatures resulted in formation of an $\alpha\text{-Fe}_2\text{O}_3$ film. The grain size was observed to increase between 350°C and 450°C . By decreasing the deposition time it was possible to grow films in which part of the Fe ions were in the divalent state.

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