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Conductivity threshold and kinetics of the phase transition in Fe_2O_3–Fe_3O_4 thin films made by chemical vapour deposition

I. A. SERBINOV*, G. A. NIKLASSON, C. G. GRANQVIST
Physics Department, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

Iron oxide films were made by chemical vapour deposition and annealing post-treatment. Optical and d.c. electrical measurements probed the $Fe_2O_3 \rightarrow Fe_3O_4$ transition. It could be understood as a thermally activated process, with an activation energy equal to the band-gap of Fe_2O_3. A.c. electrical data gave evidence against the transition being percolative.

1. Introduction and summary

This paper is devoted to iron oxide films made by chemical vapour deposition (CVD). The conductivity threshold and kinetics of the transition between Fe_2O_3 and Fe_3O_4 upon heat treatment is inferred from optical data and by d.c. and a.c. electrical measurements.

The kinetics of phase transitions is of great interest in basic physics and for many technical applications. Transformations associated with a delay time obeying an Arrhenius relation, with an activation energy given by the fundamental band-gap of the untransformed species, seem to be ubiquitous. Such transformations have been found to govern switching and breakdown in oxides of iron, chromium, nickel, silicon and aluminium [1], thermal reduction of V_2O_5 to VO_2 [2], and pyrolyzation of polyimide [3]. The main object of this work is to use d.c. electrical measurements and spectrophotometry to verify the correctness of this model also for the transformation from insulating and transparent α-Fe_2O_3 (haematite) to conducting and absorbing Fe_3O_4 (magnetite) during the heating of thin films prepared by CVD. It is known [4] that the transformation can be induced by vacuum annealing at ~450° C or by electron-beam exposure. As a further object of our work, we use a.c. electrical measurements to study the conductivity threshold of the phase transition.

Section 2 below describes the production of iron oxide thin films with different compositions by CVD followed by annealing post-treatment in a controlled atmosphere. Section 3 is devoted to d.c. electrical and optical data, from which the thermally activated transition from Fe_2O_3 to Fe_3O_4 was inferred. The kinetics was seen to be in agreement with earlier results, referred to above [1–3]. In Section 4 we discuss the a.c. conductivity and conclude that the phase transition could not be viewed in terms of simple percolation.

2. Samples

Iron oxide films can be produced by CVD using various procedures and chemicals [5]. In this work we used a three-step procedure: the first step involved CVD at atmospheric pressure, the second step comprised an oxidizing post-treatment, and the third step consisted in controlled reduction.

In order to carry out CVD we used iron acetylacetonate $Fe(C_5H_7O_2)_3$ powder heated to ~350° C in a glass reactor of volume 1 litre. The chemical was contained in a crucible put inside the reactor vessel, and deposition took place on a 76 mm × 26 mm glass substrate. A cover prevented non-gaseous products from leaving the crucible. After some initial heating, the entire reactor was filled with a brownish iron-containing vapour, whose decomposition yielded an even coating on the substrate. Typically, it took ~40 min to prepare a 0.1 to 0.2 μm thick film.

In the second step, coated substrates were heated in air at 400° C for 1 h with the purpose of preparing fully oxidized Fe_2O_3 films. The samples were then cut to ~10 mm × 20 mm in size.

As the third step in the sample preparation, we reduced the Fe_2O_3 films through annealing in a low vacuum (0.1 torr of air) at temperatures up to 460° C and for times as long as 4 h. In these latter experiments, the specimens were mounted on an electric heating element inside a vacuum chamber. Temperatures were controlled to ±5° C by a chromel–alumel thermocouple.

3. D.c. conductance and optical transmittance; kinetics of the $Fe_2O_3 \rightarrow Fe_3O_4$ transition

In earlier work, referred to in section 1 [1–3], it was found that the kinetics of various phase transitions could be understood in terms of a "delay time", after which strong changes in different physical properties take place. The delay time τ_d is given by a simple Arrhenius relation [1]

$$\tau_d = \tau_0 \exp(E/k_B t) \qquad (1)$$

where τ_0 is a reciprocal average phonon frequency, E

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* *Permanent address:* Institute of Radio Engineering and electronics, Academy of Sciences, Marx Avenue 18, Moscow, USSR.

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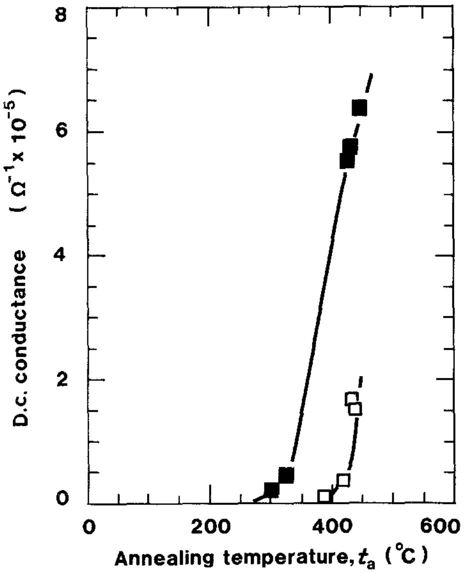

Figure 1 D.c conductance against annealing temperature for iron oxide films made by CVD. The conductance is valid for films with equal length and width. Annealing time τ_a = (□) 1 h, (■) 4 h. Curves are drawn solely to guide the eye.

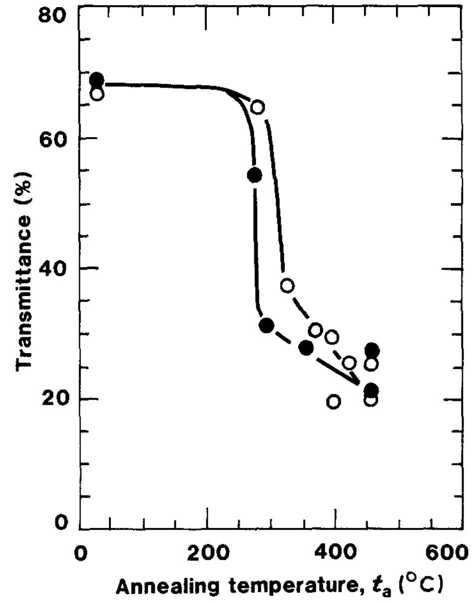

Figure 3 Transmittance at 600 nm wavelength against annealing temperature for iron oxide films made by CVD. Annealing time τ_a = (○) 25 min, (●) 120 min. Curves are drawn solely to guide the eye.

is an activation energy corresponding to the fundamental band-gap of the untransformed material, and $k_B t$ is Boltzmann's constant times the absolute temperature. The object of this section is to demonstrate that d.c. electrical as well as optical data for reduced Fe_2O_3 films can be reconciled with these notions.

Electrical d.c. conductance was measured at room temperature between silver paste contacts applied to the iron oxide films. Fig. 1 shows data for a set of samples annealed during a time τ_a between 1 and 4 h at a temperature t_a between 300 and 440° C. The change of the conductance is seen to take place in a narrow temperature interval. Extended annealing times and high annealing temperatures yield a large conductance, i.e. a partial conversion from Fe_2O_3 to Fe_3O_4.

Optical transmittance was recorded at room temperature by use of a Beckman Acta MVII spectrophotometer. Fig. 2 shows data in the $0.4 < \lambda < 0.75\,\mu m$ wavelength range for films annealed during 25 min at temperatures up to 460° C. At low t_a, strong absorption sets in at $\sim 0.6\,\mu m$. This corresponds to the thin film having a band-gap of ~ 2.1 eV, which is consistent with earlier results for Fe_2O_3 films [4, 6, 7]. After annealing at a high temperature, the absorption is increased substantially, which is indicative of a partial transformation to Fe_3O_4. The change in the transmittance is especially striking around $\lambda = 0.6\,\mu m$. Fig. 3 illustrates the transmittance at this particular wavelength as a function of annealing temperature at two annealing times. It is seen that the strong absorption sets in abruptly at about 280° C for τ_a = 120 min and at about 310° C for τ_a = 25 min.

In order to check the applicability of Equation 1, we plot conductance and transmittance against $k_B t_a \ln(\tau_a/\tau_0)$ with τ_0 set to 10^{-13} sec [1]. Fig. 4 shows that the transmittance and conductance converge

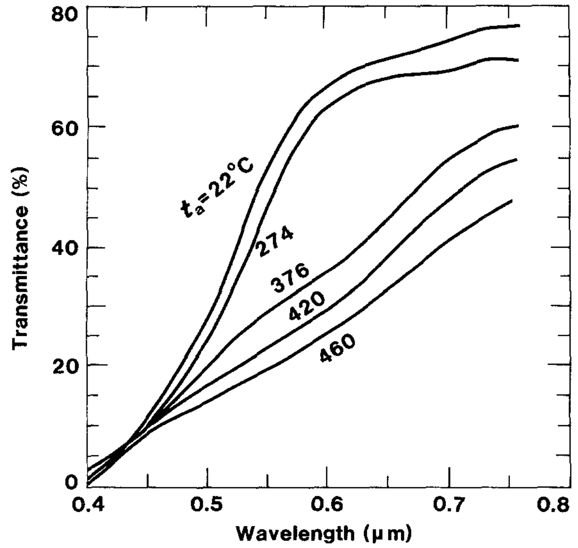

Figure 2 Spectral transmittance of iron oxide films made by CVD. Curves refer to samples annealed at various temperatures t_a and time τ_a = 25 min.

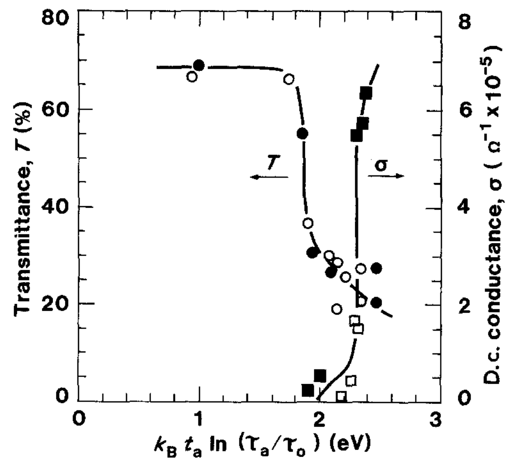

Figure 4 D.c. conductance (squares) and transmittance at 600 nm wavelength (circles) against $k_B t_a \ln(\tau_a/\tau_0)$. Annealing time τ_a = (○) 25 min, (□) 1 h, (●) 2 h, (■) 4 h. Curves are drawn solely to guide the eye. Note that different vertical scales pertain to transmittance and conductance, as indicated by the arrows.

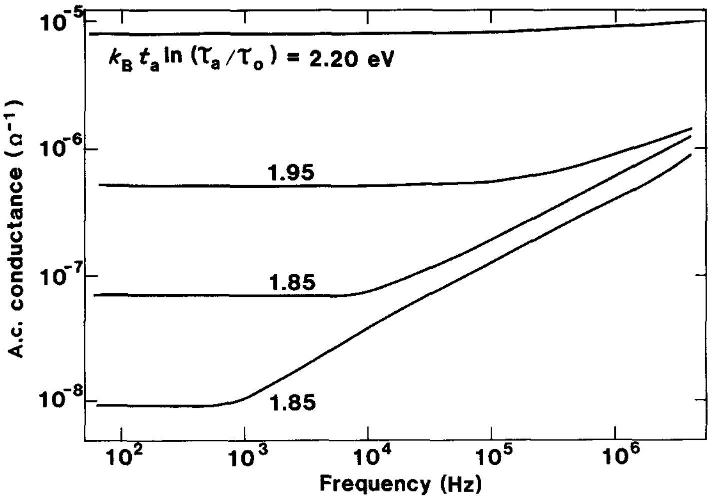

Figure 5 A.c. conductance against frequency for iron oxide films made by CVD. The conductance is valid for films with equal length and width. Curves refer to samples with different values of the parameter $k_B t_a \ln(\tau_a/\tau_0)$.

towards unique curves with strong variations when the parameter $k_B t_a \ln(\tau_a/\tau_0)$ takes on the values 1.9 and 2.3 eV, respectively. Now we put $\tau_d = \tau_a$ at the temperature t_a. It is then seen that the parameter E in Equation 1 is approximately equal to the band-gap of Fe_2O_3, which is consistent with earlier findings [1-3]. The fact that optical and electrical measurements yield somewhat different values of E is not surprising, since the transmittance probes the bulk of the films, whereas the rapid change of the conductance corresponds to a threshold at which the Fe_3O_4 phase forms an extended network throughout the specimen. Before percolation is reached, conductance may take place by hopping or tunnelling of electrons between Fe_3O_4 inclusions.

4. A.c. conductance

A.c. electrical measurements at room temperature were used to gain an increased understanding of the conductance threshold in the iron oxide films. Data were taken on samples, annealed at temperatures and times for which rapid changes in the physical properties take place, by the use of conventional techniques as described elsewhere [8].

Fig. 5 shows the a.c. conductance σ_{ac} at frequencies between 10^2 and 4×10^6 Hz for samples with the parameter $k_B t_a \ln(\tau_a/\tau_0)$ in the 1.85 to 2.20 interval, i.e. spanning the threshold range (cf. Fig. 4). The most conducting sample, with $k_B t_a \ln(\tau_a/\tau_0) \approx 2.20$, shows $\sigma_{ac} \sim 10^{-5}\,\Omega^{-1}$, with only a slight increase of the conductance towards higher frequency. The rest of the samples display conductances which are constant only at low frequencies and which increase monotonically for increasing frequency once a certain limiting frequency is exceeded. In the two least conducting samples, with $k_B t_a \ln(\tau_a/\tau_0) \approx 1.85$, the increase is by several orders of magnitude. Their conductance is seen to vary with frequency ω approximately as

$$\sigma_{ac} \propto \omega^n \qquad (2)$$

with $n \approx 0.5$.

Theoretically, a frequency dependence with $n = 0.5$ can be reconciled with diffusion of charge carriers into a semi-infinite volume [9]. Ordinary percolation theory [10, 11], on the other hand, predicts that the conductance should increase with frequency according to $n \approx 0.7$, i.e. more rapidly than found in the experiment. An entirely clearcut picture of the $Fe_2O_3 \rightarrow Fe_3O_4$ transition does not emerge from the a.c. conductance data, but it appears that the transition is not of a simple percolative character. Rather we envisage conduction within clusters, having a non-fractal structure, to dominate at high frequencies, whereas electron transfer across potential barriers separating the clusters accounts for the constant low-frequency conductance.

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