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Threshold behaviour for the electrical conductivity of V_2O_5 films reduced by heating *in vacuo*

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Thin V_2O_5 films were converted to VO_2 by heating *in vacuo*. The transformation is associated with a delay time which obeys an Arrhenius relation with an activation energy given by the bandgap of V_2O_5.

1. Introduction

This paper reports an investigation of the transformation of V_2O_5 to VO_2 in thin films subjected to heating. The main aim was to demonstrate that the transformation displays a threshold behaviour analogous to that which has been observed earlier for switching and breakdown in oxides of iron, chromium, nickel, silicon and aluminium [1], and for the pyrolisation kinetics of polyimide foil [2].

Several vanadium oxides are of considerable interest for basic studies of phase transformations as well as for technical applications related to electrical and optical devices [3–7]. In the present work we start with insulating V_2O_5 films which, according to known coexistence diagrams [8], must transform to VO_2 if heated *in vacuo* to a temperature above ~300° C.

The dioxide is metallic at temperatures exceeding ~70° C, and hence it is possible to study the transformation at elevated temperature by simple resistance measurements. Section 2 describes the preparation of samples. Data on the time-dependent conductivity at different temperatures are reported in Section 3. The time dependence exhibits threshold behaviour with a "delay time" which we find in Section 4 to obey an empirical Arrhenius-type relation.

2. Samples and measurement technique

Thin V_2O_5 films were prepared by thermal evaporation of 99.6% pure V_2O_5 powder from a VO_2-coated tantalum boat on to ordinary 1 mm thick glass slides. The type of glass is believed to be irrelevant for our results. The deposition rate was 0.5 to 1 nm $\sec^{-1}$. The pressure during the evaporation was $\sim 10^{-5}$ torr. As-deposited films had an amber yellow colour, which is characteristic of V_2O_5.

We investigated 150 nm thick films prepared as described above as well as 360 and 80 nm thick films which had been converted first to VO_2 by heating *in vacuo* and then back to V_2O_5 by a subsequent heating in air at 400° C for 2 h. Film thicknesses were determined using a mechanical stylus instrument (Tencor Alpha-Step with a stated accuracy of 2 nm).

In order to allow electrical measurements, we attached aluminium foil electrodes to the vanadium oxide films using silver paste. The distance between the electrodes was 5 to 15 mm. The samples were mounted on an electric heating element inside a vacuum chamber evacuated to ~0.1 torr. The heater could reach a stable temperature $\lesssim 400°$ C within ~10 min. Temperatures were determined to ±5° C by a chromel–alumel thermocouple. The relation between conductivity and temperature was measured continuously on a chart recorder (Watanabe MC 641).

3. Results

Fig. 1 shows electrical conductivity, σ, as a function of time, τ, at different temperatures for vanadium oxide films with three thicknesses. In all cases, the conductivity displays step-like changes when plotted on a logarithmic time axis. With one exception, the change occurs in a well-defined time interval. A certain delay-time, τ_d, can be uniquely defined as the time it takes to reach the maximum derivative in the shown relations between σ and τ. One curve (thickness 360 nm, temperature 420° C) yields a two-step behaviour which is probably caused by sample inhomogeneities. A high temperature and a small film thickness lead to a short delay time. We note that a threshold behaviour analogous to that observed here has been reported for V_2O_5 films subjected to ion bombardment *in vacuo* [9].

The overall conductivity change may be explained as follows. When a non-conducting V_2O_5 film is heated *in vacuo*, there will be a gradual increase in the density of oxygen vacancies. After some time, the vacancy density is so large that metallic VO_2 nuclei begin to form. When the metal fraction reaches the percolation threshold there will be a rapid transformation to a long-range metallic state. The conductivity in the metallic state is governed by electron scattering against defects whose type and abundancy depend on the treatment of the film. It is, therefore, not surprising that the films shown in Fig. 1 exhibit somewhat erratic conductivities.

The metallic state corresponds to the tetragonal

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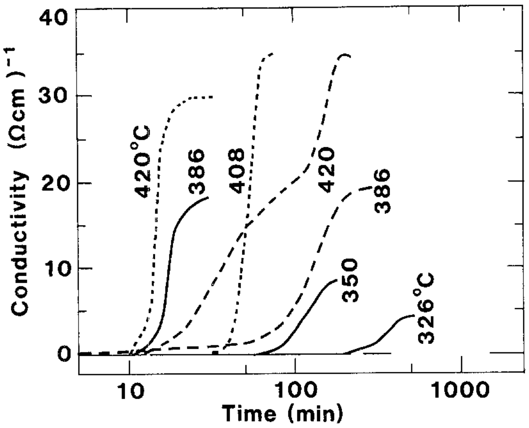

Figure 1 Time-dependent electrical conductivity for vanadium oxide films with thickness, *d*, of (----) 80 nm, (——) 150 nm, and (– – –) 360 nm. Measurements were conducted at temperatures between 420 and 326° C, as shown in the figure.

high-temperature phase of VO_2 which is clear from the fact that heat-treated films displayed the well known [3–7, 10] semiconductor–metal transition at ~ 70° C. This transition was most apparent in thick films annealed at high temperature.

The pre-threshold conductivity showed some interesting features, which are illustrated in Figs 1 and 2. The 360 nm thick films a showed a monotonic slow increase of conductivity with time before the rapid onset of conductivity, which is clearly seen in Fig. 1. For the 150 nm thick films, on the other hand, Fig. 2 shows an order-of-magnitude decrease of σ before the transition to a metallic state. An analogous behaviour was found for 80 nm thick films. The origin of these pre-threshold phenomena is not known.

4. Discussion and conclusion

We now analyse the delay time, τ_d, and show that it can be understood from the simple empirical expression

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

where τ_0 represents a reciprocal average phonon frequency, ΔE is an activation energy corresponding to the fundamental bandgap, and $k_B T$ is Boltzmann's constant times the temperature. An equation analogous to Equation 1 was shown earlier to describe the delay time for switching and breakdown in oxides of iron, chromium, nickel, silicon and aluminium [1], and the pyrolysation kinetics of polyimide foil [2]. Heuristic arguments in favour of the expression were given previously [1] and are not repeated here.

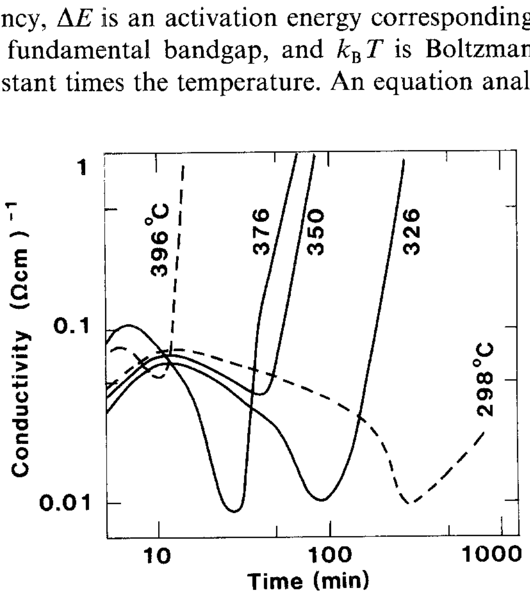

Figure 2 Time-dependent electrical conductivity for 150 nm thick vanadium oxide films. Measurements were conducted at temperatures between 396 and 298° C, as shown in the figure.

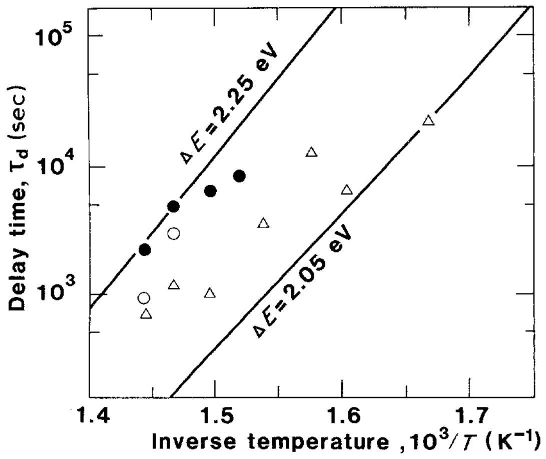

Figure 3 Delay time plotted against inverse temperature for vanadium oxide films with thicknesses, *d*, of (○) 80 nm, (△) 150 nm and (●) 360 nm. Straight lines were obtained from Equation 1 with $\tau_0 = 10^{-13}$ sec and ΔE as shown in the figure.

Fig. 3 shows log τ_d plotted against T^{-1} for several vanadium oxide films. The delay times were evaluated as mentioned above. However, the exact procedure for obtaining τ_d is not of importance for our arguments. Because of the scatter in the individual data points, it is not possible to extract an unambiguous activation energy. Therefore we use Equation 1 in the analysis, and set $\tau_0 = 10^{-13}$ sec. The lines in Fig. 3 were drawn with ΔE equal to 2.05 and 2.25 eV. By choosing these specific values, lines are obtained which pass through the most widely separated data points, and thus the experimental data can be reconciled with values of ΔE between these extrema.

The value of ΔE is not sensitive to the value assumed for τ_0. The fundamental absorption edge of V_2O_5 has been reported several times in the literature [11–13] and values between 2.3 and 2.36 eV for bulk specimens and between 1.95 and 2.18 eV for thin films have been stated. The excellent agreement between these absorption edges and the parameter ΔE in Equation 1 is striking. It is interesting to note that the bonding energy of the most weakly bound oxygen in metal oxides correlates well with the energy gap [14]. Presumably the transformation from V_2O_5 to VO_2 occurs by removal of the most weakly bound oxygen atom.

In conclusion, we have studied the transformation $V_2O_5 \rightarrow VO_2$ by electrical measurements on thin films. The transformation is associated with a delay time which is consistent with a simple Arrhenius relation with an activation energy given by the fundamental absorption edge of V_2O_5 and a prefactor corresponding to an average phonon frequency.

Acknowledgements

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