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Electrical conductivity of thermally grown titanium oxide films

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The *V–I* characteristics of thermally grown titanium oxide films on titanium are described and are explained using a model for current transport in the films.

1. Introduction

The structure [1–3], mechanism of oxide growth [4–6] and characterization [7–9] of titanium oxide have been studied extensively. It appears that titanium oxide films exhibit interesting electrical characteristics which can be exploited for electronic applications, e.g. memory switching [10–12]. In view of this, systematic investigations of thermally grown titanium oxide films have been carried out and these are described below.

2. Sample preparation

Titanium oxide was grown on titanium sheets 200 μm thick by thermal oxidation in air, steam or dry oxygen. Oxidation has been carried out at different temperatures in the range 600 to 1000° C for different durations ranging from 15 to 300 min. The oxide films which were initially insulating, were rendered semiconducting by reducing them partially through heating in a vacuum of $\sim 10^{-5}$ torr. Heating at 500° C for 300 min followed by annealing at 200° C for 350 min has been found to be optimum for partial reduction of the oxide. After this process, the oxide films were found to exhibit n-type conductivity. The oxide is then lapped on one side and contact is made with the titanium by using a conducting paint. Aluminium was deposited on the other side of the titanium oxide to serve as an electrode. The aluminium–titanium oxide–titanium overlay structure was subjected to a process of stabilization by repeatedly subjecting it to a voltage varying from 10 V to 200 V for a duration of 10 to 60 min, depending on the resistance of the specimens.

3. *V–I* characteristics

The *V–I* characteristics of all the stabilized samples were measured at different temperatures ranging from 25 to 100° C. Typical characteristics are shown in Fig. 1, from which it may be seen that the *V–I* characteristic is nonlinear at low voltages but tends to become linear at higher voltages. With increase in temperature, the characteristic then shifts towards lower voltages. Plots of log I against log V, shown in Fig. 2 are found to be linear, thus indicating that *V–I* can be represented by the relation

$$I = KV^{\alpha} \tag{1}$$

where α is the varistor nonlinearity factor. The value of α is found to vary between 1.5 and 2.5 in the temperature range for the samples studied. The variation of resistance of the samples with temperature, obtained from the measured *V–I* characteristics is shown in Fig. 3. It can be seen that the films exhibit negative temperature coefficients of resistance. From these characteristics, log R against $(1/T) - (1/T_0)$ variations have been plotted for all the samples. These plots, shown in Fig. 4, are also linear thus indicating that the films exhibit a resistance variation with temperature according to the relation

$$R = R_0 \exp\left[B\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2}$$

where B is the thermistor constant. The value of B obtained from these plots is found to lie in the range 100 to 400° K.

4. Current transport in titanium oxide films

The *V–I* characteristics described above can be explained by analysing the carrier transport in the titanium oxide film. It is proposed that the oxide film is polycrystalline in nature and that it is the transportation of carriers across the grain boundaries by a thermionic emission process which gives rise to the observed nonlinear *V–I* characteristics at low voltages. The linearity at high voltages can be attributed to the resistance due to the grain coming into series with the grain boundary.

To determine the validity of the conduction process for the oxide proposed above, an analysis has been carried out by taking a simplified model for the polycrystalline film. The film is assumed to consist of cubes of single-crystal grains surrounded by grain boundaries as shown in Fig. 5. Considering one grain and its grain boundary, the relation between the applied voltage, V, and the current, I, can be expressed as

$$V = V_g + Ir \tag{3}$$

where V_g is the voltage across the grain boundary and r is the bulk resistance of one grain.

If the oxide film is made up of n such elements in series and m such series in parallel then the total voltage, V_T, across the film can be expressed as

$$V_T = nV_g + I'R_s \tag{4}$$

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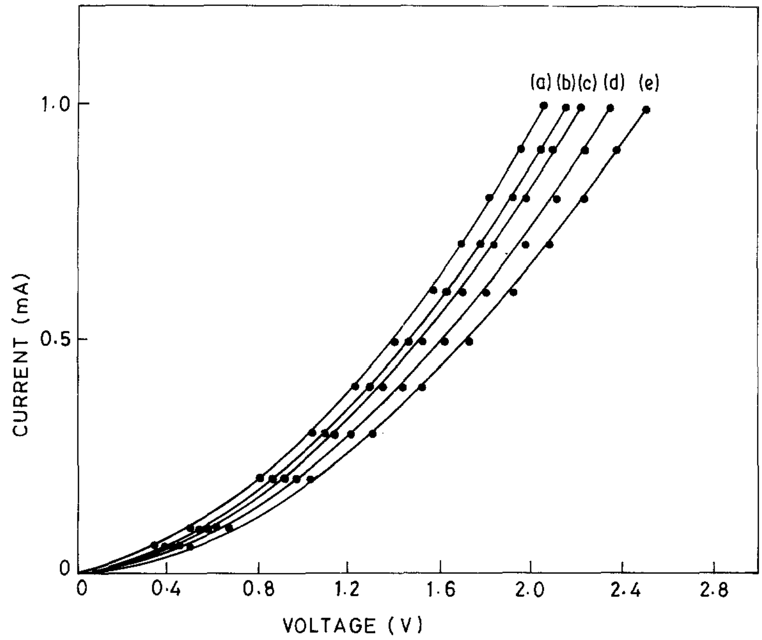

Figure 1 V–I characteristics of titanium oxide samples at different temperatures. Steam oxidation, 800° C, 300 min. T(° C) = (a) 100, (b) 90, (c) 80, (d) 60, (e) 40.

where R_s is the total resistance of the network given by $R_s = rn/m$, and I' is the total current through the film given by $I' = Im$. From Equation 4, V_g can be expressed as

$$V_g = \frac{V_T - I'R_s}{n} \qquad (5)$$

This voltage, V_g, determines the current transport across any grain boundary. The current across a boundary by thermionic emission can be expressed as

$$I' = aAT^2 \exp\left[-\left(\frac{V_B - eV_g}{KT}\right)\right] \qquad (6)$$

where A is a constant of thermionic emission, a is the cross-sectional area of current flow and V_B is the barrier potential at the grain boundary. Substituting for V_g from Equation 5, Equation 6 can be rewritten as

$$I' = aAT^2 \exp - \left[\frac{V_B - e(V_T - I'R_s)\,n}{KT}\right] \qquad (7)$$

This indicates that, from the measured V–I characteristics, the plot of log I' against $(V_T - I'R_s)$, should be linear. To obtain this variation, the value of R_s has been obtained from the V–I characteristics at high voltages at which the current is decided essentially

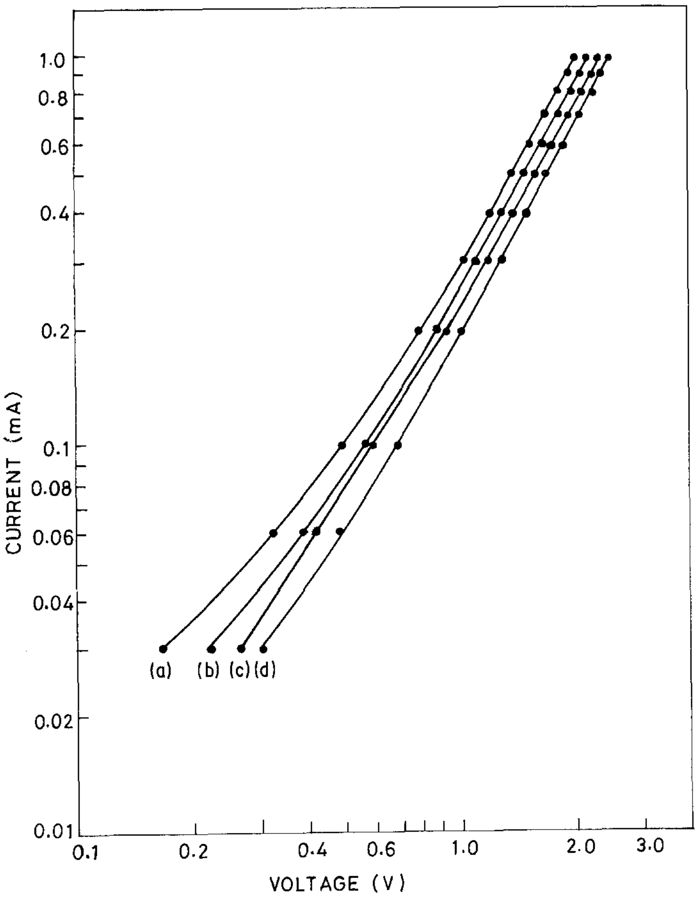

Figure 2 ln$V$–ln$I$ characteristics of titanium oxide plotted from the V–I characteristics. T(° C) = (a) 100, (b) 80, (c) 60, (d) 40.

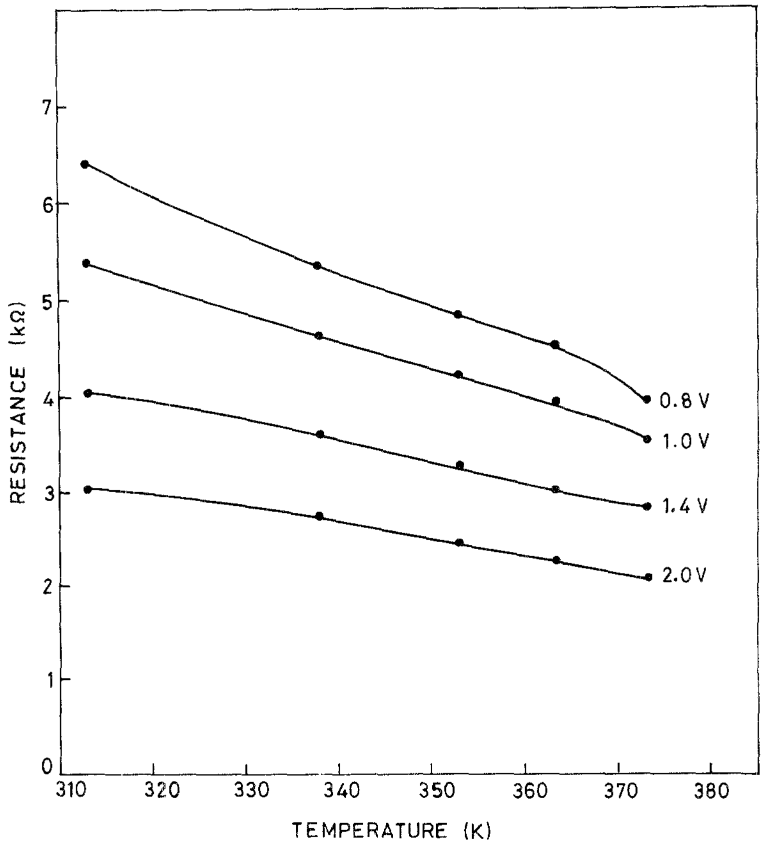

Figure 3 R–T characteristics at different voltages.

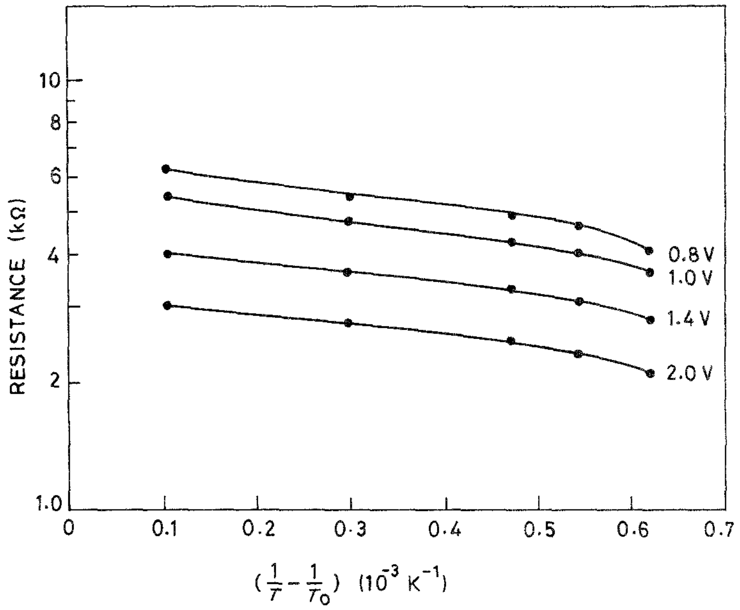

Figure 4 $\ln R$ against $(1/T) - (1/T_0)$ characteristics plotted from R–T characteristics.

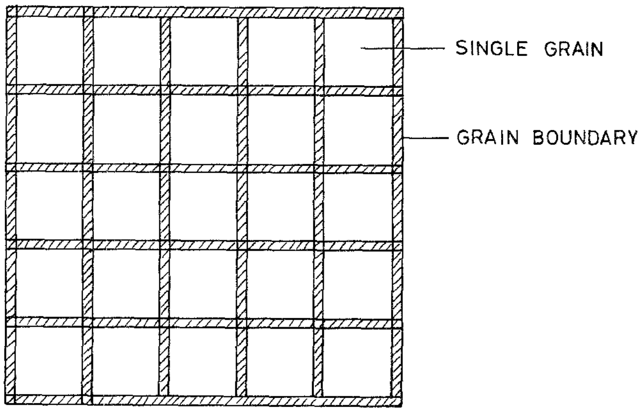

Figure 5 Structure of titanium oxide film assumed for analysis.

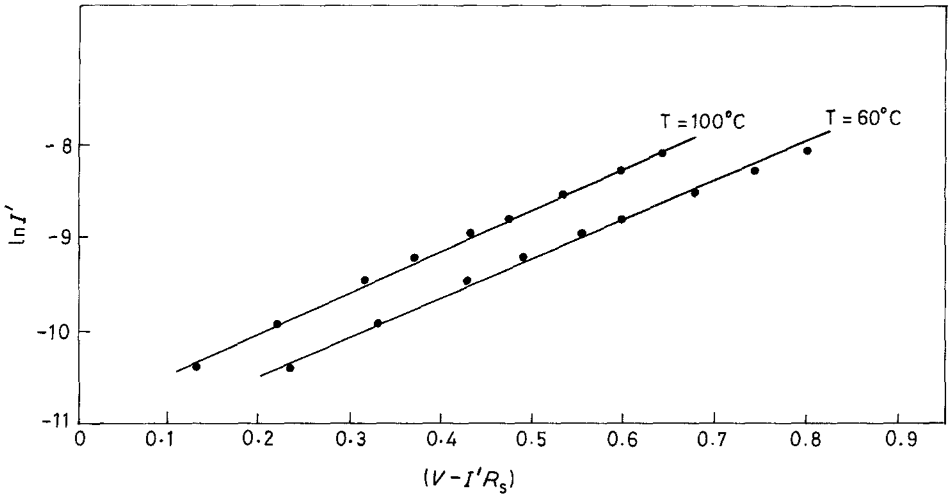

Figure 6 Plot of ln$I$ against $(V–I'R_s)$ at different temperatures.

by the bulk resistance. The plot of ln I' against $(V - I'R_s)$ obtained from the $V–I$ characteristics is shown in Fig. 6. From this figure, it may be seen that the plot is linear thus supporting the model proposed for the conduction in the oxide film. The effect of temperature on the observed $V–I$ characteristics is also explained by the proposed model, through the temperature dependence of the thermionic emission across the grain boundary.

The characteristics of thermally grown titanium oxide films reported here suggest that these can be useful as varistors and thermistors when the variation of resistance required is not very large.

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