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Thermopower measurements on SiO_x thin films

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Thermopower and d.c. electrical conductivity measurements have been carried out between 125 and 625 K on SiO_x thin films, 130 nm thick, deposited on to Corning 7059 substrates *in vacuo* $\simeq$ 1 mPa at 1.5 nm sec^{-1}. The thermopower, d.c. conductivity and their respective activation energies are fitted to a polynomial expression in $1/T$. Below 400 K, the thermopower is negative, at 400 K the thermopower activation energy is approximately zero and the dominant current carriers are holes at the valence band edge, between 400 and 470 they are polaronic holes, between 470 and 590 K non-polaronic holes, and above 590 K electrons. Energy band diagrams are proposed for each temperature range studied.

1. Introduction

Insulating thin films of SiO_x have been studied in detail for many years. The starting material is conventional evaporation is usually silicon monoxide, the structural formula of which is written SiO; this formula was also assumed to be applicable to the thin film material. However, investigations have indicated that (i) the starting material is probably a stoichiometric mix of silicon and some form of silicon oxide, such as β-chrystobolite [1, 2]; (ii) the unannealed thin film material is amorphous and is best described by the formula SiO_x with $1 \leqslant x < 2$ (x depends critically on the deposition conditions).

The exact values of x for the films discussed in this paper are unavailable at present but investigations are underway using a technique which has been applied successfully to GeO_x [3]. Basically, the Ge3d X-ray photoelectron spectroscopy (XPS) core spectra of reactively evaporated GeO_x thin films were simulated by assuming that, following oxidation, the primary coordination sphere consists of a germanium atom surrounded by either $-GeO_x$ groups, with the retention of a Ge–Ge bond, or $-OGeO_x$ groups into which an oxygen atom is inserted after a Ge–Ge bond is broken. Shifts in the binding energy of the Ge3d core spectra as the environment of the germanium atom alters are analysed using an electronegativity scale given by Sanderson [4].

Both low and high electric field conduction experiments have been investigated fully in SiO_x. Servini and Jonscher [5], for example, found that the mode of conduction is ionic at low electric fields and electronic at high fields. However, to our knowledge, one property of an evaporated SiO_x thin film which does not appear to have been discussed in the literature is its thermopower. Combined with a knowledge of the d.c. activation energy, the sign and magnitude of the thermopower gives essential information for establishing an energy band diagram for SiO_x.

2. Experimental procedure

Thin films of SiO_x (Union Carbide Ltd, select grade) having a planar geometry, 1.5 cm × 3.0 cm in size, were evaporated *in vacuo* $\simeq$ 1 mPa on to Corning 7059 borosilicate glass substrates, cleaned by conventional techniques, and maintained at 293 K during deposition. The electrodes were of aluminium. Both the film thickness ($\simeq$ 130 nm) and the deposition rate ($\simeq$ 1.5 nm sec^{-1}) were monitored using a calibrated quartz crystal oscillator unit. The thermopower was measured between 200 and 625 K and the d.c. electrical conductivity between 125 and 525 K. The circuitry has been discussed fully in a previous paper [6] and will not be considered further here. Noise signals are a problem when measuring Seebeck voltages in high-resistive films, such as SiO_x. Each individual measurement may be subject to an error $\simeq$ 20%.

Preliminary experimentation determined that current levels were enhanced under daylight conditions. Typically, the Seebeck voltage was about 5% higher than the "dark" value. Hence, all the results presented here were made under dark conditions.

3. Results

The relative thermopower, S, of a deposited SiO_x planar structure is defined in terms of the absolute thermopowers $S(SiO_x)$ and $S(Al)$, respectively, of the oxide film and electrode material by

$$S = S(SiO_x) - S(Al) \qquad (1)$$

We have determined $S(Al)$ to be $-40\,nV\,K^{-1}$, which is very small compared with the measured values of S. Hence it is reasonable to put

$$S \simeq S(SiO_x) \qquad (2)$$

Fig. 1 depicts the variation of S with the mean substrate temperature, T. It can be seen that S is: (i) negative below 300 K, increasing to about $-6000\,\mu V\,K^{-1}$ at 200 K; (ii) positive between 300 and 580 K, which

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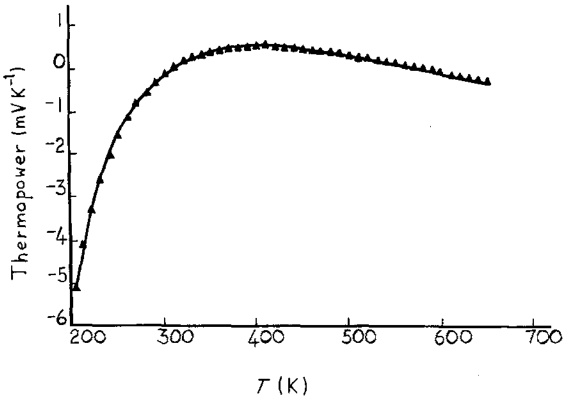

Figure 1 Variation of the thermopower of SiO_x thin films with mean temperature.

implies that the dominant charge carriers are positive holes; (iii) thermally activated between 400 and 650 K; (iv) negative above 580 K.

The results presented in Fig. 1 can be expressed in terms of a polynomial in $1/T$, i.e.

$$S = A + B/T + C/T^2 + \cdots + \quad (3)$$

where $T = (T_1 + T_2 + T_s)/3$; T_1 is the source temperature, T_2 is the sink temperature and T_s is the substrate temperature. The activation energy, $E_s(T)$, is given by

$$E_s(T) = \mathrm{d}S/\mathrm{d}(1/T) = B + 2C/T \quad (4)$$

A reasonable fit with the experimental results occurs with: $A = -5.09 \times 10^{-3}\,\mathrm{V\,K^{-1}}$, $B = 4.57\,\mathrm{V}$, $C = -928\,\mathrm{V\,K}$. The variation of $E_s(T)$ with T is displayed in Fig. 2; 4.57 eV is the asymptotic value of $E_s(T)$ at high temperatures.

As the variation of S with temperature T is known, both the Peltier coefficient, π, and the Thomson coefficient, τ, can now be calculated. π is related to S and T through

$$\pi = ST \quad (5)$$

Hence, using Equation 3, we have

$$\pi = -5.09 \times 10^{-3}\,T + 4.57 - 928/T \quad (6)$$

Fig. 3 shows that π has a maximum value of about 0.22 V around 420 K. The Thomson coefficient, τ, is given by

$$\begin{aligned}\tau &= T\,\mathrm{d}S/\mathrm{d}T \quad (7)\\ &= -4.57/T + 1856/T^2\end{aligned}$$

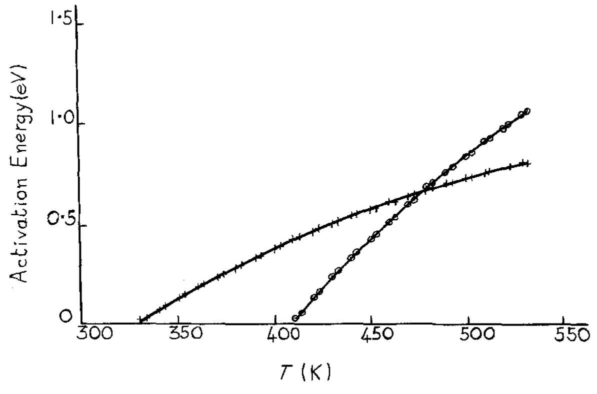

Figure 2 Variation of (○) thermopower activation energy and (×) d.c. activation energy with mean temperature.

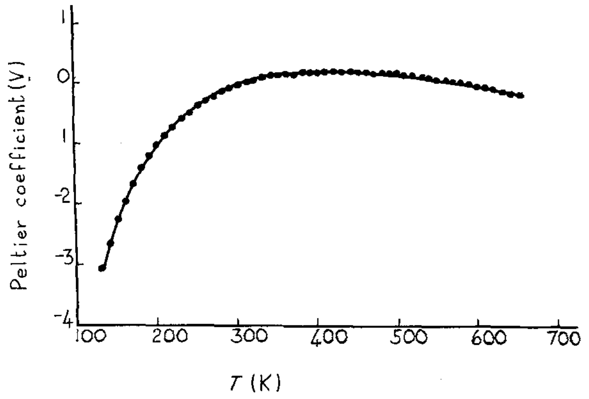

Figure 3 Variation of Peltier coefficient with mean temperature.

It can be seen from Fig. 4 that τ decreases smoothly with increase in temperature, changing sign at 400 K, the temperature at which S is a maximum.

The variation of the d.c. electrical conductivity, σ, with $1/T$ is depicted in Fig. 5. It shows that σ falls rapidly between 530 and 330 K and then remains constant in value down to about 120 K. Therefore, σ cannot be represented by the usual Arrhenius-type relation in which the activation energy, $E_\sigma(T)$ is single valued. $E_\sigma(T)$, plotted in Fig. 2, was obtained by determining the slope of ln σ at various temperatures.

We propose that a more appropriate expression for σ is

$$\ln\sigma = \ln[ec(E)\mu(E)] - A'/kT + B'/kT^2 - \ldots \quad (8)$$

where e is the electronic charge, $c(E)$ is the carrier concentration and A' and B' are constants. The temperature-dependent activation energy, $E_\sigma(T)$, may now be determined to be $(A' - 2B'/T)$. A reasonable fit with the experimentally derived values of $E_\sigma(T)$ may be obtained if A' is equal to 2.13 eV and B' is 349 eV K. Then

$$E_\sigma(T) = 2.13 - 698/T \quad (9)$$

4. Discussion

As can be seen from Fig. 1, the demarcation temperature between positive and negative values of S is about 300 K. The negative region requires further investigation because although the results seem to suggest that a phonon-drag component is adding to a diffusion component S_d to give the measured thermopower S, this explanation is doubtful because the films are amorphous.

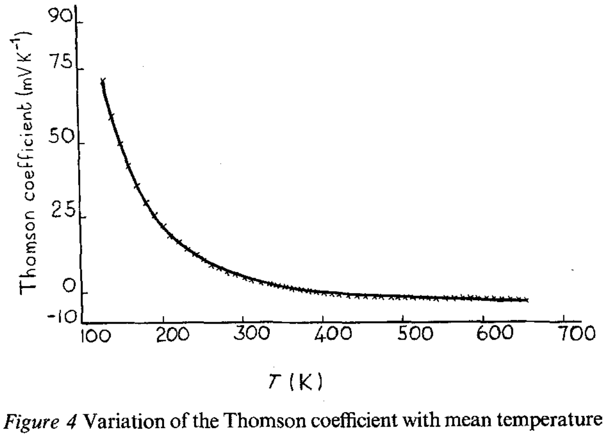

Figure 4 Variation of the Thomson coefficient with mean temperature.

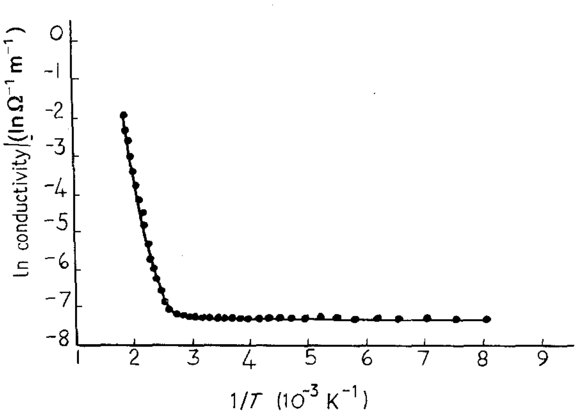

Figure 5 Variation of the d.c. conductivity, σ, with reciprocal of the substrate temperature.

At 400 K, S_d is positive and $E_s(T)$ is close to zero, with respect to the valence band. This suggests that hole conduction is occurring (with the Fermi level practically coincident with the valence band edge). Between 400 and 473 K, S_d is activated and $E_\sigma(T)$ is greater than $E_s(T)$, which, following Mott and Davis [7], implies that polaronic holes are the dominant current carriers. Between 473 and 590 K, S_d is positive and $E_s(T)$ is now greater than $E_\sigma(T)$ – the current carriers are non-polaronic holes. Above 590 K, conduction is mainly by electrons because the sign of the thermopower is now negative.

Shabalov and Feldman [8] have carried out a.c. conductivity measurements on SiO_x thin films. They concluded that the charge carriers are a mixture of hopping holes and polarons. Steele and Beynon [6] observed small polaronic hole conduction in Au/SiO_x thin cermet films (16 vol % Au) between 330 and 510 K.

We suggest that a three-carrier conduction model is essential for explaining results in SiO_x. This model has been used by Kishimoto and Morigaki [9] with amorphous Si/Au and by Beyer and Stuke [10] with amorphous germanium. In general, the measured thermopower, S, is the sum of the individual thermopowers, S_i, generated by each carrier multiplied by an appropriate weighting factor, σ_i, expressed in terms of the d.c. conductivity. That is

$$\begin{aligned} S &= \Sigma\sigma_i S_i/\Sigma\sigma_i \\ &= (\pi^2 k^2 T/3e)\,[(\delta \ln \sigma/\delta E)_{E=E_F}]\,(\sigma_F/\sigma_{tot}) \\ &\quad + (k/e)\,\{[E_F(T) - E_v)]/kT + A_v\}\,(\sigma_h/\sigma_{tot}) \\ &\quad - (k/e)\,\{[E_c - E_F(T)]/kT + A_c\}\,(\sigma_e/\sigma_{tot}) \end{aligned} \qquad (10)$$

The first term is the contribution to the thermopower of holes at the Fermi level, i.e. at the valence band edge, the second term is the contribution of holes in the acceptor localized states and the third term is the contribution of electrons in donar-localized states.

A set of energy-band diagrams can now be constructed to show the movement of the Fermi level with temperature. As $E_s(T)$ in Fig. 2 tends to zero below 400 K, we may infer that the Fermi level is coincident with the valence-band edge at such temperatures (see Fig. 6a). Then as the temperature increases, the Fermi level rises until at 480 K (Fig. 6b) we find that $[E_F(T) - E_v]$ is equal to $[E_A(T) - E_v]$, where $E_A(T)$ is the bottom of the band of acceptor states. At 500 K $E_\sigma(T)$ is 0.73 eV and $E_s(T)$ is 0.85 eV, which means that the width of the acceptor energy distribution can be calculated to be 0.12 eV (Fig. 6c). Our value for $E_\sigma(T)$ agrees fairly well with that obtained by Morley *et al.* [11] between 297 and 410 K. The position of the Fermi level at $T \rightarrow \infty$ is shown in Fig. 6d. The energy band gap has the value of the constant B in Equation 4 whilst the position of the impurity conduction band relative to the top of the valence band is equivalent to constant A' in Equation 8. The rapid variation in E_F with temperature, and the slower variation in $E_A(T)$, are surprising. Therefore, the energy band diagrams should be regarded as preliminary attempts only at this stage. An improvement in the thermopower signal : noise ratio will help to elucidate the conduction process further.

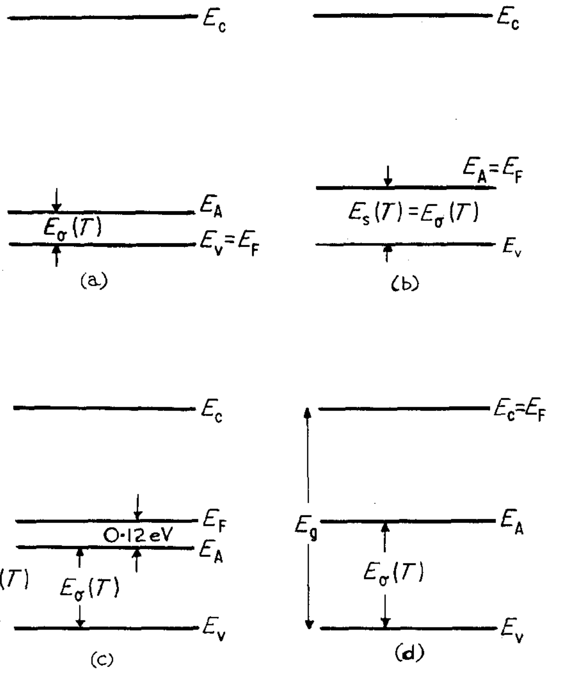

Figure 6 Energy band diagrams for SiO_x at different temperatures: (a) < 410 K, (b) 480 K, (c) 500 K, (d) $T \rightarrow \infty$.

Al-Ani *et al.* [12] determined the optical energy gap, E_{opt}, to be 2.5 eV for an R/P ratio $\simeq 9 \times 10^3$ nm sec^{-1} Pa^{-1}. Thus the mobility gap, assumed to be 2 E_{opt}, is about equal to 5 eV, which is in reasonable agreement with Fig. 6d. The difference in the values can be attributed to variations in the deposition conditions in the two cases.

According to Hübner [13], the energy gap $E_g(x)$ of SiO_x depends on the value of x. He obtained the following equation, which relates $E_g(x)$ (eV) to x

$$E_g(x) = 2.5 + 6.25x - 1.5x^2 \qquad (11)$$

For our SiO_x films, and using the value of 4.57 eV for E_g obtained with the help of Equation 4, we calculate x to be 0.36. That is, our films are deficient in oxygen. The major uncertainty with this calculation lies in whether Equation 11 can be applied in a universal way, as the exact form of the expression will obviously depend on the deposition parameters.

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