

Conduction mechanisms deduced from thermoelectric power and direct-current conductivity measurements in co-evaporated Mn/SiO_x thin films

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The thermoelectric power and direct-current (d.c.) conductivity of co-evaporated Mn/SiO_x films deposited at the rate of 0.5 nm s⁻¹, 100 nm thick and containing 1, 3 and 5 at% Mn have been measured over the temperature ranges 258–588 K and 110–575 K, respectively. Thermoelectric power and d.c. conductivity measurements suggest that, over the temperature range 258–360 K, conduction occurs by hopping due to delocalized electrons at the Fermi level and electrons in donor localized states, intrinsic over the temperature range 360–558 K and metallic like above 558 K. The d.c. conductivity is activated over the whole temperature range investigated.

1. Introduction

Thermoelectric power measurements provide the most reliable information about the nature of charge carriers and together with the direct-current (d.c.) conductivity allow the conduction mechanisms operative in the films to be investigated.

There are two basic methods of measuring the Seebeck coefficient or relative thermoelectric power: integral and differential methods [1, 2]. In the integral method, the temperature of one junction of the sample is held at a fixed temperature, T_0 (≈ 273 K), whilst the temperature, T_h , of the other junction is varied and the Seebeck voltage is measured. By convention, the Seebeck voltage is measured with respect to the hotter junction. The Seebeck coefficient or relative thermoelectric power at a selected temperature, T , can be obtained from the slope of a Seebeck voltage, V , versus T_h graph. Large thermal gradients are an inherent feature of this method. This means that samples of an extended length (about 3–5 cm) must be used. However, as the length of the sample increases, the resistance also increases. The higher concentration of SiO_x also produces highly resistive films (as in the present study). It is difficult to measure the Seebeck voltage accurately, especially at higher temperatures, owing to the loading error of electrometer. Therefore, thermoelectric power measurements are carried out using a differential method. In this method, a small thermal gradient ΔT ($= T_1 - T_2$) is applied across a short (1–2 cm) sample and gives rise to the Seebeck voltage. In this method, ΔT is kept constant whilst T_1 and T_2 are varied. The relative thermoelectric

power or Seebeck coefficient is obtained from the slope of the graph of the Seebeck voltage, V , versus mean temperature T ($= (T_1 + T_2)/2$).

There are various techniques for preparing thin films: thermal evaporation; single-boat evaporation; co-evaporation; sputtering; electron-beam evaporation; flash evaporation; sputtering (d.c., radio-frequency, magnetron, etc.) The characteristics of thin films strongly depend upon the deposition technique used to prepare them, their composition and deposition parameters, such as deposition rate, substrate temperature, thickness and pressure. The co-evaporation technique [3] for the fabrication of thin films for mixing two dielectric oxides is preferred over films prepared by single-boat evaporation. The deposition parameters can be closely controlled with this technique and, as a result, the film properties are more reproducible.

In our previous papers, thermoelectric power and d.c. conductivity measurements on co-evaporated Mn/SiO_x films for various compositions, 10 at% Mn [4] and 20–100 at% Mn [5], have been published. In 10 at% Mn films [4], below 500 K, conduction occurs by electron hopping whereas hole conduction dominates above 500 K. In 20–100 at% Mn films [5], three conduction regions have been identified: firstly, p type, via non-polaronic holes and small polarons, secondly intrinsic and thirdly metallic.

In this paper we present the results of thermoelectric power and d.c. conductivity measurements on co-evaporated Mn/SiO_x films containing a higher concentration of SiO_x and also conduction mechanisms operative in these films.

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2. Experimental procedure

Mn/SiO_x films of various compositions (1, 3 and 5 at% Mn) were deposited on Corning 7059 alkali-free aluminosilicate glass substrates *in vacuo* (about 1 mPa) from two tantalum boat-shaped filaments by co-evaporation [3] using 99.9% pure manganese flakes (Johnson and Matthey, Materials Technology, UK) and 99.9% pure select grade vacuum-baked silicon monoxide powder (Aldrich, UK). The thermoelectric power samples had a planar geometry, 1.0 cm × 1.2 cm in size, whereas d.c. conductivity samples possessed a van der Pauw clover-shaped geometry with an active region of 0.3 cm × 0.3 cm.

The deposition rate for the Mn and SiO_x sources and film thickness were controlled using two calibrated quartz crystal oscillators. The mean deposition rate was 0.5 nm s⁻¹ and the film thickness of all samples was 100 nm, as measured by multiple-beam interferometry with an Ångströmer (Sloan instruments model M – 100), and checked using an Alpha-step Research and Development profilometer (model 200, Tencor instruments, UK). Aluminium was used as the electrode material in all cases.

The thermoelectric power, *S*, was measured using a differential technique [1] *in vacuo* (about 1 mPa) in the temperature range 258–588 K. The Seebeck voltage was measured using a Keithley 617 programmable digital electrometer with an input resistance of about 200 TΩ. A temperature difference of 10 K was maintained across the sample. Four values of the Seebeck voltage were measured by altering the direction of the temperature gradient and reversing the polarity of the electrometer; an average value was obtained and *S* calculated from the slope of a Seebeck voltage versus mean temperature graph. The d.c. conductivity measurements were performed using the standard van der Pauw [6] technique *in vacuo* (about 1 mPa) in the temperature range 110–575 K. In order to remove defects and to obtain consistent values, temperature cycling was repeated until the thermoelectric power and d.c. conductivity variation was reversible. The

reproducibility of the results was confirmed by repeating measurements on various samples of the same composition, prepared under identical conditions. The atomic concentration of Mn and the degree of oxidation in the films was determined using X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded *in vacuo* (better than about 0.27 μPa) with a VG Escalab 210 spectrometer (Fisons Surface Science) using Al Kα (1486.6 eV) radiation. Charge correction of the data was performed by referring to the C 1s peak at 284.6 eV. The samples were analysed immediately after evaporation to keep surface contamination to a minimum.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

A typical X-ray photoelectron spectrum of co-evaporated Mn/SiO_x films containing 5 at% Mn and 100 nm thickness is shown in Fig. 1. The presence of the C 1s peak most probably arises from back-scattering by rotary pump oil vapours during deposition. The core level spectra for the Mn 2p doublet, Si 2p and O 1s peaks are shown in Fig. 2a, b and c, respectively.

Values of the core level binding energies are listed in Table I. It can be seen that there is no obvious systematic dependence on composition. The binding energies of the Si 2p_{1/2} peak lie in the range 102.2–102.8 eV. These values do not agree with the corresponding values for either SiO (101.2 eV) or SiO₂ (103.4 eV) [7–9]. This indicates that there is a higher atomic proportion of oxygen in the films than in silicon monoxide. The ratio of atomic concentration of oxygen to silicon oxide was calculated to be 1.8; the oxide is best represented by the formula Si₅O₉.

3.2. Thermoelectric power and d.c. conductivity

The relative thermoelectric power, *S*, between a co-evaporated Mn/SiO_x thin film and an Al contact may

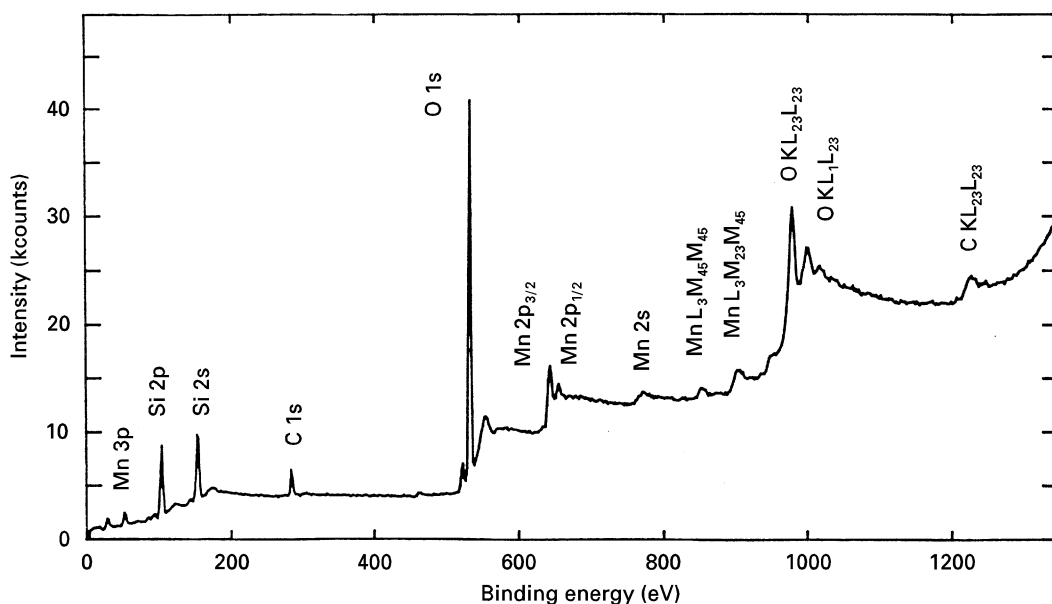


Figure 1 X-ray photoelectron spectrum for co-evaporated Mn/SiO_x film (5 at% Mn; 100 nm thick; deposited at 0.5 nm s⁻¹).

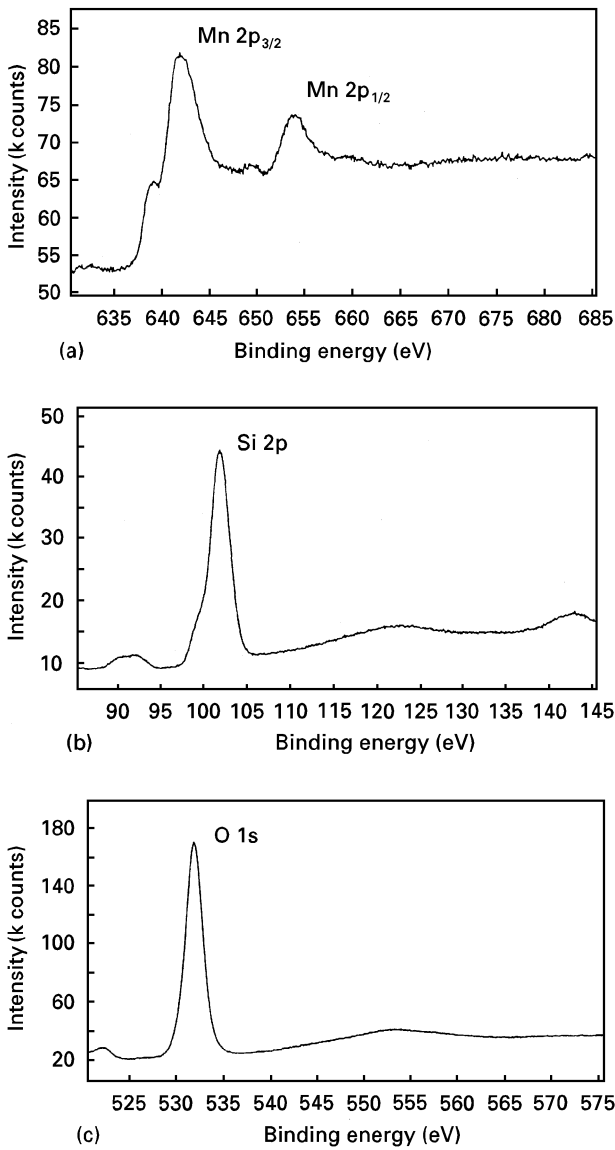


Figure 2 Narrow XPS scan for co-evaporated Mn/SiO_x film (5 at% Mn; 100 nm thick; deposited at 0.5 nm s⁻¹): (a) Mn 2p_{3/2} and 2p_{1/2} peaks; (b) Si 2p peak; (c) O 1s peak.

TABLE I XPS core-level binding energies of various compositions of co-evaporated Mn/SiO_x films

Mn (at%)	XPS core-level binding energy (eV)			
	Mn 2p _{1/2}	Mn 2p _{3/2}	Si 2p	O 1s
1	653.8	641.9	102.8	532.0
3	653.6	641.5	102.7	531.7
5	654.2	642.3	102.2	532.0

be equated with the absolute thermoelectric power of the film because S_{A1} is negligibly small (-40 nV K⁻¹) compared with the experimentally determined values. Fig. 3 shows how S varies with mean sample temperature, T , for various compositions. S displays three quite distinct temperature characteristics.

(i) S is small, negative and relatively independent of temperature between 258 and 360 K, approaching -25 , -15 and -10 μ V K⁻¹ in 1, 3 and 5 at% Mn films, respectively, indicating that the dominant charge carriers are hopping electrons.

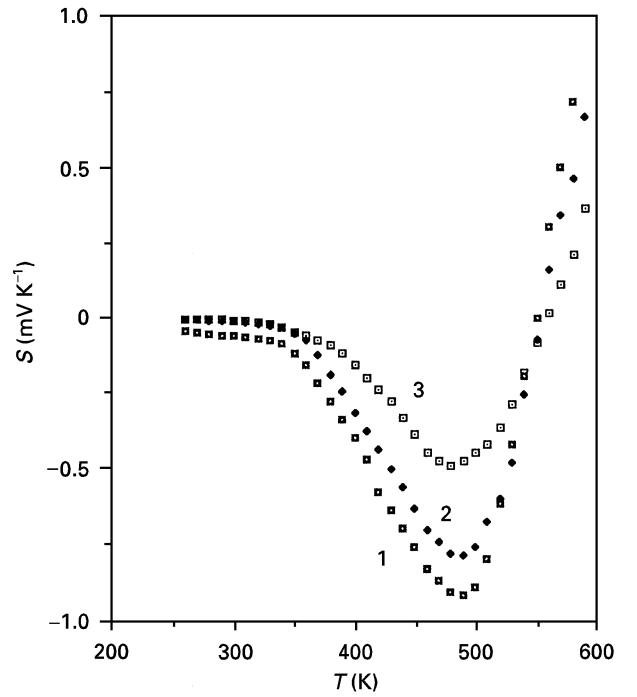


Figure 3 Variation in thermoelectric power, S , with temperature, T , for various compositions of co-evaporated Mn/SiO_x films (100 nm thick; deposited at 0.5 nm s⁻¹): data 1, 1 at% Mn; data 2, 3 at% Mn; data 3, 5 at% Mn.

(ii) S increases negatively above 360 K, attaining values of -0.9 , -0.8 and -0.5 mV K⁻¹ at 488, 488 and 478 K in 1, 3 and 5 at% Mn, respectively, and above 488 K in 1 and 3 at% Mn and 478 K in 5 at% Mn; S increases positively becoming zero ($p > n$) at 558 K, indicating that intrinsic conduction is occurring.

(iii) Above 558 K, S increases positively ($p \geq n$) with increasing temperature to about 0.95, 0.65 and 0.35 mV K⁻¹ at 588 K, in 1, 3 and 5 at% Mn, respectively, indicating that the dominant charge carriers are holes and that metallic-like behaviour occurs.

Fig. 4 gives the corresponding variation in the d.c. conductivity σ with temperature between 293 and 575 K for 1 at% Mn and between 110 and 575 K for 3 and 5 at% Mn; σ increases with increasing temperature for all compositions over the whole temperature range.

3.3. Conduction mechanisms

3.3.1. Hopping conduction

A negative, small and fairly constant thermoelectric power below 360 K suggests that delocalized electrons and electrons in donor localized states dominate the conduction process and that conduction occurs by electronic hopping. Table II lists the temperature range over which hopping conduction is occurring in Mn/SiO_x films (obtained from Fig. 3). Zaidi *et al.* [4] found that the thermoelectric power (in microvolts per Kelvin) in 10 at% Mn films can be expressed as a polynomial in T , having the form

$$S = -5.7 + 4.2 \times 10^{-2} T - 1.0 \times 10^{-4} T^2 + 8.3 \times 10^{-8} T^3 \quad (1)$$

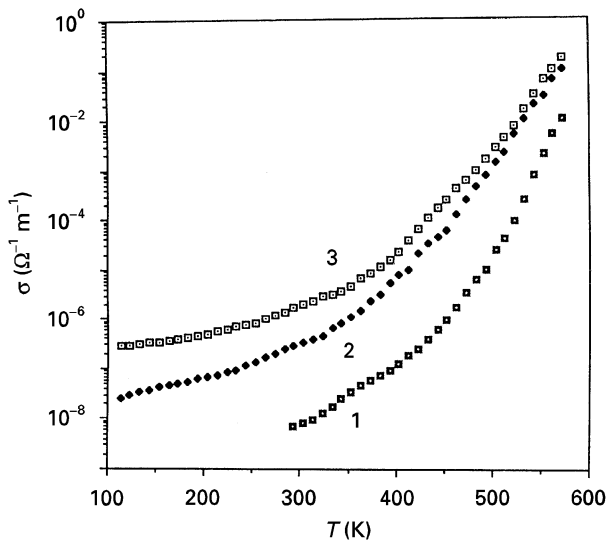


Figure 4 Variation in d.c. conductivity, σ , with temperature, T , for various compositions of co-evaporated Mn/SiO_x films (100 nm thick; deposited at 0.5 nm s⁻¹): data 1, 1 at% Mn; data 2, 3 at% Mn; data 3, 5 at% Mn.

TABLE II Hopping, intrinsic and metallic conduction in various compositions of co-evaporated Mn/SiO_x thin films over various temperature ranges

Mn (at%)	Temperature range (K)		
	Hopping conduction	Intrinsic conduction	Metallic-like conduction
1	258–360	360–558	>558
3	258–360	360–558	>558
5	258–360	360–558	>558

The observed behaviour of the thermoelectric power in this compositional region suggests that three conduction processes may be occurring over the temperature range investigated, represented by

$$S = \frac{\sigma_p S_p - \sigma_e S_e + \sigma_h S_h}{\sigma_h + \sigma_e + \sigma_p} \quad (2)$$

The term $\sigma_h S_h$ in Equation 2 is important because it shows the contribution of hopping electrons to the thermoelectric power. According to Mott and Davis [10], when states are delocalized and conduction is due to electrons at the Fermi level, the thermoelectric power is given by

$$S = \frac{\pi^2 k^2 T}{3e} \left. \frac{d(\ln \sigma)}{dT} \right|_{E=E_F} \quad (3)$$

where k is Boltzmann's constant and e is the electronic charge. It is proposed that the first two terms in Equation 1 characterize this mode of conduction, in accordance with the work of Mott and Davis [10]. Thus Equation 1 suggests that three conduction processes may be occurring in Mn/SiO_x films over the temperature range investigated.

The constant value of the thermoelectric power implies that the electron concentration is constant whereas the increase in d.c. conductivity (Fig. 4)

suggests that the electrons have an activated mobility. The mobility can be expressed as [11, 12]

$$\mu_e = \mu_0 \exp\left(\frac{-E_H}{kT}\right) \quad (4)$$

where E_H is the hopping energy. Steele and Beynon [13] using Au/SiO_x and Zaidi *et al.* [4] using Mn/SiO_x films containing 10 at% Mn obtained similar results.

Following Beyer and Stuke [14] and Mott and Davis [15] with amorphous (a-Ge) and amorphous Si, small values of the thermoelectric power are observed at low temperatures because the density of states at the Fermi energy level is large and conduction occurs by hopping. Chopra and Nath [16] with a-Ge and Cu/Ge thin films stated that the low-temperature thermoelectric power can be understood in terms of hopping between localized states at the Fermi level. Grigorovici *et al.* [17] found that the thermoelectric power of a-Ge is constant and negative in the lower temperature range; electrons are provided by some compensated donors, and the Fermi level E_F ($= \mu' T$) where μ' is the chemical potential) lies between the acceptor energy level E_A and the valence band edge E_V . In this temperature region $E_A - \mu' T$ is positive and the thermoelectric power is negative.

3.3.2. Intrinsic conduction

For temperatures above about 360 K, the thermoelectric power increases negatively for all compositions. The negative increase in thermoelectric power and the increase in d.c. conductivity (Fig. 4) is believed to be a consequence of intrinsic conduction.

Goldsmid [18] suggested that, depending on the concentration of donor or acceptor impurities, conduction by both electrons and holes becomes appreciable in narrow-band materials if the temperature is sufficiently high. This is a mixed-conduction range, wherein appreciable number of electrons are excited from the valence band. In this case, MacDonald [19] and Wilson [20] have shown that the thermoelectric power, S_{int} , should be expressed as

$$S_{int} = \frac{S_p \sigma_p - S_n \sigma_n}{\sigma_p + \sigma_n} \quad (5)$$

where σ_n and σ_p are the contributions to the electrical conductivity from electrons and holes and S_n and S_p are the respective thermoelectric powers. The electrons and hole concentrations are equal ($n = p$) when intrinsic conduction occurs, but the electron mobility is greater than that holes ($\mu_n > \mu_p$). Therefore, the overall sign of the thermoelectric power is negative.

According to Valdes [21] and Kittel [22], the thermoelectric power in an intrinsic semiconductor behaves in a similar way to an n-type semiconductor because the signs are negative in both cases. This statement is necessary to interpret the intrinsic results. The intrinsic conduction ranges for all compositions are listed in Table II. The temperatures quoted are similar to those found previously by Zaidi *et al.* [5] for 40, 50, 70, 80 and 90 at% Mn/SiO_x films (above

355 K), and by Steele *et al.* [23] from Hall measurements on 2 at% Au/SiO_x films (above 420 K).

3.3.3. Metallic-type conduction

Above 558 K for 1, 3 and 5 at% Mn films, the thermoelectric power is positive ($p \gg n$) and increases in value as the temperature increases; this property is similar to a metal. It is possible that the impurity band (formed by localized states in the band gap, due to addition of Mn) and valence band overlap above 558 K. Table II lists the temperature ranges for metallic conduction. This behaviour has previously been observed in 10 at% Mn films above 500 K [4], 20 and 40 at% Mn films above 410 and 450 K, respectively, and 60 and 100 at% Mn films above 460 K [5]. The thermoelectric power may be expressed as [24]

$$S_m = \frac{\pi^2 k^2 T}{eE_F} \quad (6)$$

The value of the Fermi energy, E_F , in Equation 6 is usually smaller in degenerate semiconductors than in metals and, as a result, S_m is larger. Also, the increase in both thermoelectric power and d.c. conductivity with increasing temperature indicates that carrier concentration and not mobility is activated; conduction occurs via extended states in the valence band. When the mobility edge is reached and conduction becomes a higher-mobility process via extended states, the mobility is expected to decrease as the temperature increases. The theoretical expression for the extended states is given by [25]

$$\mu_E = \text{constant } T^{-3/2} \quad (7)$$

which shows that μ_E decreases as T increases.

3.4. Conduction model: three-carrier model

The present thermoelectric power results for Mn/SiO_x films can be explained by the three-carrier model proposed by Beyer and Stuke [14]. The results are similar to those for a-Ge [14] and Au/Si films [26]. The resultant thermoelectric power may be considered to be the sum of individual contributions, S_j , multiplied by a weighting factor, defined in terms of the d.c. conductivity σ_j , as [19]

$$S = \frac{\sum_j \sigma_j S_j}{\sum_j \sigma_j} \quad (8)$$

Applying this model to the three-carrier model for Mn/SiO_x films enables the thermoelectric power to be expressed as

$$S = \frac{S_{DL}\sigma_{DL} - S_L\sigma_L + S_h\sigma_h}{\sigma_{DL} + \sigma_L + \sigma_h} \quad (9)$$

The three terms in Equation 9 represent the contribution, $S_{DL}\sigma_{DL}$, of delocalized electrons near the Fermi-energy level, the contribution, $S_L\sigma_L$, of electrons in donor localized states and the contribution, $S_h\sigma_h$, of holes in the valence band. The three-carrier model has previously been applied to explain thermoelectric power results with Mn/SiO_x films [4, 5] and Au/SiO_x films [13].

4. D.c. conductivity

Fig. 4 shows that the d.c. conductivity, $\sigma_{d.c.}$, increases non-linearly with increasing temperature for all compositions of Mn/SiO_x films. The curved characteristics imply that the d.c. conductivity activation energy E_σ cannot be represented by one single expression but requires a spectrum of activation energies. The expression for E_σ for 10 at% Mn films at 293 K [4] is

$$E_\sigma(\text{eV}) = 0.05 - 8.4 \times 10^{-4} T + 3.2 \times 10^{-6} T^2 \quad (10)$$

$\sigma_{d.c.}$ is activated for all compositions over the whole temperature range and the film structure is predominantly an island type. This type of structure has previously been observed in 20–50 at% Mn films [5]. $\sigma_{d.c.}$ for this type of film is written as [23]

$$\sigma_{d.c.} = \sigma_0 \exp\left(-\frac{E_F - E_{\max}(T) - E_h(T)}{kT}\right) \quad (11)$$

where σ_0 is a constant, $E_{\max}(T)$ is the impurity state energy and $E_h(T)$ is the hopping energy of charge carriers. The conduction mechanism in these films can be explained quantitatively by invoking Hill's dominant-current model [27]. This assumes that the largest contribution to the d.c. conductivity at a temperature T arises from localized states situated at an energy $E_{\max}(T)$ away from the Fermi level.

5. Conclusions

Three conduction mechanisms have been identified in Mn/SiO_x films: electronic hopping below 360 K, intrinsic over the temperature range 360 to 558 K and metallic like above 558 K. Thermoelectric power results are explained using a three-carrier model. The d.c. conductivity increases with increasing metallic content. D.c. conduction is activated and the films have an island structure.

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