Effects of composition and substrate temperature on the a.c. properties of co-evaporated Mn/SiO$_x$ thin films

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Capacitance, a.c. conductance and loss factor have been measured in Cu–Mn/SiO$_x$–Cu sandwich structures with compositions 1, 3, 5 and 10 at% Mn in the frequency range 10–10^6 Hz between temperatures of 110 and 500 K. The capacitance has a weak minimum at 1.0 MHz for all temperatures, whilst the a.c. conductance increases between four and eight orders of magnitude for temperatures of 150 and 473 K, respectively. Various a.c. conduction models have been considered, and it has been concluded that correlated barrier hopping best describes the results. The Goswami–Goswami model was used to describe the variation of loss factor with temperature and composition.

1. Introduction

a.c. conductivity has been observed in every amorphous semiconductor or insulator. The variation with frequency of the real part of the a.c. conductivity is able to give information about deep defect states associated with impurities, irregularities and discontinuities, which for a thin film are functions of preparation technique and deposition parameters.

The a.c. conductivity, $\sigma(\omega)$, generally, obeys the relation

$$\sigma(\omega) \propto \omega^s \qquad (1)$$

in the frequency range 10–10^6 Hz. The exponent s has values which are of the order of unity, and may be weakly temperature-dependent [1].

The purpose of this paper is to present results of various a.c. measurements: capacitance, conductance and loss factor obtained in co-evaporated Mn/SiO$_x$ thin films, and to determine a possible conduction mechanism.

2. Experimental procedure

a.c. measurements of capacitance, conductance and loss factor have been made on Cu–Mn/SiO$_x$–Cu thin-film sandwich structures *in vacuo* ~ 1 mPa in the frequency range 10 to 4×10^6 Hz between 110 and 500 K. The films were deposited on Corning 7059 alkali-free glass substrate by co-evaporation *in vacuo* ~ 1 mPa. The manganese content of the films was determined using X-ray photoelectron spectroscopy. All the a.c. measurements were performed using a Hewlett-Packard Analyser (model 4192A LF) in the parallel mode. The built-in frequency synthesizer was able to be set to any frequency within the range 5 Hz to 13 MHz with maximum resolution of 10^{-3} Hz and an accuracy of ± 50 p.p.m. at 296 ± 5 K. The measuring range of the capacitance lies within 0.1×10^{-12} to 0.1 F, of the conductance between 1×10^{-4} and 12.99 S and of tan δ between 1×10^{-4} and 19.99. All have a basic accuracy of $\pm 0.1\%$ and a resolution of 4.5 digits.

The connections between the sandwich device and the impedance analyser were made with coaxial cable. The length of the cable was kept as short as possible to minimize stray capacitance around component leads and lead inductance: in high resistive materials, the effect of cable length increases markedly at frequencies > 1 MHz. A zero-offset adjustment function automatically eliminated parasitic effects due to stray capacitance and residual resistance. The a.c. signal applied across the device was maintained at 0.5 V (RMS) with zero d.c. bias.

3. Results and discussion

The variation of capacitance with frequency for films, 200 nm thick, containing 1, 3, 5 and 10 at% Mn at 293 K is shown in Fig. 1. It can be seen that the capacitance decreases slowly as frequency increases, attaining a minimum value at about 0.2 MHz for all compositions before increasing rapidly to the maximum frequency of 4.0 MHz; the maximum value of dC/df below 0.2 MHz occurs at 473 K. Fig. 2 shows the variation of capacitance with frequency for a 1 at% Mn film at 150, 200, 293, 373 and 473 K. At any given frequency, the capacitance increases with increase in temperature.

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It is possible to account for the results in Figs 1 and 2 in qualitative terms by treating the metal–insulator sandwich configuration as a parallel-plate capacitor of capacitance C, given by

$$C = \varepsilon_0 \varepsilon' A / d \qquad (2)$$

where ε_0 is the permitivity of free space ($= 8.85 \times 10^{-12} \ \mathrm{F \, m^{-1}}$), ε' is the dielectric constant of the material, A is the active area and d is 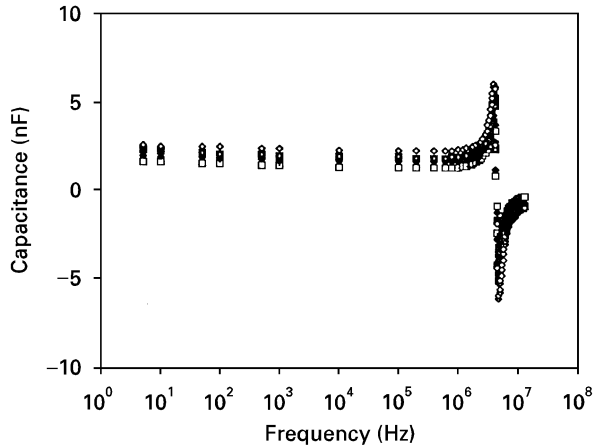the film thickness. A mixed metal/insulator thin-film system at low metal content generally consists of metallic islands within an insulating matrix. The increase in capacitance with metallic content may be considered to arise from the contribution of micro-capacitors in series/parallel combination, consisting of metal-island electrodes with a SiO_x dielectric. Let there be n capacitors (each of capacitance C) in series and N such branches in parallel, ignoring any resistive component. Then, it can be shown that the total capacitance, C_T, is given by NC/n. As the width of the film is larger than the thickness, $N > n$, and C_T is larger than C. From Equation 1, an increase in size of the metallic islands and a decrease in inter-island separation results in an increase in C and, hence, C_T. The dependence of capacitance on temperature can be considered similarly.

Table I lists values of the dielectric constant for various compositions at selected frequencies. At each frequency, ε' increases with manganese content, whilst at each composition, ε' has a minimum between 0.1 and 0.6 MHz.

Fig. 3 shows the variation of the a.c. conductance, $G_{a.c.}$, with frequency in 1 at % Mn films at different substrate temperatures. The contribution of d.c. conductivity was subtracted from the total a.c. conductivity measurements. $G_{a.c.}$ increases slowly with frequency below about 1 kHz but increases by about four orders of magnitude above 1 kHz. The a.c. conductance follows a power-law dependence on frequency which has the same form as Equation 1, namely $G_{a.c.} \propto \omega^s$.

Table II lists calculated values of s in three frequency ranges. It can be seen that s decreases with increase in substrate temperature in each frequency range. However, it is unclear if the large values of s (>2.0) below 293 K in column 4 have any real significance. They may be a consequence of a large experimental error.

The a.c. conductivity activation energy is shown in Table III for 1 at % Mn films. In all cases, the activation energy increases with increase of frequency at given substrate temperature and with increase in temperature at given frequency. Hence, the activation energy, E_A, is given by

$$E_A \propto \omega^a T^b \qquad (3)$$

where a and b are both greater than 1.

The strong frequency dependence of $G_{a.c.}$ at high frequencies and the low E_A at lower temperatures suggests that conduction is governed by a hopping mechanism [2]. Pollak and Geballe [3] first suggested

Figure 1 The variation of capacitance with frequency for various compositions of co-evaporated Mn/SiO$_x$ films at room temperature: ($\square$) 1 at % Mn, ($\blacklozenge$) 3 at % Mn, ($\blacksquare$) 5 at % Mn, ($\diamond$) 10 at % Mn.
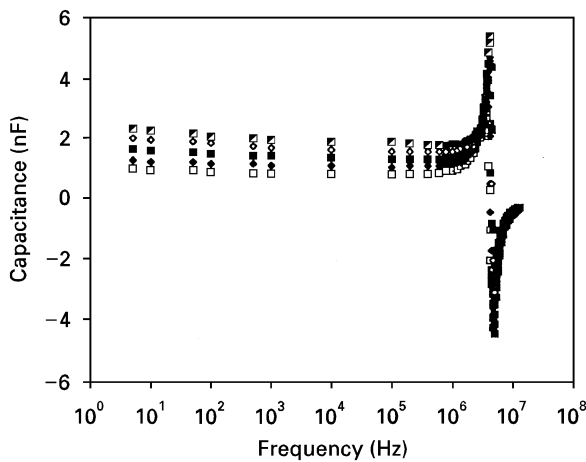

Figure 2 The variation of capacitance with frequency for co-evaporated Mn/SiO$_x$ films (1 at % Mn, 100 nm) at different substrate temperatures: ($\square$) 150 K, ($\blacklozenge$) 200 K, ($\blacksquare$) 293 K, $\diamond$) 373 K, ($\blacksquare$) 473 K.

TABLE I The values of dielectric constant ε' at room temperature for various compositions of co-evaporated Mn/SiO$_x$ films at different fixed frequencies

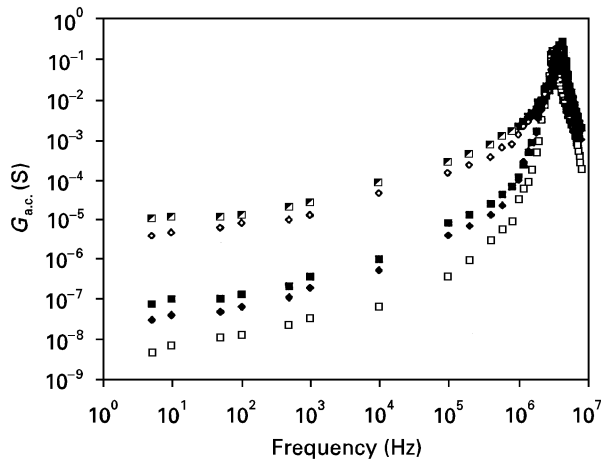| Composition (at % Mn)	Dielectric constant, ε', at different frequencies							
	10 Hz	10^2 Hz	10^3 Hz	10^4 Hz	10^5 Hz	6×10^5 Hz	1×10^6 Hz	2×10^6 Hz
1	3.55	3.34	3.17	3.05	2.98	3.01	3.12	3.75
3	4.27	4.05	3.89	3.82	3.77	3.78	3.88	4.52
5	4.97	4.66	4.45	4.38	4.34	4.34	4.44	5.07
10	5.74	5.58	5.43	5.31	5.24	5.27	5.38	6.01

Figure 3 The variation of a.c. conductance, $G_{a.c.}$, with frequency for co-evaporated Mn/SiO$_x$ films (1 at % Mn, 100 nm) at different substrate temperatures: ($\square$) 150 K, ($\blacklozenge$) 200 K, ($\blacksquare$) 293 K, ($\diamond$) 373 K, (◪) 473 K.

TABLE II The values of index s for 1 at % Mn in co-evaporated Mn/SiO$_x$ films at different substrate temperatures in different frequency ranges.

Temperature (K)	s at different frequencies		
	10^2–10^3 Hz	10^3–10^5 Hz	10^5–10^6 Hz
150	0.34	1.27	5.61
200	0.32	1.10	4.54
293	0.26	0.96	3.28
373	0.22	0.70	2.33
473	0.16	0.68	2.03

TABLE III The values of the a.c. conductivity activation energies, E_A, for 1 at % Mn in co-evaporated Mn/SiO$_x$ films at different substrate temperatures in different frequency ranges

Frequency (Hz)	Activation energy (eV)			
	150–200 K	200–293 K	293–373 K	373–473 K
10^2	2.94×10^{-5}	2.96×10^{-4}	6.92×10^{-3}	3.08×10^{-2}
10^3	9.81×10^{-5}	5.0×10^{-4}	1.31×10^{-2}	2.86×10^{-2}
10^4	2.81×10^{-4}	2.82×10^{-3}	3.01×10^{-2}	0.12
10^5	1.04×10^{-3}	6.56×10^{-3}	8.54×10^{-2}	0.41
2×10^5	3.52×10^{-3}	2.93×10^{-2}	0.14	0.61
4×10^5	6.27×10^{-3}	4.58×10^{-2}	0.31	1.04
1×10^6	4.08×10^{-2}	0.15	0.95	2.24

that $\sigma_{a.c.}$ behaves as Equation 1. This was extended to include the effect of temperature. Various theoretical investigations [4–8] and experimental investigations [9–12] suggest that $\sigma_{a.c.}$ should obey the universal law

$$\sigma_{a.c.} \propto \omega^s T^n \qquad 0 \leqslant s \leqslant 1; 0.1 \leqslant n \leqslant 0.4 \quad (4)$$

The theoretical models which support Equation 4 can be divided into three groups: quantum mechanical tunnelling (QMT) [13]; correlated barrier hopping (CBH) [4]; quantum-mechanical tunnelling

of small polarons (QMTSP) [6]. The QMT model ascribes a.c. loss to a relaxation process arising from electronic or atomic tunnelling between equilibrium sites. It predicts s (lying in the range $(0, 1)$) to be temperature-independent but frequency-dependent. The CBH model is concerned with the hopping of two electrons from a D$^-$ to a neighbouring D$^+$ centre over the potential barrier between them. It predicts that s should be less than 1, decreasing with increasing temperature. The QMTSP model is concerned with carriers trapped at structural defects, i.e. small polarons, tunnelling between states lying close to the Fermi level. It predicts that s will increase with increasing temperature and that the tunnelling distance, and hence the a.c. conductivity, will decrease at high frequencies. The QMT and QMTSP predictions do not fit the data in Table I, because s decreases with increase in temperature. This conclusion also fits data for Mn/SiO$_x$ films prepared by single-boat evaporation [14].

s is related to the optical band gap energy, E_0, via [1]

$$s = [1 - (6kT/W_M)] \quad (5)$$

where W_M is equal to $2 (E_0 - E_a)$. Equation 5 indicates that s must be less than 1. Thus there is reason to suspect either the accuracy of the s-values in column 4 of Table I due to a high experimental error in $G_{a.c.}$ or the validity of the CBH model: $s > 1$ below 200 K between frequencies of 10^3 and 10^5 Hz and below 473 K at frequencies $\geqslant 10^5$ Hz. Using experimental values of E_0 [15] and E_a at 293 K, s is computed to lie between 0.96 and 0.94 for 1 at % Mn to 10 at % Mn films. These values agree with the experimental result for the 1 at % Mn film in the frequency range 10^3–10^5 Hz (Table I) but is over three times larger than the values in the 10^2–10^3 Hz range.

Fig. 4 shows the variation of loss factor, $\tan \delta$, with frequency for 1, 3, 5 and 10 at % Mn films at 293 K. It can be seen that $\tan \delta$ decreases with increase in metallic content and that there is a minimum value ($\tan \delta_{min}$) at 0.25 MHz for all compositions. The reason for $\tan \delta$ varying in this way with manganese composition may be due to a reduction in the number of weak percolation paths through the SiO$_x$ insulating matrix. Fig. 5 shows the variation of $\tan \delta$ with frequency for 1 at % Mn films at different substrate temperatures; like Fig. 4, $\tan \delta$ has a minimum. Although $\tan \delta$ decreases as temperature increases, the minimum shifts towards higher frequencies.

The presence of $\tan \delta_{min}$ and its shift towards higher frequencies with increasing temperature may be explained using the Goswami and Goswami model [16]. It considers the thin film to be equivalent to a capacitor, C, in parallel with a resistance, R, and the combination in series with the resistance, r, of the leads. It may be shown that

$$\tan \delta = 1/\omega RC + \omega rC \quad (6)$$

In the low-frequency region where $1/\omega RC \gg \omega rC$, we have
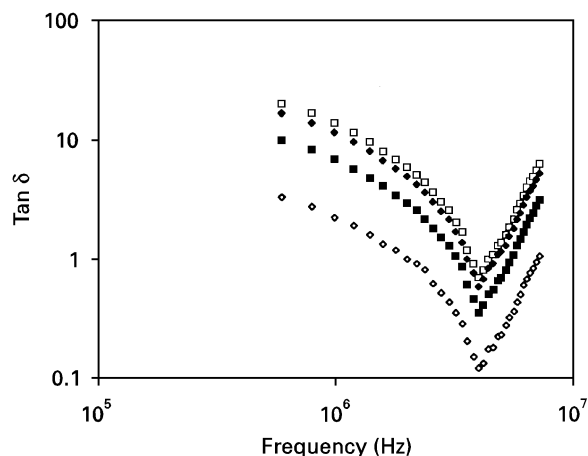
$$\tan \delta = 1/\omega RC \quad (7)$$

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Figure 4 The variation of loss factor $\tan\delta$ with frequency for various compositions of co-evaporated Mn/SiO_x films at room temperature: ($\square$) 1 at % Mn, ($\blacklozenge$) 3 at % Mn, ($\blacksquare$) 5 at % Mn, ($\diamond$) 10 at % Mn.
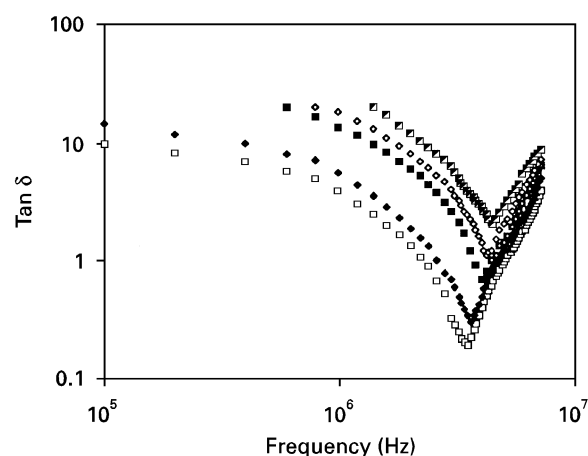

Figure 5 The variation of loss factor $\tan\delta$ with frequency (1 at % Mn, 100 nm) of co-evaporated Mn/SiO_x films at different substrate temperatures: ($\square$) 150 K, ($\blacklozenge$) 200 K, ($\blacksquare$) 293 K, ($\diamond$) 373 K, ($\boxslash$) 473 K.

This indicates that $\tan\delta$ decreases with increasing frequency. In the high-frequency region, $1/\omega RC \ll \omega rC$, and

$$\tan\delta = \omega rC \tag{8}$$

Here, $\tan\delta$ increases with increasing frequency. The loss factor has a minimum value at a frequency, given by

$$\omega_{min} = 1/C(rR)^{1/2} \tag{9}$$

For ω_{min} to shift towards higher frequencies as temperature increases, R must decrease more rapidly than C increases (r remains constant).

4. Conclusion

a.c. measurements in Mn/SiO_x films appear to support Elliot's correlated barrier hopping model of conduction within certain temperature and frequency regimes: in 1 at % Mn films, below 473 K and frequencies $< 10^3$ Hz and above 293 K at frequencies between 10^3–10^5 Hz. Capacitance varies with temperature having a minimum at a frequency of 0.2 MHz. The loss factor has a minimum value at 0.4 MHz for all compositions, and shifts towards higher frequencies as temperature increases for each composition.

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