

Effect of composition on optical properties of co-evaporated Mn/SiO_x, Cr/SiO_x and Cu/SiO_x cermet thin films

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Optical absorption spectra of amorphous Mn/SiO_x, Cr/SiO_x, and Cu/SiO_x cermet films, 300 nm thick, with compositions from 0 to 25 at% Mn, Cr and Cu, respectively, prepared by co-evaporation at 293 K *in vacuo* have been investigated. The linearity of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ graphs in the high absorption region for all the cermet films indicates that indirect photon transitions in k-space are involved in the absorption process. Tauc's rule is also confirmed. In all cases the optical energy gap decreases significantly with increasing metallic content of the films and the width of the tail of localized states increases.

1. Introduction

The study of optical absorption spectra, and particularly the absorption edge, has been one of the productive tools for (a) investigating optically-induced transitions and (b) obtaining information about the band structure, density of states at the valence and conduction band edges, the refractive index, the energy spread of localized tail states and the optical energy gap in both crystalline semiconductors and non-crystalline materials.

There are two types of optical transitions at the fundamental absorption edge: direct and indirect; these depend on the energy band structure. Optical measurements can help to distinguish between them. With direct transitions, the minimum in the conduction band and the maximum in the valence band lie at the same point in k-space. The absorbed photon interacts with an electron at the top of the valence band, raising it to the minimum in the conduction band with no significant change in the momentum $\hbar k$, since the absorbed photon has negligible momentum. The allowed transitions are governed by the k-conservation rule in which electrons with a wave vector in the valence band make only vertical transitions to states in a higher band having the same vector. Non-vertical transitions are forbidden. With indirect transitions, the interaction of electrons with lattice vibrations (phonons) takes place, resulting in a change in the momentum of the electron. This momentum change is either taken up, or given up, by phonons to satisfy the conservation of momentum due to the change in the electron's wave vector. In other words, the minimum in the conduction band lies in a different region of k-space from the maximum in the valence band, and a direct optical transition from the top of the valence band to the bottom of the conduction band (minimum energy gap) is forbidden.

In order to evaluate the optical energy band gap for amorphous materials, the variation in the absorbance versus energy of an incident photon needs to be fitted to a theoretical expression. Generally, two theoretical approaches are used: one proposed by Urbach [1] and the other by Tauc *et al.* [2], derived in a more general form by Davis and Mott [3].

Urbach [1] proposed that the absorption coefficient $\alpha(\omega)$ at lower absorption levels (i.e. $\alpha < 10^6 \text{ m}^{-1}$) is an exponential function of photon energy of the form:

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \quad (1)$$

where α_0 is a constant, \hbar is the reduced Planck constant and E_e (also known as the Urbach energy) [1–3] is interpreted as the width of the tail of localized states in the normally forbidden band gap, associated with the amorphous nature of the materials. The value of E_e can be obtained from a graph of $\ln \alpha$ versus $\hbar\omega$. This relation has been found to hold for many amorphous, or glassy, materials in the lower region of the absorption edge.

Tauc *et al.* [2] considered that such absorption edges in amorphous materials can arise from inter-band transitions involving the tails of localized states, where the density of states falls off exponentially. He proposed that the absorption coefficients above $\sim 10^6 \text{ m}^{-1}$ are related to photon energy via:

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^2/\hbar\omega \quad (2)$$

where B is a constant equal to $(4\pi\sigma_0/ncE_e)$, in which σ_0 is the d.c. electrical conductivity extrapolated to absolute zero, n is the refractive index and E_{opt} is the optical band gap. In this case $\alpha(\omega)$ is considered to be the absorption coefficient for non-direct transitions.

Davis and Mott [3] generalized Tauc's rule and suggested that for $\alpha(\omega) < 10^6 \text{ m}^{-1}$, there is usually an

Urbach tail whilst for $\alpha(\omega) > 10^6 \text{ m}^{-1}$ the absorption edge has the form

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^m/\hbar\omega \quad (3)$$

where B is as previously defined, and m is an index which can take values that depend on the nature of the electronic transitions in k -space. $m = 2$ for an indirect-allowed transition, $m = 3$ for an indirect-forbidden transition, $m = 1/2$ for a direct-allowed transition and $m = 3/2$ for a direct-forbidden transition [4].

In this paper optical measurements on Mn/SiO_x, Cr/SiO_x and Cu/SiO_x cermet thin films, prepared by co-evaporation are reported. The data are analysed to obtain values of E_{opt} and E_c , and their dependence on composition. The results are used to investigate the applicability of the Urbach equation at low absorption and the Tauc and Mott models at high absorption.

2. Experimental details

Mn/SiO_x, Cr/SiO_x and Cu/SiO_x cermet thin films were deposited on Corning 7059 alkali-free aluminosilicate glass substrates at 293 K *in vacuo* ~ 1 mPa from two molybdenum boat-shaped filaments by co-evaporation [5] using 99.9% pure manganese flake, 99.99% pure chromium and copper powder (Johnson & Matthey Materials Tech., UK) and 99.9% pure select grade/vacuum-baked silicon monoxide powder (Aldrich, UK). The deposition rate and film thickness were controlled using two calibrated quartz crystal oscillators. The mean deposition rate for the cermet films was about 0.5 nm s^{-1} and the film thickness of all samples reported here is 300 nm, as measured by multiple-beam interferometry with an Angstromer (Sloan Instruments, Model M-100) and checked using an alpha-step 200 R & D profilometer (Tencor Instruments, UK).

The atomic percentage of Mn, Cr and Cu in the films was determined using X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded with a VG ESCALAB 210 spectrometer (Fisons Surface Science) using AlK α (1486.6 eV) radiation. Charge correction of the data was performed by reference to the carbon (1s) peak at 284.6 eV. The samples were analysed immediately after evaporation to keep surface contamination to a minimum. The residual pressure in the XPS spectrometer was better than $0.27 \mu\text{Pa}$ during the analysis.

The optical absorption measurements were made at 293 K using a Perkin-Elmer Lambda 9 double-beam spectrophotometer in the wavelength region 280 to 900 nm. The effect of substrate on the optical absorption was eliminated by placing a similar cleaned uncoated Corning 7059 glass substrate in the reference beam. Data were recorded using the Perkin-Elmer software package PECSS version 4.01. $\alpha(\omega)$ was calculated using the following relation

$$\alpha(\omega) = 2.303 A/d \quad (4)$$

where d is the thickness of the film and A is the absorbance, defined as $A = -\log_{10} T$, where T is the transmittance.

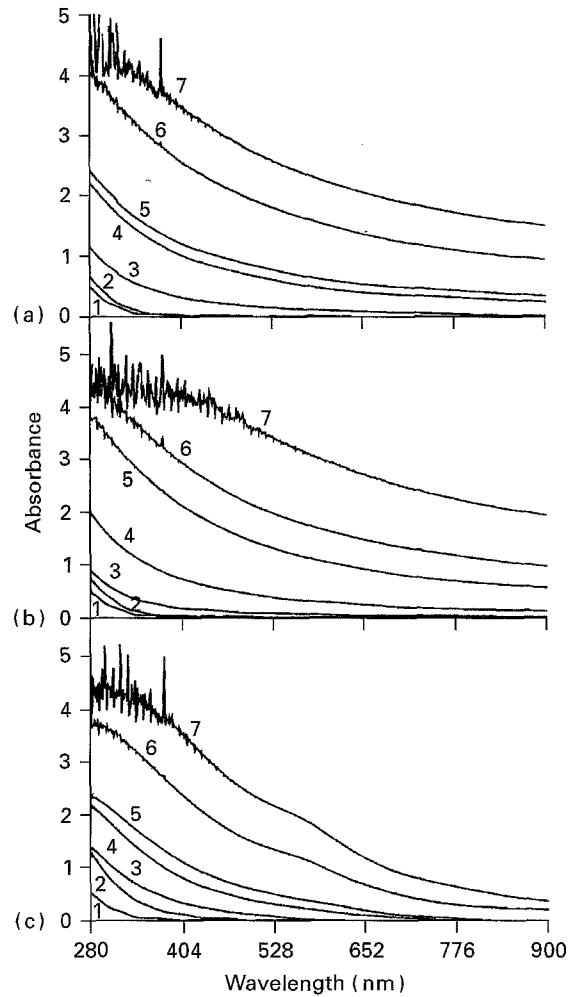


Figure 1 Optical absorption spectra at 293 K of (a) Mn/SiO_x (b) Cr/SiO_x (c) Cu/SiO_x cermet thin films prepared by co-evaporation at 293 K for various compositions, (1) 0 at% (2) 1 at% (3) 5 at% (4) 10 at% (5) 15 at% (6) 20 at% (7) 25 at%; thickness 300 nm; deposition rate 0.5 nm s^{-1} .

3. Results

Fig. 1 shows the variation of optical absorbance with wavelength for co-evaporated M/SiO_x cermet thin films (M = Mn, Cr, Cu) of various compositions. As the M content in the films increases, the absorbance increases and the absorption edge shifts towards longer wavelengths. Fig. 2 shows corresponding graphs of $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$. They approach linearity at high absorbance values. The values of optical band gap E_{opt} derived from the limiting behaviour at high ω for all the compositions are listed in Tables I–III. E_{opt} decreases monotonically as the M content increases. B does not change systematically with composition but in all cases the values are of the order of $10^7 \text{ m}^{-1} \text{ eV}^{-1}$ which are comparable with the theoretical values [3]. Graphs of $\ln \alpha(\omega)$ versus $\hbar\omega$, plotted in accordance with Urbach's law, are shown in Fig. 3. The limiting slopes at low ω give the values of E_c listed in Tables I–III. For some samples interference features are seen in the spectra. Because of this, measurement of the limiting slopes is subject to some error. It is clear, however, that the values of E_c increase as the at% of M in the films increases.

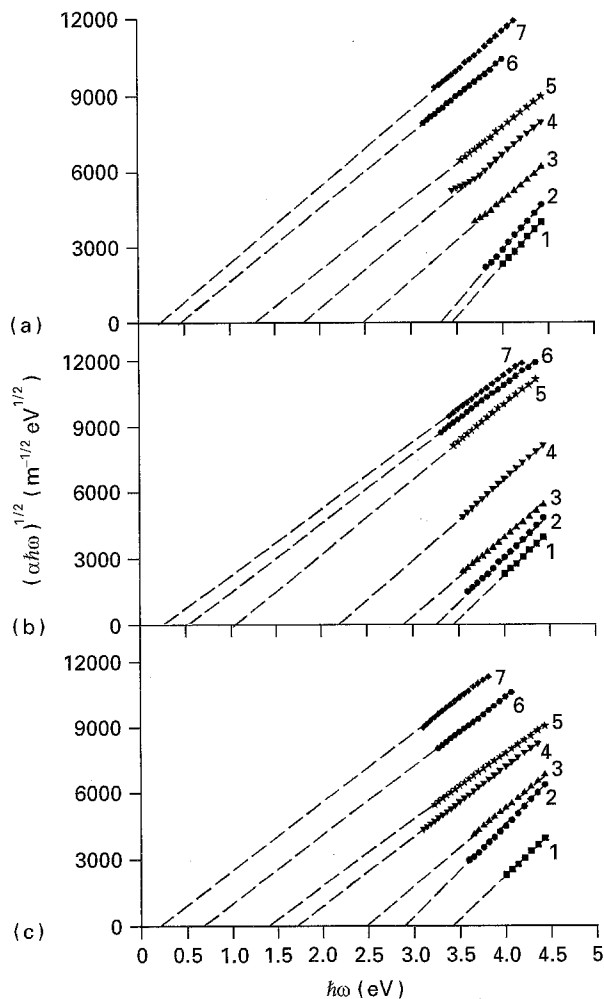


Figure 2 Data of Fig. 1 replotted in terms of indirect transitions for various compositions of (a) Mn/SiO_x (b) Cr/SiO_x (c) Cu/SiO_x cermet thin films (1) 0 at % (2) 1 at % (3) 5 at % (4) 10 at % (5) 15 at % (6) 20 at % (7) 25 at %.

4. Discussion

The optical absorption edges for all compositions are exponential-like, and shift towards longer wavelengths as the Mn, Cr and Cu content of the films increases. They are typical of amorphous materials [6]. The exponential region in the absorption edge is suggested to be evidence for localized states [7]. In every case $\alpha(\omega)$ is greater than 10^6 m^{-1} throughout the wavelength range studied; nevertheless the validity of Urbach's rule in the lower absorption region of the spectra is observed. All the graphs in Fig. 2 are linear in the high absorption region with $m = 2$ (in Equation 3) for all the cermet thin films, indicating that indirect photon transitions are involved in the absorption process and also confirming that the films obey Tauc's rule. It has been shown by a number of workers that Davis and Mott's relation (Equation 3) with $m = 2$ gives the best fit for optical absorption data particularly in the high absorption region for many glasses [8–10], amorphous thin film oxides [11–14] and cermet thin films [15–17].

In all cases, E_{opt} decreases significantly as the Mn, Cr or Cu content increases. The decrease in E_{opt} with composition can be attributed to an increase in the degree of disorder of the system. The large values of

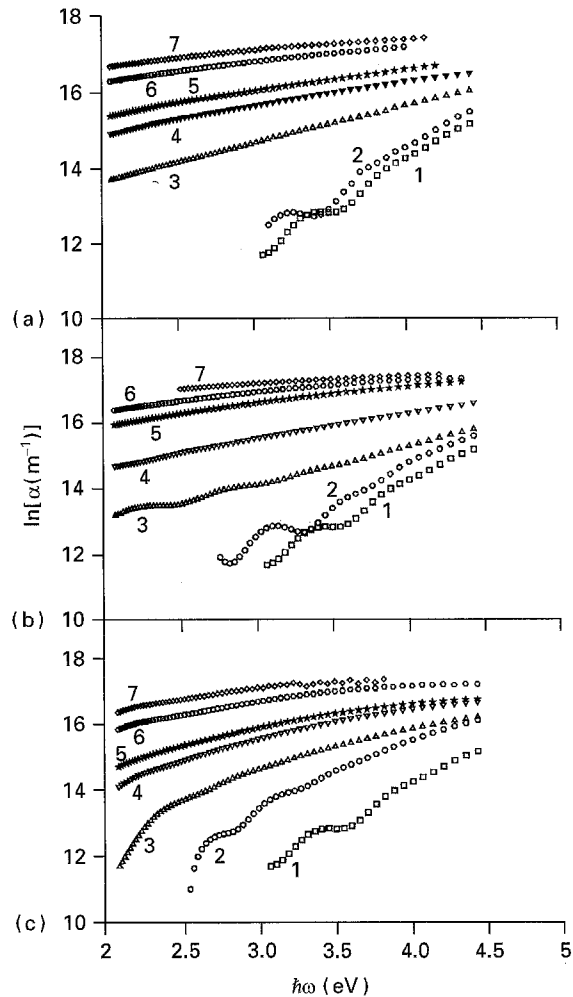


Figure 3 Data of Fig. 1 replotted using Equation 1 for various compositions of (a) Mn/SiO_x (b) Cr/SiO_x (c) Cu/SiO_x cermet thin films (1) 0 at % (2) 1 at % (3) 5 at % (4) 10 at % (5) 15 at % (6) 20 at % (7) 25 at %.

TABLE I The dependence of E_{opt} and E_c for various compositions of Mn/SiO_x cermet thin films prepared by co-evaporation at 293 K, thickness 300 nm and deposition rate 0.5 nm s^{-1}

Composition (at % Mn)	E_c (eV)	E_{opt} (eV)	$10^{-7} B$ ($\text{m}^{-1} \text{ eV}^{-1}$)
0	0.39	3.40	1.581
1	0.43	3.27	1.729
5	1.01	2.48	1.022
10	1.52	1.85	0.845
15	1.74	1.30	0.834
20	2.38	0.40	0.822
25	2.88	0.20	0.921

TABLE II The dependence of E_{opt} and E_c for various compositions of Cr/SiO_x cermet thin films prepared by co-evaporation at 293 K, thickness 300 nm and deposition rate 0.5 nm s^{-1}

Composition (at % Cr)	E_c (eV)	E_{opt} (eV)	$10^{-7} B$ ($\text{m}^{-1} \text{ eV}^{-1}$)
0	0.39	3.40	1.548
1	0.42	3.24	1.620
5	0.94	2.85	1.177
10	1.23	2.22	1.368
15	1.79	1.05	1.147
20	2.29	0.51	0.960
25	2.97	0.25	0.951

TABLE III The dependence of E_{opt} and E_c for various compositions of Cu/SiO_x cermet thin films prepared by co-evaporation at 293 K, thickness 300 nm and deposition rate 0.5 nm s⁻¹

Composition (at % Cu)	E_c (eV)	E_{opt} (eV)	$10^{-7} B$ (m ⁻¹ eV ⁻¹)
0	0.39	3.40	1.581
1	0.46	2.87	1.839
5	0.58	2.49	1.307
10	0.92	1.72	1.030
15	1.13	1.38	0.887
20	1.67	0.70	0.991
25	2.14	0.22	1.035

E_c in all cermets suggest that these materials are highly disordered at this deposition rate. Increased disorder and the presence of defects increase the number of the localized states [18, 19]. As a consequence, E_{opt} decreases. Other workers have observed a decrease in the optical band gap of SiO_x with the addition of metals. The systems Ba/SiO [20, 21], SiO/In₂O₃ [22], SiO/V₂O₅ [23], GeO₂/SiO_x [19], SiO/B₂O₃ [24], SiO_x/SnO [25] and Cu/SiO_x [17] all show behaviour qualitatively in accord with that observed here.

The linearity in the graphs in Fig. 3 indicates an exponential dependence of $\alpha(\omega)$ on photon energy $\hbar\omega$, suggesting that these films obey Urbach's rule. The values of E_c are very much larger than the values quoted for a range of amorphous semiconductors [26, 27] and vary quite significantly with composition for all cermet films. The increase in the energy spread of localized tail states with increase of M content has been observed by many workers: Al-Ani *et al.* [15] and Reza-ur-Rahim [28] in Mn/SiO_x cermet thin films (using single boat evaporation), Al-Saie *et al.* [16] in Cu/GeO₂ cermet thin films, Khan and Beynon [17] in Cu/SiO_x cermet thin films, Islam [29] in SiO/SnO₂ amorphous thin films, Khan and Hogarth [25] in SiO_x/SnO amorphous thin films and Moridi and Hogarth [8] for Cu/Ca₃(PO₄)₂ glasses.

Many theoretical and experimental explanations [30–35] have been given to explain the Urbach absorption edge in amorphous materials but the exact nature of the physical origin of this is still uncertain [36]. Unambiguous interpretation requires that the effect of temperature be adequately accounted for [15]. Redfield [32] suggested that this behaviour is due to the frequency-dependent fluctuations of micro-fields caused by impurities. This is closely related to an electron-impurity scattering process which results in lattice distortion and band-tail behaviour in amorphous materials. Dow and Redfield [33] suggested that it arises from an electric field broadening of an exciton associated with structural disorder in many amorphous materials. Tauc [34] suggested that the behaviour is due to electronic transitions between localized states in the band edge tails, the densities of which are assumed to fall off exponentially with energy and the width of the tail E_c being dependent on composition and deposition parameters. Davis and Mott [3, 27], on the other hand questioned this suggestion on the grounds that the slopes of the observed exponential

edges obtained from Equation 1 are very much the same in many semiconductors, giving values of E_c within a narrow range.

In the present work, the values of E_c are much larger and vary quite significantly with composition. These observations are at variance with Davis and Mott's suggestions and lend support to Tauc's model in which the Urbach edge can be expected to show a significant compositional dependence.

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