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Structure and optical properties of vacuum-deposited scandium films on crystalline substrates

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Thin films of scandium have been deposited in high vacuum on to amorphous and crystalline substrates at room temperature. These films were examined by X-ray diffraction and transmission electron microscopy to study the structure and orientation of films of various thicknesses. It was observed that thin scandium films evaporated on to air-cleaved mica and rock-salt substrates have a polycrystalline structure. The variation of the refractive index *n*, the extinction coefficient *k* and optical conductivity $\sigma_1(\omega)$ with wavelength were studied. Measurements were made in the spectral region from 2.5 to 40 μm.

1. Introduction

Scandium is the lightest member of the rare earth group of elements and the first transition metal in the periodic table. The scandium atom has three outer valence electrons beyond the argon core. In its general chemical metallurgical and physical behaviour it is similar to those observed for the other rare earth metals, but there are a number of significant differences due to its smaller size and its larger electron negativity value [1]. Some of its electrical and magnetic properties are quite sensitive to impurities, especially at low temperature. These properties make it attractive in some technological applications.

Gorodetskii and Shevlyakov [2] investigated the structural transitions and electronic properties of scandium films adsorbed on the (1 1 2) face of tungsten. The structure of scandium films on a (1 0 0) face of tungsten was investigated by LEED (low-energy electron diffraction). Scandium crystals grow on tungsten crystal with their (1 0 0) face oriented parallel to the substrate surface [3].

The band structures, density of state curves and Fermi surfaces are presented for the hexagonal close-packed configurations of scandium, titanium, yttrium and zirconium, as calculated by the cellular method [4] and by using the augmented plane-wave (APW) method [5]. Two very different Fermi surfaces were obtained by the investigators. The differences are not due to the methods used but rather to the differences in the potentials used according to Fleming and Loucks [5]. The density of states at the Fermi surface is calculated to be 1.3 and 2.3 two-spin states per atom per electron volt by Altmann and Bradley [4] and by Fleming and Loucks [5], respectively.

Cullen and Callen [6] in an attempt to explain the magnetic susceptibility values suggested that scandium has two overlapping bands with a large density of states.

From the analysis of the NMR relaxation time, Fradin [7] suggested that the valence band has 0 to 20% S-character and 80 to 100% d-character; Masuda and Hashimoto [8] suggested there are only 0.07 S ($\sim$2%) electrons in the valence band; and Ross *et al.* [9] estimate 2.4 to 15% S-character in the conduction electrons at the Fermi surface. These results are reasonably consistent but are significantly lower than the suggested values of 50% S- and d-character by Manninen [10] and Gschneidner [11].

The aim of the present work is to study the growth and orientation of scandium films condensed from the vapour phase on crystalline substrates. The optical properties of evaporated scandium were investigated in region from 2.5 to 40 μm.

2. Experimental technique

Scandium of purity 99.999% was thermally evaporated using molybdenum boats in a vacuum atmosphere of $\sim 10^{-4}$ Pa and thin films were deposited on freshly cleaved rock-salt and mica substrates. The thickness of the films were determined by multiple-beam interferometry techniques [12]. Films of thickness ranging from 20 to 240 nm were prepared with a deposition rate of about 5 nm sec^{-1}. The films were investigated by means of an X-ray diffractometer (Philips D 500) and transmission electron microscope (Zeiss EM 10). The optical transmittance in the range 2.5 to 40 μm was measured for films deposited on to potassium bromide and mica substrates using a double-beam Beckman 4220 spectrophotometer which gives values of transmission accurate to 1%.

3. Results and discussion

Studies of the microstructure of vacuum-deposited thin films, particularly in relation to their nucleation and growth, have been made by numerous investigators [13–16]. The crystallite size of a vapour-deposited polycrystalline film increases with the increasing surface mobility of adatoms and clusters

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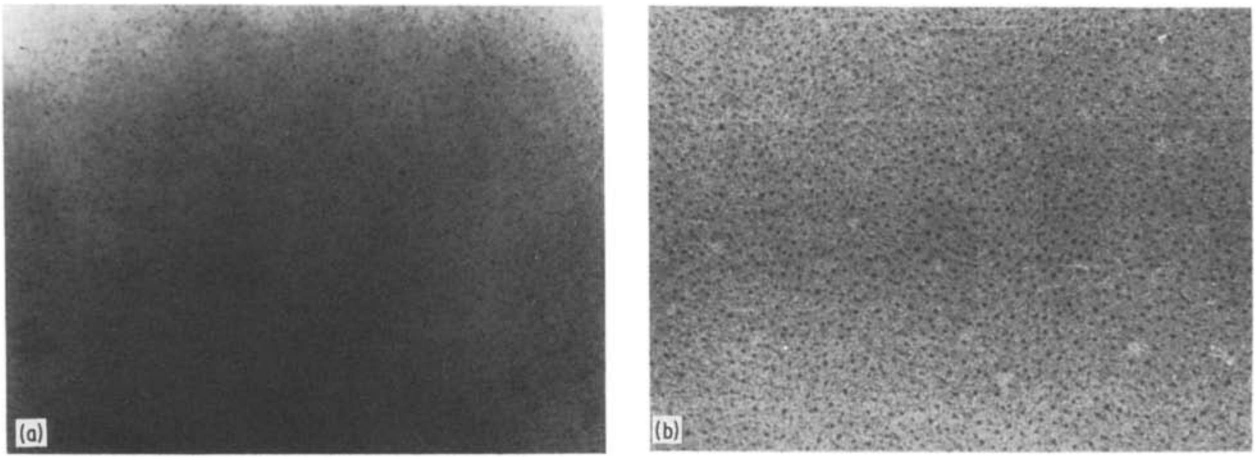

Figure 1 Electron micrographs (× 15 000) of scandium films deposited on mica. Film thickness (a) 30, (b) 42 nm.

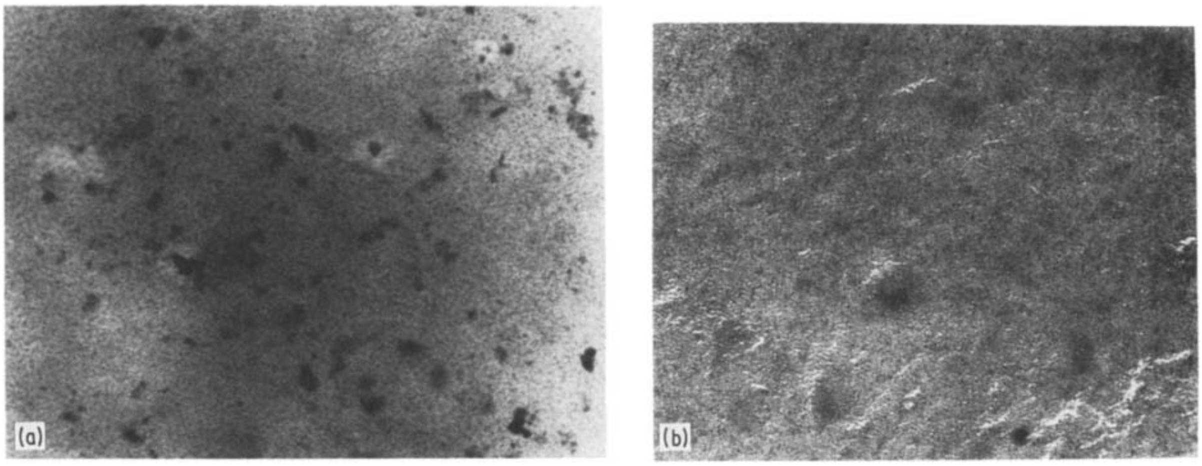

Figure 2 Electron micrographs (× 7500) of scandium films deposited on rock-salt. Film thickness (a) 60, (b) 75 nm.

during deposition. Therefore, the crystallite size is expected to increase with increasing substrate temperature, rate of deposition, velocity of the vapour atoms parallel to the surface, inertness and smoothness of the surface, etc.

Electron micrographs (Figs 1 and 2) show the morphology of scandium films deposited on to the cleavage surface of mica and rock-salt, respectively. The steps on the substrate surface act as preferential nucleation sites. It is apparent that grains grow and become uniformly distributed as the thickness increases. Grain growth occurs by coalescence of nuclei.

The electron diffraction patterns of scandium films of thickness 75 nm deposited on the two crystalline substrates indicate polycrystalline structure (Fig. 3). Figs 4a and b show X-ray diffraction patterns of 75 nm films deposited on to mica and rock-salt substrate, respectively. The X-ray data are given in Table I compared to the ASTM card file data. The analysis indicated that films deposited on mica are randomly oriented, in agreement with the electron diffraction. However, films deposited on rock-salt show a predominant orientation.

In conclusion, scandium films deposited on the cleavage plane of mica are polycrystalline with a small grain size, even for 75 nm thick films. However, in

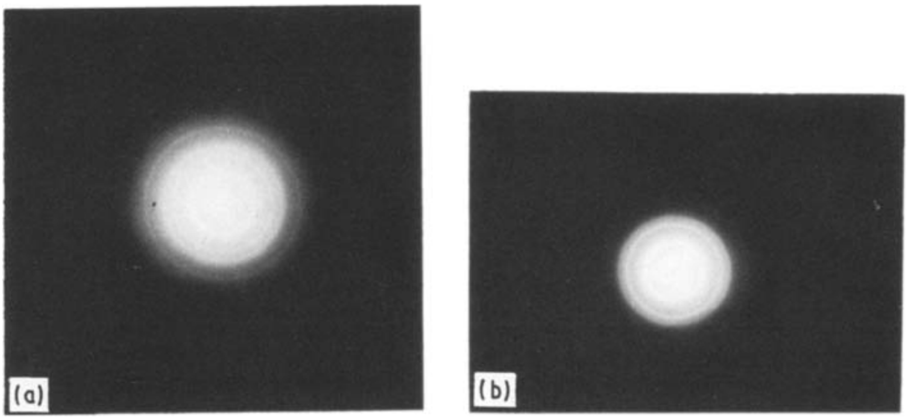

Figure 3 Electron diffraction patterns of 75 nm films deposited on (a) mica and (b) rock-salt.

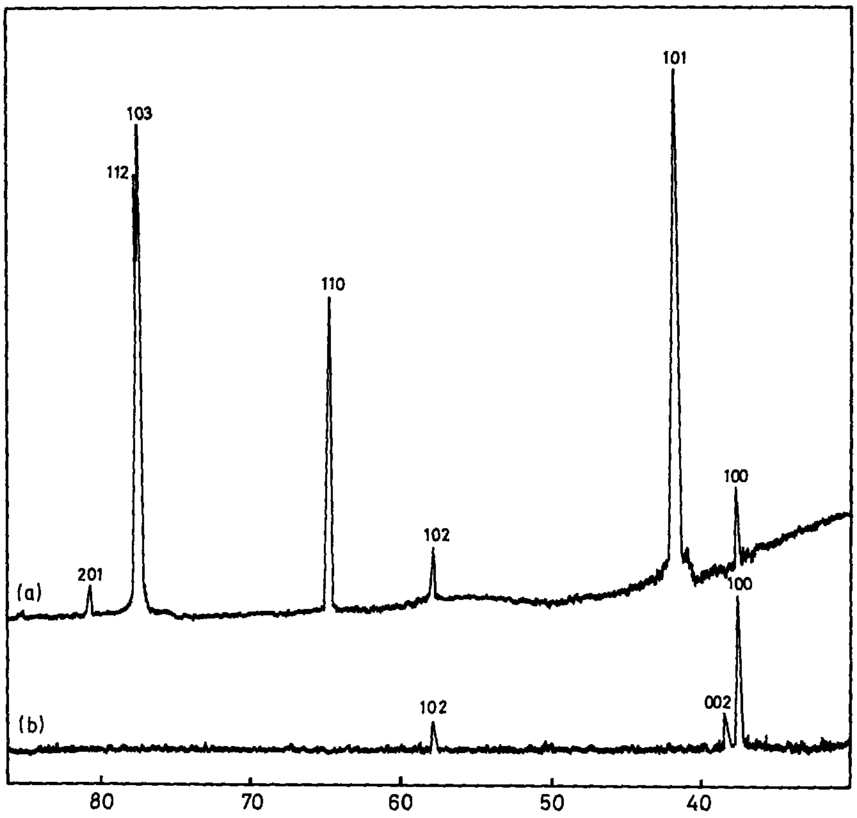

Figure 4 X-ray diffraction patterns from thin films of scandium deposited on (a) mica and (b) rock-salt. Scale readings are 2θ (deg).

case of deposition on the cleaved surface of rock-salt, the films have a polycrystalline structure with a predominant orientation of the (1 0 0) plane parallel to the substrate surface and the films become nearly continuous for a 75 nm thick film.

The optical constants of a metal are functions of the influence of an electromagnetic wave on the behaviour of the electrons within the metal. It would thus seem that if the optical constants of thin films are different from the constants of the bulk metal, and if they vary with the thickness of the film, it is because the structures of the bulk metal and of films of various thicknesses are all different.

The variation of the transmittance T of scandium films deposited on to two different substrates (potassium bromide and mica sheet discs) with the wavelength λ is shown in Figs 5a and b. The transmittance increases gradually as the wavelength increases, moreover, the transmittance decreases on increasing the film thickness. It is noticeable that the wavelength at the transmittance maximum increases with increasing film thickness (Fig. 5a). Following Tubbs [17] and Brattain and Briggs [18] the absorption index k and the index of refraction n for a thick absorping film ($4\pi kd > \lambda$) are given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{1}$$

$$T = \frac{16 n_1 (n^2 + k^2)}{[(n + n_1)^2 + k^2]\,[(n+1)^2 + k^2]} \times \exp(-4\pi kd/\lambda) \tag{2}$$

where T and R are the intensities of the transmitted and reflected light, respectively, n_1 is the refractive index of the substrate and d is the film thickness.

The dependence of k and n on λ, for a thick scandium film (d = 240 nm) on a potassium bromide substrate and for d = 50 nm on a mica sheet substrate, calculated by the above formula, is shown in Figs 6a and b. As seen from Fig. 6, the extinction coefficient (k) increases with the increase of wavelength, but the refractive index (n) decreases with the increase of the wavelength to about 4.5 μm and then increases again.

TABLE I X-ray diffraction data of scandium films deposited on mica and NaCl

Substrate	$d_{\text{calc.}}$	$(I/I_0)_{\text{calc.}}$ (%)	$d_{\text{X-ray}}$	hkl	$(I/I_0)_{\text{X-ray}}$ (%)
mica	2.79188	25	2.846	100	20
	2.509	100	2.52	101	100
	1.8609	14	1.935	102	30
	1.6728	59	1.648	110	10
	1.43162	89	1.493	103	20
	1.43006	81	1.394	112	15
	1.3839	7	1.381	201	15
NaCl	2.8507	100	2.846	100	20
	2.7776	48	2.627	002	35
	1.829	40	1.935	102	30

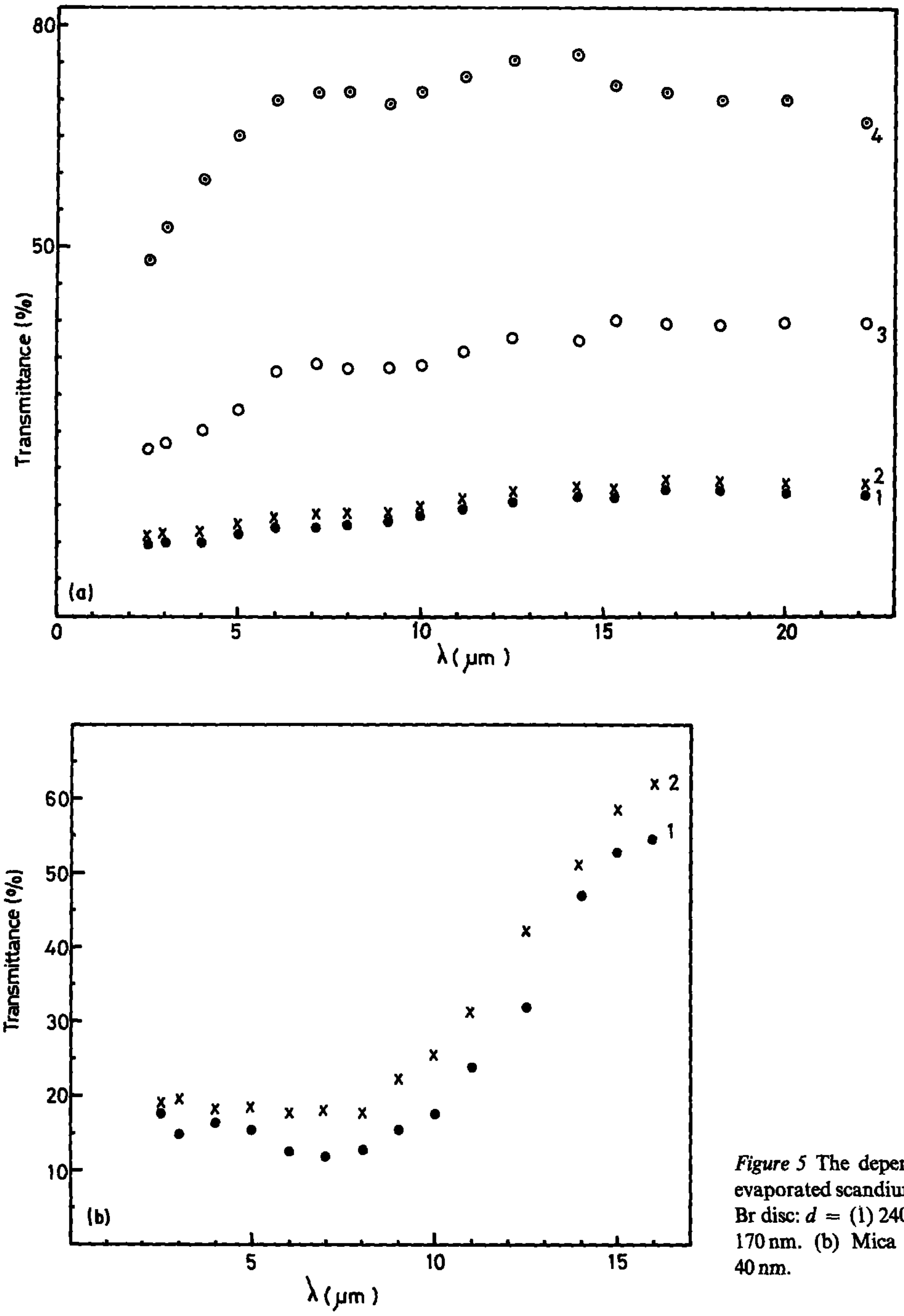

Figure 5 The dependence of the transmittance of evaporated scandium films on the wavelength. (a) K Br disc: d = (1) 240 nm, (2) 225 nm, (3) 200 nm, (4) 170 nm. (b) Mica substrate: d = (1) 50 nm, (2) 40 nm.

Fig. 6a shows the presence of maximum k and minimum n at about 4.5 μm.

In the infrared region where the photon energy does not exceed the threshold of internal photo-effect, the optical data in this frequency range reflect the relaxation processes, the electronic system being excited by the alternating electric field of the light waves. The behaviour of the spectral dependence of the IR optical conductivity can be investigated by plotting $\sigma_1(\omega) = \omega nk/2\pi = nkc/\lambda$ against photon energy (Fig. 7). The curve shows that the IR conductivity increases with the increase of photon energy. It can be seen from Fig. 7 that well-defined structures are shown at $\hbar\omega$ = 0.23, 0.34 and 0.45 eV and shoulders at 0.08, 0.1 and 0.15 eV. The intraband transitions were not easily identified since the relation between Reε (Real dielectric constant) and λ^2 was not linear. Since there is no experimental evidence on this metal as yet, some more work is needed at longer wavelengths for one to be able to separate the intraband and interband transitions.

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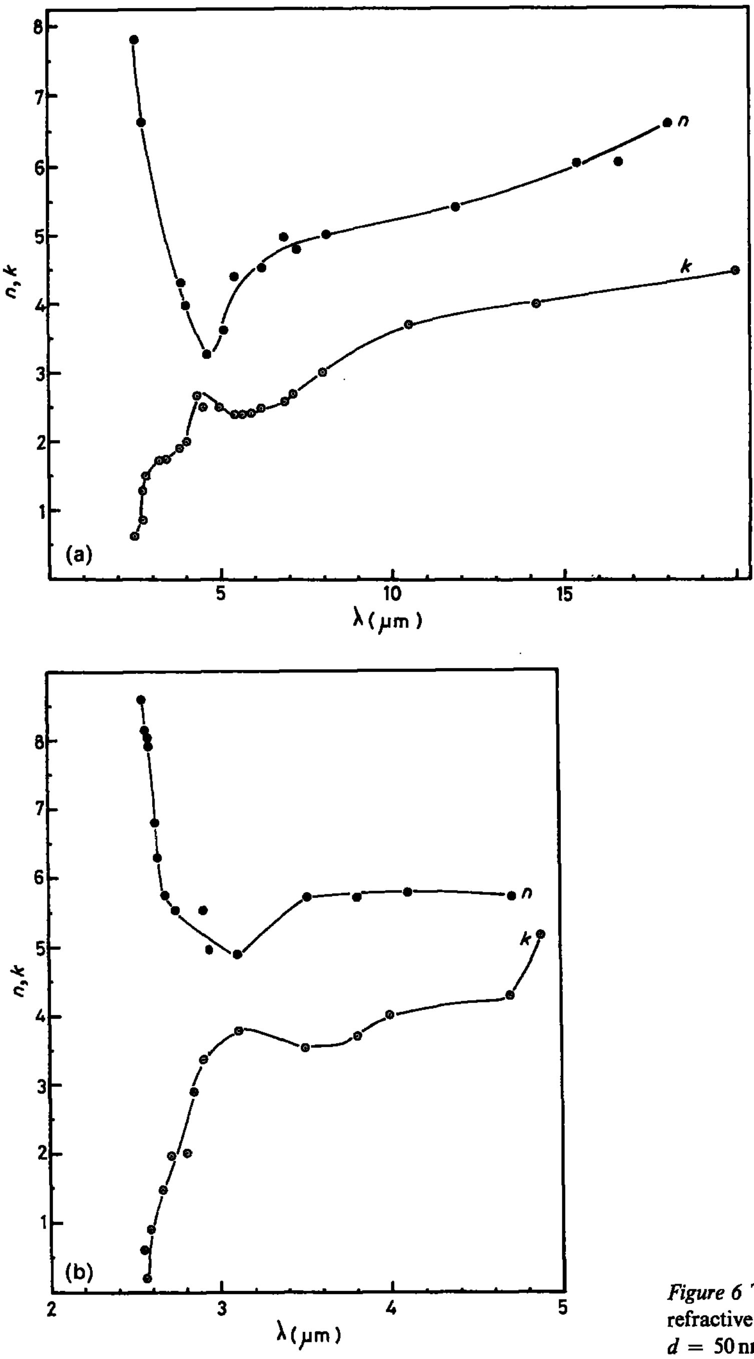

Figure 6 The dependence of the extinction coefficient, k, and the refractive index, n, on wavelength, (a) $d = 240$ nm on KBr disc; (b) $d = 50$ nm on mica substrate.

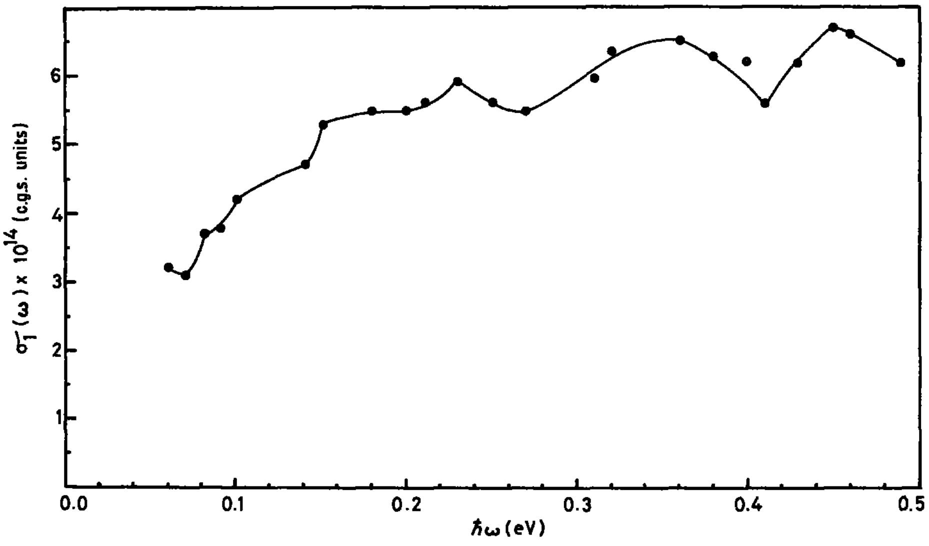

Figure 7 Variation of $\sigma_1(\omega)$ with $\hbar\omega$ in the IR region on KBr disc.

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