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## OPTICAL PROPERTIES OF AMORPHOUS AND A1-TYPE ANTIMONY TELLURIUM AND IODINE

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Measurements were made of reflectance, transmittance and coating thicknesses of optical systems consisting of glass substrates coated at 4.2°K with amorphous Sb, Te or I single layers or with B1-type CaO base films and A1-type Sb, Te or I pseudomorphic overlays. A combination of the measured values allowed us to determine the optical constants and the reflectance of amorphous and A1-type Sb, Te and I. The results obtained in the 0.6–4  $\mu$  spectral interval (corresponding to the 2.07–0.31 eV photon energy range) for films thicker than 70 nm (where size effects were found to vanish) are presented and discussed here. Let us emphasize that the amorphous phase exhibits semimetallic (Sb) or semiconducting (Te and I) behaviour, whereas the A1-type modification behaves in typically metallic fashion.

### INTRODUCTION

A1-type metallic superconducting Sb [1,2], Te [3,4] and I [5] were obtained in the form of metastable pseudomorphic overlays by vapour-quenching at 4.2°K on very smooth, optically polished alkali-zinc borosilicate glass substrates that had been quench-coated at the same temperature with base films of B1-type oxides able to promote pseudomorphism: MnO or CaO for Sb and Te; CaO or SrO for I. The aim of this paper is to present and discuss the findings of a study of the optical constants, in the 0.6–4  $\mu$  wavelength range, of the A1-type modification quench-condensed on CaO, which are compared with those of an amorphous Sb, Te and I phase that forms when the quench-deposition takes place in the absence of the base film. The study has been completed by using the optical constants of the A1-type and amorphous modifications for calculating their reflectance at normal incidence.

### EXPERIMENTAL

The specimen preparation technique was detailed elsewhere [1,3,5], together with a description of the base-film and overlay crystal structure and the overlay electrical properties in the normal and superconducting states. It must be pointed out that the films were deposited at 0.8–1.2 nm/sec rates in a vacuum chamber which operated at about  $10^{-9}$  Torr and that the residual gas was rarefied air. To determine the optical constants, combined measurements were made of the following quantities: the reflectance at the film-coated substrate side,  $R$ , of the substrate/base-film and sub-

strate/base-film/overlay systems or the substrate/amorphous-film system; the transmittance  $T$  of the substrate/base-film/overlay system or the substrate/amorphous-film system; the thicknesses  $s_1$  and  $s_2$  of the overlay or the amorphous film and the base film.  $R$  and  $T$  were measured at normal incidence with a double-beam spectrophotometer, precalibrated so that the substrate can be assumed to be semi-infinite.  $s_1$  and  $s_2$  were determined with a quartz-crystal oscillator whose resonance frequency changes with mass loading, by deriving the density of the B1-type and A1-type films from the lattice constant deduced from electron-diffraction patterns and assuming that the density of the amorphous films is the same as that of the ordinary A7-type Sb, A8-type Te and orthorhombic I (which is quite reasonable, since careful electron-diffraction and electron-microscope investigations show that in effect the amorphous films have an amorphous-like microcrystalline structure and consist of very fine grains of the above types). The study was restricted to specimens with  $s_1 = 10$ –100 nm and  $s_2 > 10$  nm, since deposits thinner than 6–8 nm are not yet isotropic and homogeneous, as shown by electron-transmission micrographs, and A1-type overlays thicker than 110–120 nm are already too absorbing for a reliable measurement of  $T$ .

### THEORETICAL CONSIDERATIONS

$R$  and  $T$  of the substrate/base-film/overlay and substrate/amorphous-film systems can be expressed, respectively, by the relations [6,7]



$$R = \left| \frac{r_1 + r_2 \exp(-2i\alpha_1) + r_3 \exp[-2i(\alpha_1 + \alpha_2)] + r_1 r_2 r_3 \exp(-2i\alpha_2)}{1 + r_1 r_2 \exp(-2i\alpha_1) + r_1 r_3 \exp[-2i(\alpha_1 + \alpha_2)] + r_2 r_3 \exp(-2i\alpha_2)} \right|^2$$

$$T = \frac{n_s}{n_0} \left| \frac{t_1 t_2 t_3 \exp[-i(\alpha_1 + \alpha_2)]}{1 + r_1 r_2 \exp(-2i\alpha_1) + r_1 r_3 \exp[-2i(\alpha_1 + \alpha_2)] + r_2 r_3 \exp(-2i\alpha_2)} \right|^2 \quad (1)$$

$$R = \left| \frac{r_1 + r_2 \exp(-2i\alpha_1)}{1 + r_1 r_2 \exp(-2i\alpha_1)} \right|^2, \quad T = \frac{n_s}{n_0} \left| \frac{t_1 t_2 \exp(-i\alpha_1)}{1 + r_1 r_2 \exp(-2i\alpha_1)} \right|^2, \quad (2)$$

where  $n_s$  and  $n_0$  are the indices of refraction of the substrate and vacuum,  $r_i$  and  $t_i$  are the amplitude reflection and transmission coefficients at the overlay/vacuum or amorphous-film/vacuum ( $i = 1$ ), base-film/overlay or substrate/amorphous-film ( $i = 2$ ) and substrate/base-film ( $i = 3$ ) interfaces and  $\alpha_i$  is the phase thickness of the overlay or amorphous film ( $i = 1$ ) and base film ( $i = 2$ ).

These parameters may be written in the known forms

$$r_1 = \frac{n_0 - n_1 + ik_1}{n_0 + n_1 - ik_1}, \quad r_2 = \frac{n_1 - ik_1 - n_2}{n_1 - ik_1 + n_2}, \quad r_3 = \frac{n_2 - n_s}{n_2 + n_s}$$

$$t_1 = \frac{2n_0}{n_0 + n_1 - ik_1}, \quad t_2 = \frac{2(n_1 - ik_1)}{n_1 - ik_1 + n_2}, \quad t_3 = \frac{2n_2}{n_2 + n_s}$$

$$\alpha_1 = \frac{2\pi(n_1 - ik_1)s_1}{\lambda}, \quad \alpha_2 = \frac{2\pi n_2 s_2}{\lambda} \quad (3)$$

where  $\lambda$  is the radiation wavelength,  $n_1$  and  $k_1$  are the optical constants of the overlay or amorphous film (i.e. the real and imaginary parts of its refractive index) and  $n_2$  is the index of refraction of the base film. Note that, obviously, in the coefficients  $r_2$  and  $t_2$  of the substrate/amorphous-film system  $n_2$  must be replaced by  $n_s$  and that  $n_2$  can be derived from the measured values of  $s_2$  and reflectance  $R$  of the substrate/base-film system by using the expression [6]:

$$R = \frac{(n_s^2 + n_2^2)(n_2^2 + n_0^2) - 4n_s n_2 n_0 + (n_s^2 - n_2^2)(n_2^2 - n_0^2) \cos(4\pi n_2 s_2 / \lambda)}{(n_s^2 + n_2^2)(n_2^2 + n_0^2) + 4\pi n_s n_2 n_0 + (n_s^2 - n_2^2)(n_2^2 - n_0^2) \cos(4\pi n_2 s_2 / \lambda)} \quad (4)$$

Introducing eqs. (3) into (1) and (2), and inserting the measured values of  $R$ ,  $T$ ,  $s_1$  and  $s_2$  and the values of  $n_2$  deduced from (4), a system is obtained whose unknowns are  $n_1$  and  $k_1$ . Eq. (4) and this system were solved by limited series expansions of the transcendental functions. The results found for  $s_1 > 70$  nm (where  $n_1$  and  $k_1$  exhibit size-independent bulk values  $n_{1b}$  and  $k_{1b}$ ) in the spectral interval from 0.6 to 4  $\mu$  (corresponding to the 2.07–0.31 eV photon energy range) are shown in Figs. 1–3 together

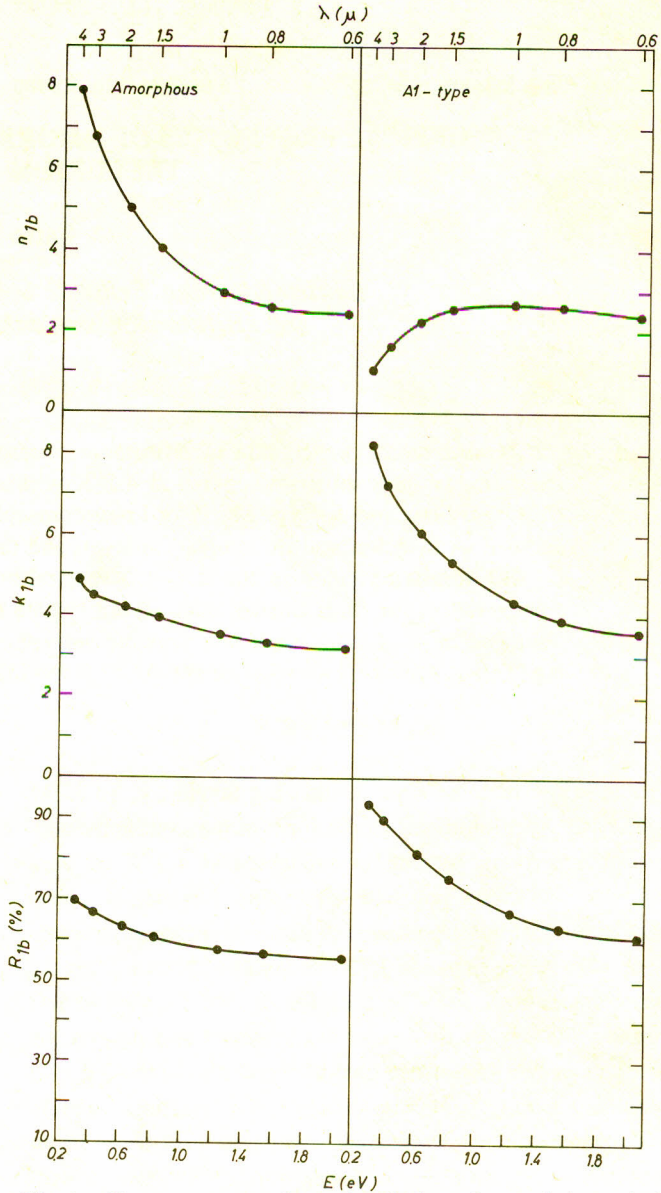


Fig. 1. Photon energy and wavelength dependence of the optical constants  $n_{1b}$  and  $k_{1b}$  and the reflectance at normal incidence,  $R_{1b}$ , of amorphous and A1-type bulk Sb. The circles represent values determined by averaging those derived from measurements of reflectance  $R$ , transmittance  $T$  and coating thicknesses of a large number of glass plates coated with amorphous Sb or B1-type CaO and A1-type Sb.  $R$ ,  $T$  and the thicknesses were measured with a precision of about  $\pm 0.1\%$ . This accuracy, together with the observed departure of the values obtained for some specimens from an ideal Gaussian-type distribution, results in a maximum error of  $\pm 1.2\%$  (not shown in the figure) in the determination of  $n_{1b}$  and  $k_{1b}$ .

with the values of the bulk reflectance at normal incidence of the A1-type and amorphous phases, derived from the well-known formula

$$R_{1b} = \frac{(n_{1b} - n_0)^2 + k_{1b}^2}{(n_{1b} + n_0)^2 + k_{1b}^2} \quad (5)$$



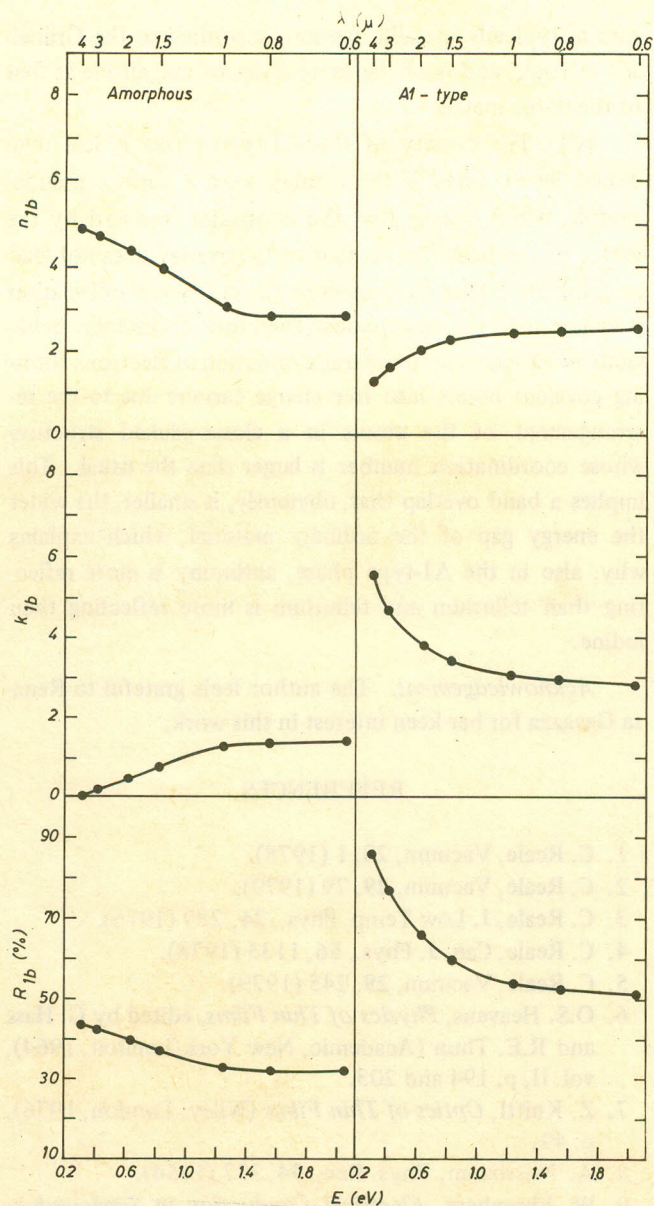


Fig. 2. Photon energy and wavelength dependence of the optical constants  $n_{1b}$  and  $k_{1b}$  and the reflectance at normal incidence,  $R_{1b}$ , of amorphous and A1-type bulk Te.

The structural data are given in Table 1.

### RESULTS

The findings of the present investigation may be summarized as follows:

**Real Part of the Refractive Index.**  $n_{1b}$  is higher in the amorphous than in the A1-type material, except for antimony at  $\lambda = 0.6-0.8 \mu$  and iodine at  $\mu = 0.6-0.2 \mu$ .  $n_{1b}$  of the amorphous phase increases with  $\lambda$ , except for iodine at  $\lambda = 0.6-1.5 \mu$ , whereas  $n_{1b}$  of the A1-type modification behaves oppositely, except for antimony at  $\lambda = 0.6-1 \mu$ .

**Imaginary Part of the Refractive Index.**  $k_{1b}$  is always higher in the A1-type than in the amorphous material.  $k_{1b}$  of the amorphous phase increases with  $\lambda$  in antimony and

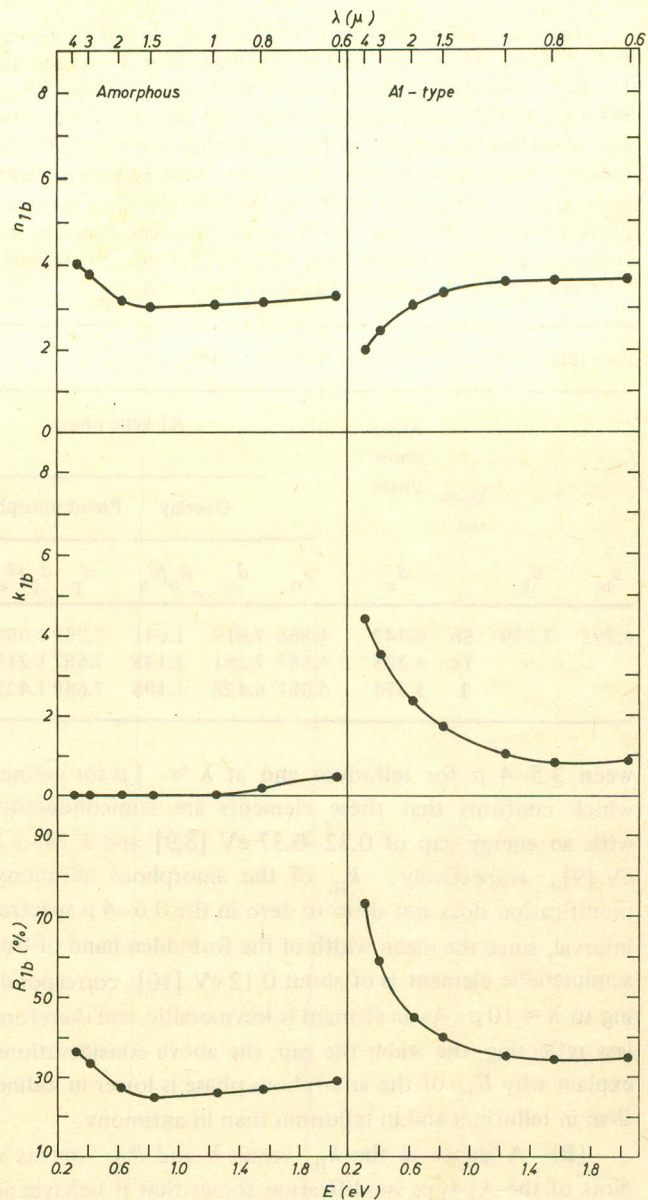


Fig. 3. Photon energy and wavelength dependence of the optical constants  $n_{1b}$  and  $k_{1b}$  and the reflectance at normal incidence,  $R_{1b}$ , of amorphous and A1-type bulk I.

decreases with increasing  $\lambda$  in tellurium and iodine, whereas  $k_{1b}$  of the A1-type modification increases with  $\lambda$  in all three materials, except for iodine at  $\lambda = 0.6-0.8 \mu$ .

**Reflectance.**  $R_{1b}$  is always higher in the A1-type than in the amorphous material.  $R_{1b}$  increases with  $\lambda$  in both amorphous and A1-type materials (except for the amorphous tellurium at  $\lambda = 0.6-0.8 \mu$ , amorphous iodine at  $\lambda = 0.6-1.5 \mu$  and A1-type iodine at  $\lambda = 0.6-0.8 \mu$ ), but the increase is much sharper in the A1-type than in the amorphous modification.

### DISCUSSION AND CONCLUSIONS

(A)  $k_{1b}$  of the amorphous phase drops to zero at  $\lambda$  bet-



Table 1. Lattice constant at 4–7°K,  $a_i$ , in Å, and/or density at 4–7°K,  $d_i$ , in g/cm<sup>3</sup>, of CaO B1-type base films ( $i = b$ ) and Sb, Te and I amorphous single layers ( $i = a$ ), A1-type overlays ( $i = o$ ) and ideal A1-type pseudomorphs ( $i = p$ ) with the same lattice constant as the base films ( $a_p = a_b$ ). The values which are means of those obtained for a large number of samples, were determined with an accuracy of approximately +0.1%. Note that in effect the amorphous films have an amorphous-like microcrystalline structure and consist of very fine A7-type (Sb), A8-type (Te) and orthorhombic (I) grains and that  $d_o$  is higher than  $d_a$  but lower than  $d_p$ .

Base film		Sb, Te or I film					
Material	Amorphous phase	A1-type phase					
		Overlay		Pseudomorph			
$a_b$	$d_b$	$d_a$	$a_o$	$d_o$	$d_o/d_a$	$d_p$	$d_p/d_a$
4.795	3.379	Sb 6.742	4.866	7.019	1.041	7.335	1.088
		Te 6.325	4.887	7.261	1.148	7.687	1.215
		I 5.374	5.081	6.428	1.196	7.648	1.423

ween 3.5–4  $\mu$  for tellurium and at  $\lambda \approx 1 \mu$  for iodine, which confirms that these elements are semiconductors with an energy gap of 0.32–0.37 eV [8,9] and 1.24–1.3 eV [9], respectively;  $k_{lb}$  of the amorphous antimony modification does not drop to zero in the 0.6–4  $\mu$  spectral interval, since the mean width of the forbidden band of this semimetallic element is of about 0.12 eV [10], corresponding to  $\lambda \approx 10 \mu$ . As an element is less metallic, and therefore less reflecting, the wider the gap, the above considerations explain why  $R_{lb}$  of the amorphous phase is lower in iodine than in tellurium and in tellurium than in antimony.

(B) A glance at the  $k_{lb}$  versus  $\lambda$  and  $R_{lb}$  versus  $\lambda$  plots of the A1-type modification shows that it behaves as expected for typical metals, which have no energy gap. This is consistent with the results of previous investigations, which showed that the A1-type antimony [1], tellurium [3] and iodine [5] may become superconductors and that in the normal state their resistivity increases with tempera-

ture in typically metallic fashion, according to the Grüneisen relation, and is of the same order of magnitude as that of the noble metals.

(C) The density of the A1-type phase is less than would be expected if the overlay were a perfect pseudomorph, which means that the constraint imposed by the lattice of the base film to that of the overlay does not lead to complete lattice fit. However, the A1-type modification is denser than the amorphous. Therefore, its metallic behaviour is attributable to the transformation of electrons forming covalent bonds into free charge carriers due to the rearrangement of the atoms in a closer-packed structure whose coordination number is larger than the usual. This implies a band overlap that, obviously, is smaller, the wider the energy gap of the ordinary material, which explains why, also in the A1-type phase, antimony is more reflecting than tellurium and tellurium is more reflecting than iodine.

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