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OPTICAL PROPERTIES OF TIN IN THE 2.5 —40 μ REGION

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The optical constant n and k of evaporated tin deposited on different substrates were determined in the 2.5 — 40 μ region by measuring its transmittance. From these values the second step was carried out for the determination of other physical parameters of tin films. These parameters were the density of conduction electrons N, the effective collision frequency of the electrons ν_0, the plasma fraquency ω_0, the velocity on Fermi surface V_0, the effective area of the Fermi surface A_{eff} and the absorption coefficients A. The energy-loss functions for surface and volume plasmons show sharp peak at 7.69 μ. These values are compared with those found in earlier works.

1. Introduction

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[1,2].

The optical constants of metals depend strongly on the conduction electron density as well as on the interaction of electrons with phonons. Golovashkin et al.[3] carried out a simultaneous study of the optical, electrical and several other properties of white tin, evaporated in vacuum onto a glass substrate. The optical constants of tin were measured at temperatures of 4.2, 78 and 293 K in the wavelength range 0.9—12 μ. The temperature dependence of the electron-phonon collision frequency was determined in the case of high-energy light quanta[4].

The optical constants of tin at room temperature have been determined by Motulevich and Shubin[5], as well as by Hodgson[6]. The results reported in Ref. 5 refer only to the spectral range 1.3—6.3 μ. They agree well with the results of Golovashkin et al.[3]. Hodgson[6] gave his results only in the form of a graph of the dependences of $\log (k^2 - n^2 + 1)$ and $\log (nk/\lambda)$ on $\log \lambda$.

Near-normal incidence-reflectance data on vacuum-evaporated white tin films, produced in situ, are presented for incident photon energies from 2.1 to 4.5 eV. In addition, the real part of the refractive index has been measured from 14.5 to 20.5 eV by the critical-angle method. Separation of the dielectric constants into contributions due to free and bound electrons indicates interband transitions at 1.2 ± 0.1 and 24.5 ± 0.1 eV, and a further interband transitions at approximately 3 eV. Then the energy-loss functions for surface and volume plasmons show sharp peaks at 9.2 and 13.4 eV, respectively, in agreement with electron-energy-loss measurements[7]. Finally, Comins[8] have measured the optical constants of liquid tin by an ellipsometric method at wavelengths mainly in the infrared region, of up to 8 μm and at temperatures up to 1200 °C.

2. *Experimental techniques*

Tin films were obtained by evaporating tin of 99.99% purity from a molybdenum boat on two different substrates freshly cleaved surface of mica and KBr discs at room temperature. A pressure of 10^{-4} Pa was maintained in the apparatus. The optical constants of these films were determined from the transmission curves over the spectral range from 2.5 — 40 μ using a recording double beam spectrophotometer type Beckman IR 4220 which gives transmission data accurate to 1%. The thickness of all these layers was measured by an interference method[9].

3. *Results and discussion*

It is well known that with specified values of temperature and wavelength the optical constants of a thin film of given thickness are functions of a certain number of factors: the type of support and the temperature of the support at the instant of the evaporation, the speed with which the film has been prepared, the degree of vacuum in which the evaporation took place, the type of preparation used and the nature of the residual gas. On the other hand, under well-defined conditions of evaporation the optical constants have been found to vary with the thickness of the film; the temperature and the wavelength of the radiation used in the determination of the constants[1].

For a thick absorbing film, the transmittance of a film of index $n - \mathrm{i}\,k$ and thickness t is given by[10,11]

$$T = \frac{16\, n_0\, (n^2 + k^2) \exp(-\, 4\pi\, kt/\lambda)}{[(n+1)^2 + k^2]\, [(n_0 + n)^2 + k^2]} \quad n > n_0 \ldots \qquad (1)$$

The reflectance in air, for normal incidence is given by

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

The extinction coefficient k can be determined at any wavelength from the slope of the curve of ln transmission against thickness for that wavelength according to the equation[10,11]

$$k = \frac{\lambda}{4\pi}\left(\ln\frac{1}{T_1} - \ln\frac{1}{T_2}\right)/(t_1 - t_2). \tag{3}$$

The variation in the transmittance T of tin films of different thicknesses onto two different substrates with variation in wave number in inverse centimeters is shown in Fig. 1. The transmittance increasses gradually as the wavelength increases, moreover, the transmittance decreases on increasing the film thickness and for thickness $t \approx 150$ nm the film becomes opaque in case of KBr disc and 120 nm in case of mica substrates.

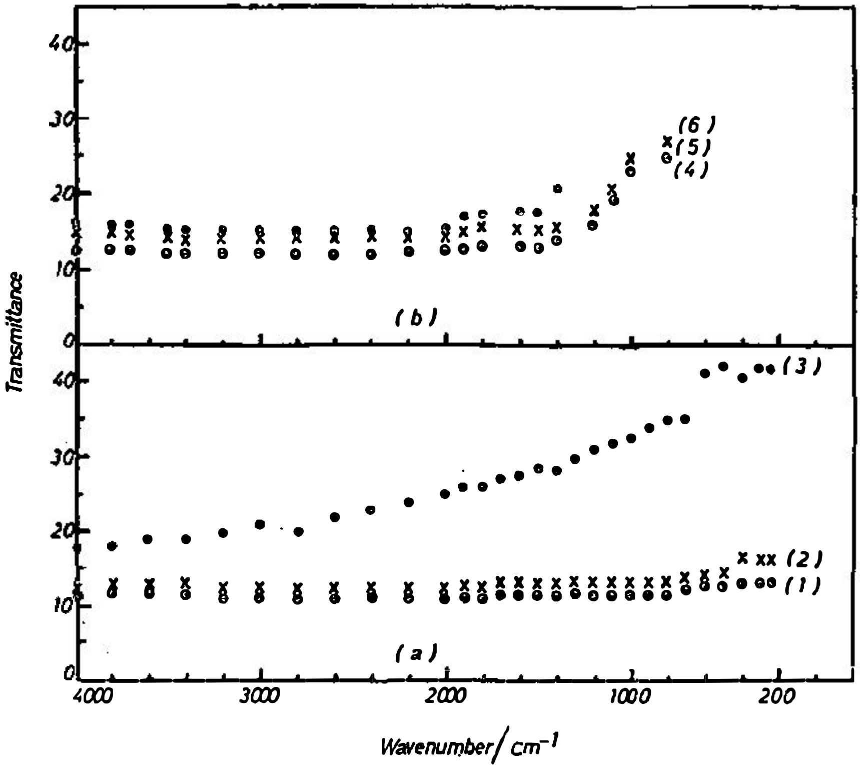

Fig. 1. Relation between transmittance and wavenumber.
(a) on KBr disc, 1 — t = 150 nm; 2 — t = 130 nm; 3 — t = 90 nm.
(b) on mica substrate, 4 — t = 120 nm; 5 — t = 110 nm; 6 — t = 100 nm.

The spectral behaviour of the real (n), and imaginary (k) part of the refractive index of tin films could be estimated from Eqs. (1) and (3). Fig. 2 shows the variation of n and k with wavelength for tin films deposited on KBr disc and mica substrates, respectively.

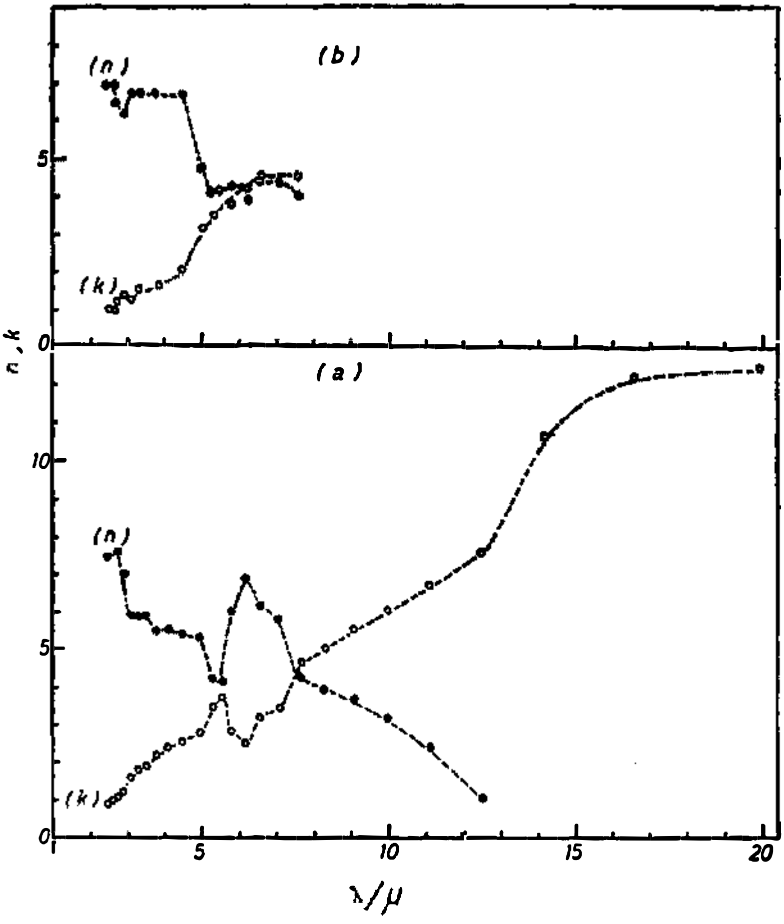

Fig. 2. The dependence of the extinction coefficient (k) and refractive index (n) on wavelength.
(a) $t = 150$ nm on KBr disc.
(b) $t = 120$ nm on mica substrate.

The electronic theory of metals leads to the following expression[12)]

$$\mathrm{Re}\,\varepsilon = \varepsilon_0 - \frac{4\pi Ne^2}{m(\omega^2 + \nu_0^2)}$$

$$\cong \varepsilon_0 - \frac{\omega_0^2}{(\omega^2 + \nu_0^2)} \tag{4}$$

where N is the concentration of the conduction electrons (cm^{-3}), e is the electronic charge, $m^* = 1.26\,m$ for tin[13)], m is the mass of the free electron, ω is the light frequency, ν_0 is the effective collision frequency of the conduction electrons and ω_0 is the plasma frequency. In terms of Drude's relation

$$\bar{\varepsilon} = \varepsilon - i\frac{4\pi\,\bar{\sigma}(\omega)}{\omega} = (n - \mathrm{i}\,k)^2 \tag{5}$$

one obtains,

$$\mathrm{Re}\,\sigma(\omega) = \frac{\omega\,\mathrm{Im}\,\varepsilon}{4\pi} = \frac{n\,k\,\omega}{2\pi} = \frac{Ne^2\,\nu_0}{m(\omega^2 + \nu_0^2)}. \tag{6}$$

When $\omega \to 0$, $\mathrm{Re}\,\sigma(\omega) \to \sigma_{dc}$, hence,

$$\sigma_{dc} = \frac{Ne^2\,\tau}{m} \tag{7}$$

where τ is the relaxation time and is equal to one half the time between two collisions.

In the spectral region $\omega_0^2 \gg \omega^2 \gg \nu_0^2$ one obtains

$$\mathrm{Re}\,\varepsilon = \varepsilon_0 - \frac{\omega_0^2}{\omega^2} \cong \varepsilon_0 - \frac{4\pi\,Ne^2}{m\,\omega^2} = \varepsilon_0 - \frac{Ne^2\,\lambda^2}{\pi\,m\,c} \tag{8}$$

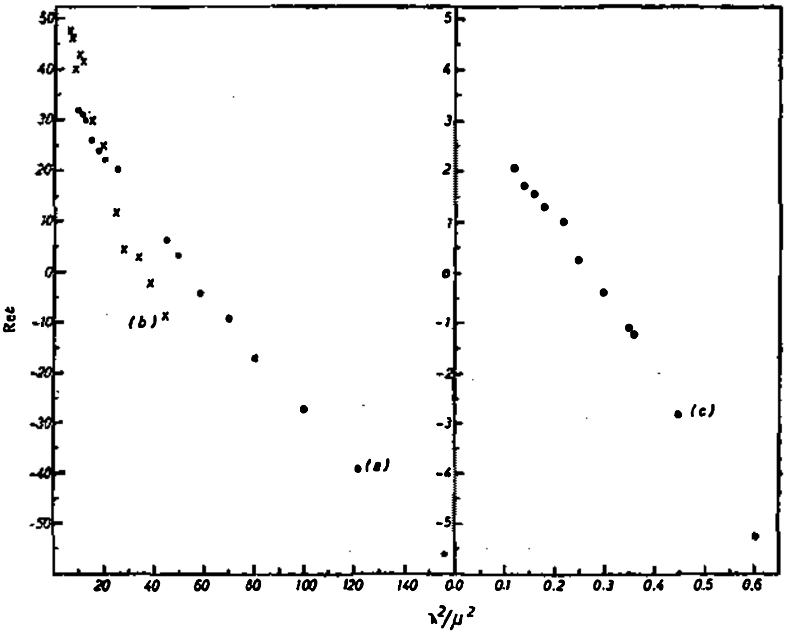

Fig. 3. The dependence of the real dielectric constant Re $\varepsilon = n^2 - k^2$ on the wavelength (λ^2).
(a) Tin deposited on KBr disc.
(b) Tin deposited on mica substrate.
(c) Tin deposited on fused silica.

and the relation between Re ε and λ^2 should be linear. Fig. 3 shows such a relation in the visible and infrared region. The data were fitted with a correlation coefficient of 98.8%, 98.3% and 96.5% for a fused silica substrat, KBr disc and mica substrate, respectively, using a mini-computer Tr-59. If one considers $\omega \approx \nu_0$ Eq. (8) can be written in the form

$$\mathrm{Re}\,\varepsilon = \varepsilon_0 - \frac{Ne^2\,\lambda^2}{\pi\, m\, c^2}. \tag{9}$$

The value of N determined from the slope of the linear plot from relation (9) is given in Table 1.

As $\lambda^2 = 0$ the intercept on the ordinate axis gives $\varepsilon_l = 4.2$, 33.04 and 54.6 for a fused silica substrate, KBr disc and mica substrate, respectively. The value of ε_l, , KBr disc, could be taken as a good agreement with the known theoretical value of bulk tin[14] which is equal to 23.8.

The value of the relaxation time τ was determined according to the Drude equations which may be rewritten as

$$n^2 - k^2 - \varepsilon_l = 2nk\,\omega\tau = \frac{Ne^2}{\cancel{m\,\varepsilon_0}}\,\frac{\tau^2}{1 + \omega^2\,\tau^2}. \tag{10}$$

Therefore, the value of the relaxation time τ was calculated to be 0.21×10^{-14} s at $\lambda = 2.5$ μ which is in reasonable agreement with the published theoretical values of tin[15] (0.23×10^{-14} s).

By taking account of the fact that the measured dc conductivity[16] of the sample was $\sigma_{dc} = 2.24 \times 10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ it can be calculated from equation (7) that $\nu_0 = 1.899 \times 10^{14}\ \mathrm{s}^{-1}$. This value is smaller than the values estimated by Golovashkin et al.[3] and Macrae et al.[7] which are $2.26 \times 10^{14}\ \mathrm{s}^{-1}$ and $2.38 \times \times 10^{14}\ \mathrm{s}^{-1}$, respectively. On the other hand, the value of ω_0 was calculated as follows[17]

$$\omega_0 = \left(\frac{4\pi\, Ne^2}{\varepsilon_l\, m}\right)^{1/2} \tag{11}$$

and found to be $1.272 \times 10^{15}\ \mathrm{s}^{-1}$ which corresponds to $\lambda \sim 7.7$ μ, that is, the short wavelength limit of the spectral region which is studied. Given the values of N and ν_0 it is possible to evaluate the contribution of conduction electrons to the absorption A_{el}. By using the approximate expression[12]

$$A_{el} \approx \nu_0 \left(\frac{m}{\pi\, e^2\, N}\right)^{1/2} \tag{12}$$

the value $A_{el} \approx 5.19\%$ is obtained. Thus the contribution of conduction electrons to the absorption in tin in the wavelength region of interest here is clearly very small. In the calculation presented above, it was assumed that skin effect is normal in tin. Knowing the value of N, one can make the following evaluations. According to the equation[18]

$$V_0 = \left(\frac{h}{m}\right)\left(\frac{3N}{8\pi}\right)^{1/3} \tag{13}$$

the velocity on the Fermi surface is $V_0 \approx 0.921 \times 10^8$ cm/s which agrees with the value obtained from the optical measurements of tin[3,4] ($V_0 = 0.93 \times 10^8$ cm/s), and the mean free path length[16] is $l \sim 0.0391$ μ. The skin depth δ changes from 0.41 to 0.139 μ as the wavelength varies from 2.5 μ to 33.3 μ as a result of which the condition for normal skin effect ($l \ll \delta$) is well satisfied over the whole region under investigation.

The values of the effective area of the Fermi surface A_{eff} were determined in case of infrared and visible regions taking into account the following equation

$$A_{eff} = 4\pi (3\pi^2 N)^{2/3}. \tag{14}$$

The results of the analysis of the experimental data are listed in Table 1.

TABLE 1.

	Visible region	Infrared region	
		KBr disc	Mica substrate
Density of conduction electron N/cm^{-3}.	2.55×10^{22}	1.68×10^{22}	2.1×10^{22}
Density of conduction electron N/atom.	0.688	0.455	0.57
Fermi velocity V_0/cm s^{-1}.	1.06×10^8	0.92×10^8	0.989×10^8
Relaxation time τ/s.	15×10^{-16}	0.526×10^{-14}	0.398×10^{-14}
Aera of Fermi surface A_{eff}/cm^{-2}.	1.04×10^{17}	0.788×10^{17}	$0,914 \times 10^{17}$
Plasma frequency ω_0/s^{-1}.	4.38×10^{15}	1.272×10^{15}	1.106×10^{15}
Contribution of conduction electrons to the absorption A_{el}.	14.8%	5.19%	6.14%

The comparison between the physical parameters in the two regions.

It is clear from Table 1 that there are great differences between these values. This discrepancy may be due to that the skin anomalous effect could be obviously found in case of visible region than in case of infrared.

Besides, it was found that the values of the relaxation time τ and the number of the conduction electrons N obtained from infrared measurements could be taken as reasonable values rather than those obtained from visible measurements. On the other hand, comparing with the known value of Fermi velocity V_0 of bulk tin, it was found that V_0 obtained from the visible measurements was higher, while that obtained from infrared measurements was nearly the same. The high value of V_0 could be attributed to the fact that the photon energy $h\nu$ in case of visible region is larger than that in case of infrared.

The study of the anomalous skin effect showed that the amount of this anomaly is much greater in case of visible than in case of infrared. This is because the energy of photon in case of visible is much higher than in case of infrared leading to the movement of conduction electrons which would travel a considerable distance free from the applied electromagnetic field.

The volume $-\operatorname{Im}\left(\frac{1}{E}\right)$ and surface $-\operatorname{Im}\left(\frac{1}{E+1}\right)$ energy loss functions are proportional to the characteristic energy loss of fast electrons traversing the bulk and surface of the material, respectively. They are related to the real (ε_1) and imaginary (ε_2) part of the dielectric constant by the relations:

$$-\operatorname{Im}\left(\frac{1}{E}\right) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}, \quad -\operatorname{Im}\left(\frac{1}{E+1}\right) = \frac{\varepsilon_2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2} \tag{15}$$

where E is the complex dielectric constant.

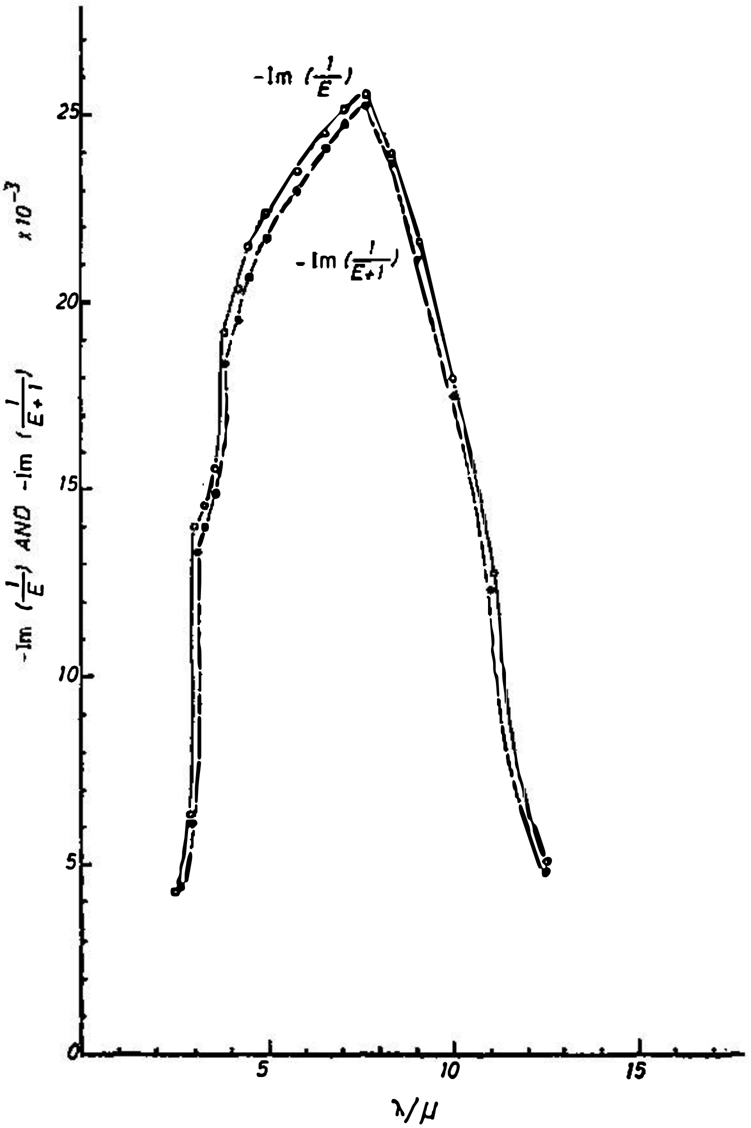

Fig. 4. The behaviour of both the volume and surface energy loss functions as a function of wavelength. t = 150 nm tin deposited on KBr disc.

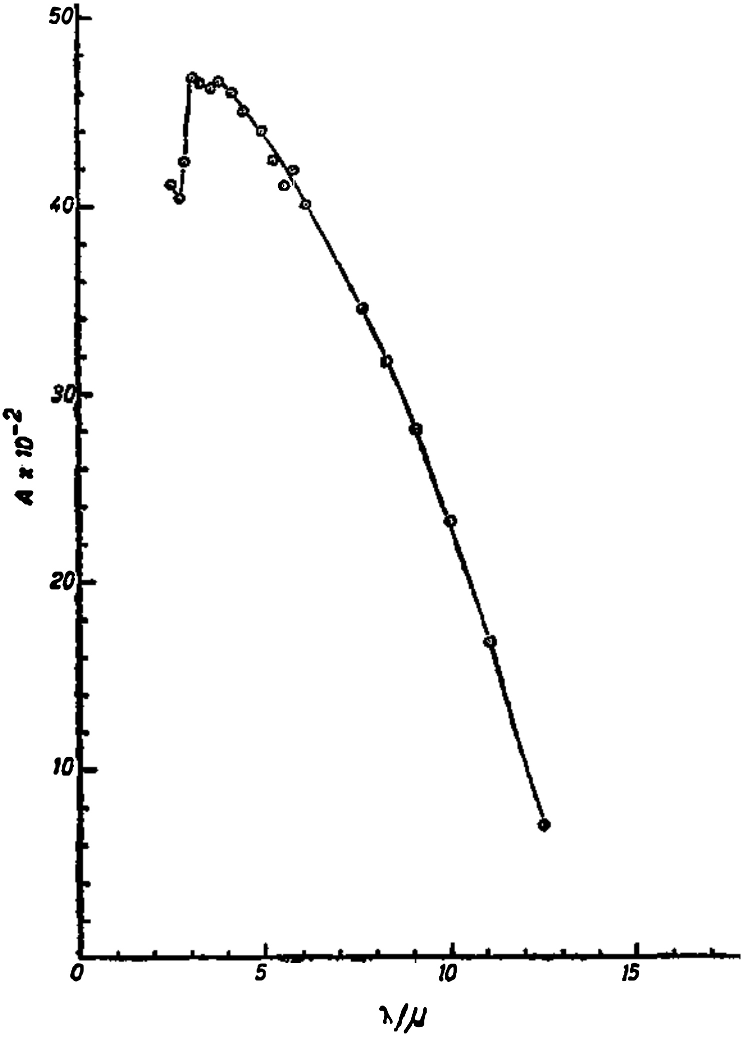

Fig. 5. The variation of the coefficient of energy absorption with the wavelength. $t = 150$ nm tin deposited on KBr disc.

Fig. 4 illustrates the behaviour of both the volume and surface energy loss functions. In Fig. 4 the $-\operatorname{Im}\left(\frac{1}{E}\right)$ and the $-\operatorname{Im}\left(\frac{1}{E+1}\right)$ function shows a sharp maximum at $\sim 7.7\ \mu$. The sharpness of this maxima indicates that both energy losses should be observed when fast electrons traverse tin films.

Along with optical constants (n) and (k), the absorption coefficient A is of great importance in the description of a metal. The determination of the absorption coefficient[10] for normal incidence $A = 4n/[(n+1)^2 + k^2]$ indicated the presence of a sharp peak in the 3.1 — 3.8 μ region (Fig. 5).

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OPTIČKA SVOJSTVA KOSITRA U PODRUČJU 2,5—40 μ

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Određene su optičke konstante *n* i *k* u području 2,5—40 μ za kositar naparen na različite substrate pomoću mjerenja transmitivnosti. Pomoću tih vrijednosti određeni su ostali fizički parametri tankih filmova: gustoća vodljivih elektrona, efektivna frekvencija sudara, Fermijeva brzina, veličina Fermijeve površine i apsorpcioni koeficijenti. Funkcije gubitka energije za površinske i volumne plazmone imaju oštar maksimum na 7,69 μ. Ove vrijednosti uspoređene su sa onima iz prijašnjih radova.