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OPTICAL PROPERTIES OF BISMUTH IN INFRARED AND VISIBLE REGION

SIHAM MAHMOUD

Physics Department, National Research Centre, Cairo, A. R. E.

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Thin bismuth films of thickness in the range from 20 to 250 nm were prepared by thermal evaporation under vacuum conditions of 10^{-4} Pa. The films were deposited onto mica discs and quartz with the rate of 2 nm/s. The values of refractive index, extinction coefficient, dielectric constant, optical conductivity and some physical data of bismuth films were estimated in the infrared and visible region by using transmission technique.

1. Introduction

The optical properties of bulk and thin bismuth films have been investigated by a number of authors[1-9]. Markov and Lindstrem[1] have measured the optical constants of bismuth films sublimed on rocksalt and nitrocellulose substrates of thicknesses 0.1 to 1 μ in the wavelength range from 3 to 15 μ by measuring the reflectance and transmittance of the films, where distinct interference patterns were obtained.

Markov et al.[9], have measured the optical constants of bulk bismuth. The samples were made from bismuth whose purity was 99.97%. The samples were prepared by mating in a mold and then polished electrolytically. By measuring the reflectance in the wavelength range from 3 to 36 μ, an absorption band was found in the vicinity of 27 μ and the concentration of conduction electrons was found to be 5×10^{19} cm^{-3}. The properties of Bi were traeted from the band model viewpoint with a forbidden band gap $\Delta E_0 \cong 0.04$ eV.

Harris et al.[3], have measured the optical constants of Bi deposited onto a free Al_2O_3 substrates, the deposits were heated for several hours at 453 K. Transmittance and reflectance measurements were made at a number of fairly closely spaced wavelengths, from 15 to 150 μ. All samples show reflectance minimum and transmittance maximum near 30 μ. The dielectric constant for these deposits have been found to approach zero values near the wavelength of the reflection minimum.

Potapov[4] has measured the refractive index and absorption index for polycrystalline samples of Bi, Sb, Bi + 0.5% Te. The measurements were carried out by the absorption method in the interval of wavelengths 1—14 μ at 2.5 K. The samples of pure Bi were in the form of a polycrystal measuring 5 × 16 mm and 2 mm thick. They were prepared in vacuum by pouring out spectroscopically pure bismuth, subjected to zone purification on a glass plate, this was followed by electrolytic polishing. The ratio of the resistance ϱ of the sample at room temperature and at liquid helium temperature was found to be ϱ (300 K)/ϱ (4.2 K) = = 130. The real and imaginary components of the permitivity ε were calculated and compared with the data derived from Abrikosov's theory[5]. It is shown that in the case of Bi + 0.05% Te the behaviour of the real and imaginary parts of the dielectric constant differs little from the behaviour of the corresponding quantities for Sb and Bi. The optical constants for the principal directions of single crystals of Bi have been determined over the range 0.4 to 11.0 μ. The absorption curves for Bi show that the minimum energy gap for this series of interband transitions occurs at wavelengths longer than 11 μ and the $n^2 - k^2$ curves [where n, k are the refractive index and the extintion coefficient of bismuth, respectively] indicate that this gap is not closely approached in either of the principal directions at the limits of Lenham measurements[10]. This contradicts the results of Hodgson[7] for a polycrystalline bulk specimen.

2. *Experimental techniques and data analysis*

The investigated bismuth layers were obtained by vacuum evaporation on mica-sheet discs for IR and quartz for visible region. The evaporation temperature was maintained at about 333 K, which ensured average rates of evaporation of 2 nm/s, in 10^{-4} Pa vacuum. Bismuth (99.99%) was evaporated using helical tungsten filament. A multibeam interferometer method[11] was used for measurement of the thickness. The transmission spectra (on mica substrate) and absorbance spectra (on quartz substrate) were obtained wirth the help of an 4220, 5260 Beckman double beam spectrophotometer with an accuracy of 1% used in the infrared and visible region, respectively.

Data analysis

A detailed examination of the electromagnetic solution for transmission through a semi-transparent metal film was found helpful in designing appropriate samples[12]. Suppose that the metal film is supported, and therefore bounded, on the side by a glass or quartz substrate and bounded on the other side by air as shown in Fig. 1. Assume that monochromatic light of unit intensity is incident through air of refractive index n_1 onto a metal film with refractive index n_2 and extinction coefficient k. When the thickness of the films is small enough, a measurable intensity of light T emerges into the substrate of refractive index n_3. The experimentally measured intensity T' which passes through the substrate is smaller than T because of internal reflections within the substrate. The exact solution for T in Fig. 1 is rather clumsy algebraically, therefore only the approximation for large thicknesses will be given here[13, 14]:

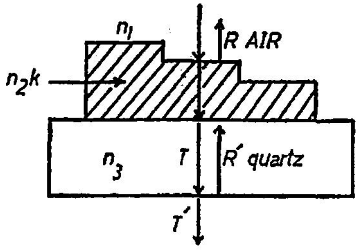

Fig. 1. Schematic diagram of the film/substrate structures.

$$T = C \exp\left(-4\pi kt/\lambda\right) \tag{1}$$

where

$$C = \frac{16 n_1 n_3 (n_2 + k)^2}{[(n_2 + n_1)^2 + k^2]\,[(n_2 + n_3)^2 + k^2]}. \tag{2}$$

An examination of the derivation of Eq. (2) shows that the exponential term arises from absorption in the metal film and that the pre-exponential factor C is associated with reflection as at the film boundaries.

3. Results and discussion

A convenient way of discussing the optical properties[15] of metals related to their electronic structure is to divide them in two classes, free (intraband) and bound electron effects. In metals the absorption related to the intraband transitions is very large because of the high density of free carriers.

This confirmed that the contributions to the dielectric constant of free and bound electrons are additive and that the free carrier contribution to the dielectric constant decreases rapidly with increasing frequency[16]. Thus the influence of the conduction electrons will be more important in the infrared. The interband transitions start at a definite minimum frequency, and therefore the infrared region of the optical properties of metals is governed exclusively by the behaviour of free electrons.

Fig. 2 shows the dependence on wavelength of the refractive index (n), the absorption coefficient (k) and optical conductivity (σ) for bismuth films deposited on freshley cleaved mica substrate. The calculated values of n, k are compared with the data measured by different authors, where the data of Markov and Lindstrem[1)] were measured for an evaporated bismuth layer about 1 μ thick (deposited onto rocksalt substrate); the data of Markov and Khaikin[2)], for electrolytically polished bismuth, and Hodgson's data[7)] on mechanically polished bismuth. It is readily seen that the results differ considerably each from other. These differences can be explained by differences in surface structure. Mechanical polishing of bismuth produces a cold-worked surface layer of varying structure, while electropolishing does not leave a surface layer of different structure. Evaporated bismuth layer has a structure which differs greatly from the usual structure of bulk bismuth (the specific resistivity of evaporated bismuth is three times as great as that of the bulk metal[17)], etc.).

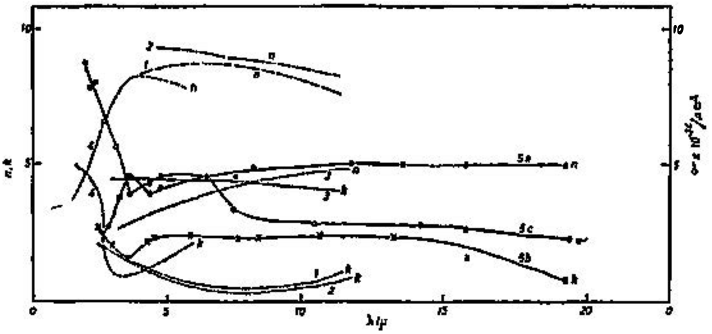

Fig. 2. The dependence of the extinction coefficient (k), refractive index (n) and optical conductivity (σ) on wavelength (λ).

1 — From Ref. 1 (for 890 nm film);
2 — From Ref. 1 (for 560 nm film);
3 — From Ref. 2;
4 — From Ref. 7;
5 — Present work, for bismuth film deposited on mica substrate ($t = 250$ nm).

As is seen from Fig. 2, there is maximum of (n) and minimum of (k) at about 4 μ. Hodgson[7)] assumed that the position of the maximum of n (minimum of k) determines the width of the forbidden band of bismuth. The experimental results may be interpreted in the following way. The energy gap between the first filled band and the conduction band of bismuth is about 0.3 eV, corresponding to the absorption minimum at about 4 μ. The absorption radiation of wavelength greater than 4 μ is due to electronic transitions within the conduction band[18)]. A determination of the width of the forbidden band from present data gives a value of 0.298 eV. The deviation in the position of the maximum n and the related deviation in the width of the forbidden band could have been caused by the structural peculiarities of evaporated bismuth.

Fig. 2 shows a plot of $2nk/\lambda$ versus λ. The curve shows that the IR conductivity decreases with λ in the short wavelength region, then it increases with λ at higher wavelengths. This anomalous behaviour can be interpreted taking into consideration the Harris and Loeb[19)] theory for the variation of conductance with wavelength in thin metal films. These are the *condenser effect* and the *relaxation effect*. The *condenser effect* is due to nonconducting regions which can intercept electric current. Such imperfections act as condensers that have an infinite impedance toward direct current, but whose impedance decreases with increasing frequency. Thus the effective conductance in the infrared tend to decrease with increasing wavelength if there are imperfections acting as condensers. The *relaxation effect* causes the induced electron motion to lag behind an imposed radiation field so that the amount of energy absorbed is less than it would be if the field and the current were in phase. This lag inceases with increasing frequency. Therefore, due to the *relaxation effect*, the effective optical conductivity should increase with the increase of the wavelength in the infrared region. Harris and Corrigan$^{20)}$ had derived the following expression for the IR conductivity due to the *relaxation effect* (using Drude's equation)

$$\sigma(\omega) = \left[\frac{\sigma_n(0)}{(1+\omega\,\tau_n)^2} + \frac{\sigma_p(0)}{(1+\omega\,\tau_p)^2}\right] \qquad (3)$$

where τ_n, τ_p are isotropic relaxation times for the electrons and holes, and $\sigma_n(0)$, $\sigma_p(0)$ are the d. c. electrical conductivity for the electrons and holes, respectively. Therefore, the optical conductivity should vary with the wavelength as:

$$\frac{\sigma(\omega)}{\sigma(0)} \cong \left[1 + (2\pi\, c\, \tau)^2 \frac{1}{\lambda^2}\right]^{-1}. \qquad (4)$$

The anomaly due to the *condenser effect* is very pronounced in thin films of good conductors (silver and aluminium)$^{21)}$, while the anomaly due to the finite relaxation time of the electrons is pronounced in thicker films of poor conductors. Bismuth is not as good conductor as are silver and aluminium, nor it is very poor conductor. Therefore, both the *condenser* and the *relaxation effects* may occur simultaneously. However, at longer wavelengths the predominant mechanism will be the *relaxation effect*, which explains the increase of $\sigma(\omega)$ at longer wavelengths. In Fig. 3a, absorbance spectra are shown for samples of three thicknesses: 20, 25 and 30 nm. The absorbance decreases gradually as the wavelength decreases, however, the absorbance increases on increasing the film thickness. This phenomenon has been noted by other workers$^{22)}$.

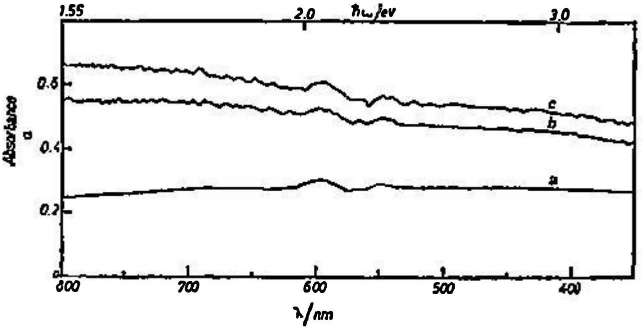

Fig. 3a. Spectral behaviour of bismuth films:
(a) $t = 20$ nm, (b) $t = 25$ nm, (c) $t = 30$ nm.

The values of n, the refractive index k, the extinction coefficient and σ, the optical conductivity (Fig. 4) can be calculated from values of transmission spectra and are shown in the graph (3 b). As is seen from Fig. 4, the extinction coefficient (k) decreases with the increase of photon energy and thickness, but the refractive index (n) increases with the increase of photon energy and thickness.

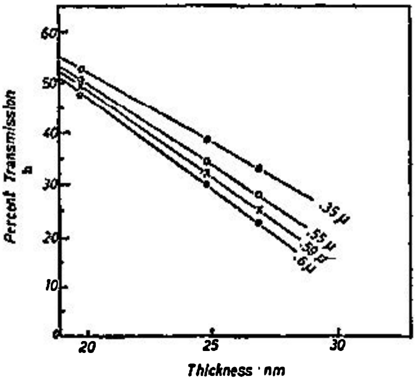

Fig. 3b. Transmittance versus thickness at different wavelengths.

The conduction electron density N, the velocity of electrons on the Fermi surface v, and the frequency of electron collisions ν_0, were determined using the following formulae[23]:

$$N = \frac{0.1115 \cdot 10^{22}}{\lambda^2} \frac{(n^2 + k^2)^2}{k^2 - n^2} (1 - B_1)^{-1} \tag{5}$$

$$\frac{\nu_0}{N} = 1.69 \cdot 10^{-6} \lambda \frac{2nk}{(n^2 + k^2)^2} (1 - B_2) \tag{6}$$

$$B_1 = \frac{3v}{8c} \left[\frac{1 + (n/k)^2}{1 + (\nu_0/\omega)^2} \right]^{1/2} \left[\cos (Q_1 - Q_2) + \frac{2nk}{k^2 - n^2} \sin (Q_1 - Q_2) \right] \tag{7}$$

$$B_2 = \frac{3v}{8c} \left[\frac{1 + (n/k)^2}{1 + (\nu_0/\omega)^2} \right]^{1/2} \left[\cos (Q_1 - Q_2) - \frac{k^2 - n^2}{2nk} \sin (Q_1 - Q_2) \right]. \tag{8}$$

Here, $\tan Q_1 = \hbar/k$, $\tan Q_2 = \omega/\nu_0$, ω is the angular frequency of light, λ is the wavelength of light in microns, and c is the velocity of light in vacuum. The calculations were carried out by the method of successive approximations. In the zeroth approximation, one assumes that[24] $B_1 = B_2 = 0$. This corresponds to the normal skin effect.

The results of the determinations of the density for various wavelengths are given in Fig. 5a which shows clearly its remarkable constancy in the visible region.

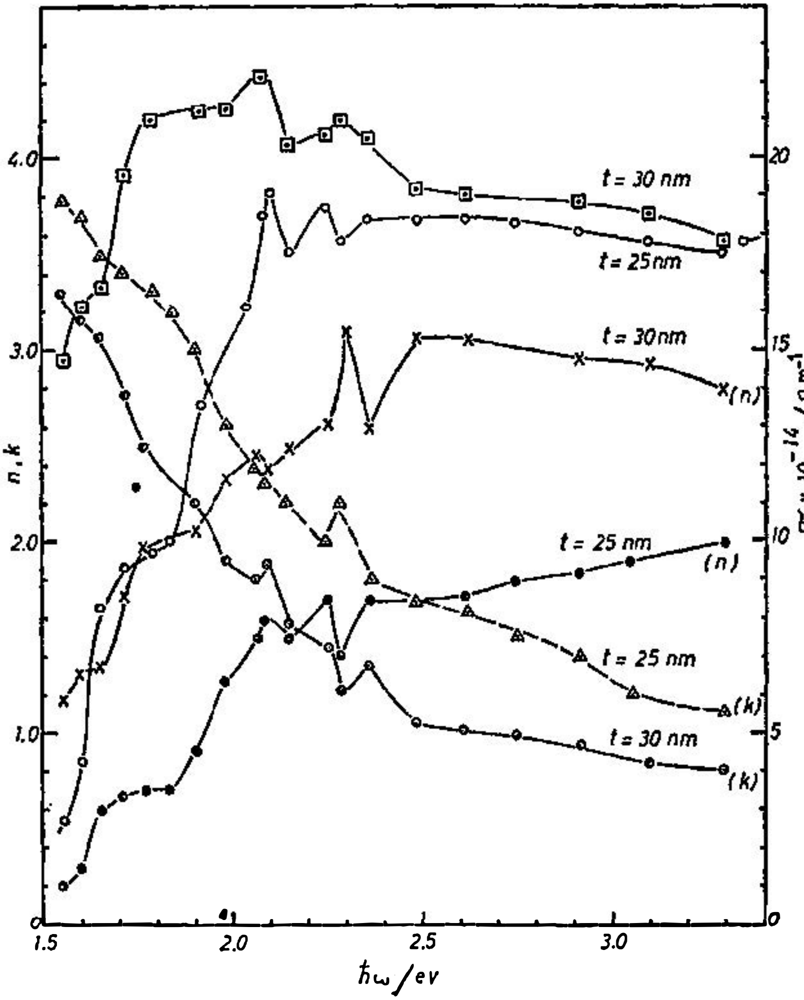

Fig. 4. Dependence of the extinction coefficient (k), refractive index (n) and optical conductivity (σ) on photon energy for bismuth film deposited on quartz (t = 25 nm and 30 nm).

The dependence of the electron collision frequency, ν_0, found from the optical data from the long wavelength end of the spectral range on λ is given in Fig. 5b. From this figure we cannot use the short-wavelength part of the spectrum where the influence of the electron-electron collisions is dominant. In the long-wavelength region, the influence of the electron-electron collisions is extremely small compared with the strong electron-phonon interaction[25].

For $\lambda = 0.8$ μ ($\omega = 23.6 \cdot 10^{14}$ s^{-1}) we have $\omega^2/\nu^2 = 1.01 \cdot 10^2 \gg 1$. On the other hand, the value of ω_0 was calculated as follows[26]

$$\omega_0 = \left(\frac{4\pi e^2 N}{m}\right)^{1/2} \tag{9}$$

and found to be $8.97 \cdot 10^{15}\,s^{-1}$. Given the values of $N(2.53 \cdot 10^{22}\,cm^{-3})$ and $\nu_0(2.344 \cdot 10^{14}\,s^{-1})$, it is possible to evaluate the contribution of conduction electrons to the absorption A_{el}. By using the approximate expression[27]

$$A_{el} \approx \nu_0 \left(\frac{m}{\pi e^2 N}\right)^{1/2} \tag{10}$$

$A_{el} \approx 5\%$ is obtained. Thus the contributions of conduction electrons to absorption in bismuth in the wavelength region of interest here is clearly small and agrees with the value obtained from Markov's measurements[2].

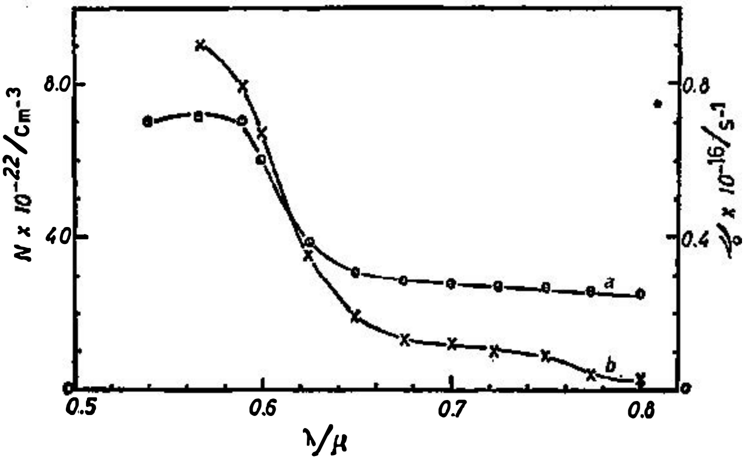

Fig. 5 a) Conduction electron density (N) versus wavelength (λ).
5 b) Electron collision frequency (ν_0) versus wavelength (λ).

In the calculations presented above, it was assumed that the skin-effect in bismuth is normal. Knowing the values of N and ν_0, one can make the following evaluation. According to the equation[28]

$$v_0 = \left(\frac{h}{m}\right)\left(\frac{3N}{8}\right)^{1/3} \tag{11}$$

the velocity on the Fermi surface is $v_0 \sim 1.05 \cdot 10^8$ cm/s, which agrees with the value obtained from the optical measurements of bismuth[2].

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OPTIČKA SVOJSTVA BIZMUTA U INFRACRVENOM I VIDLJIVOM PODRUČJU

SIHAM MAHMOUD

Physics Department, National Research Centre, Cairo, A. R. E.

UDK 538.958

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Tanki bizmutovi filmovi debljine 20 do 250 nm preparirani su metodom termalne evaporacije u vakuumu od 10^{-4} Pa. Primjenom transmisione tehnike određeni su indeks loma, koeficijent ekstinkcije, dielektrična konstanta, optička vodljivost i druga svojstva bizmutovih filmova u infracrvenom i vidljivom području.