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SOME OPTICAL PROPERTIES OF BiI_3 FILMS

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The optical properties of high quality BiI_3 films were investigated near the fundamental absorption edge. The absorption coefficient near the absorption edge is well described by Urbach's rule. The large peak near 2.0 eV is ascribed to direct excitonic transition near the edge. The absorption bands at 2.03 eV and 2.39 eV are attributed to the spin-orbit splitting of the low energy iodine doublet.

1. Introduction

Recently much research and attention has been devoted to the optical properties of halides with layer structures[1]. BiI_3 is one of a large number of layer compounds, it possesses a general structural modification and is related to rhombohedral system (sp. gr. C_{3i}^2). The atomic arrangement is in the form of layers of Bi and I ions oriented perpendicular to the *c*-axis, being stacked as I-Bi-I ... I-Bi-I. The Bi ions occupy one third of the octahedral holes formed by adjacent layers of closed packed I ions. The bond inside layers are ionic-covalent, and the adjacent composite (I-Bi-I) layers are held by Van der Waals forces. The crystallographic direction C_3 is perpendicular to the cleavage plane, and cleavage occurs parallel to (001) plane across the Van der Waals forces between adjacent composite I-Bi-I layers[2]. Optical measurements on the interband transitions in bulky BiI_3 crystals have been carried out by several authors. but the results are not in well agreement among different research groups. The difference can be largely ascribed to the difference in sample quality.

The aim of the present contribution is to investigate the optical properties and the fundamental absorption of thin films of BiI_3 prepared by thermal evaporation. The optical constants have been calculated and important data on the interband transitions have been obtained.

2. *Experimental*

Polycrystalline films were deposited by thermal evaporation in vacuum ($7 \times \times 10^{-4}$ Pa) at an evaporation rate 3 nm/s. In the region of intense absorption, the value of the absorption coefficient lies between 10^5 to 10^6 cm^{-1}, therefore, evaporated films few nanometers thickness were used for optical measurements. The microstructure of BiI_3 films, supported on amorphous carbon substrate, was investigated with an electron microscope. It was found to consist of small crystals (a few nanometer in size) which were mostly oriented with the *c*-axis perpendicular to the carbon film, while the (001) plane is parallel to the substrate. Since both carbon and fused silica glass provides amorphous substrates, epitaxial growth should not occur and the observations are likely to be applicable to BiI_3 evaporated onto fused silica plates. Optical transmission measurements were made over the range 300 nm to 800 nm with Beckmann UV 5230 recording spectrophotometer. The thickness of the films was determined by Tolansky's interference method[3].

3. *Results and discussions*

Fig. 1 shows the variation of the transmission of thin films of BiI_3 evaporated onto fused silica plates with the wavelength. The absorption increases as the wavelength decreases.

The problem of a plane electromagnetic wave of wavelength λ passing at normal incidence from a medium of refractive index n_1 into a homogenous plane parallel specimen of index $n - ik$, on a substrate of refractive index n_2 was treated by classical electromagnetic theory. For a thick absorbing film ($4\pi kd > \lambda$) the intensity of transmitted light can be expressed as[4]

$$T = \frac{16\, n_1 n_2 (n^2 + k^2)}{[(n_1 + n)^2 + k^2]\,[(n_2 + n)^2 + k^2]} \exp\left(-\frac{4\pi\, kd}{\lambda}\right). \qquad (1)$$

Plotting ln T versus d for different λ, the extinction coefficient k can be determined at each λ from the slope of the curve, hence n values can be calculated from the preexponential factor after substituting for the corresponding values of k, T, d, n_2 and with $n_1 = 1$ (for air). The variation of the real and imaginary parts of the refractive index and the dielectric constants n, k, ε_r and ε_i with the photon energy are shown in Figs. 2 and 3. A characteristic peak appears at 2.03 eV. The dependence of the surface loss $\left(-\operatorname{Im}\frac{1}{\varepsilon^*}\right)$ and bulk loss $\left(-\operatorname{Im}\frac{1}{\varepsilon^* + 1}\right)$ functions on the photon energy are shown in Fig. 4.

The absorption coefficient can be calculated from the extinction coefficient k, through the relation

$$a = \frac{4\pi k}{\lambda}. \tag{2}$$

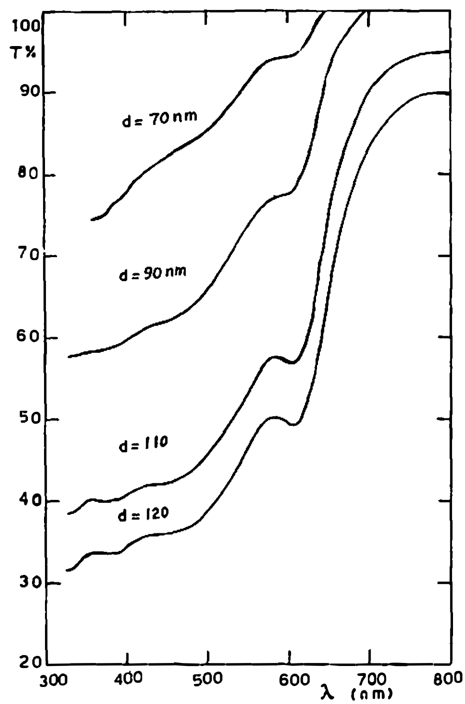

Fig. 1. Spectral dependence of the transmission of thin BiI_3 films.

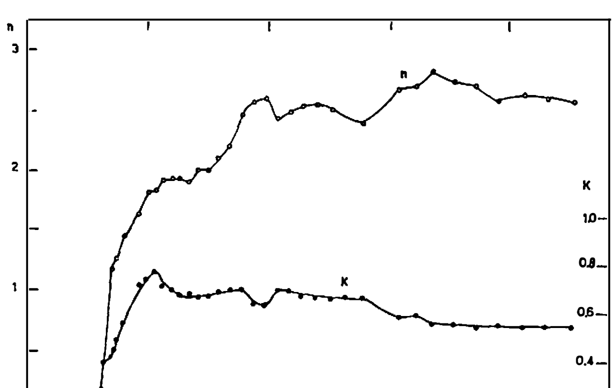

Fig. 2. The dependence of the real and imaginary parts of the refractive index on the photon energy.

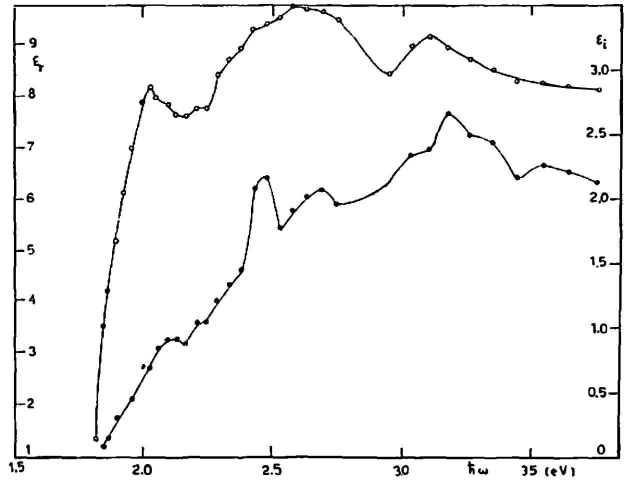

Fig. 3. The dependence of the real and imaginary parts of the dielectric constants on the photon energy.

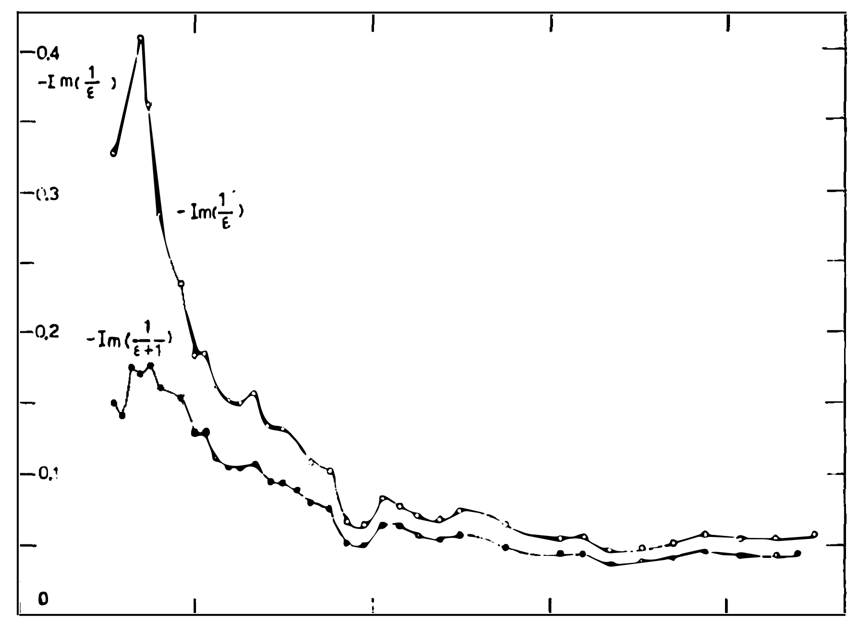

Fig. 4. The variation of the surface loss and bulk loss functions with photon energy.

Fig. 5 shows the variation of α with the photon energy. BiI_3 films show a strong absorption band near the fundamental absorption edge, and the intrinsic energy gap is $E_g = 1.76$ eV. A value of $E_g = 1.7$ eV for BiI_3 crystals has been estimated[11,12].

Critical information about the energy band structure ca be obtained from the analysis of the experimental data. The type of transition can be verified from the dependence of the absorption edge on photon energy. On plotting ln α against $\hbar\,\omega$ a straight line is given (Fig. 6), therefore, the absorption coefficient varies exponentially with photon energy and is well described by Urbach's empirical relation[5])

$$\alpha = \alpha_0 \exp\left[-\sigma (E_0 - \hbar\omega)/kT\right] \quad (3)$$

which was first proposed by Urbach for silver halides[5]) and also described the long wavelength tail of the localized exciton band in potassium halides[6-8]). The steepnes parameter σ depends on the temperature and decreases rapidly below a

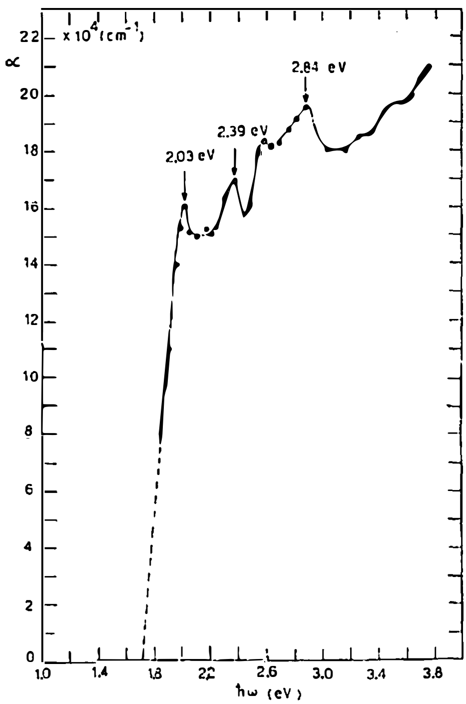

Fig. 5. The dependence of the absorption coefficient on photon energy.

temperature corresponding to some effective phonon energy, and E_0 is a constant. The best fit to the experimental data for BiI_3 can be obtained using $\sigma = 1$and $E_0 = 2$ eV. Mahr[9]) had proposed a comprehensive equation to describe the band shape due to localized excitons in ionic crystals, which reduces to Urbach's equation for small σ but gives a Gaussian shape near the band maximum as shown in Fig. 6. The exponential edge is ascribed to electric field ionization of the exciton. This exponential behaviour follows from assumption that the absorption coefficient near the edge can be written as weighted average of the absorption coefficients for excitons in a distribution of uniform electric fields which presumably arise from optical phonons and impurities. The tail observed in absorption spectra of BiI_3 can be attributed to the effect of the optical phonons in accordance with Toyozawa's mechanism[10], for Urbach's rule.

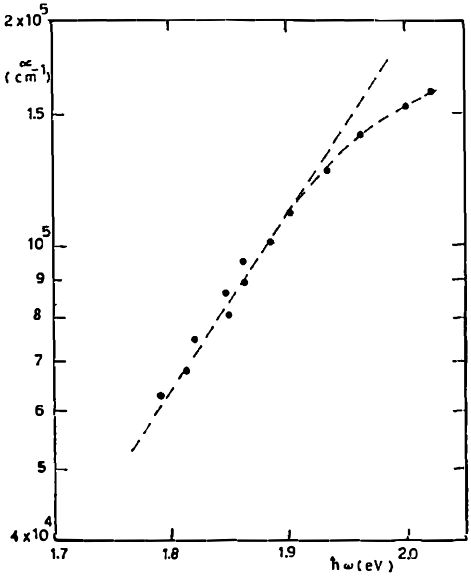

Fig. 6. Semilogarithmic plot of α versus photon energy.

Beside the intrinsic absorption peak, two absorption peaks were observed at 2.03 eV and 2.39 eV (Fig. 5). The interpretation of the interband transitions may be explained by considering the excitation state of iodine atom. The outer electronic configuration of the I^- ion is $5p^6$, while that of Bi^{3+} is $5d^{10}$ $6s^2$ $6p^3$. In BiI_3 crystal lattice, linear combination of the atomic orbitals gives the valence band as a combination of the $5p$ wavefunctions of I^- ions and $6s$ wavefunctions of Bi^{3+} ions, while conduction band (empty) will be a combination of $6p$ wavefunctions of Bi^{3+} ions and has a p-like character. The lowest excited states in free I^- ions are $5p^5$ $6s$ and $5p^5$ $6p$. In BiI_3 layer lattice I^- ions are situated in a strong electric field due to the existence of Bi^{3+} neighbours on one side and I^- ions on the other side. This electric field will hybridize the $6s$ and $6p$ wavefunctions giving a pair of hybrids excited levels. Each hybrid will split into a doublet by spin-orbit interaction. This excited level scheme was predicted for similar layered materials[13,14] and seem to be true for BiI_3. The two absorption bands at 2.03 eV and 2.39 eV could be attributed to transitions from the split valence band to higher excited levels, the energy separation of the absorption bands, 0.36 eV being a measure of the spin-orbit splitting of the low energy iodine doublet. Since spin-orbit interaction is related to deep orbitals, the crystal field will not affect strongly the splitting value $\Delta^{s.o.}$ which for BiI_3 crystal is equal to 0.45 eV[15]. A similar absorption doublet, having an energy separation of 0.46 eV, has been observed in SbI_3[16].

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NEKA OPTIČKA SVOJSTVA BiI_3 FILMOVA

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Istražena su optička svojstva BiI_3 filmova u području fundamentalne apsorpcije. Koeficijent apsorpcije opisan je Urbachovim pravilom. Široki vrh oko 2.0 eV pripisan je direktnim ekscitonskim prijelazima u blizini apsorpcijskog ruba. Područja apsorpcije na 2.03 eV i 2.39 eV pripisuju se spin-orbitalnom cijepanju niskoenergetskog dubleta joda.