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Photodecomposition of BiI_3 films

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The effect of illumination on the transmittance and the structure of BiI_3 films was investigated. Photoexcitation was found to induce structural variation and decomposition of the films into metallic bismuth and free iodine. Moreover, measurements of the electrical conductivity during heating show thermal decomposition of the films and it was found that the temperature of decomposition depends on the thickness of the film.

1. Introduction

The transport processes and structural changes which appear under photoexcitation are of importance for the understanding of the properties of semiconductors. Ovshinsky [1] have demonstrated that xenon flash-lamp irradiation of amorphous semiconductors leads to major changes of optical transmission and reflectivity. These changes are sufficiently stable to permit the use of these semiconductors as imaging media [2].

BiI_3 is one of a large number of halides with layer structures [3], it possesses a general structural modification and is related to the rhombohedral system with space group 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 close-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 (0001) across the van der Waals forces between adjacent composite I–Bi–I layers [4].

The optical and electrical properties of BiI_3 have been studied [5–7]. BiI_3 is an ionic semiconductor the conductivity of which depends on the concentration of impurities, connected with the deviation from the stoichiometric composition, which is in the iodine side because of its rapid sublimation [6, 7].

The aim of the present contribution is to investigate the effect of illumination on the physical properties and structure of BiI_3 films and to explain the mechanism of photodecomposition of BiI_3 films.

2. Experimental procedure

BiI_3 films were prepared by vaccum deposition at an evaporation rate of 1 nm sec^{-1} in a vacuum of 10^{-4} Pa onto fused silica plates. Film thickness was measured by the Tolansky interference method [8]. The prepared films were subjected to illumination from a tungsten lamp (6 V, 30 W) with a filter at a wavelength, λ, of 710 nm so that the radiation corresponds to the intrinsic absorption edge of BiI_3. Transmission measurements were carried out using a Beckmann UV 5230 type* double-beam recording spectrophotometer.

Structural changes were investigated by the X-ray diffraction technique using a Siemens D-500 type* X-ray diffractometer.

Electrical conductivity measurements were carried out using predeposited gold electrodes set 5 mm apart. A sensitive Keithly 610 C type electrometer, capable of measuring currents as low as 10^{-13} A and a stabilized d.c. voltage supply were used.

*Obtained from Central Services Laboratory, National Research Centre, Cairo, Egypt.

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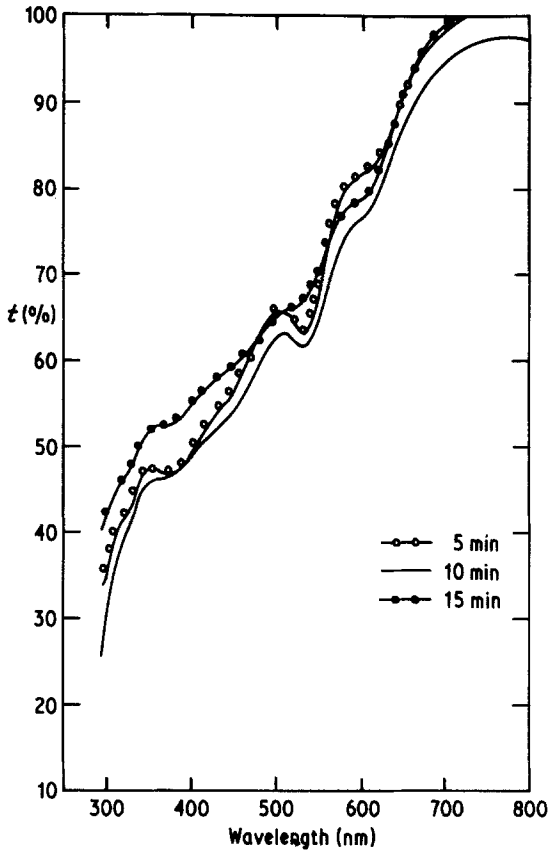

Figure 1 Spectral dependence of the transmission, t, of BiI_3 film, of 50 nm thickness, subjected to different periods of illumination: 5, 10 and 15 min.

3. Results and discussion

Fig. 1 shows the spectral distribution of the transmission for a thin BiI_3 film of thickness, d, of 50 nm, subjected to different periods of illumination: 5, 10 and 15 min. It is clear from Fig. 1 that the transmittance varies with the period of illumination and that the peaks observed near 350 nm and 550 nm which are attributed to the spin–orbit splitting of the excited iodine ion [9–11] are smeared out on illumination for long periods. Moreover, Fig. 1 indicates that a higher overall transmission occurs after 5 and 15 min of illumination than after 10 min; in other words, the maximum overall absorption occurs after 10 min of illumination. Two factors may explain this behaviour. Firstly, the deposition of metallic bismuth modifies the absorption properties of the film and the overall absorption is the sum of the absorption due to BiI_3 crystallites and metallic bismuth. Secondly, the decomposition rate, has time dependence, which may reach a maximum value after 10 min illumination with increased absorption.

Analysis of the X-ray diffraction patterns for BiI_3 film before and after illumination (Fig. 2b and c) for 15 min, shows the presence of metallic bismuth as well as BiI_3 crystallites. This indicates that BiI_3 undergoes a partial photodecomposition when it is exposed to illumination corresponding to its intrinsic absorption edge. The mechanism of decomposition can be written as

$$2\,BiI_3 \xrightarrow[h\nu]{\lambda = 710\,\text{nm}} 2\,Bi\downarrow + 3\,I_2 \qquad (1)$$

where h is Planck's constant and ν is the frequency.

Fig. 3 shows the variation of the electric current with temperature for thin BiI_3 film of 50 nm thickness. The current rises exponentially with temperature, with an activation energy of 0.2 eV, reaches a maximum at 440 K and then decreases abruptly. BiI_3 is an anionic semiconductor in which the current is carried mainly by iodine ion vacancies [6] with a slight contribution of electrons, and the activation energy obtained can be considered as the migration energy of the anions. The abrupt fall of the current above 440 K is attributed to the migration of the iodine ions towards the anode and bismuth ions towards the cathode and the subsequent formation of a depletion layer near the cathode, which can be observed visually. The formation of the depletion layer can be attributed to the difference in mobilities between the charge carriers and, since the layer is formed at the cathode, it may be concluded that the mobility of the iodine ion vacancies is greater than that of bismuth ions. Moreover, it was observed that the temperature at which the abrupt fall of the current occurs depends on the thickness and shifts towards higher temperatures on increasing film thickness.

For thick films ($d > 500$ nm) which approach bulk properties, the behaviour of the current–temperature dependence under illumination differs as shown in Fig. 4. Four distinct regions can be observed: the first (1) at low temperatures corresponds to the migration of anions with an activation energy, $E_1 = 0.28$ eV; the second (2) is attributed to the scattering of charge carriers at the grain boundaries, which increases in the case of thick films; the third (3) shows a rapid fall due to the trapping of mobile charge carries by bismuth ions and the formation of bismuth atoms, which is indicative of photodecomposition; and the fourth (4) with an activation energy

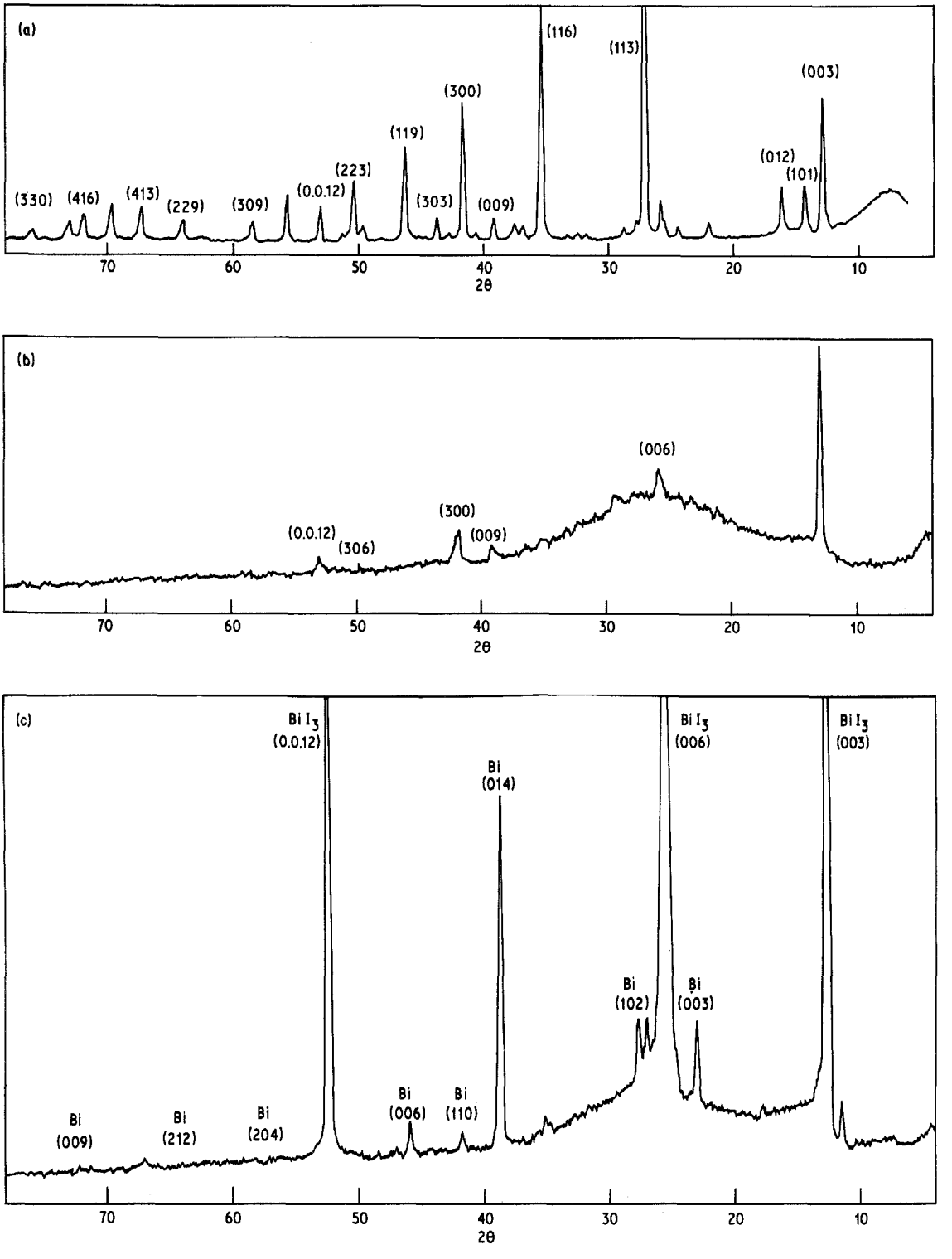

Figure 2 X-ray diffraction patterns for: (a) BiI_3 powder; (b) BiI_3 film of thickness 300 nm; and (c) BiI_3 film of thickness 300 nm subject to illumination for 15 min.

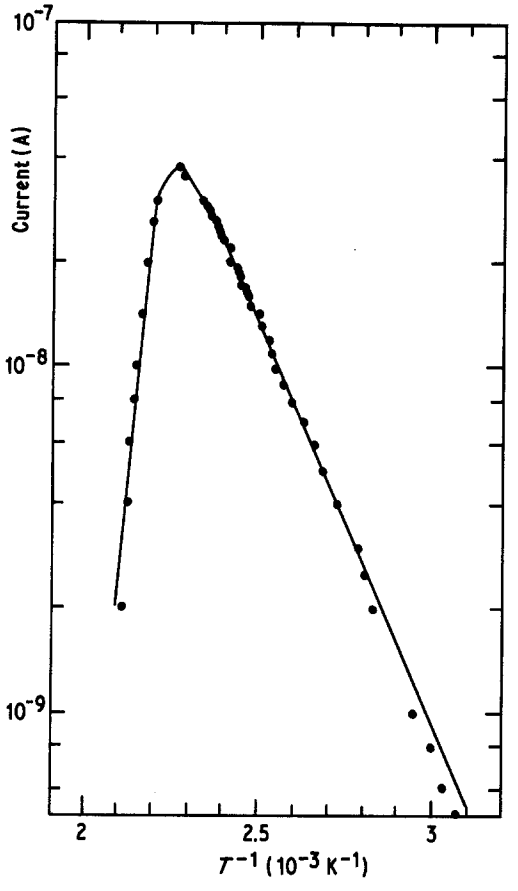

Figure 3 Temperature dependence of electric current for thin BiI_3 film of thickness 50 nm.

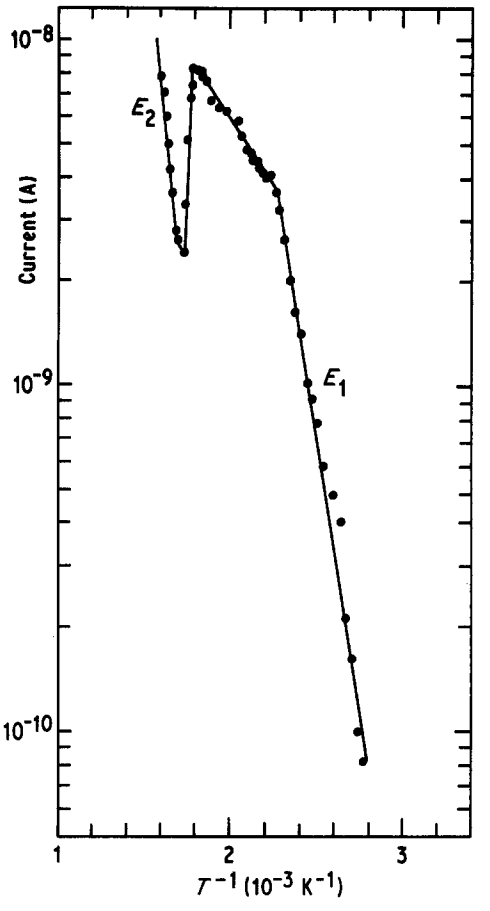

Figure 4 Temperature dependence of electric current for BiI_3 film of thickness 500 nm, under illumination.

$E_2 = 1.037$ eV, may be attributed to intrinsic conduction due to both types of carriers. The activation energy E_2 can be written as

$$E_2 = E_{\text{migration}} + E_{\text{formation}}, \qquad (2)$$

where E_1 in Fig. 4 can be considered as the migration energy, while $E_{\text{formation}}$ is the energy of formation of one carrier. Substituting values in the above equation, one obtains

$$E_{\text{formation}} = 0.757 \text{ eV},$$

and therefore the total energy of formation for four carriers is 3.028 eV.

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