



## Bias voltage controlled photoluminescence from $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films

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### ARTICLE INFO

#### Keywords:

Thin films  
Chemical Spray Pyrolysis  
Indium sulfide  
Photoluminescence quenching  
Voltage dependence

### ABSTRACT

$\beta$ -In<sub>2</sub>S<sub>3</sub> thin films were deposited on Indium Tin Oxide substrates using the Chemical Spray Pyrolysis technique. Metal contact was deposited over the  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin film to form a hetero-structure of the type ITO/ $\beta$ -In<sub>2</sub>S<sub>3</sub>/Metal. The intensity of two photoluminescence emissions from the  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin film, centered at 520 and 690 nm could be varied by the application of an external bias voltage to this hetero-structure. The emissions could be switched on or off depending upon the magnitude of the external applied bias voltage. Thus the presence of two conducting states in this hetero-structure could be identified. The temporal variation in intensity of the photoluminescence emission with the application of the bias voltage has also been studied. The condition under which photoluminescence quenching occurs has been represented by a first order differential equation between diffusion length and carrier concentration.

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### 1. Introduction

Starting from a II–VI compound, a variety of semiconductors can be built by replacing the divalent metal by other metals or combinations of them [1]. Replacement of the divalent metal by one of the Group III–B elements leads to a defect structure of the formula M<sub>2</sub>×<sub>3</sub> in which the non-metallic constituent X forms a cubic or hexagonal closed pack structure, where a part of the cation sites (normally occupied in the Zincblende, Wurtzite, or similar lattices), remains vacant [2]. Different defect structures are found for several of the Group III Group VI compounds [3]. Unusual features are expected to arise because of the defect structure.

$\beta$ -In<sub>2</sub>S<sub>3</sub> is a III–VI compound, which is by birth n-type, with ordered vacancies in the III-sub lattice. The interest in this material is stimulated due to its application in optoelectronic devices like thin film solar cells, red and green phosphors for picture tubes of television, dry cells and photochemical cells [4–10]. With optimal physical

properties,  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films meet the requirements of a window material or buffer layer for photovoltaic structures [4].  $\beta$ -In<sub>2</sub>S<sub>3</sub> can be deposited by various soft techniques and the band gap can be varied between 2.0 and 2.45 eV, depending upon the film composition [11–15].

Photoluminescence (PL), a non-contact, non-destructive spectroscopic tool, has been used as a “memory read” tool in polymer based devices [16]. PL spectra give characteristic information, which has been routinely used to study the defects in semiconductors (Sc) [17]. Such non-destructive “read” tools will end destructive read out. PL properties of  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films were found to show interesting features [18]. The PL study of stoichiometric  $\beta$ -In<sub>2</sub>S<sub>3</sub> thin films showed that the emission bands were due to ‘Donor Acceptor Pair (DAP)’ recombination [18]. In the present work we report on the bias dependence of PL from the ITO/ $\beta$ -In<sub>2</sub>S<sub>3</sub>/Metal structure. The present work was aimed at drawing a correlation between the PL emission from this hetero-structure and the bias voltage applied across it. We have theoretically modeled a general condition for the semiconducting thin film under which the PL emission would be quenched with the application of an external bias voltage.

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## 2. Experimental

$\beta$ - $\text{In}_2\text{S}_3$  thin films were prepared using Chemical Spray Pyrolysis (CSP) technique. Solutions of indium chloride ( $\text{InCl}_3$ ) and thiourea were mixed and sprayed on to indium tin oxide (ITO) coated soda lime glass substrates maintained at 573 K [19]. A 0.3  $\mu\text{m}$ -thick  $\beta$ - $\text{In}_2\text{S}_3$  film with preferential orientation along the (2 2 0) plane was grown on the ITO substrate. Structural, chemical and electrical properties of  $\beta$ - $\text{In}_2\text{S}_3$  thin films grown by this method have been reported elsewhere [19]. The In/S molar ratio was maintained at 2/8 for deposition of the films used in this study because of its optoelectronic properties [18,19]. Photoluminescence studies were carried out at room temperature. The samples were optically excited using the 325 nm line of a He–Cd laser (Kimmon Koha Ltd.). The diameter of the excitation beam spot was 1.2 mm, which had a power of  $\sim 20$  mW. The emission was collected using a spectrophotometer (USB 2000-ocean optics). Electrodes were deposited using silver paste so as to obtain a sandwich structure for the device. PL response for the hetero-structure under different bias voltage was studied.

## 3. Results and Discussion

Two PL emissions were detected from the hetero-structure: (1) A green emission centered on  $\sim 520$  nm and (2) A red emission centered on  $\sim 690$  nm. The dependence of the PL emission spectra for the hetero-structure on the bias voltage is as shown in Fig. 1. As the bias voltage was increased beyond 6 V, PL emission was not detected from the structure. This voltage dependence remained identical when the polarity at the ITO and metal contacts were interchanged. This phenomenon of switching “off” the PL emission by application of a bias voltage is more generally termed as PL quenching, which has been studied earlier in photo-generated or electro-chemically doped material and in metal–insulator–semiconductor structures [20,21]. With increase in bias voltage at constant excitation intensity it was most probable that the generated electrons/holes were carried towards the

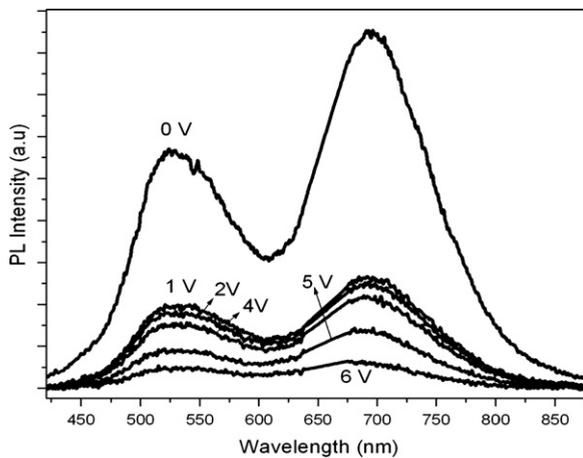


Fig. 1. PL emission spectra recorded at different bias voltages for the ITO/ $\beta$ - $\text{In}_2\text{S}_3$ /Metal hetero-structure.

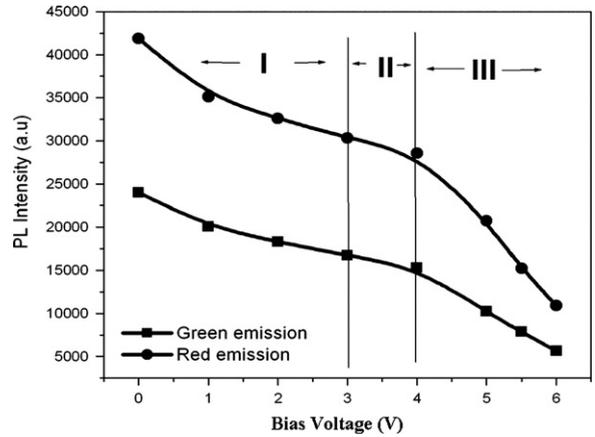


Fig. 2. Plot of absolute PL emission intensity (photon counts) versus the applied bias voltage for the ITO/ $\beta$ - $\text{In}_2\text{S}_3$ /Metal hetero-structure.

respective electrodes, which increased the current through the hetero-structure and caused the PL intensity to decrease.

Fig. 2 shows the plot of the absolute PL emission intensity (photon counts) versus bias voltage for the hetero-structure. The plot shows that there were three regimes in the voltage dependence of PL quenching in the device. In region I the slope defined as change in PL intensity per unit change in applied bias voltage was larger for the red emission compared to that for the green emission. In region II the slopes had minimum magnitude indicating a saturation behavior. In region III the slope for the red emission had maximum magnitude. It was observed that when the device is applied with a bias voltage the PL emission intensity was always lower than the intensity that was observed under zero bias state. A change in input voltage by 6 V decreased the PL emission intensity by 10 orders for the red emission while the intensity was lowered only by 5 orders for the green emission. These results proved that the red emission was very sensitive to the bias voltage in this hetero-structure.

Since carriers are generated by photo-excitation it is generally true that the excess carriers generated can be mathematically represented by relation [22]

$$\Delta n = G\tau \quad (1)$$

where  $G$  is the photo-excitation rate ( $\text{m}^{-3} \text{s}^{-1}$ ) and  $\tau$  is the carrier lifetime.

By the balance equation for the space distribution of the light-generated electrons and holes the bias dependence of PL can be explained using the relation

$$G = \mu E(\partial n / \partial x) + (n / \tau) \quad (2)$$

where  $\mu$  is the mobility and  $E$  the electric field. The first term on the RHS of Eq. (2) represents the excess carrier generated by the external bias  $V$  within a length  $\partial x$  of the semiconductor. Since the PL intensity strongly depends on the field strength and not on the carrier lifetime above 4 V bias, it may be assumed that the high electric fields results in reducing Eq. (2) to  $G=0$ , i.e. the field moves the electrons and holes in the opposite direction and

prevents them from recombining. If we assume that there is a uniform electric field given by

$$E = (D/\mu\tau) \quad (3)$$

where  $D$  is the diffusion length, then the condition for photoluminescence quenching by an external bias reduces to

$$\partial n/\partial x = -n/D \quad (4)$$

Thus when condition represented by Eq. (4) is physically satisfied in the thin film structure PL quenching occurs under the influence of the external bias voltage.

An application of the field dependence of PL was realized when the bias condition of the structure was back read from of the intensity of PL emission. This kind of non-contact “reading” of the state of a device has many important applications in telecommunication and in encoders and decoders of memory chips [8,2]. This effect could be used in reading input channels (i.e. bias voltages) serially, which will allow the PL emission intensity to vary by  $\sim 10$  orders across the hetero-structure. The difference between the PL emission intensity for the red emission (690 nm) at bias states  $V_i$  and  $V_i + \Delta V_i$  for the corresponding change in bias voltage  $\Delta V_i$ , defined as  $(\Delta PL/\Delta V_i)$  was plotted against the bias voltage  $V_j (=V_i + \Delta V_i)$  as shown in Fig. 3. The plots represent bias voltage sensitivity curves under different initial biased states of  $V_i=0, 1, 2$  and  $3$  V for the hetero-structure. The bias state of the hetero-structure could be best read (decoded) as evident from the Fig. 3, when the intensity of PL emission from the hetero-structure under a biased state was compared with PL emission intensity at zero bias state. This showed that the electric field sensitivity of PL emission for the hetero-structure was highest when initial condition is taken as zero bias state. Thus ability of the PL emission in the structure to “read” a change in bias voltage could be demonstrated. The difference in slope of the plots when the hetero-structure was initially at a bias of  $0$  V and at other biased states different from  $0$  V demonstrates the “read” capability of PL.

The temporal dependence of PL intensity upon the application of a bias voltage shows the real time decrease in built-in potential for the semiconductor thin film. This

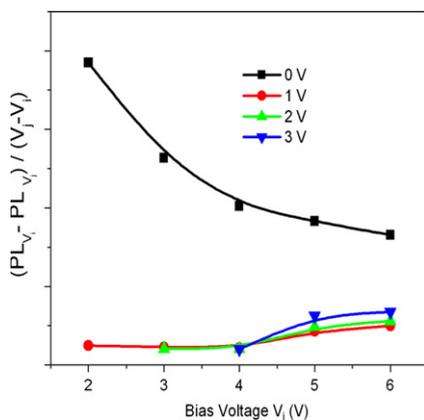


Fig. 3. Plot of  $(\Delta PL/\Delta V)$  versus bias voltage for the PL emission at 690 nm from the ITO/ $\beta$ - $\text{In}_2\text{S}_3$ /Metal hetero-structure.

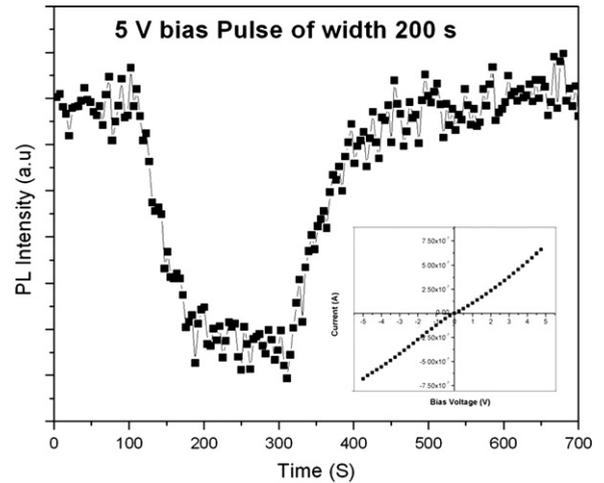


Fig. 4. Temporal dependence of PL emission at 690 nm for the ITO/ $\beta$ - $\text{In}_2\text{S}_3$ /Metal device structure for a 5 V bias pulse. Inset shows the dark  $I$ - $V$  for  $\beta$ - $\text{In}_2\text{S}_3$  thin films.

temporal behavior can be used to measure the effect of diffusion of carriers. *In situ* PL response of the hetero-structure was as shown in Fig. 4. The figure shows the temporal behavior of PL intensity with the application of a 5 V bias voltage to the hetero-structure. Approximately 200 s was taken for the PL intensity to reach a stable level after the application of a bias voltage. This condition of the hetero-structure – a 5 V bias applied across it – can be assigned to a high conducting state. This was evident from the  $I$ - $V$  measurements for  $\beta$ - $\text{In}_2\text{S}_3$  as shown in inset of Fig. 4. Thus the application of 5 V bias can be considered as a “write” process. When the bias voltage is switched off we have found that the  $\beta$ - $\text{In}_2\text{S}_3$  thin films retain the high state for about  $\sim 120$  s during which the PL emission intensity increases and gradually grows back to the zero bias level. PL intensity was  $\sim 10$  times greater when the bias voltage was removed to “erase” the high state and induce the low state. The speed of response of the  $\text{In}_2\text{S}_3$  system has been investigated by us earlier and was found to be highly dependent on the composition of the film [23]. Tang et al. reported that the photosensitivity and speed of response could be improved with the incorporation of  $\text{Cu}^+$  cation into the  $\beta$ - $\text{In}_2\text{S}_3$  system [24]. It remains to work in the direction of increasing the response time for the hetero-structure fabricated by us so as to find commercial applications for  $\beta$ - $\text{In}_2\text{S}_3$  based hetero-structure.

#### 4. Conclusions

A device structure based on  $\beta$ - $\text{In}_2\text{S}_3$  thin films prepared using CSP technique has been fabricated. The structure showed two PL emission peaks, whose intensities could be controlled by the application of a bias voltage. PL could be switched off from the hetero-structure by applying a bias voltage greater than 6 V. Thus the existence of two states in the hetero-structure was clearly identified using PL. In one state (bias greater than 6 V) the radiative recombination efficiency is zero whereas in the other state (with any bias voltage less than 6 V) radiative

recombination efficiency is greater than zero. A general condition for PL quenching to occur under the influence of an external bias voltage has been obtained in this work. The temporal dependence of PL intensity on the applied bias voltage was studied, which indicated the possibility of exploiting this structure for memory storage application.

### Acknowledgement

The authors are grateful to DRDO, Government of India, for funding the research work through project nos: ERIP/ER/0203393/M/01 and ERIP/ER/0402118/M/01.

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