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## LETTER TO THE EDITOR

# The effect of indium on the electronic properties of arsenic triselenide

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**Abstract.** A preliminary investigation of the effects of doping arsenic triselenide with indium was carried out. Measurements of DC conductivity, photomobility and optical absorption were performed. We find a significant improvement in the main transport properties. The findings are explained in terms of a shift of the valence band edge towards the centre of the mobility gap as a function of doping rather than a shift of the Fermi level towards the band edge.

Currently there is an interest in arsenic/selenium compounds because of their electrical and photoconductive properties, the main applications being in xerographic and xeroradiographic systems where they are used as photoreceptors. For xeroradiographic systems, in particular, the aims are to improve the sensitivity of the x-ray plates and the reproducibility of output (Aiyah *et al* 1993, Leiga 1989). For the purpose of this letter we examine the effect of adding indium on factors which affect the sensitivity such as the DC conductivity, mobility and lifetime of  $\text{As}_2\text{Se}_3$ .

It is well known, there being only a few exceptions, that the chalcogenides cannot be doped effectively by quenching from the melt, the distinctive feature being the independence of the DC conductivity upon additive concentration. There is some evidence, however, that atoms introduced using a 'cold' deposition technique such as RF cosputtering do control the electrical properties. This method introduced by Ovshinsky and co-workers was called chemical modification (Ovshinsky 1977, Kolomiets 1983, Barclay *et al* 1985). Below we present an investigation into the effects of adding indium on the transport properties and on the density of states profile  $N(E)$  found in  $\text{As}_2\text{Se}_3$ .

Samples in the thickness range 5–10  $\mu\text{m}$  were prepared by cosputtering indium with arsenic triselenide. The amount of additive was varied by covering a small amount of the sputter target area with indium. X-ray microanalysis of the films showed that the atomic percentage of indium was in good agreement with the target coverage calculations. The x-ray microanalysis also revealed that the atomic percentage ratio of As/Se was almost the same as that of the target material. Electron micrographs of the films showed them to be homogeneous down to a resolution of 50  $\text{\AA}$  suggesting that indium was entering the films in a well distributed matter. On the whole, no huge variation in the main electronic characteristics with increasing indium content was found. Thus during the presentation and analysis of the results more attention will be paid to the results that are most contrasting, those from the least heavily doped sample, 0.2 at.%, and the most heavily doped sample, 4 at.%.

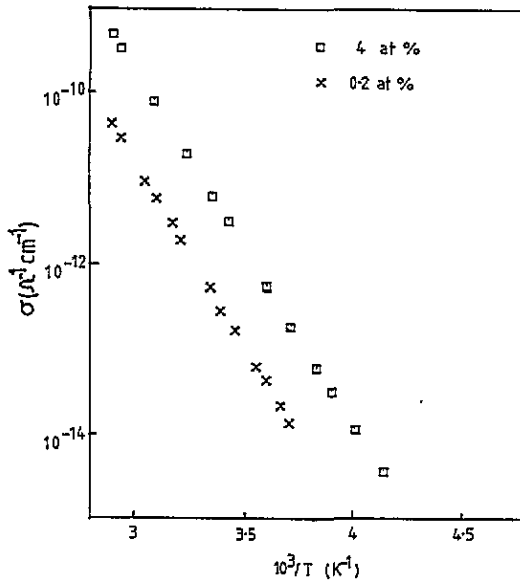


Figure 1. A plot of DC conductivity versus inverse temperature showing the increase in conductivity with increasing impurity content.

Table 1.

%In (at.%)	$E_{\sigma} \pm 0.01$ (eV)	$\sigma_{RT}$ ( $(\Omega \text{ cm})^{-1}$ )	$\sigma_0$ ( $(\Omega \text{ cm})^{-1}$ )	$E_0 \pm 0.01$ (eV)
4	0.89	$8 \times 10^{-12}$	1550	1.72
0.2	0.91	$6 \times 10^{-13}$	250	1.74
Undoped	0.93	$5 \times 10^{-14}$	50-100	1.76

The DC conductivity for both samples is illustrated in figure 1. Values for the room temperature conductivity ( $\sigma_{RT}$ ), zero-field activation energy ( $E_{\sigma}$ ) and the conductivity pre-exponential ( $\sigma_0$ ) are provided in table 1. From the table it can be seen that there is only a small decrease in activation energy as a function of doping. However, the introduction of indium increases the pre-exponential by two orders of magnitude. Such large values are indicative of a conduction mechanism that involves extended states. One can also observe from table 1 that there is a shrinkage in the optical gap,  $E_0$ , (a red shift of only  $\sim 0.04 \pm 0.01$  eV) as a function of doping.

Table 2.

%In (at.%)	$E_{\mu} \pm 0.01$ (eV)	$\mu_d(\text{pre})$ ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$N_{E_2}$ ( $\text{cm}^{-3}$ )
4	0.41	1120	$1 \times 10^{18}$
0.2	0.43	105	$3 \times 10^{18}$
Undoped	0.44	10	$8 \times 10^{18} - 2 \times 10^{19}$

The photomobility estimated from the rise of the photocurrent following step illumination is shown in figure 2. An interesting feature here is the slight decrease in activation energy,  $E_{\mu}$ , from  $0.43 \pm 0.01$  eV in the 0.2 at.% sample to about  $0.41 \pm 0.01$  eV in the 4 at.% sample while the mobility pre-exponential increases by over an order of

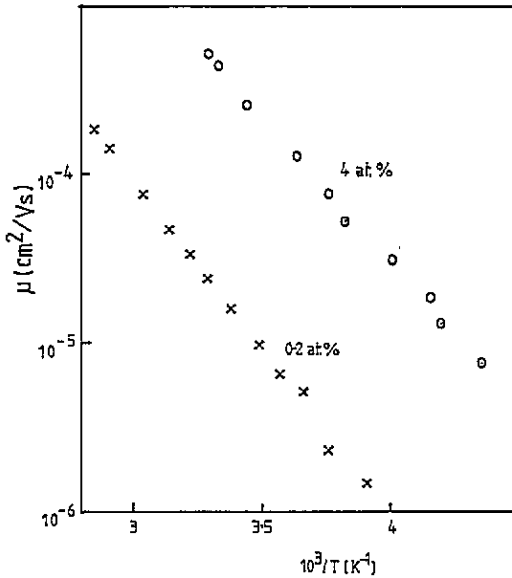


Figure 2. The variation in hole mobility as a function of doping.

magnitude (see table 2). We must add that the decay time,  $t_{1/2}$ , which is the time required for the photocurrent to fall to half its value after switching off the illumination, remained almost constant as a function of doping. This time is representative of a trap limited lifetime and had a room temperature value of about 2 ms.

As with undoped material, the magnitude of the pre-exponentials for both the DC conductivity and the photomobility suggest that conduction is via extended states. Assuming that this is the dominant mechanism it is possible to obtain a trap density by combining conductivity and mobility data as follows (Fisher *et al* 1976)

$$N_t = \frac{\sigma}{e\mu_d} \exp(E_\sigma - E_t)/kT \quad (1)$$

where  $E_t$  is the trap depth. The results of applying (1) to the data are shown in table 2. Here it is worth noting that the value of the trap density,  $N_{E_2}$ , found for the doped samples at an energy depth  $\sim 0.43$  eV which is roughly the same energy as the  $E_2$  level in undoped material (Barclay 1994) is lower than that found for undoped material by about a factor of 10. It can also be shown from the mobility pre-exponential since  $\mu_{d(\text{pre})} = \mu_d(N_v/N_{E_2})$  that there is an increase in the density of states at the valence band edge,  $N_v$ , with increasing amounts of additive. This implies that the impurities are incorporated in a manner that leads to a lowering of the trap density at the  $E_2$  level (see below). One should also mention that the increase in mobility is approximately the same as that of the conductivity and that the decrease in activation energy of the DC conductivity masks that of the photomobility. Thus the transport properties have improved significantly with an increase in  $\mu\tau$  of  $\sim 100$  based on the mobility pre-exponential values. The correlation in behaviour for both data sets suggests that a shift in the valence band edge has occurred rather than a shift in the Fermi level position. This supposition is supported by the valence band edge density calculations.

Our findings can thus be explained by the build up of new localized states at the valence band edge resulting in a shift in the conduction channel of  $\sim 0.03$  eV towards mid-gap for the most heavily doped sample. This is because the magnitude of the shift of the optical

gap energy and the change in  $\Delta E_{\mu}$  are similar taking into account experimental error. Furthermore, transient and steady photoconductivity studies (Barclay 1994) confirm our findings and studies performed elsewhere come to similar conclusions. For example, Pfister and Morgan (1980) interpret their results in terms of a shift in conduction channel caused by the creation of impurity-related valence bands states which extend  $\sim 0.1$  eV above the hole transport states. They suggest that the localized states that widen the band tail can be attributed to the additives being incorporated in neutral bonding configurations. Thus the valence requirements are satisfied in support of Mott's earlier prediction (Mott 1969) that these glasses cannot be doped.

At this point it is worth looking at the possibility of explaining the data in terms of defect models. One model proposed by Street and Mott (1975) and Mott *et al* (1975) involves charged lattice defects ( $D^+$ ,  $D^-$ ,  $D^0$ ) which are situated in the band gap. No continuous distribution of defects is implied. Prior interpretation of transient photocurrents has placed  $D^-$  at the  $E_2$  defect level (Adriaenssens 1990). If this were the case then the introduction of indium would lead to a reduction in the density of  $D^-$ . However the present author's work on undoped material suggests that the defects are neutral rather than charged (Barclay 1994). One must also take into account that some authors interpret their results using a broad featureless density of states which is difficult to explain in terms of charge defects (Monroe and Kastner 1986). A model which incorporates both features is the one introduced by Klinger and Karpov (1982) which specifically couples a continuous distribution of gap states to discrete transition energies. Adriaenssens (1990) has found some compatibility with his data but found the negative effective correlation energy to be too high. He suggested that refinements are required before it can be applied with any accuracy. We are in agreement with his suggestion.

It has been demonstrated that the addition of indium improves the transport properties of amorphous triselenide considerably. We find a red shift in the optical gap which is similar in magnitude to the decrease in DC conductivity and mobility activation energies. This suggests a modification of the conduction channel rather than a shift of the Fermi level. In support of this we find an increase in the valence band density of states whilst the trap density at the  $E_2$  level is found to decrease.

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