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# Preparation and properties of $Bi_{2-x}As_xS_3$ thin films by solution-gas interface technique

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**Abstract.** The solution gas interface technique by which thin films of $Bi_{2-x}As_xS_3$ were deposited is described in this paper. The semiconducting properties of the interface grown $Bi_{2-x}As_xS_3$ thin films are studied. The optical absorption, dark resistivity and thermoelectric power of the films were studied and results are reported.

**Keywords.** Solution-gas interface technique; $Bi_{2-x}As_xS_3$ films; resistivity.

## 1. Introduction

During the last few years, mixed semiconductors, especially chalcogenides, have been extensively studied because of their proven and potential applications in thin film technology. Among the compound semiconductors, sulphides of arsenic, antimony and bismuth are important due to their photoconductive and photovoltaic properties (George and Radhakrishnan 1979; Curran *et al* 1982; Bhattacharya and Pramanik 1982; Andreichin 1970; Ghosh and Verma 1979). We have recently reported the growth of thin films of $As_2S_3$, $Sb_2S_3$ and $Bi_2S_3$ by our newly developed solution-gas interface (SGI) technique (Pawar and Bhosale 1984; Pawar *et al* 1983). Thin films of these compounds can be obtained by vacuum evaporation, spray pyrolysis, dip and dry and solution growth techniques (Ghosh and Verma 1979; Pawar *et al* 1984; Nayak *et al* 1982; Pramanik and Bhattacharya 1980). Amongst these techniques SGI technique is relatively new, inexpensive, simple and convenient for the deposition of uniform large area thin films. In order to devise a simple method of controlling the composition of the individual metal ions in the chemically grown films, we have studied their optical and transport properties and the results are reported in this paper. These results are used to deduce the variation in optical gap ($E_g$) as a function of composition ($x$).

The mixed $Bi_2S_3$-$As_2S_3$ system can be one of the promising materials for the photovoltaic energy conversion, because of the availability of the bandgap between 1·4 eV and 2·4 eV to cover the maximum portion of the solar spectrum. Therefore, attempts have been made to establish the feasibility of producing this system in thin film form using SGI technique and to investigate the energy gap and dark resistivity of the material as a function of $x$.

## 2. Experimental

Thin films of $Bi_{2-x}As_xS_3$ were deposited onto the glass substrates in the following manner. The solutions were prepared using analar grade bismuth and arsenic salts by adding together clear solutions of $BiCl_3$, $3H_2O$ (0·1 M) and $AsCl_3$ (0·1 M) in the volumetric ratio by varying the relative proportion of $BiCl_3$ and $AsCl_3$ so as to get Bi : As ratio from $x = 0$–2. The solutions were mixed thoroughly and the final solution was exposed to hydrogen sulphide ($H_2S$) gas. The experimental set-up was described earlier (Pawar *et al* 1983; Pawar and Bhosale 1984). In brief, it consists of a gas chamber filled with pure and dry $H_2S$ gas at a desired pressure, solution container which is specially designed to remove the solution from its bottom without disturbing the solution surface and uniform gas exposure unit. Cleaned and dry glass substrates (size 2·5 cm × 1 cm) which were kept on a rectangular glass stand in the container were immersed in the solution. The solution was exposed to $H_2S$ gas. A thin solid film is formed at the interface of the solution and gas. The solution is drained slowly from the bottom of the solution container and a uniform large area film remained on the glass substrates. The films were washed, dried and preserved in dark desiccator for further study. The films prepared with different Bi : As ratios are denoted as, $S_{2·0:0·0}$, $S_{1·5:0·5}$, $S_{1·0:1·0}$, $S_{0·5:1·5}$ and $S_{0·0:2·0}$, where subscripts denote the Bi : As ion ratios. The band gap of the deposited material was determined by recording the absorption spectrum in the wavelength range between 4000 and 8000 A° using a spectrophotometer (Carl Zeiss Jena). The dark resistivity measurements were carried out in the temperature range between 300 and 600 K, while thermovoltage was recorded in the temperature range between 300 and 450 K using d.c. microvoltameter (PP 9004).

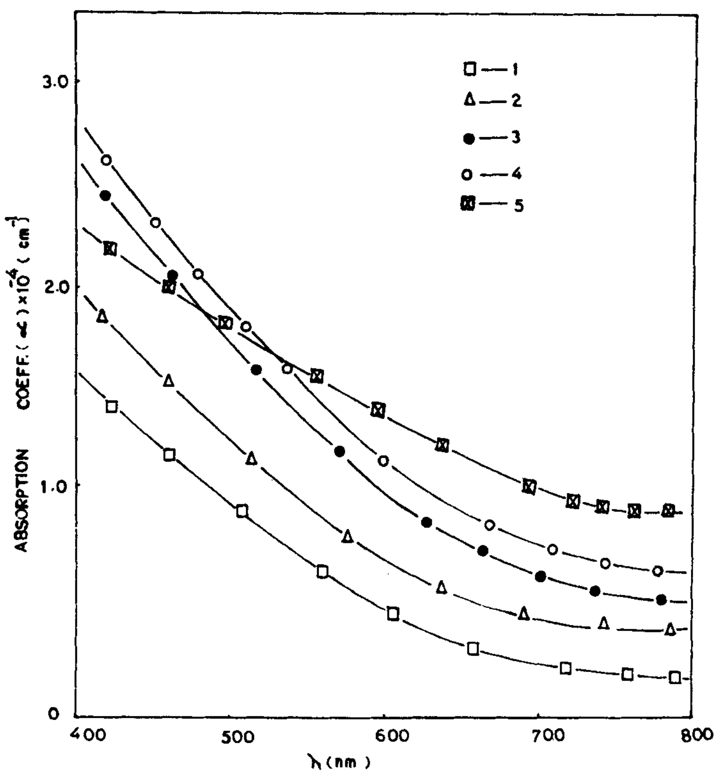


**Figure 1.** Variation of absorption coefficient α as a function of wavelength (λ) for the samples, (1) $S_{2·0:0·0}$ (2) $S_{1·5:0·5}$ (3) $S_{1·0:1·0}$ (4) $S_{0·5:1·5}$ (5) $S_{0·0:2·0}$.

## 3. Results and discussion

It is well known that the fifth group elements Bi, Sb and As have a strong affinity towards chalcogen ions and form stable chalcogenide compounds. Based on the experimental evidence a new deposition method is being proposed for the mixed thin film semiconductors. Similar to solution growth techniques, the growth of $Bi_{2-x}As_xS_3$ thin films takes place at the interface of the solution and gas. Due to cation-anion interaction of the arsenic, bismuth and sulphide ions a thin solid film of mixed $Bi_{2-x}As_xS_3$ is formed at the interface of solution and gas.

The quality and uniformity of the $Bi_{2-x}As_xS_3$ thin films prepared by the SGI technique depend on various preparative conditions, including the composition of the mixed solution, pH, surface tension, temperature, gas exposure time and gas pressure. Keeping all these parameters constant the composition of $AsCl_3$ and $BiCl_3$ solutions was taken to vary from 0–2. The $Bi_{2-x}As_xS_3$ thin films in the present investigation were formed using 0·1 M bismuth and arsenic chloride solutions with pH range between 2 and 4 at room temperature.

Variation of absorption coefficient ($\alpha$) with wavelength ($\lambda$) is shown in figure 1. The steep fall in $\alpha$ is ascribed to the absorption edge of the semiconductor. The value of $\alpha$ for all the films lies in the order of $10^{-4}$ $cm^{-1}$ which is characteristic of the direct transition. Figure 1 shows that the absorption edge shifts towards the shorter wavelength side with increase in the arsenic composition in the film. This reveals that the bandgap of $Bi_{2-x}As_xS_3$ film increases with increasing composition of arsenic in the film. Figure 2 shows that the variation of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for a typical film

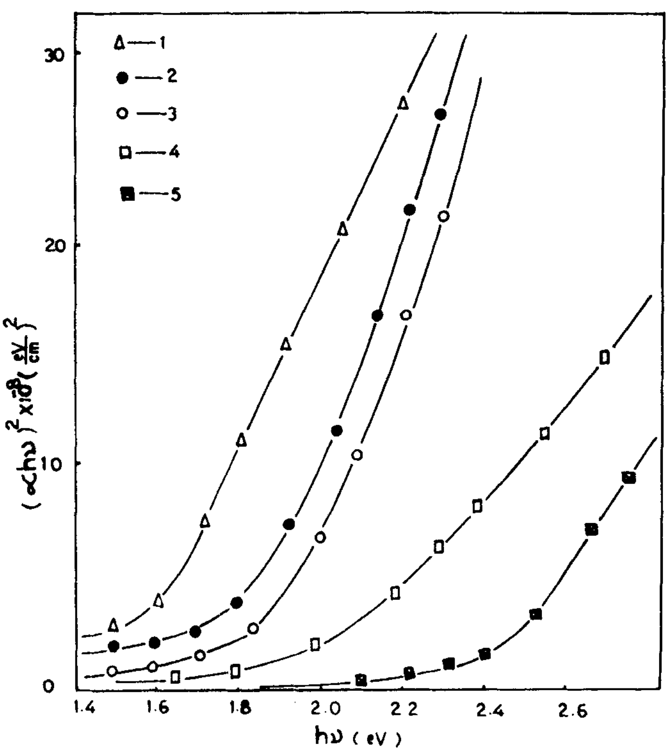


**Figure 2.** Plots of $(\alpha h\nu)^2$ vs $(h\nu)$ for the samples. Details same as in figure 1.

is linear and shows strong absorption near the bandgap region. Extrapolation of this plot to energy axis gave the bandgap varying from 1·5 eV for pure $Bi_2S_3$ to 2·42 eV for pure $As_2S_3$ thin films. Figure 3 shows the experimental curve of $E_g$ vs $x$. The dependence of energy gap $E_g$ on $x$ is obtained from the position of the symmetry point $x$ which has been selected in accordance with the values for pure compounds of $Bi_2S_3$ and $As_2S_3$.

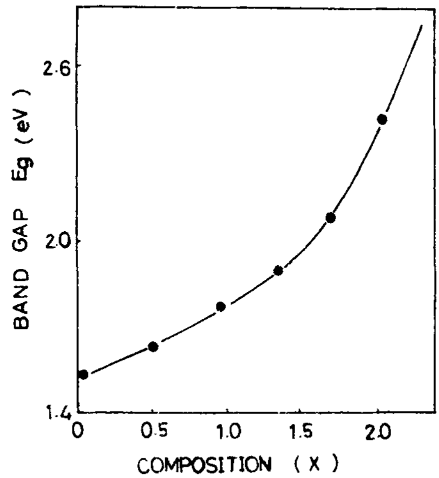


**Figure 3.** Variation of bandgap ($E_g$) as a function of composition ($x$) for $Bi_{2-x}As_xS_3$ films.

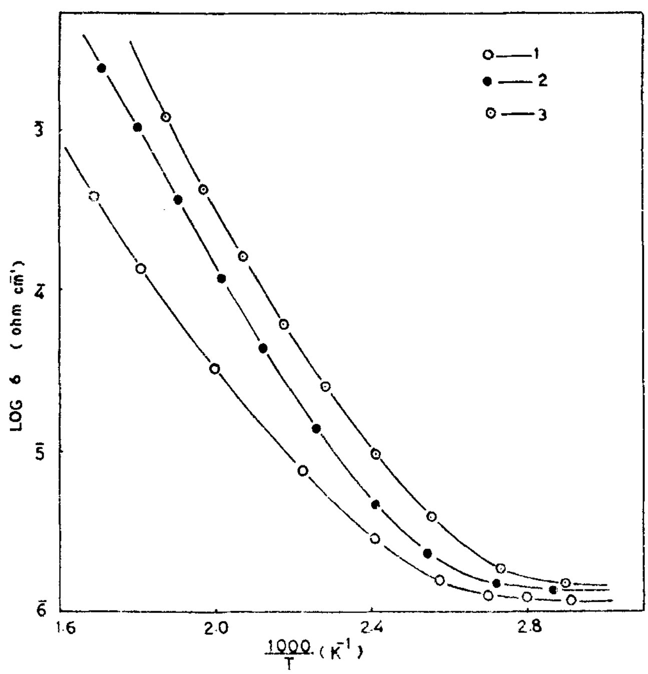


**Figure 4.** Plot of log $\sigma$ vs $1/T$ for the typical samples (1) $S_{2\cdot0:0\cdot0}$ (2) $S_{1\cdot0:1\cdot0}$ (3) $S_{0\cdot0:2\cdot0}$.

The nonlinear variation of $E_g$ with $x$ is similar to the results reported by other workers in case of $Cd_{1-x}Zn_xS$ thin films (Agnihotri and Gupta 1979; Mbow *et al* 1982).

In the present investigation variation of resistivity with reciprocal of temperature is studied for all films. The films have high electrical resistance in comparison to single crystals of $Bi_2S_3$ and $As_2S_3$ (Andreichin 1970; Bhattacharya and Pramanik 1982). The resistivity lies in the range of $10^8$ to $10^9$ ohm cm at room temperature. The resistance is generally high for films prepared by solution growth techniques, presumably due to the discontinuity and thickness of the films. The activation energy of the films deposited by SGI technique is high as compared to single crystals, perhaps due to high specific resistivity. The plot of log $\sigma$ vs $1/T$ for three typical samples are shown in figure 4. The slope of the plots gives two activation energies at lower and higher temperature region which can be attributed as follows. At higher temperatures, excessive evaporation of sulphur from the films takes place with a pronounced reduction in resistance (Krishnamoorthy and Shivakumar 1984), while at lower temperature conduction of electrons takes place in the extrinsic region of the semiconductor. The $Bi_{2-x}As_xS_3$ films show $n$-type conduction in accordance with pure $Bi_2S_3$ thin films.

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