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Short communication

The p-type doping of vacuum deposited ZnTe thin films with bismuth by a new technique of using nano-spheres

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ABSTRACT

The present paper reports the successful doping of vacuum evaporated zinc telluride (ZnTe) thin films with bismuth by a new technique of using nano-spheres. The discontinuous films of bismuth (the dopant material), containing bismuth in the form of nano-spheres, were prepared by vacuum evaporation and the ZnTe films were then deposited on top of them. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to ascertain the formation of discontinuous bismuth films and the proper diffusion of bismuth in ZnTe films, respectively. After doping, the carrier concentration of the ZnTe films was found to increase by an order of the magnitude. The electrical conductivity also improved significantly. The photoconductivity and photo-response properties of the doped films were also analysed.

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1. Introduction

Zinc telluride belongs to the II–VI group of semiconductor compounds and like other members of the group, it has many attractive potential applications in the field of optoelectronics. The material has a direct bandgap of 2.26 eV (at 300 K) [1,2], which corresponds to the pure green region of the electromagnetic spectra, and hence it is seen as a potential material for the fabrication of green LEDs [3–6]. Besides ZnTe is also a promising material for the fabrication of various devices such as THz emitters and detectors [3,7], photodetectors etc.

ZnTe has a strong preference to p-type conductivity. The n-type doping is very difficult to achieve due to the self-compensation property of ZnTe. Vacuum deposited ZnTe thin films usually have an excess of tellurium content at low substrate temperatures, and exhibit p-type conductivity [8]. The p-type conductivity can be improved by doping. Many dopant materials, like antimony [9], copper [10], arsenic [11] etc., have been used as p-type dopants for ZnTe films. In the present research work an attempt has been made to dope vacuum deposited ZnTe thin films with bismuth, a less studied dopant material, and a new doping technique has been employed to achieve proper diffusion of the dopant material.

2. Experimental details

The deposition of bismuth and ZnTe were done in two separate deposition cycles. Bismuth films were prepared by vacuum evaporating 99.999% pure bismuth ingots (procured from Sisco Research Labs, India) in a molybdenum boat. In order to obtain discontinuous bismuth films, the glass substrates were heated to a temperature of about 453 K. The zinc telluride films were then deposited on these discontinuous bismuth films at room temperature. High purity (99.99%) ZnTe ingots (Aldrich) were used as source material and molybdenum boat was used to evaporate the source. The thickness of the ZnTe films was about 500 nm in all the samples. The depositions were carried out in vacuum better than 10^{-5} Torr, inside a 12 in. vacuum chamber (HINDHIVAC 12A4D). In order to study the effects of annealing, the films were annealed in a hot air oven at 523 K for 4 h. SEM images of the bismuth films were obtained by a JEOL JSM 5800 scanning electron microscope. The atomic percentage of bismuth in the doped films was determined by the energy dispersive analysis of X-rays (EDAX) using an EDAX unit attached to the JEOL JSM 5800 SEM. XRD analysis was performed using a Rigaku Miniflex XRD unit (operating voltage 30 kV, CuKα radiation of wavelength 1.54 Å). For electrical measurements silver ohmic contacts were made on the films by vacuum deposition .The carrier concentration, conductivity and carrier mobility of the doped and undoped films were determined by Hall effect analysis. The electrical measurements were obtained by Keithley Multimeter (Model 2002). The photoconductivity of the doped and undoped films were studied by using a photoconductivity measurement setup comprising of a 150 W Xe arc source

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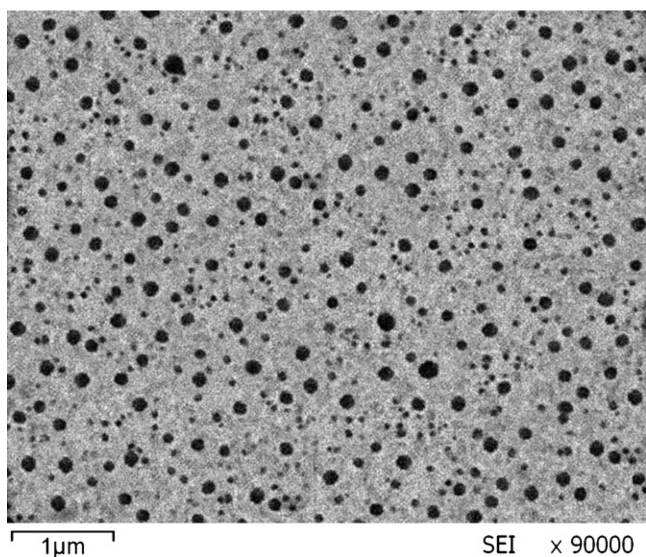

Fig. 1. The SEM images of discontinuous bismuth film (grown at a substrate temperature of 453 K) showing bismuth nano-spheres.

(Newport), a monochromator with photo-multiplier tube detector (PI-Acton) and an optical chopper (Holmarc, India). The variation of film resistance with ambient temperature was determined by placing the film in a hot air oven and then measuring the resistance at different temperatures using Keithley Multimeter (Model 2002).

3. Results and discussions

The doping of a vacuum deposited thin film can be accomplished either by co-evaporation of the film material and the dopant or by depositing the two materials, as two separate layers, one after the other. In the later method, also known as sandwich method, one has to ensure that the dopant is properly diffused into the material and has not remained as a separate layer. Although annealing can produce some degree of diffusion, the dopant layer may still remain intact in some places. In such cases the electrical conduction may take place largely or entirely through the low resistance dopant film, rather than the semiconductor film, giving a false impression of improvement in electrical conductivity. This possibility makes the conventional sandwich technique non-reliable. In the present research work a different approach has been employed to ensure the proper diffusion of the dopant. The bismuth films, i.e. the dopant material, are intentionally made discontinuous so that the possibility of an intact dopant layer can be completely ruled out. Since the dopant layer is discontinuous any conduction must take place only through the ZnTe material and hence the results obtained are reliable.

In the case of physical vapor deposition, the film material deposited on a substrate re-evaporates continuously. However, the rate of such re-evaporation will be very low at low substrate temperatures. If the substrate temperature is increased to about 2/3rd of the bulk melting point of the material, or above, then the rate of re-evaporation increases considerably and the resultant film may become discontinuous. This is due to the fact that the melting point of the material in thin film form, under reduced pressure, is usually 2/3rd of its melting point in the bulk form. Under such condition the film will be discontinuous and islands of the film will be in the form of spherical liquid drops [12,13]. This condition can be easily achieved for low melting point materials like bismuth. Bismuth has a melting point of about 545 K in bulk form. Hence the melting point of bismuth in thin film form, under reduced pressure, will

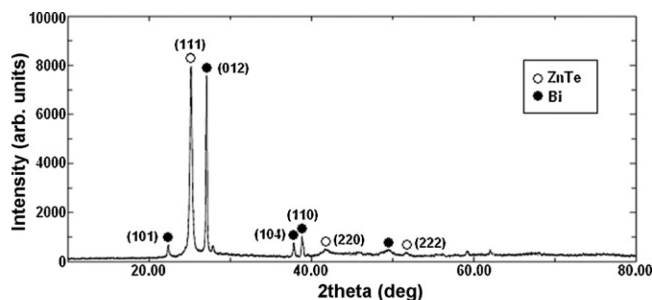

Fig. 2. The XRD pattern of ZnTe film deposited on a continuous bismuth film (deposited at a substrate temperature of 300 K).

be around 360 K. If the substrate temperature is increased beyond this value then the resulting bismuth film will be discontinuous [14]. In the present research work a substrate temperature of about 453 K was used to obtain discontinuous bismuth films containing nano-spheres of bismuth.

The formation of discontinuous bismuth films was confirmed by obtaining the SEM images of the films. Fig. 1 shows the SEM image of the discontinuous bismuth film. The individual bismuth nano-spheres are clearly visible. The average size of the nano-spheres was about 100 nm. The ZnTe films were deposited on these discontinuous bismuth films. The fact that the above technique results in proper diffusion of the bismuth material is well illustrated by the XRD patterns shown in Figs. 2 and 3. Fig. 2 shows the XRD pattern of ZnTe film deposited on top of a continuous bismuth film deposited at room temperature. In this pattern, a large peak corresponding to bismuth is clearly visible which is due to the poor diffusion of the bismuth material. However, the peak reduced drastically in Fig. 3(a), which corresponds to the ZnTe film deposited on discontinuous bismuth film, indicating proper diffusion of bismuth. The diffusion of bismuth was further enhanced by annealing as shown in Fig. 3(b).

The carrier concentration, resistivity and hole mobility of both doped and undoped films, determined from Hall effect analysis, are tabulated in Table 1. In the table, sample 1 represents undoped ZnTe film while all other samples are doped samples deposited on Bi nano-spheres. The third column of the table gives the atomic per-

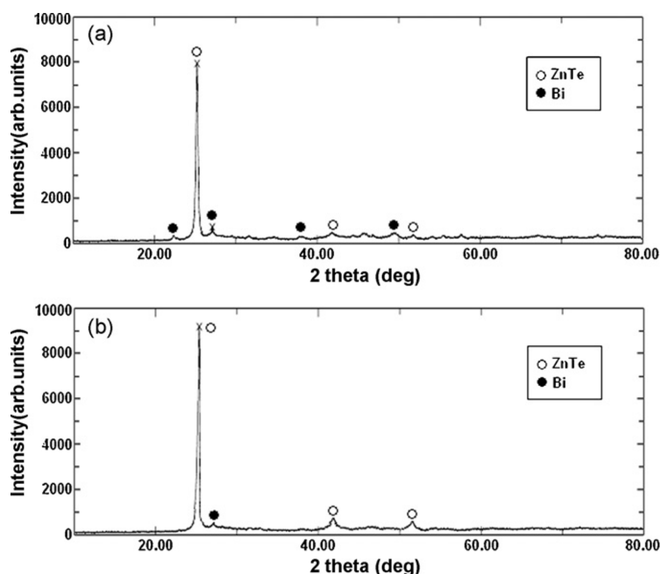

Fig. 3. The XRD patterns of ZnTe films deposited on discontinuous bismuth films (deposited at a substrate temperature of 453 K), (a) before annealing and (b) after annealing at 523 K for 4 h.

Table 1
The electrical properties of doped and undoped ZnTe films.

Sample	Annealing	Atomic percentage of bismuth	Carrier concentration ($\times 10^{20}$ m^{-3})	Resistivity (Ω m)	Hole Mobility (cm^2/V s)
Sample 1 (Undoped)	–	0 (Undoped)	3.47	13.2	13.6
Sample 2	–	0.18	42.7	1.19	12.3
Sample 2	At 523 K for 4 h	0.18	70.3	0.74	12.0
Sample 3	–	0.23	68.1	0.88	10.6
Sample 3	At 523 K for 4 h	0.23	86.3	0.68	10.2
Sample 4	–	0.32	73.4	0.85	9.8
Sample 4	At 523 K for 4 h	0.32	97.9	0.69	9.2

centage of bismuth in the films. The atomic percentage of Bismuth increases as we go from sample 2 to sample 4 and corresponding increase in carrier concentration was observed. This indicates that the increase in free carrier concentration is due to the increase in the dopant bismuth atoms. The carrier concentration increased by an order of the magnitude in the doped films. Almost 30 times increase in the carrier concentration can be seen in sample 4 after annealing. A significant decrease in electrical resistivity can also be observed. However, the hole mobility decreased marginally in the doped films. This is normally observed in doped materials mainly due to the increase in ionized impurities [15]. The ionized impurities impede the flow of charge carriers and hence reduce their mobility.

The variation of resistance R with ambient temperature T was studied for both doped and undoped films and the resultant graphs are shown in Fig. 4. The resistance decreased with the increase in ambient temperature for both doped and undoped films. This result, particularly for doped films, confirms the fact that the electrical conduction is actually taking place through the semiconductor material, ZnTe, and not through the metal dopant bismuth. The graphs show two distinct regions corresponding to extrinsic and intrinsic conduction at lower and higher temperatures respectively. The bandgap and activation energies of the doped and undoped films were determined from the graphs shown in Fig. 4 using the equation,

$$E = 2k \times \text{Slope} \quad (1)$$

where k is the Boltzmann's constant. If slope of the extrinsic region is considered then E will represent the activation energy and if slope of the intrinsic region is taken then E represents the bandgap. The bandgap and activation energies of both doped and undoped films were determined from the graphs shown in Fig. 4. No significant change in the bandgap of the material was observed after doping and the value was found to be about 2.25 eV. The activation energy decreased marginally from 0.89 eV (for undoped films) to 0.78 eV (for doped films).

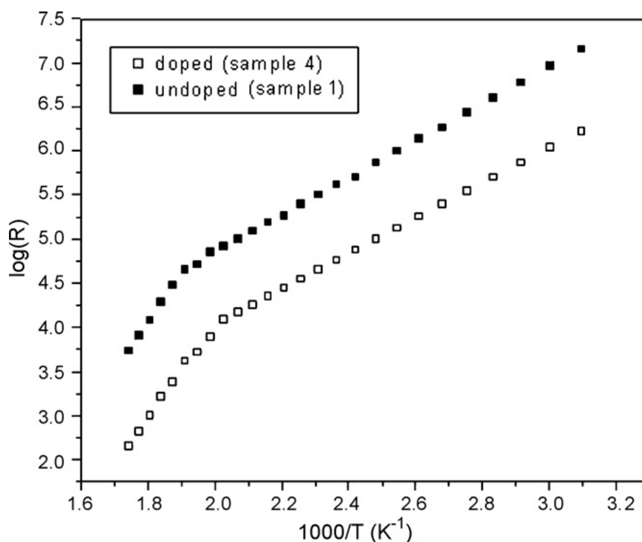

Fig. 4. The variation of log(R) with 1/T for undoped and bismuth doped ZnTe films.

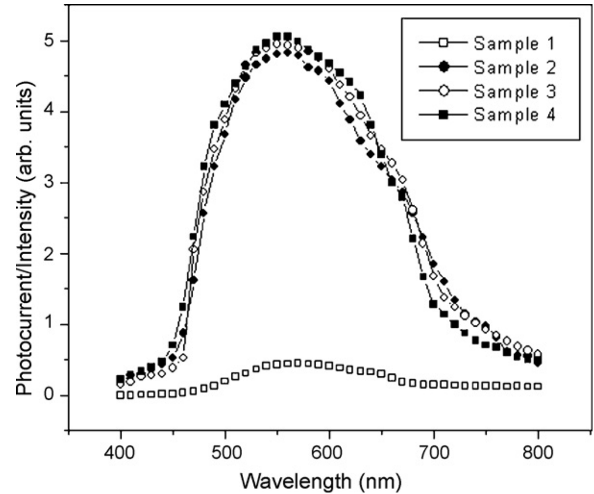

Fig. 5. The spectral response curves of undoped and bismuth doped ZnTe films.

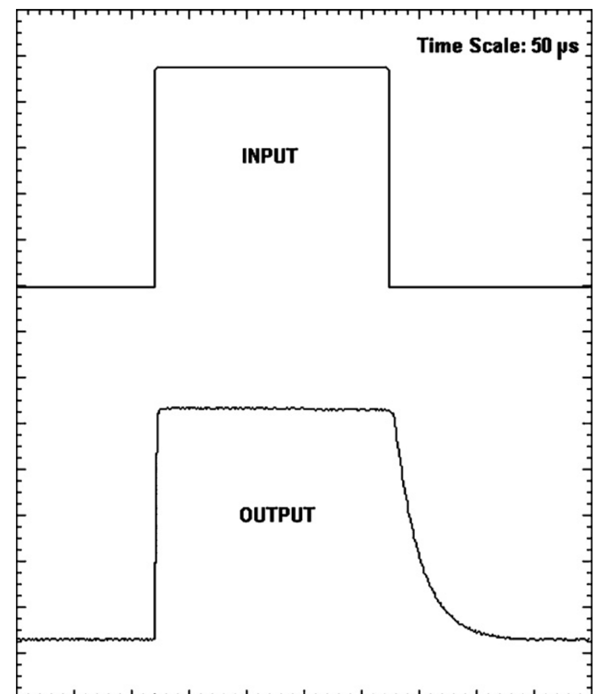

Fig. 6. The photo-response of bismuth doped ZnTe film (sample 4) for pulsed light input.

Fig. 5 shows the normalized spectral response curves for both doped and undoped ZnTe films. All the curves show a maximum at about 550 nm which corresponds to the bandgap of the ZnTe material. The photocurrent increased significantly, about 10 times, after doping. This increase is due to the increased electrical conductivity of the doped films. The rise and decay time of the photocurrent were determined by obtaining a photo-response curve of the films for pulsed light input as shown in Fig. 6. No significant change in rise and decay time was observed. This result follows from the fact that the hole mobility of the films changes only marginally after doping.

4. Conclusion

Vacuum deposited ZnTe films were successfully doped with p-type dopant bismuth. The new technique of using dopant material in the form of nano-spheres was found to be effective in achieving proper diffusion of the dopant material. The carrier concentration of the ZnTe films increased by an order of the magnitude after doping. Significant improvement in electrical and photoconductivity were also observed for doped films.

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