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Formation of nanodots and enhancement of thermoelectric power induced by ion irradiation in PbTe:Ag composite thin films

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ABSTRACT

Present study demonstrates an enhancement in thermoelectric power of 10% Ag doped PbTe (PbTe:Ag) thin films when irradiated with 200 keV Ar ion. X-ray diffraction showed an increase in crystallinity for both PbTe and PbTe:10Ag nano-composite films after Ar ion irradiation due to annealing of defects in the grain boundaries. The preferential sputtering of Pb and Te ions in comparison to Ag ions resulted in the formation of nano-dots. This was further confirmed by X-ray photoelectron spectroscopy (XPS). Such an enhancement in thermoelectric power of irradiated PbTe:10Ag films in comparison to pristine PbTe:10Ag film is attributed to the decrease in charge carrier concentration that takes part in the transport process via restricting the tunneling of carriers through the wider potential barrier formed at the interface of nano-dots.

1. Introduction

There has been considerable research interest in improving the thermoelectric energy conversion efficiency of PbTe based materials both in bulk and thin film forms [1]. The efficiency of any thermoelectric material is determined by figure of merit $ZT = S^2\sigma T/\kappa$, where S is the thermoelectric power (also termed as Seebeck coefficient); σ is the electrical conductivity; k is the thermal conductivity, which consists of two factors, viz. (i) the lattice thermal conductivity (k_l), and (ii) the electronic thermal conductivity (k_e) and T is the absolute temperature. Therefore, the numerator part of the above expression known as power factor ($PF = S^2\sigma$) must be enhanced with simultaneous reduction in thermal conductivity. Since last decade, efforts have been made to enhance the thermoelectric (TE) properties using various approaches. An extensive work has been carried out on Pb based chalcogenides due to their applications over a wide temperature range. Among all Pb based chalcogens, the PbTe shows the best TE properties and used in the most modern TE generators, particularly for mid-temperature range (500–900 K) power generation applications [3].

Heremans et al. demonstrated that Tl doped PbTe alloy can achieve ZT of 1.5 at 773 K [4]. Later, Yanzhong et al. found ZT ~1.4 at 750 K in sodium-doped PbTe. Yanzhong's group showed that both Tl and Na alter the electronic structure of the crystal which increases electrical conductivity. Rogacheva et al. [5] investigated the effect of Bi element on TE properties of PbTe and obtained maximum values of thermoelectric power ($P = 39 \times 10^{-4}$ W/m K^2) at $x \sim 0.25$. Among all these elements, Ag has also been reflected as one of the potential dopants to improve the TE properties of PbTe. Dow et al. [6] studied the result of Ag and Sb doping on the TE of PbTe and found that maximum value of ZT is ~0.27 at 723 K for $Pb_{1-x}Ag_xTe$ alloys for $x = 0.1$. The PbTe:Ag nanocomposites have improved TE properties, with power factor of 18.78×10^{-4} W m^{-1} K^{-2} with room temperature thermal conductivity of 1.69 W m^{-1} K^{-1} [7]. Besides doping, ion beam processing of materials is one of the attractive ways of enhancing TE properties. It provides an important means of nanostructuring which results in the improvement of thermoelectric power. An enhancement in TE properties using 5 MeV Si ion irradiation in superlattices namely Bi_2Te_3/Sb_2Te_3 was reported with an increase in the thermoelectric power from 30 to 55 mV/K at 300 K [8]. Gupta et al. reported 40% enhancement in thermoelectric power at 520 K after irradiation with 100 MeV Ag ion beam [9]. Thus, ion irradiation is one of the effective tools to modify TE properties in a controlled manner.

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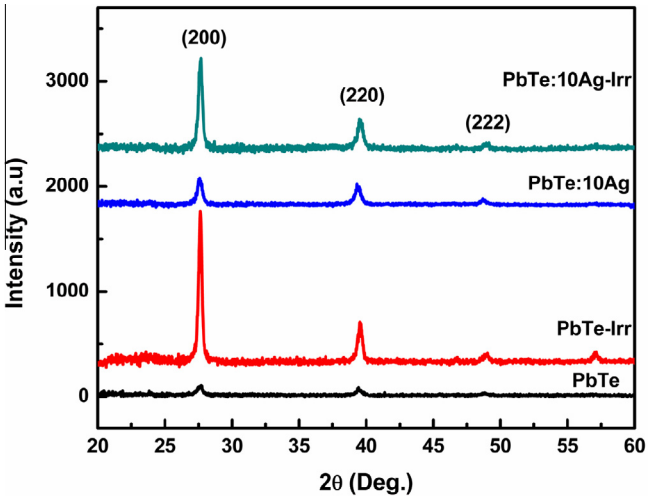

Fig. 1. XRD spectra of PbTe, PbTe:10Ag, PbTe-Irr and PbTe:10Ag-Irr films in the 2θ range of 20–60°.

Table 1
Peak position, FWHM and grain size corresponding to (200) XRD peak.

	Position 2θ (deg.)	FWHM (deg.)	Grain size (nm)
PbTe	27.58	0.49	18.6
PbTe-Irr	27.62	0.29	31.4
PbTe:10Ag	27.58	0.42	22.2
PbTe:10Ag-Irr	27.63	0.34	28.2

The present study focuses on the enhancement of thermoelectric power of doped and undoped PbTe thin films using low energy ion beam irradiation. Previously, it was reported that 10% Ag doping enhances thermoeletric power by nearly 30% [10]. However, further increase of Ag doping to 20% in PbTe enhances the thermoelectric power to only 10% in comparison with undoped PbTe. Therefore, it indicates that the chemical doping can enhance thermoelectric properties only up to a limited extent. This motivated us to explore alternate approaches for further enhancement of thermoelectric power. From earlier studies, ion beam irradiation has been used as an important tool to tune the TE properties by controlling the ion beam parameters [8,9,11]. Therefore the present work attempts to study the combined effect of Ag addition and ion beam irradiation on PbTe thin film.

2. Experimental procedure

The thin films of PbTe and 10% Ag incorporated PbTe of thickness ~60–70 nm were prepared by thermal evaporation technique on quartz substrate under high vacuum condition at Panjab University, Chandigarh. The as deposited PbTe and Ag incorporated thin films were then irradiated with 200 keV Ar^+ ion beam at a fluence of 3×10^{15} ions/cm^2 with 500 nA ion current using low-energy ion beam facility (LEIBF) at IUAC, New Delhi. The irradiation was done at room temperature and the chamber pressure was maintained at 10^{-6} Torr. The ion fluence of 7×10^{14} ions/cm^2 is needed to get 1 dpa (displacement per atom) for PbTe using TRIM (Transport of Ions in Matter) simulation. Therefore, to make sure the displacement of all the atoms from their lattice site we have irradiated the samples with four times higher fluence (30×10^{14} ions/cm^2) than required for 1 dpa. For convenience hereafter, the pristine PbTe, 10% Ag incorporated PbTe, 200 keV Ar^+ ion irradiated PbTe and 10% Ag incorporated PbTe thin films will be denoted as PbTe, PbTe:10Ag, PbTe-Irr and PbTe:10Ag-Irr, respectively. X-ray diffraction (XRD) measurements were performed at glancing angle of 2° to identify the crystalline phases in the films using a Bruker D8 advance diffractometer with Cu Kα (1.54 Å) X-ray source. X-ray photoelectron spectroscopy (XPS) measurement was done to determine the surface elemental composition on the films using a VG instrument having system resolution ~0.9 eV and Mg source, at IOP, Bhubaneswar. Scanning electron microscopy (SEM) was used for the surface study. Four probe and bridge method [12] were respectively used to measure the electrical resistivity (ρ) and thermoelectric power (S) of the films. The carrier density and mobility were determined by Hall effect measurement using a magnetic field of 0.57 Tesla at room temperature.

3. Results and discussion

3.1. X-ray diffraction study

Fig. 1 shows the glancing angle XRD spectra of pristine and irradiated PbTe and PbTe:10Ag films. These measurements were carried out at a glancing angle of 2°. The diffraction peak at $2\theta = 27.5°$, is the characteristic peak for crystalline PbTe and corresponds to (200) planes (Fig. 1). Peak intensity increases and full width half maximum (FWHM) decreases for the irradiated films. The estimated values of grain sizes using Scherrer equation were found to be 18.6 nm, 22.2 nm, 31.4 nm and 28.2 nm, respectively, for PbTe, PbTe:10Ag, PbTe-Irr and PbTe:10Ag-Irr corresponding to (200) plane (Table 1) and it shows that the grain size increases with Ag addition. A substantial increase in the peak intensity was observed for the Ar ion irradiated PbTe and PbTe:10Ag films. The electronic and nuclear energy losses in the present case for 200 keV Ar^+ ion beam in PbTe film are nearly the same (~45 eV/Å). It has been reported by Bai et al. that the grain boundaries and interfaces serve as effective sink for the radiation induced point defects (interstitial and vacancies) created by nuclear energy loss [13]. The present experimental results are consistent with the expectation that the grain boundaries absorb defects which results in the increase in crystallinity. The crystallization of thin film by low energy ion irradiation has also been observed earlier by other groups [14].

3.2. SEM study

Fig. 2 shows the SEM images of PbTe, PbTe-Irr, PbTe:10Ag, and PbTe:10Ag-Irr films. The PbTe:10Ag film shows nanosize islands like structures having dimension ~60 nm × 150 nm on the surface of the sample. The grain size of PbTe thin film has been estimated from Image J software. The grain size of irradiated PbTe film is ~40 nm which is ~15–20 nm greater than pristine PbTe film. The nanosized grain transforms into nanodots of diameter ~140–160 nm on irradiation. Elemental composition of above nanostructures were examined using an energy dispersive spectrometer (EDS) equipped with SEM. The elemental compositions at two different points A (at nanostructures) and B (on flat region) for each sample are given in Table 2. From EDS measurement, it is identified that the nano-size islands like structures of PbTe:10Ag film are Pb rich regions while outside this region, Pb and Te are in 1:1 stoichiometry. This shows that the formation of nanostructures are due to precipitation of Pb on the surface due to formation of $Ag_{2-x}Te$ alloy [2]. The EDS measurement of PbTe:10Ag-Irr film shows that the nanodots also contains all three elements Pb, Te and Ag with higher concentration of Ag in comparison to that present in nanostructures of PbTe:10Ag film. The transformation of nanostructure into nanodots may be because of preferential sputtering of Pb and Te in comparison to Ag. The sputtering yields of