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PbTe nanocrystal formation by interface mixing of Te/Pb bilayer using low energy ions

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ABSTRACT

PbTe nanocrystals are synthesised using low energy ion beam mixing of a Te/Pb bilayer on a Si substrate. The bilayer films are irradiated using 90 keV Ar$^+$ ions and 140 keV Kr$^+$ ions at different fluences ranging from 3×10^{15} ions/cm^2 to 3×10^{16} ions/cm^2. The samples are characterised by resonant Rutherford backscattering spectrometry (RRBS) for determination of presence of oxygen and for ion beam mixing analysis. The simulation of RRBS spectra reveals the mixing of Te and Pb layers with ion irradiation and sputtering of Te and Pb. High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) are used to study the phase formation and change in surface morphology of the pristine and irradiated films. HRTEM confirms the formation of PbTe nanocrystals of ~3–5 nm. The present work reveals that local spherical thermal spike contributes significantly to the mixing process whereas the possibilities of mixing at interface by ballistic process and radiation enhanced diffusion are rather low.

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1. Introduction

PbTe is a low band gap (0.25 eV at 0 K) semiconductor with a high melting point (1200 K) which can be used in various potential applications such as thermoelectric (TE) applications (600–900 K), IR photo detector and ultra high density optical data storage [1,2]. PbTe possesses both p-type and n-type conductivity depending on excess of Te and Pb excess respectively [3]. Synthesis of PbTe to enhance the TE efficiency is highly desirable in the current scenario. Furthermore, PbTe nanocrystals formation has attracted much interest due to their unique properties leading to enhancement in thermoelectric properties [4]. Extensive chemical routes [5–9] have been developed to synthesise PbTe nanocrystals to control their size and shape using different capping agent, surfactant, reaction time, precursor molar ratio and other synthesis parameters. Control of surface energy may result in different shapes of nanostructures with narrow size distributions. However, formation of PbTe nanocrystals with purity, stoichiometry and without any extrinsic doping, etc., seems to be a very tedious task. This limitation motivated us to look for other synthesis techniques, which

can synthesise the PbTe nanocrystals with better control over shape and size of the nanocrystals to enrich the properties. Antipov et al. [9] synthesised the PbTe nanoparticles using CW laser irradiation of PbTe thin film. However, they got bimodal size distribution which had prominent maxima at ~100 nm and 300 nm. The low energy ion irradiation is of interest to many researchers and has been used widely for the formation of different nanostructure with different combinations of systems for various applications [10–15]. In the past, some research groups have reported low energy ion irradiation by different ions Ar, Kr or Xe ions with hundreds of keV energy for the interface mixing of bilayer/multilayer such as in miscible systems (Ag–Ge bilayer [16], Au–Ge bilayer [17], Cu–Ge [18]) and in immiscible system (Ag–Fe bilayer/multilayer [19,20]). Low energy ion beam mixing can also be used to synthesise thermoelectric materials [21,22] with the required stoichiometry by deposited energy at the interfaces of bilayer with selective ion fluence. Ibrahim and Thompson [21] reported ion beam mixing in Bi/Sb system and formation of Bi–Sb alloy with Sb content ranging from 5% to 49% using 80 keV Ar$^+$ and 120 keV Kr$^+$ ions. Benenson et al. [22] have also reported ion beam mixing in Bi/Te system using 130 keV Kr ions at a fluence of 8×10^{15} ions/cm^2 to investigate thermoelectric properties in Bi$_2$Te$_3$ alloys. The basic mechanism of alloy formation during ion beam mixing using low energy ions can be attributed to several processes such as ballistic processes (cascade mixing, recoil mixing), thermal spike (local or global) and radiation

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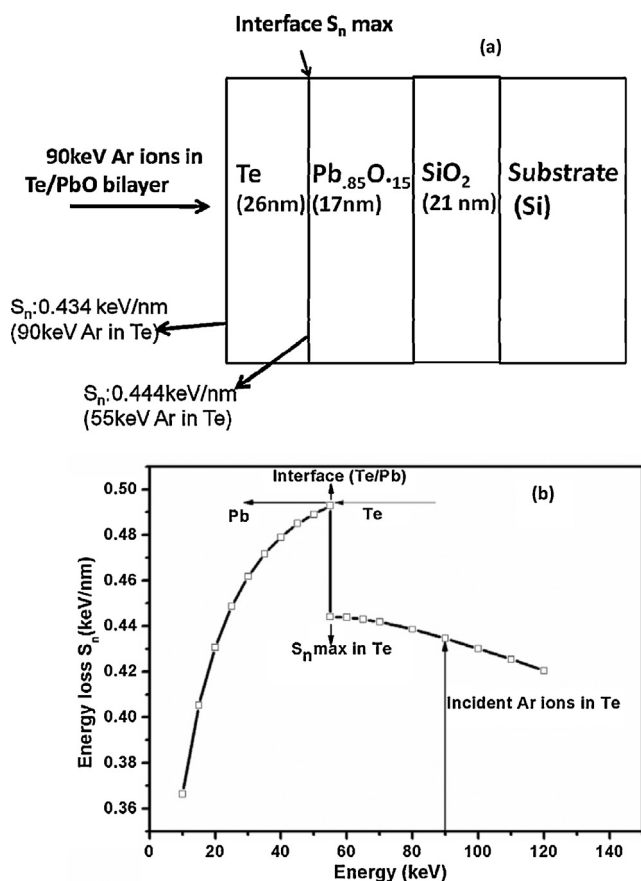*E-mail addresses:* srashti.3@gmail.com (S. Gupta), dka4444@gmail.com (D.K. Avasthi).

Fig. 1. (a) Schematic of Te/Pb bilayer and (b) selection of incident energy for Ar$^+$ ions with maximum energy loss at the interface (Te/Pb).

enhanced diffusion (RED) under different processing conditions [23–29]. Ion beam mixing is influenced by various parameters such as deposited energy density, ion fluence, atomic mass, atomic number of the target material and incident ions.

Laser and ion beam irradiation of material have shown their potential to form different nanostructures on the surface. However, as discussed above PbTe nanoparticle synthesised by CW laser irradiation of PbTe thin film are too large in size to show the nanodimensional effect [9]. This limitation can be overcome with the use of low energy ion irradiation. Ion beam irradiation provides an alternate direction in research that extends the interest in a broad spectrum like control of shape and size, alloy formation of material.

In this study, we investigated the formation of PbTe semiconductor nanocrystals by ion beam mixing of the Te/Pb bilayer using Ar$^+$ and Kr$^+$ ions and studied the effect of deposited energy density on the efficiency of interface mixing. The mechanism underlying the ion beam mixing is also discussed in light of various models, reported in the literature for different systems, depending on different ion beam parameters and bilayer parameters. This study is aimed to identify the most probable mixing mechanism in Pb/Te bilayer system and effect of nuclear energy loss in the mixing.

2. Experimental

Te/Pb bilayer samples (Te was the top layer), with thicknesses as shown in Fig. 1, were synthesised using thermal evaporation on Si substrates and on carbon coated Cu grids under the pressure of ~3–4 × 10^{-6} mbar at room temperature. These bilayer samples (Te/Pb) were irradiated at room temperature at different ion fluences ranging from 3 × 10^{15} to 3 × 10^{16} ions/cm^2 using 90 keV Ar$^+$

and 140 keV Kr$^+$ ions. Thickness of each layer (Te, Pb) and incident energy of the ions are selected to get maximum nuclear energy loss at the interface (Te/Pb) which is calculated by the SRIM software [30]. Deposited energy in bilayer is shown in Fig. 1 for the case of Ar$^+$ ions. Nuclear energy loss (S_n) for 90 keV Ar$^+$ ions is 0.434 keV/nm near the surface of Te layer, which increases with depth and reaches maximum (S_{nmax}) ~0.444 keV/nm after travelling a depth of Te layer ~26 nm, i.e., at Te/Pb interface as shown in Fig. 1. Nuclear energy loss (S_n) for 140 keV Kr$^+$ ions at the surface of the sample (Te) is ~1.373 keV/nm. The average projected range for 90 keV Ar$^+$ ions and 140 keV Kr$^+$ ions in Te/Pb bilayer is ~70 nm (i.e. ions should stop in substrate ~70 nm). These samples were characterised by resonant RBS (RRBS), X ray diffraction (XRD), atomic force microscopy (AFM) and transmission electron microscopy (TEM) before and after ion irradiation. RRBS was performed using 3.048 MeV He$^+$ ions at scattering angle of 165° at IUAC, Delhi to detect the content of oxygen before and after irradiation. RUMP software has been used for RBS analysis [31]. Grazing incidence XRD measurements were performed using a Bruker D8 advance diffractometer with CuKα (1.5406 Å) X-ray source at a grazing incidence angle 2° and with a scan speed of 0.5°/min to investigate the pristine and ion irradiated samples. TEM investigations were carried out using Libra 2000 FE HRTEM equipped with energy dispersive X-ray (EDS) analysis for selective samples. Gatan software has been used for the analysis of HRTEM images of samples. Atomic force microscopy was used for surface roughness measurement of all samples before and after ion irradiation using Nanoscope IIIa at IUAC, Delhi.

3. Results and discussion

3.1. Interface study by resonant Rutherford backscattering spectrometry (RRBS)

Resonant RBS (RRBS) spectra of pristine and samples irradiated by 90 keV Ar$^+$ ion and 140 keV Kr$^+$ ion at different ion fluences ranging from 3 × 10^{15} to 3 × 10^{16} ions/cm^2 are shown in Fig. 2 (a–e). Pristine sample shows two separate edges of Pb and Te. The Rutherford Backscattering Manipulation Program (RUMP) simulations show that the thickness of the top layer (Te) is ~26 nm and that of Pb layer is ~18 nm. There is a PbTe layer of thickness ~2 nm at the interface, which may be due to the mixing of Pb and Te due to the roughness at the interface. The Pb layer is partially oxidised with atomic composition of Pb (86 at%) and O (14 at%). A SiO$_2$ layer of thickness ~21 nm on the surface of the Si substrate is also present as deduced from the simulated RBS spectrum.

There is a clear shift of Pb peak towards the higher energy side in the sample irradiated at the lowest ion fluence of 3 × 10^{15} ions/cm^2 (shown in Fig. 2(b)), which signifies the diffusion of Pb atoms towards the surface. On further increasing ion fluence, there is a reduction in the yield of Pb and Te peaks (shown in Fig. 2(d)), which is the signature of sputtering of Te and Pb with increasing ion fluence. The inset of RRBS spectra shows desorption of oxygen with increasing ion fluence. Simulation of Ar$^+$ ions at the lower fluence of 3 × 10^{15} ions/cm^2 shown in Fig. 2(c) reveals that the PbTe has grown at the interface and form intermixed layer of thickness of PbTe (M_{th} ~25 nm) with unmixed Pb and Te atoms. As the ion fluence increases to 5 × 10^{15} ions/cm^2 rest of the Pb and Te atoms are consumed in mixing to form PbTe layer. On further increasing the ion fluence, sputtering of PbTe starts to occur, which results in the decrease of PbTe film thickness. Furthermore, the experimental data are inadequate for quantitative estimation of mixing rate due to the strong mixing and sputtering of both elements Pb and Te even at initial ion fluence itself. However, qualitatively the mixing rate (k) is deduced using $k = \Delta M_{th}^2 / \Phi$, and the value of k was found to be ~20.8 nm^4 for Ar ions.