Journal of Alloys and Compounds 612 (2014) 98–102

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

# Effects of homogeneous irradiation of electron beam on crystal growth and thermoelectric properties of nanocrystalline bismuth selenium telluride thin films

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ARTICLE INFO

*Article history:*
Received 21 January 2014
Received in revised form 21 May 2014
Accepted 21 May 2014
Available online 2 June 2014

*Keywords:*
Electron beam irradiation
Thermoelectrics
Nanocrystalline
Bismuth selenium telluride

ABSTRACT

The effects of homogeneous irradiation of electron beam (EB) on the crystal growth and thermoelectric properties of nanocrystalline bismuth selenium telluride thin films were investigated. The thin films were prepared using a flash evaporation method, after which EB irradiation was performed under $N_2$ at room temperature at an accelerated voltage of 0.17 MeV. SEM revealed that the untreated thin film was composed of a large quantity of rice-like nanostructures. With increasing the EB irradiation dose, a number of nanodots with diameters of less than 10 nm became visible on the surface of the rice-like nanostructures. The crystallinity and the crystal orientation were enhanced with increasing EB irradiation dose while the average crystal grain size remained almost the same size as that of the untreated thin film. In terms of thermoelectric properties, the mobility of the thin films was enhanced as the EB irradiation dose was increased while the carrier concentration was not greatly changed. As a result, both the electrical conductivity and the Seebeck coefficient were improved with increasing EB irradiation dose. Consequently, even though there is still room for further improvement, the power factor was enhanced around sevenfold (from 0.14 to 0.96 μW/cm/K$^2$) by the EB irradiation treatment.



## 1. Introduction

The development of electrical power sources such as solar cells and thermoelectric devices becomes increasingly important year by year. Thermoelectric device can directly convert thermal energy by means of the Seebeck effect, allowing electricity to be produced using waste heat from automobiles or industrial plants [1]. In addition, thermoelectric device can also directly pump heat through the Peltier effect, which is used for the temperature control of laser diodes to pump heat from the thermal spots [2]. The efficiency of thermoelectric energy conversion of such a device depends on the dimensionless figure of merit ($ZT$) defined as $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively.

Among the many kinds of thermoelectric materials, bismuth telluride based alloys are of great interest not only because they are the best near room temperature thermoelectric materials available, with a highest $ZT$ of close to 1.0, but also due to the potential for improving their $ZT$ values by structural modification. Thin film technology enables the preparation of material in amorphous and crystalline state. To date, many researchers have investigated the size effect on the transport properties [3–5]. For instance, Venkatasubramanian et al. produced a layered $Bi_2Te_3/Sb_2Te_3$ superlattice and did measure a $ZT$ of 2.4 using metal–organic chemical vapor deposition [6], and Harman et al. obtained a $ZT$ of 1.6 for a PbSeTe-based quantum dot superlattice fabricated using molecular beam epitaxy [7]. None of these results have been reproduced until now. In these cases the key for improving the $ZT$ is phonon scattering by controlling the size of structures while maintaining high crystallinity. However, while these deposition methods are suitable for producing nanosized structures with higher crystal quality, the apparatus is complicated and the deposition rate is low, resulting in a high manufacturing cost. Conversely, conventional deposition methods such as flash evaporation [8,9], sputtering [10,11] and electrodeposition [12,13] are able to reduce the manufacturing cost but it is challenging to achieve nanostructuring with high

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http://dx.doi.org/10.1016/j.jallcom.2014.05.146
0925-8388/

crystallinity. In general, the most common method for improving the crystallinity is thermal annealing, but the crystal grains also grow up simultaneously during this process.

Electron beam (EB) irradiation treatment is one method proposed to improve the crystallinity. The mechanism of EB irradiation-induced crystallization is thought to be due to energy dissipation based on EB irradiation-assisted atomic rearrangement [14–16]. In Fe–Zr–B alloys, a nanocrystalline structure has previously been produced by effective EB irradiation while controlling the irradiation dose [17]. However, there have been few reports on the fabrication of thermoelectric material nanocrystalline structures using EB irradiation treatment.

In this study, we investigated the effects of EB irradiation on the crystal growth and thermoelectric properties of nanocrystalline bismuth selenium telluride thin films. We fabricated bismuth selenium telluride thin films using a flash evaporation method, and then treated them by EB irradiation. The structural and the thermoelectric properties of the EB irradiated thin films were analyzed. Finally, we discussed the relationship between the EB irradiation dose, nanostructure, and the thermoelectric properties of the thin films.

## 2. Experimental

Bismuth selenium telluride thin films were fabricated on glass substrates (size: 50 mm × 25 mm, 1.1 mm thick) by a flash evaporation method. The detailed experimental setup has been described in our previous work [18]. In brief, the distance between tungsten boat and substrate was set to 200 mm. The starting material was spherical bismuth selenium telluride powder with an average diameter of 200 μm prepared by a centrifugal atomization method [19]. For the thin film deposition, we first loaded the starting powder in the vessel, and placed the glass substrate on the holder. The chamber was evacuated to $1.4 \times 10^{-3}$ Pa and then a current of 80 A was applied to the tungsten boat until the temperature of the substrate reached 200 °C. Finally, by tilting the powder vessel gradually, the powder was fed onto the tungsten boat, which evaporated them on to the glass substrate. We confirmed that the resulting films had a uniform thickness across the substrate, approximately 500 nm.

Next, the bismuth selenium telluride thin films were homogenously irradiated with an Electron-curtain processor at room temperature (Type CB175/15/180L, Energy Science Inc., Iwasaki Electric Group Co., Ltd.) [20–22]. A tungsten filament in a vacuum was used to generate an electron beam with an electric voltage of 0.17 MeV and an irradiating current of 2.0 mA. The samples were irradiated with the electron beam through a titanium window attached to a 24 cm-diameter vacuum chamber. To prevent oxidation, the samples were kept in a nitrogen atmosphere of 0.1 MPa with a residual oxygen concentration of less than 0.04%. The flow rate of the nitrogen gas was 1.5 L/s.

The surface morphology of thin films was investigated by scanning electron microscopy (SEM; S-4800, Hitachi). The crystallographic properties of the thin films were evaluated by X-ray diffraction (XRD; Mini Flex II, Rigaku) using the Cu Kα line ($\lambda$ = 0.154 nm). The average crystal grain size was estimated from the full width at half maximum of the XRD peaks using Scherrer's equation. The carrier concentration and the mobility of the thin films were measured at room temperature using a Hall effect measurement system (HMS-3000, Ecopia). The in-plane electrical conductivity of the thin films was measured at room temperature by a 4-point probe method (RT-70 V, NAPSON). The in-plane Seebeck coefficient was also measured at room temperature. One end of the thin film was connected to a heat sink and the other end to a heater. The Seebeck coefficient was determined as the ratio of the potential difference along the film to the temperature difference, which was measured using two *K*-type thermocouples of 0.1 mm in diameter pressed on to the thin films. The distance between the thermocouples was 13 mm. The in-plane power factor, $S^2\sigma$ was calculated from the measured electrical conductivity and the Seebeck coefficient.

## 3. Results and discussion

### 3.1. Structural properties of bismuth selenium telluride thin films

Fig. 1 shows the surface morphology of the bismuth selenium telluride thin films imaged by SEM. In Fig. 1(a), the SEM image of the untreated thin film shows that it was composed of a large quantity of rice-like nanostructures with diameters of 10–20 nm and lengths of up to 30–100 nm that were bonded with each other. The surface morphology of the thin films treated with an EB irradiation dose of 0.22 MGy was similar to that of the untreated thin film (Fig. 1(b)). In contrast, when the EB irradiation dose increased up to 0.43 MGy, the surface morphology was drastically changed. A number of nanodots with diameters of less than 10 nm were observed on the surface of the rice-like nanostructures (Fig. 1(c)). Furthermore, when the EB irradiation dose increased up to 1.07 MGy, the surface morphology obtained at this dose was similar to that of the thin film obtained at a dose of 0.43 MGy, but the boundaries of nonodots seemed to become clearer (Fig. 1(d)).

The X-ray diffraction patterns of the bismuth selenium telluride thin films obtained after different various EB irradiation doses are shown in Fig. 2. All peaks in the patterns corresponded to the reflections of the rhombohedral phase of $Bi_2Te_3$ (JCPDS 15-0863). The XRD peaks of (0 1 5) and (1 1 10) were mainly observed in the untreated thin films but their intensities were still low, which revealed that the untreated thin films contain amorphous phase. Only the (0 1 5) peak was enhanced with increasing EB irradiation dose. In particular, when the EB irradiation dose was 0.43 MGy, the (0 1 5) peak was greatly enhanced, and other peaks became weak or even disappeared. This trend corresponded to the change of surface morphology at this EB irradiation dose. Therefore, we think that the nanodots on the rice-like structures were composed of crystalline phase, and the further generation of nanodots led to the higher crystallinity.

Fig. 3 shows the relationship between the EB irradiation dose and the crystallographic properties (crystal orientation and average grain size) of the obtained bismuth selenium telluride thin films. In Fig. 3(a), the crystal orientation is defined as the ratio of the XRD peak of (0 1 5) to the sum of all the XRD peaks. The crystal orientation of the untreated thin film was 0.52. Compared with the standard pattern of $Bi_2Te_3$ (JCPDS 15-0863) and SPS (spark plasma sintering) samples [23], the untreated thin film exhibited a similar crystal orientation. The crystal orientation was linearly enhanced with EB irradiation up to 0.43 MGy, reaching 0.91. This indicated that significant preferential orientation along the (0 1 5) plane of bismuth selenium telluride crystal had been successfully developed. The crystal orientation was saturated at approximately 0.9 even if the EB irradiation dose was further increased. While the mechanism of this preferentially orientated crystal growth is not yet clear, several modified techniques have previously been used to achieve preferential orientation along the (0 1 5) plane [24–26]. In Fig. 3(b), the estimated crystal grain size of the untreated thin film was 13 nm. The crystal grain size was slightly enlarged with increasing the EB irradiation up to 0.43 MGy, and it reached 18 nm. No further increase in crystal grain size with EB irradiation dose was observed above 0.43 MGy. The growth of crystal grain size with increasing EB irradiation dose was negligible in scale compared with that reported for thin films treated with thermal annealing [27–29]. Therefore, the EB irradiation treatment crystallized partially the films and promoted a preferred grain orientation while maintaining the crystal grains at a relatively small size. These nanostructures are possible to reduce the thermal conductivity of the thin films. Fig. 4 shows the relationship between the EB irradiation dose and the atomic composition of the bismuth selenium telluride thin films. With increasing EB irradiation dose, the atomic composition of tellurium was slightly increased and that of bismuth was slightly decreased, while the selenium composition was almost constant throughout all the samples. The deviation range of the atomic composition of the films treated with EB irradiation was within ±1.5% for all the elements. Hence, we think that the treatment of EB irradiation at an electric voltage of 0.17 MeV did not cause significant damage by which atoms were removed from the surface of thin films.