Abstract
Bismuth Telluride is the most efficient thermoelectric material near room temperature with the highest figure of merit. It is known that figure of merit can be improved in nanostructures. This paper reports the synthesis of highly uniform and single crystalline BiTe nanobelts by a simple catalyst free vapor transport method. The morphology, structure, phase purity and stoichiometry of the nanobelts were investigated by x-ray diffraction, scanning electron microscopy, transmission electron microscopy and x-ray energy-dispersive spectrometry. The results revealed the growth of hexagonal BiTe nanobelts along (110) planes. A probable growth mechanism is discussed. This simple approach will provide growth of BiTe nanobelts and related chalcogenides, which could be used as a potential material for future solid state thermoelectric devices.

Introduction
Bismuth Telluride is a thermoelectric material with the highest figure (ZT) of merit near room temperature. With respect to the Bi and Te binary composition, several forms of this material are known to occur [1–6]. Layered structure is the characteristic of this material and the properties strongly depend on the stoichiometry. Thermoelectric and structural properties were correlated for the homologous series of this material viz, Bi4Te5, Bi6Te7, Bi8Te9, BiTe, Bi4Te3, Bi2Te and Bi7Te3 [7, 8]. The nanostructures of these materials can be prepared by various physical as well as solution-based chemical methods such as thermal evaporation [6, 7, 9], molecular beam epitaxy [7], solvothermal method [10] and template assisted electrodeposition [2, 7]. Zhou et al studied the lattice dynamics of BiTe nanotubes synthesized by solvothermal method [10]. They analyzed the micro-Raman scattering spectra and confirmed these materials exceptional thermoelectric performance. Hsin et al prepared BiTe and Bi4Te3 nanostructures of these materials can be synthesized bismuth telluride nanowires with a composition which correspond to a composition between the Bi4Te5, Bi6Te7, Bi8Te9 and BiTe phases by catalytic growth and post annealing [7, 11]. They also studied the thermoelectric properties of these nanowires. Schönherr et al and Wei et al prepared Bi4Te3 nanobelts by the vapor–liquid–solid (VLS) growth mechanism using TiO2 and Au nanoparticles respectively, as a catalyst [6, 9]. In contrast to Bi4Te3, material, BiTe was a non-toxic thermoelectric material and shows the higher value of ZT than Bi2Se3 and Bi2Te3 near the room temperature (320 K) [12–14]. Different forms of BiTe nanostructures, such as nanoparticles [15], nanowires [16, 17], nanosheets [18], heterostructures [19] have been synthesized successfully until now. The general growth mechanism is catalyzed vapor transport to enhance the yield and length [9].

The crystal structure of BiTe consists of two layers of TeBiTeBiTe sandwiched with one layer of BiBi, which is stacked along the c axis of a hexagonal lattice [19]. In vacuum deposition process, the difference in vapor pressures of Bi and Te (Te > Bi) can lead to the deviation from the stoichiometric composition due to the re-evaporation of Te element from the deposited film [20]. It is known that the low thermoelectric (TE) figure of merit of bulk materials can be increased in nanostructures due to the enhancement of density of states near the Femi level, suppression of thermal conductivity by phonon-boundary scattering and due to the modification of
and then purged with Ar gas for 30 min. In a typical experiment, the precursor Bi$_2$Te$_3$ powder is removed to remove any impurities and to maintain an inert atmosphere, the furnace was evacuated to less than 100 mTorr. The hexagonal BiTe structure is highly pure.

**Results and discussion**

A typical horizontal two-zone temperature furnace with a 1 inch diameter quartz tube, as shown by a layout in Scheme 1, was used to grow BiTe NBs. The setup is equipped with pressure and mass flow controllers. In order to remove any impurities and to maintain an inert atmosphere, the furnace was evacuated to less than 100 mTorr and then purged with Ar gas for 30 min. In a typical experiment, the precursor Bi$_2$Te$_3$ powder (0.08 g, 99.999%, Sigma-Aldrich) placed in an alumina boat and kept at the centre of the upstream zone, was evaporated at a temperature of 500 °C maintaining a pressure of 10 Torr. The heating rate was 50 °C min$^{-1}$. The vapors carried over by Ar carrier gas, at a flow rate 50 sccm, were deposited on to Si substrates placed at a distance d from the alumina boat kept at the junction between downstream and upstream. The experiment was performed for 30 min, keeping a steady flow rate and pressure. The downstream was not heated during the course of the experiment. After the completion of the experiment the furnace was allowed to cool down to room temperature. Experiments were also performed at different upstream temperatures of 500 °C–550 °C, pressures 10 and 15 Torr and Ar gas flow rate of 50–250 sccm. All these trials yielded NBs of similar morphology and structure on the substrate, but the overall percentage (number) of deposition of NBs varied. For instance, NBs were deposited on the substrate at all the temperature intervals between 500 °C and 550 °C along with a few plate like structures. However above 550 °C, mostly the deposition was in the form of plate like structures. The pressure range 10–15 Torr is observed to be optimum for NB deposition. As far as the Ar gas flow rate is concerned, all the flow rate intervals between 50 sccm to 250 sccm deposited NBs on the substrate. However higher flow rate deposited more plate like structures and less NBs. The optimum Ar gas flow rate was observed to be ~50 sccm. The NBs that had grown on the substrate were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). The crystal structure of the final product on the substrate were examined by XRD using Cu Kα radiation ($\lambda = 1.5418 \text{ Å}$). The morphology, structure and phase purity of the NBs were investigated by SEM and TEM. The TEM images, high-resolution TEM (HRTEM) images, and selected area electron diffraction (SAED) patterns were obtained on a JEOL JEM-2100F TEM operated at 200 kV. Chemical composition of the individual NB was examined by energy dispersive x-ray spectroscopy (EDS) attached to the TEM. The EDS of the samples were also performed with SEM as well. The samples for TEM analysis were prepared either by dispersing the NBs in solvent followed by placing a drop of the solution on a carbon coated copper grid or by dragging the grids along the surface of the sample.

**Experimental**

Figure 1(a) depicts the XRD pattern of the as-grown NB ensemble. The Bragg diffraction peaks were indexed to the hexagonal BiTe structure (ICPDS file: 83–1749), implying the growth of hexagonal BiTe NBs. Table 1 displays the details on the angle 2θ, interplanar spacing d and the corresponding (hkl) values. The XRD spectrum did not exhibit any significant characteristic Bragg peak of Bi or Te metal, which excludes significant Bi/Te phase segregation and formation of Bi/Te metal clusters/precipitates in the BiTe. Figure 1(b) shows the morphology of NBs as examined by SEM using a Philips XL30SFEG. The inset depicts the magnified image of a typical NB. Figures 1(c) to (f) show a series of SEM images from low to high magnifications deposited at various...
temperatures to demonstrate the morphology of the NBs at various deposition conditions. The deposition temperatures were 500 °C, 550 °C, 520 °C and 540 °C respectively. The pressure is ∼10 Torr and Ar gas flow rate is ∼50 sccm. All the NBs showed similar morphology irrespective of deposition conditions. A representative TEM image from a NB that is deposited at 540 °C and of width 60 nm is shown in figure 2(a). The bright and dark stripes or ripple like contrast in the TEM image is due to strain resulting from the bending of the belt with respect to electron beams [25, 26]. The inset in figure 2(a) depicts the SAED patterns from the NB that shows a regular diffraction spot pattern, reflecting the single-crystalline nature of the NB. The diffraction spots pattern were indexed to hexagonal BiTe structure (JCPDS file: 83–1749), in agreement with XRD pattern of NB ensemble and the growth direction of NB was along (110) plane. The lattice spacing of 0.229 nm and 0.129 nm were identified as (110) and (128) planes, respectively of hexagonal BiTe. The HRTEM image measured from the NB in panel ‘a’ is depicted in figure 2(b) which shows clear lattice fringes, reflecting the single crystalline nature of NB and is structurally uniform without any dislocation. An estimate of 0.229 nm lattice spacing perpendicular to the growth direction of the NB was shown in figure 2(e).
to the growth direction is in agreement with (110) growth direction. Inset in the figure indicates the growth direction of nanobelt. Inset shows SAED pattern, indexed to hexagonal BiTe structure. The lattice spacing of 0.129 nm was identified as the interplanar distance of (128) plane. (b) Representative HRTEM image of the nanobelt shown in panel (a). The lattice spacing 0.229 nm corresponds to the interplanar distance of (110) plane. Inset in the figure shows the two dimensional Fast Fourier transform. (c) And (d) TEM images at various magnifications prepared at 500 °C and 550 °C respectively.

Table 1. Details on 2θ, interplanar distances (d) and (hkl) for BiTe.

| 2θ  | d-spacing (Å) | (hkl) |
|-----|---------------|-------|
| 23.50 | 3.78          | 011   |
| 27.60 | 3.23          | 104   |
| 35.06 | 2.56          | 107   |
| 38.02 | 2.37          | 018   |
| 40.78 | 2.29          | 110   |
| 45.09 | 2.01          | 115   |
| 49.95 | 1.82          | 024   |
| 55.09 | 1.67          | 0113  |
| 56.97 | 1.62          | 208   |
| 62.50 | 1.49          | 1112  |
| 66.37 | 1.41          | 214   |
| 72.40 | 1.29          | 128   |
| 74.23 | 1.27          | 300   |

Figure 2. (a) Representative TEM image of BiTe nanobelt grown along (110) plane at 540 °C. The arrow mark indicates the growth direction of nanobelt. Inset shows SAED pattern, indexed to hexagonal BiTe structure. The lattice spacing of 0.129 nm was identified as the interplanar distances of (128) plane. (b) Representative HRTEM image of the nanobelt shown in panel (a). The lattice spacing 0.229 nm corresponds to the interplanar distance of (110) plane. Inset in the figure shows the two dimensional Fast Fourier transform. (c) And (d) TEM images at various magnifications prepared at 500 °C and 550 °C respectively.
shows that Bi and Te are the major elements in the NB (lines due to Cu are from the TEM grid). A quantitative analysis indicates that the atomic percentage of Bi is around 51.32 (mass percentage is around 63.33) and that of Te is around 48.68 (mass percentage is around 36.67) that is close to an atomic ratio of 1:1, confirming the growth of BiTe NB. Repeated measurements in different samples deposited at various deposition temperatures yielded the same result.

Several mechanisms including vapor-liquid-solid (VLS) mechanism and vapor-solid (VS) mechanism were proposed to explain the growth of NBs [27–29]. The former is generally the case when a catalyst is used for the growth, and after the growth, liquid droplets can be found at the tips of the NBs. In our TEM images, no droplets were found at the tip of the NB and hence the growth mechanism is likely to be the conventional VS process.
Radial growth and axial growth coexists in the nanostructure growth. If the axial growth is faster than radial growth, non uniformity of radial growth results leading to the growth of belt like morphology. In fact, a clear explanation for the growth of belt like morphology is still unclear, though there are some speculative reports [27, 28, 30, 31]. It is argued that growth temperature and super saturation ratio are the two dominant factors controlling the morphology of nanostructures during growth. Dai et al envisaged that higher temperature and larger supersaturation ratio facilitate the belt like growth [27].

In our case the NBs were synthesized by heating the precursor, Bi₂Te₃, at a temperature range of around 500 to 550 °C. Above this temperature, instead of NBs more or less plate like structures or layered structures were formed on the substrate (figure 4). During heating, Bi₂Te₃ dissociates and non-congruent evaporation results [32, 33]. The vapors carried over by Ar carrier gas was deposited on the substrate. Te has high vapor pressure than Bi. This could lead to the deviation from the stoichiometric composition while depositing on the substrate. After the deposition, BiTe NBs must have grown by self-seeded process through diffusion and reaction. It is to be noted that although the downstream is not heated during the course of experiment, the substrates kept at a small distance from the upstream will be, in general, at a higher temperature than the room temperature. Due to high substrate temperature some fraction of deposited Te element, which is the more volatile, could be re-evaporated from the substrate favoring the formation of BiTe composition [34]. The sticking coefficient of Bi-Te system can also be a factor facilitating the growth of BiTe phase. The sticking coefficient of elements that adhere to the substrate is the ratio of adherent atomic flux to the incident atomic flux. It is known that the sticking coefficient of Bi is independent of substrate temperature and flux ratio where as that of Te strongly depends on substrate temperature. The sticking coefficient of Te decreases significantly at high substrate temperature (especially above 200 °C) resulting changes in the stoichiometry and excess of Te on the substrate may be desorbed due to temperature [34, 35].

Conclusions

In conclusion, BiTe NBs have grown on Si substrates by a simple catalyst free vapor transport method. These NBs were analyzed by XRD, SEM, TEM and EDS to determine the morphology, structure and phase purity. The results confirmed the growth of hexagonal BiTe NBs along (110) direction. A possible growth mechanism is discussed. It is expected that these NBs could be used for studies of thermoelectric and transport properties. Besides, this simple approach will provide growth of BiTe NBs and related chalcogenides, which could be used as a potential material for future solid state thermoelectric devices.

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References

[1] Kim Y, Cho S, DiVenere A, Wong G K L and Ketterson J B 2001 Phys. Rev. B 63 155306
[2] Manzano C V and Martin-Gonzalez M 2019 Front Chem. 7 516
[3] Moosavi S H, Kojda D, Kockert M, Schoenherr T, Hesjedal T, Fischer S F, Kroener M and Woias P 2017 *Proceedings* 1311

[4] Kok K Y, Ng I K, Choo T F, Saidin N B and Abdullah Y 2016 *Mater. Sci. Forum* 840 271

[5] Ng I K, Kok K Y, Rahman C Z and C A, Saidin N U, Ilias S H and Choo T F 2014 *AIP Conf. Proc.* 1525 1584 5

[6] Wei Q, Su Y, Yang C J, Liu Z G, Xu H N, Xia Y D and Yin J 2011 *J. Mater. Sci. 46* 2267

[7] Hamdou B, Kimling J, Dorn A, Pippel E, Rostek R, Woias P and Nielsch K 2013 *Adv. Mater.* 25 239

[8] Mamur H, Bhuian M R A, Korkmaz F and Nil M 2018 *Renew Sust Energ. Rev.* 82 4159

[9] Schönherr P, Tillbury T, Wang H, Haghhihirad A A, Sot V, van Aken P A and Hesjedal T 2017 *Cryst. Growth Des.* 17 1438

[10] Zhou F, Zhao Y, Zhou W and Tang D 2018 *AIP Adv.* 8 125530

[11] Hsin C L, Wingert M, Huang C W, Guo H, Shih T J, Juh J, Wang K, Wu J, Wu W W and Chen R 2013 *Nanoscale* 5 4669

[12] Deng R et al 2018 *Energy Env. Sci.* 11 1520

[13] Deng R et al 2018 *Sci. Adv.* 4 5606

[14] Zheng G et al 2017 *Energy Env. Sci.* 10 2638

[15] Akshay V R, Sureesh M V and Vasundhara M 2017 *Inorg. Chem.* 56 6264

[16] Jung S J, Park S Y, Kim B K and Kwon B 2015 *Acta Mater.* 97 68

[17] Kaur H, Sharma L, Singh S, Sivathai B, Reddy G B and Senguttuvan T D 2014 *J. Electron. Mater.* 43 1782

[18] Kusagawa K and Takashiri M 2014 *J. Alloy. Compd.* 633 480

[19] Yamane K, Kihara K and Matsumoto T 1979 *Acta Cryst.* B35 1479

[20] Kim D H, Byeon E, Lee G H and Cho S 2006 *Thin Solid Films* 510 148–53

[21] Shi L, Yu C and Zhou J 2005 *J. Phys. Chem. B* 109 22102–11

[22] Shi L, Hao Q, Yu C, Mingo N, Kong X and Wang Z L 2004 *Appl. Phys. Lett.* 84 2638–40

[23] Borca-Tasciuc D A, Chen G, Prieto A, Martin-Gonzalez M S, Stacy A, Sands T, Ryan M A and Fleuriau J P 2004 *Appl. Phys. Lett.* 85 6601–3

[24] Zhou J, Jin C, Seol J H, Li X and Shi L 2005 *Appl. Phys. Lett.* 87 133109

[25] Yoo B, Xiao F, Bozhilov K N, Herman J, Ryan M A and Myung N V 2007 *Adv. Mater.* 19 296–9

[26] Pan Z W, Dai Z R and Wang Z L 2001 *Science* 291 1947–9

[27] Chan Y F, Wang R M, Zhang H Z, Sun X C, Zhang Z S, Xing Y J and Yu D P 2004 *Micron* 35 481–7

[28] Dai Z R, Pan Z W and Wang Z L 2003 *Adv. Funct. Mater.* 13 9–24

[29] Xu B, Yang D, Wang F, Liang J and Ma S 2006 *Appl. Phys. Lett.* 89 074106

[30] Wang Q, Li G D, Liu Y L, Xu S, Wang K J and Chen J S 2007 *J. Phys. Chem. C* 111 12926–32

[31] Li J Y, Qiao Z Y, Chen X L, Cao Y G, Liu Y C and Wang C Y 2000 *Appl. Phys. A* 71 587–8

[32] Jian J, Chen X L, He M, Wang W J, Zhang X N and Shen F 2003 *Chem. Phys. Lett.* 368 416–20

[33] Shing Y H, Chang Y, Mirshafi A, Hayashi L, Roberts S S, Josefowicz J Y and Tran N 1983 *J. Vac. Sci. Technol. A* 1 503–6

[34] Mzerd A, Sayah D, Tedenac J C and Boyer A 1994 *J. Mater. Sci. Lett.* 13 301–4

[35] Mzerd A, Sayah D, Brun G, Tedenac J C and Boyer A 1995 *J. Mater. Sci. Lett.* 14 194–7