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Switching of the Natural Nanostructure in Bi_2Te_3 Bulk Materials by Low Energy Ion Irradiation

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Bismuth telluride (Bi_2Te_3) based compounds are the best choice for room temperature thermoelectric applications due to their outstanding energy conversion efficiency ($ZT = S^2\sigma/\lambda \approx 1$ at 300 K). It is a severe challenge to increase ZT since the electronic and thermal transport properties (thermopower S, electrical conductivity σ, and thermal conductivity λ) depend on each other. As a recent trend [1] to overcome this problem, advanced engineering is applied to fabricate thermoelectric nanomaterials (nanowire [2], superlattices [3], nanostructured bulk [4]) with emphasis to enhance phonon scattering and reduce thermal conductivity but to retain the crystalline structure and electronic transport properties.

We studied Bi_2Te_3 based bulk materials [5,6] and nanomaterials [7] by transmission electron microscopy (TEM) and we observed a structural modulation superimposed to the average structure which was referred to as natural nanostructure (nns) [5]. Similar to dislocations, the strain field of the nns can be imaged using two-beam diffraction conditions and we found that the nns consists of a sinusoidal displacement field with wavelength of 10 nm and amplitude of 10 pm [5]. Therefore, the nns represents a high structural disorder relevant for phonon scattering. The nns was observed in Bi_2Te_3 nanomaterials by many groups in the TEM (see references in [6]), however, its formation remained unclear.

In a recent systematic study we realized that the nns can be switched ON and OFF in a controlled way by ion etching [6]. The range of etching parameters and minimum dose for switching the nns ON and OFF will be presented. TEM specimens were prepared from p-type $(Bi_{0.26}Sb_{0.74})_2Te_3$ bulk material with the c-axis lying in the plane of the specimen (a-cut, Fig. 2a). After an initial etching the specimen was subjected to a re-etching series; the specimen was repeatedly etched at 1 and 3 keV. The formation (Fig. 1b) and removal (Fig. 1a and 1c) of the nns was clearly observed in the TEM for ion energies of 3 and 1 keV, respectively. The same ion irradiation procedure was applied on a TEM specimen obtained from n-type $Bi_2(Te_{0.91}Se_{0.09})_3$ bulk material, yielding identical results (not shown) [5]. We emphasize that the presence or absence of the nns could be seen both in the images and also in the diffraction patterns (inserts in Fig. 1). The above experiments were repeated for TEM specimens having c-axis perpendicular to the plane of specimen (b-cut samples) (Fig. 2b) and no nns formation was observed.

In a second step the effect of the etching angle was studied. One n-type and one p-type sample were etched at energies between 0.5 and 3 keV; for each energy the etching angle was increased in steps of 2° to 5°. The results are summarized in Fig. 2c, showing that with decreasing ion energy larger etching angles are required for forming the nns. Hence, the formation and removal of the nns can also be controlled by increasing or decreasing the etching angle, respectively.

Control was demonstrated by reproducing the results in six n- and p-type samples prepared from different batches, switching the nns ON and OFF twice, and verifying the results on two different ion etching machines. Controlled formation of the nns has the potential for reducing the thermal conductivity and

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could increase the thermoelectric figure of merit in Bi_2Te_3 materials. This relates particularly to nanomaterials since ion irradiation can be applied very effectively in this case.

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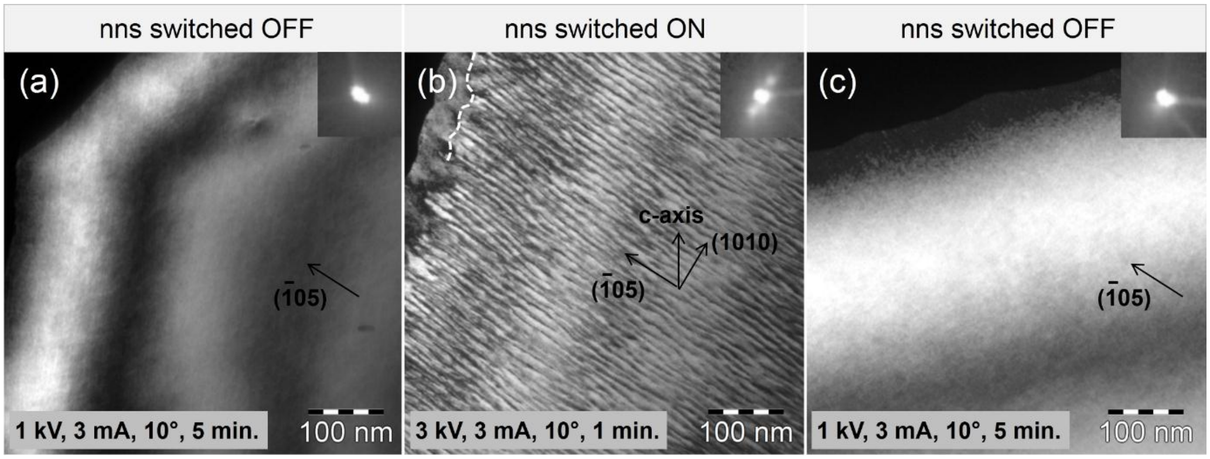

Figure 1. TEM dark-field images acquired under g = {0,1,5} two-beam conditions for imaging the nns in p-type $(Bi_{0.26}Sb_{0.74})_2Te_3$ (a–c). Etching at 3 keV (b) revealed the nns and etching at 1 keV (a and c) the nns disappeared. The inserts in the upper right corner show the {0,1,5} reflections with satellite reflection due to the nns in (b).

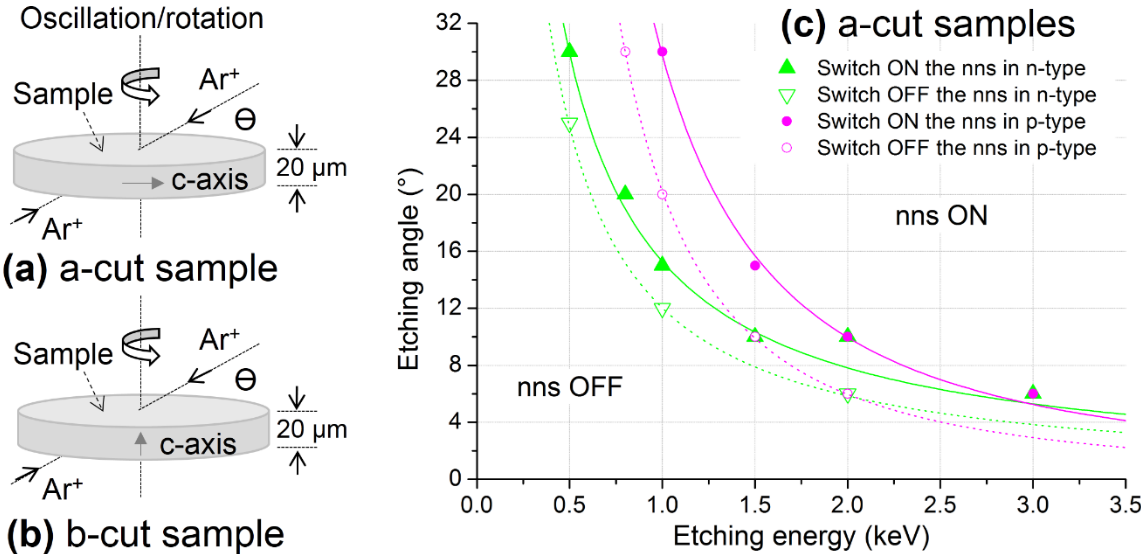

Figure 2. (a) Schematic of TEM sample orientation and etching angle applied for Ar^+ ion etching. (b) Dependence of formation and removal of the nns on ion energy and angle by Ar^+ ion irradiation for n- and p-type material. The ion source current was set to 3 mA and the etching time was 5 min.

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