Vol 17 No 1, January 2008
1674-1056/2008/17(01)/0286-04
Chinese Physics B
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Ab initio calculation of the growth of Te nanorods and Bi_2Te_3 nanoplatelets*

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(Received 16 May 2007; revised manuscript received 6 June 2007)

In this paper the growth mechanism of a Te/Bi_2Te_3 novel structure is studied by *ab-initio* calculations. The results show that the growth of Te nanorods is determined by the adsorption energy of Te atoms on different crystalline Te surfaces. The adsorption energy of Te on the Te (001) surface is 3.29 eV, which is about 0.25 eV higher than that of Te on the Te (110). This energy difference makes the preferential growth direction along the $< 001 >$ direction. In addition, the higher surface energy of Bi_2Te_3 (110) and the lattice misfit between crystalline Bi_2Te_3 and Te along $< 001 >$ direction are considered to explain the growth of the Bi_2Te_3 nanoplatelets, in which Volmer–Weber model is used. The theoretical results are in agreement with experimental observation.

Keywords: *ab initio* calculation, growth mechanism, Te nanorod, Bi_2Te_3 nanoplatelet
PACC: 7115A, 6860, 6150

1. Introduction

Understanding and controlling the growth of nanostructures and self-assembly structures are of great importance for designing and fabricating nanoscale devices.[1−4] Thermoelectric devices are used in many special applications, such as coolers and electrical power generators. The inherent efficiency of thermoelectric material is determined by a dimensionless parameter ZT (the thermoelectric figure of merit), where T is the temperature and Z characterizes the electrical and thermal transport properties of materials. At present, thermoelectric devices are made of bulk material, which have low efficiency at room temperature due to the low ZT. The important properties for high-efficiency thermoelectric materials are large Seebeck coefficient, moderate electrical conductivity, and small thermal conductivity. It has been theoretically predicted and experimentally demonstrated that nanostructure materials exhibit a high value of ZT due to enhanced thermoelectric power and electrical conductivity or reduced thermal conductivity.[5−12] A synthesis of novel composite nanostructure of Te/Bi_2Te_3[13] was reported, in which the Bi_2Te_3 nanoplatelets grew on Te nanorods by packing them along c-axial direction in a top–bottom sequence. It may be a potential thermoelectric building block due to the confined thickness of the platelet. However, the growth mechanism of Te/Bi_2Te_3 nanostructures has not been reported. In this article, we will present *ab initio* calculations of adsorption energies of Te and Bi adatoms on different surfaces of Te nanorods to explain the growth mechanism. The growth mechanism of the Bi_2Te_3 nanostructure is also discussed.

2. Method

We analyse the adsorption energies of Te adatom on different surfaces, the surface energy of Te (110) and Bi_2Te_3(110), and the lattice misfit between Bi_2Te_3 epitaxial layers and Te (110) substrate. We use *ab-initio* calculations based on density functional theory,[14] which is implemented in the Vienna *ab-initio* simulation package.[15] Perdew–Burke–Ernzerhof[16] generalized gradient approximation for the exchange–correlation energy functional, projector augmented waves method, and 227eV for cut-off energy of the plane waves basis set are employed. First, the crystal structures of the bulk Te and the bulk Bi_2Te_3 are optimized. Second, Te (110), Te (001) and Bi_2Te_3 (110) surfaces are relaxed. Third, for analysing the adsorption energies of Te adatom on different surfaces, all possible adsorption sites for Te on Te (110)

*Project supported by the National Natural Science Foundation of China (Grant No 10774176), the Nation Basic Research Program of China (Grant Nos 2006CB921305 and 2006CB806202).
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and Te (001) surfaces are optimized. The adsorption energy of each adsorption pattern on different surfaces is calculated by

$$E_{\text{adsorption}} = E - E_0 - E_{\text{adatom}}, \quad (1)$$

where E is the total energy of the surface with one adatom on a possible adsorption site, E_0 is the total energy of the corresponding clean surface, and E_{adatom} is energy of Te adatom. Fourth, for analysing the surface energy (σ) of Te (110) and Bi_2Te_3(110), we calculate total energy of Bi_2Te_3 (110) surface and Te (110) surface, respectively. And then the surface energy is calculated by Boettger equation[17]

$$\sigma = [E^N_{\text{slab}} - N\Delta E]/2A, \quad (2)$$

where

$$\Delta E = (E^N_{\text{slab}} - E^{N-2}_{\text{slab}})/2, \quad (3)$$

E^N_{slab} is the energy of surface with N layers, and A is the surface area.

3. Results and discussion

3.1. The growth mechanism of Te nanorods

In Ref.[9], the Te nanorods grow along < 001 > direction and the side surface is Te (110) according to transmission electron microscopy, scanning electron microscope and energy dispersive x-ray spectroscopy results. In our calculations, Te nanorods with Te (110), and Te (001) surfaces are considered. Figures 1(a) and 2(a) show all the possible adsorption sites for Te adatom on Te (001) and Te (110) surfaces. Figures 1(d) and 2(d) show the order of height of atomic layers.

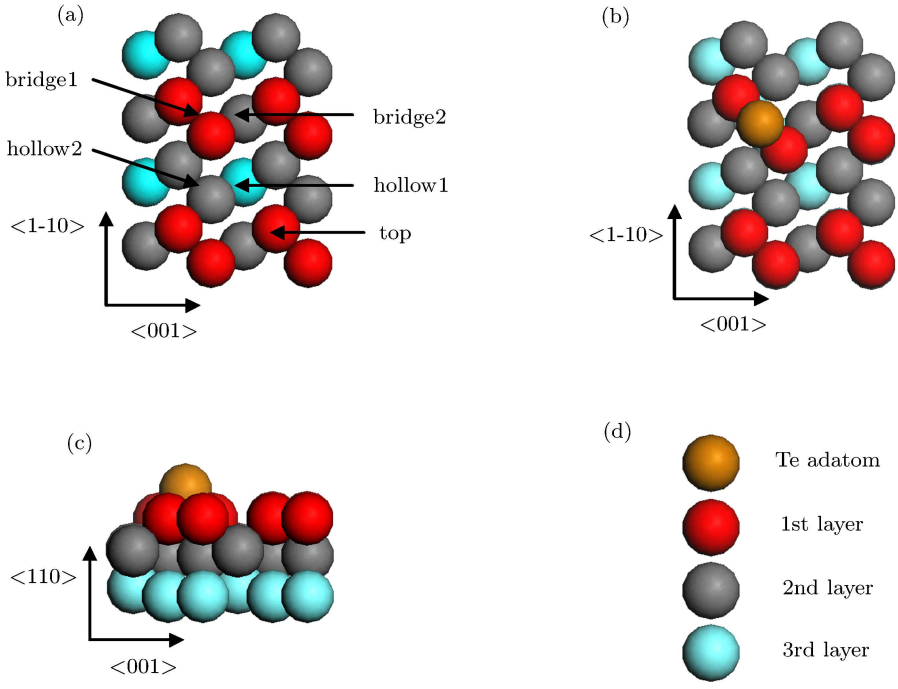


Fig.1. Adsorption of Te adatom on Te (110). (a) Five typical adsorption sites; (b) Top view of the most stable configuration for Te adsorption; (c) Side view of (b); (d) The red atom stands for the first layer of the slab, argentine for the second layer, and blue for the third layer; the brown atom stands for the Te adatom.

In the case of Te adatom on Te (110) surface, it is found that only bridge site and hollow site are possible adsorption sites. The configuration with Te adatom on the top site of Te (110) is not stable and the adatom moves to bridge site after relaxation. The most stable configuration is that the Te adatom on the bridge1 site, and the adsorption energy is 3.04eV as shown in Figs.1(b) and 1(c), which is 0.62–0.77eV higher than that of other configurations. As to the Te on Te (001) surface, *ab-initio* calculations show that the configurations with Te adatom on the top and bridge sites are not stable and the adatom moves

to the hollow sites after relaxation. The most stable configuration is the one with the Te adatom on the hollow1 site as shown in Figs.2(b) and 2(c), and adsorption energy is 3.29eV, which is 0.22–0.84eV higher than that of other configurations. Therefore, comparing the most stable configuration, we find that the adsorption energy of Te on Te (001) surface is 0.25eV higher than that of Te on Te (110) surface, implying that Te nanorods grow faster along < 001 > direction than along < 110 > direction. It is in good agreement with the experimental result.[13]

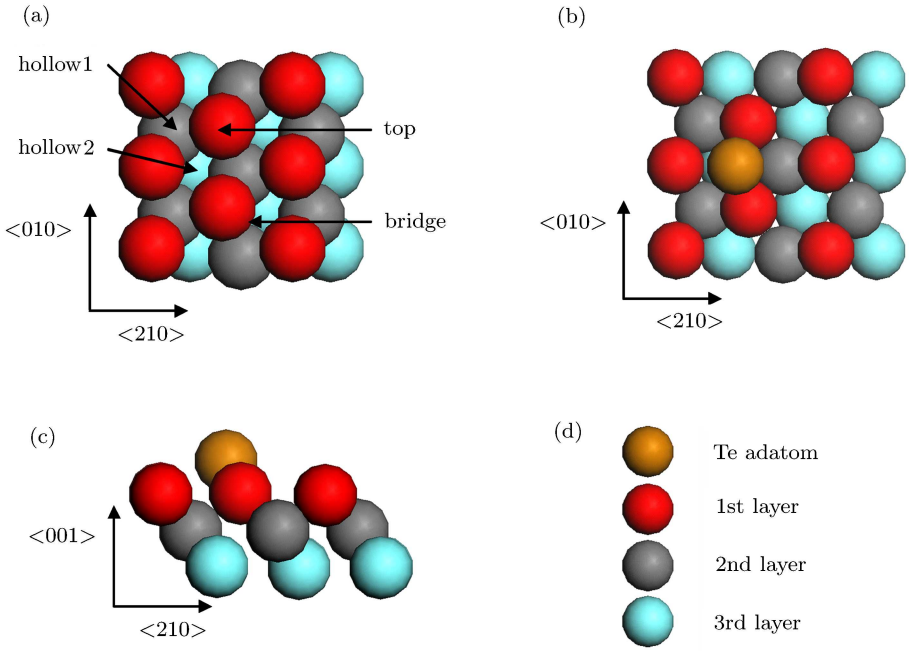


Fig.2. Adsorption of Te adatom on Te (001). (a) Four typical adsorption sites; (b) Top view of the most stable configuration for Te adsorption; (c) Side view of (b) and the lowest energy is in the case of (c), which makes the preferential growth along this direction; (d) Same to Fig.1(d).

3.2. The growth mechanism of Bi_2Te_3 nanoplatelets

In previous studies, it was found that the Bi_2Te_3 nanoplatelets grew on the side surfaces of Te nanorods along < 110 > direction and the growth of Bi_2Te_3 is restricted in < 001 > direction.[13] First, the Boettger equation is used to calculate the surface energies of both Te (110) and Bi_2Te_3 (110) surfaces. In the case of Te (110), the total energy calculations of the clean surfaces with 5–10 atom layers are carried out respectively. The area of Te (110) surface slab is fixed to 0.465nm,^{2} and the thicknesses of vacuum layers are all set to 10Å. Then the energies of single layer, ΔE (calculated by Eq.3), are obtained. They vary from –10.666 to –10.659eV. Since the relative error is only 0.07%. The mean value of ΔE (–10.661eV) is employed to calculate surface energy by using Eq.(2). The surface energy $\sigma_{\mathrm{Te}(110)}$ is 1.13eV/nm^2. In the case of Bi_2Te_3 (110), the surface area is fixed to 0.816nm^2. The thickness of vacuum layer and the number of slab layers are the same as that used in the Te (110) calculation. The total energies of the surfaces with different layers are calculated. The energy of a single layer, ΔE (calculated by Eq.3), varies from –17.794 to –17.786eV. The relative error is only 0.04%. We use the mean value of ΔE, –17.790, to calculate surface energy, which is 2.20eV/nm^2. We find that the surface energy of Bi_2Te_3 (110) (2.20eV/nm^2) is nearly twice as much as that of Te (110) (1.13eV/nm^2).

Second, we analyse the lattice misfit between Bi_2Te_3 epitaxial layer and Te (110) substrate. Te has trigonal cell structure with a_s=0.45033nm and c_s=0.59614nm. Bi_2Te_3 has hexagonal cell structure with a_e=0.44459nn, c_e=3.1826nm. The c_e is about five times as much as c_s. The lattice misfits between Te crystal and Bi_2Te_3 crystal are $f_1 = \dfrac{a_s - a_e}{a_s} = 0.3\%$, and $f_2 = \dfrac{5c_s - c_e}{5c_s} = -7.36\%$, where f_1 and f_2 are the lattice misfit of a and c direction between Te and Bi_2Te_3 crystals respectively. According to the equation $E_\varepsilon = GVf^2/(1-\upsilon)$[18] (where E_ε is the lat-

tice misfit energy, G is shear modulus, V is the volume of epitaxial island, f is the lattice misfit, and ν is Poisson's ratio), the lattice misfit energy is proportional to f^2. Thus, lattice misfit energy along $< 001 >$ direction is much higher than other directions.

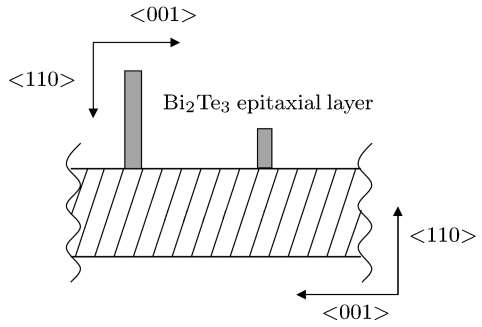


Fig.3. Schematic diagram of the growth mode of the Bi_2Te_3 nanoplatelet. The nanoplatelet is grown based on the nanorod as the substrate. This growth is caused by the lattice misfit and difference in surface energy. The growth follows Volmer–Weber model.

Based on the above theoretical consideration, it can be summarized as follows. 1) The surface energy of Bi_2Te_3 (110) is nearly twice as much as that of Te (110). 2) The lattice misfit energy is very large in c direction. Then it can be deduced that the growth of Bi_2Te_3 epitaxial layer on Te (110) substrate follows the Volmer–Weber model described in Ref.[19] (three-dimensional island growth) as shown in Fig.3. The growth of Bi_2Te_3 epitaxial layer is confined along $< 001 >$ direction due to large lattice misfit energy, and that will cause the formation of Bi_2Te_3 nanoplatelets.

4. Conclusions

Through *ab-initio* calculations, we find that the Te nanorods growth is preferentially along $< 001 >$, which is determined by the adsorption energies on different surfaces. Based on the surface energy and lattice misfit, we have also explained the growth of Bi_2Te_3 nanoplatelets on the Te nanorods. Because of large surface energy of Bi_2Te_3 (110) and large lattice misfit energy along $< 001 >$ direction, the growth of Bi_2Te_3 nanoplatelets on Te (110) follows Volmer–Weber model. Thus, Bi_2Te_3 nanoplatelets along $< 001 >$ direction are obtained. This work is helpful for understanding the formation of Bi_2Te_3 nanostructures.

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