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The fabrication of Te nanowires with different orientations by vacuum vapor deposition

Haiyong Chen [a,*], Hongliang Lu [a], Yanguang Nie [a], Jiahua Zhang [b,**], Mingzhe Zhang [a], Quanqin Dai [a], Shiyong Gao [a], Shihai Kan [a], Dongmei Li [a], Guangtian Zou [a]

[a] *State Key Laboratory of Super-hard Materials, Jilin University, Changchun 130012, PR China*
[b] *Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China*

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Abstract

We have fabricated sharp-tipped Te nanowires on a $NaNO_2$ nanoparticles substrate by vapor deposition method. These nanowires are parallel or perpendicular to c-axis of hexagonal Te depending on the source temperature. We think the sharp-tip can efficiently reduce the energy of adsorbed atoms, leading to favorable growth along its direction.

Keywords: Low dimensional structures; Growth models; Nanomaterials

1. Introduction

The fabrication and characterization of one-dimensional (1D) nanostructured materials has attracted much interest, owing to both their novel physical properties, which differ from those of bulk materials, and their potential applications in nanodevices [1–7]. Various shape of 1D nanostructured materials have been fabricated, such as nanorod, nanowires, nanoribbons and nanotube [8–11]. For a certain material, these 1D nanostructured materials are often along a certain crystallographic direction. For example, Te nanowires, nanoribbons and nanotube [12–14] are all along the c-axis of hexagonal Te crystal, because (001) direction (i.e., c-axis) is energetically most favorable. But, for studying the quantum confinement effect and optimizing the properties of 1D material, it is important to fabricate 1D material with different orientations. In this Letter, we report the fabrication of Te nanowires parallel and perpendicular to the c-axis of Te by vapor deposition method, and propose a formation mechanism of such nanowires based on the calculated barriers for an adsorbed atom hopping on (001) and (100) surfaces of Te crystals.

2. Experiments

The fabrication of Te nanowires: our experiments are performed on HUS-5GB high vacuum evaporator, which has two couples of electronic rods (marked as 1# and 2#). We clamped a molybdenum piece with the thickness of 0.3 mm between the two electronic rods (marked as 1#) as the heat source. It can endure the current of 50 A. In this experiment, the current was about 10–15 A. The other couple of rods (2#) are connected with the thermocouple pointing on the source heater or the substrate, and we controlled this switch by a lever outside the vacuum chamber. Te with 99.999% purity was placed on the molybdenum piece. $NaNO_2$ white floccules, which is a network composed of spherical $NaNO_2$ nanoparticles (about 400 nm) [15], were placed on a copper circle (∅3 mm), one millimeter far away above Te source. With the increase of the current, the Mo piece was soon heated to 523 K (573 K) at 1×10^{-3} Pa. At

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[*] Corresponding author. Tel.: +86 431 5168340; fax: +86 431 5166089.
[**] Corresponding author.
E-mail addresses: chenhy@jlu.edu.cn (H. Chen), zjiahua@public.cc.jl.cn (J. Zhang).

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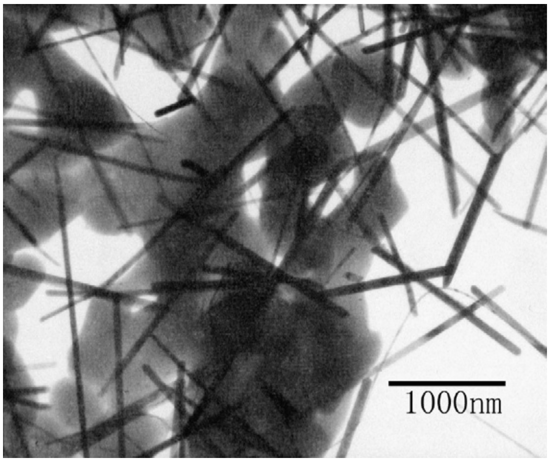

Fig. 1. (a) Te nanowires fabricated on $NaNO_2$ substrate by vapor-phase depositing method.

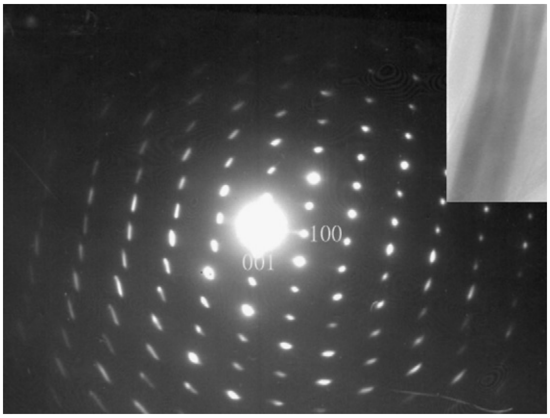

Fig. 1. (b) The SAD pattern of a Te nanowire (the insert) with the growth direction parallel c-axis.

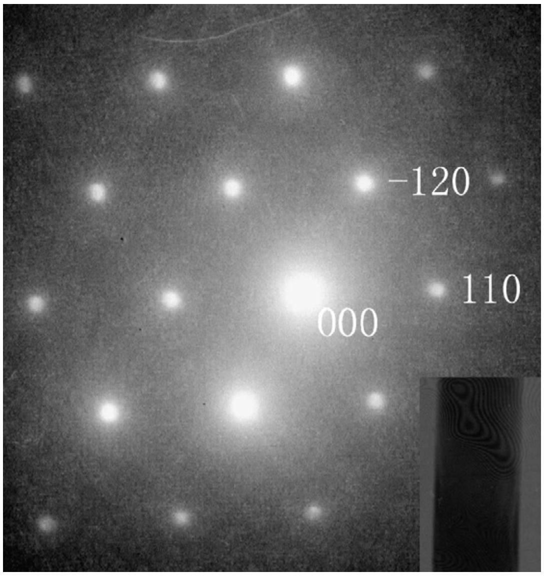

Fig. 1. (c) SAD pattern of a Te nanowire (the insert) with the growth direction perpendicular to c-axis.

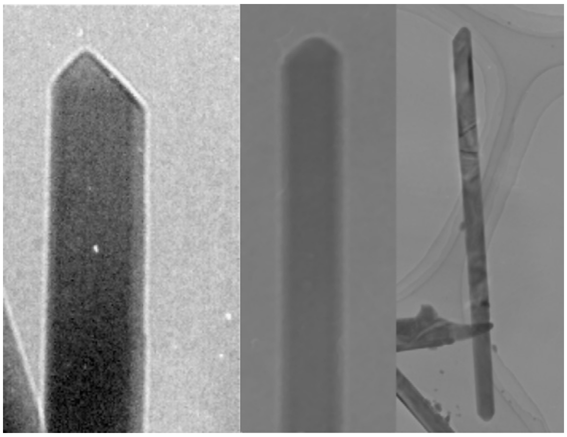

Fig. 1. (d) Some typical growth-sharp-tip (GST) of Te nanowires. (Left) a typical GST of the nanowire along c-axis; (middle) a typical GST of the nanowire perpendicular to c-axis; (right) a nanowire with tow GSTs.

the same time, the substrate temperature was 473 K. Te started to grow on the $NaNO_2$ substrate. The growth process lasted for 15 minutes. And the final floccules became black.

After the growth process, we dusted a bit of black floccules on a copper net (∅3 mm) with a support film, and use a clean glass plate to press it for a moment. This is prepared for the observation of the sample with the $NaNO_2$ substrate. Then we dropped distilled water on it several times and got the sample without $NaNO_2$ networks. The morphology and the crystal structure of these nanowires were characterized by transmission electron microscope (TEM) and selected area diffraction (SAD) on a HITACHI TEM H-8100 IV at the work voltage of 200 kV.

3. Results

As shown in Fig. 1(a), these nanowires have a width of 10–100 nm and a length of several microns.

Fig. 1(b) shows the TEM image and electron diffraction of a single wire from the Te nanowires fabricated at a substrate temperature of 473 K and a source temperature of 523 K. The longitudinal direction of this Te nanowire is parallel to (001) reciprocal lattice vector, indicating the Te nanowire is along to c-axis. This is true for all nanowires examined. However, for Te nanowires fabricated at the same substrate temperature (i.e. 473 K) and a higher source temperature of 573 K, the orientation of some Te nanowires are perpendicular to c-axis. This is shown in Fig. 1(c), which displays the TEM image and electron diffraction pattern of a Te nanowire fabricated at this condition having a longitudinal direction parallel to (−330) reciprocal lattice vector. So our experiments show that Te nanowires with different orientations can be fabricated by adjusting the source temperature.

4. Discussion

To understand our experimental observations, we propose the following explanation. As shown in Fig. 1(d), the end of each fabricated nanowire is sharp-tipped which we called the growth-sharp-tip (GST). The moving adsorbed atoms over the

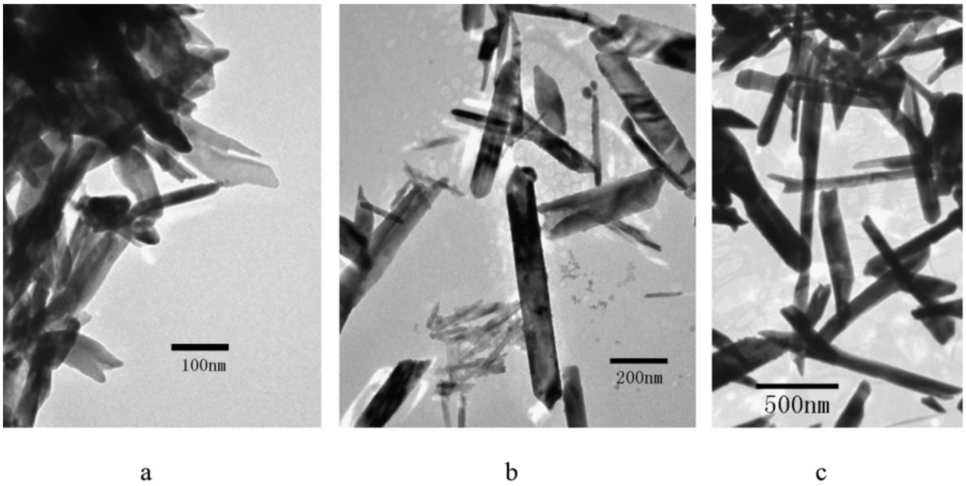

Fig. 2. (a) Te nanowires at the growth time of three minutes; (b) Te nanowires at the growth time of 7 minutes; (c) Te nanowires at the growth time of 10 minutes.

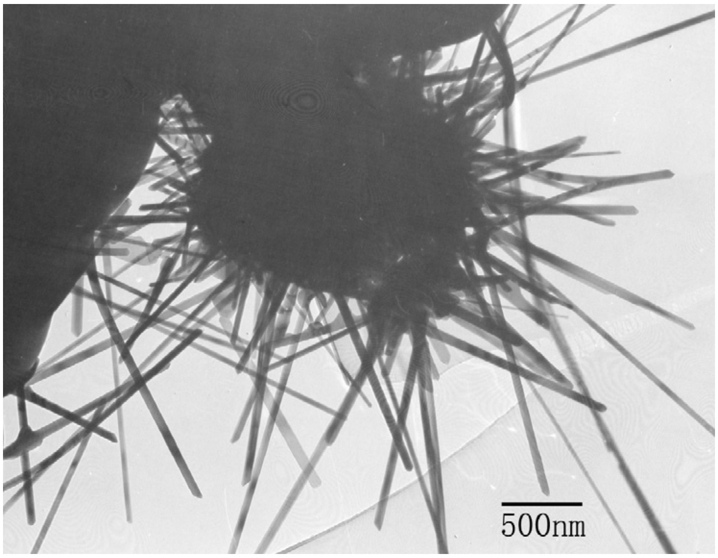

Fig. 3. Te nanowires fabricated on $NaNO_3$ substrate.

sharp tip will more frequently interact with the edges than those over the flat body of the nanowires. Considering that these adatoms will lose more energy while moving over the side edge than the flat plane, due to the atom on the edge is more yielding than the one on the plane, we can deduce that moving adsorbed atom will rapidly reduce its energy while moving on the sharp tip. This can result in adsorbed atoms mainly growing on the tip. That is to say that the growth on the tip is preferential. Hence the sharp tip induces the formation of the nanowire in the growth progress.

We have studied time dependent growth of these nanowires at the substrate temperature of 473 K and the source temperature of 523 K. We first placed three substrates above the Te source; at the growth time of three minutes, we stopped the deposition and took out the first sample; then we started the deposition again and the growth continued; the second and third samples were taken out at the growth time of 7 and 10 minutes, respectively. As shown in Fig. 2(a), (b) and (c), with the increase of the growth time, Te nanowires became longer and longer. We can find that they always grew along the direction of the tip. These observations confirm that the tip leads to the formation of the nanowire. Specially, on the picture (Fig. 2(c)) which shows a clear secondary nucleation, the new nanorod always formed on the tip of the old nanowire. This result confirms once more that the growth on the GST is preferential.

For confirming the formation of GST is mainly based on the ball shape of the substrate particles, we also deposited Te on the $NaNO_3$ network composed of spherical nanoparticles (about 500 nm) and the K_2SO_4 network composed of nanowires with the diameter of near 100 nm [16]. The condition of the Te deposition and the fabrication of the $NaNO_3$ and K_2SO_4 substrates are same with the one of $NaNO_2$ substrate. The results on the $NaNO_3$ substrate are shown in Fig. 3, we can see that sharp-tipped Te nanowires can also form with a denser nucleation than the one on the $NaNO_2$ substrate. But for the K_2SO_4 substrate with the wire shape, no such Te nanowires formed on them. So, we believe the spherical surface is important to form sharp-tipped Te nanowires.

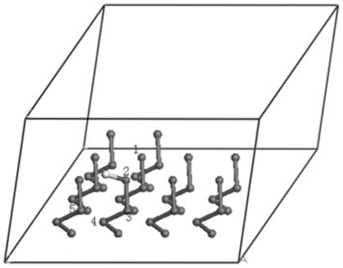

Fig. 4. The lattice used in energy barrier calculation.

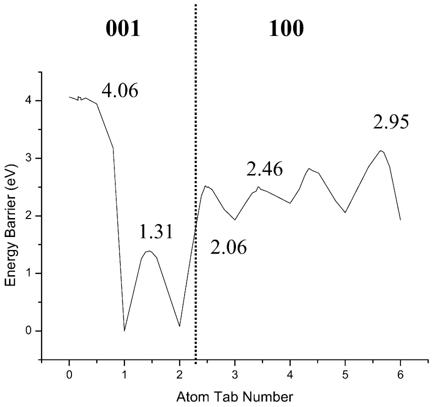

Fig. 5. The energy barriers of Te atom hopping on the surface of Te crystal (atom 6# and 3# is same atom).

In our experiments, we imagine the original tip is formed as follows. Te is deposited on the spherical surface of $NaNO_2$ nanoparticles. As the Te nuclear is growing, the stress increases in the Te-substrate interface. When the length of Te crystal is larger than a critical value, a part of Te nuclear will be separated from the surface of the substrate. The stress in this part is released, leading to easier growth on this section. This protrudent segment just is the original growth-sharp-tip (GST), having a long axis along the direction of the fast growth.

For knowing the direction of fast growth of Te crystal, we first calculated the hopping barriers on the surfaces of hexagonal Te by the CASTEP [17] module of materials studio. The options are GGA, PW91 [18] and complete LST/QST [19]. Fig. 4 is the hexagonal lattice used in calculation ($a = 22.18$ Å and $c = 15.89$ Å).[1] Atom 1# and 2# are atoms on (001) surface, and atom 2#, 3# (6#), 4#, and 5# are atoms on (100) surface. After we optimized each structure of Te adatom bonded on atom 1#, 2#, 3#, 4# and 5#, the barriers for Te adatom hopping among them were calculated.

As shown in Fig. 5, when we use the energy of Te adatom bonded on atom 1# (i.e. the stable position of (001) surface) as the zero point energy, the energy barrier of Te adatom escaping from the surface, hopping between two chains of (100) surface, hopping on one chain of (100) surface, and hopping on (001) surface is 4.06, 2.95, 2.46, and 1.31 eV, respectively.

From the results of the calculation, we can know that the energy of stable adatom on (001) and (100) surface is 0 eV (1# in Fig. 5) and 2.06 eV (3# in Fig. 5), respectively. When the source temperature is low, the supplied vapor atoms are very insufficient to occupy all the stable positions of (001) and (100) surfaces. The number of adatoms staying on (001) surface divide by the one on (100) surfaces is about $e^{-(0-2.06)\ \mathrm{eV}/k_B T}$. At our growth condition (473 K), $k_B T$ is about 0.04 eV. So most adsorbed atoms are trapped by (001) surface, leading to the growth along (001) direction is faster than the one along (100) direction.

But when the source temperature is high, the supplied vapor atoms are very sufficient. The stable positions of (100) surface will also be fully occupied because the sufficient vapor atoms are always ready to fill any vacancies. At this condition, the process of energy loss will limit the crystal growth. As shown in Fig. 5, for freshly absorbed adatoms to grow on (001) and (100) surface, it has to lose an energy of 2.7 and 1.6 eV, respectively. Suppose the rate of energy loss is constant, it will take roughly twice the time for a freshly adsorbed atom to grow on (001) surface than on (100) surface. This will lead to the growth along (001) direction is slower than the one along (100) direction.

For confirming the fast growth direction at the high source temperature is perpendicular to the c-axis, we deposited Te on the $NaNO_2$ substrate with the size of several microns at the source temperature of 573 K. After the $NaNO_2$ substrate was washed by water, we observed their morphology. As shown in Fig. 6(a) and (b), Te nuclei which lain on the support film, are some sheets with a sharp tip. From the diffraction pattern, we can find (100), (101) and (110) diffraction circles, but (001) diffraction circle cannot be seen. This indicates that the fast growth directions of these nuclei sheets are perpendicular to the c-axis of Te. This result is consistent with the one of our calculation.

In a summary, when the source temperature is low (high), and the source vapor pressure is low (high), the growth on (001) surface is faster (slower) than the one on (100) surface. So the long axis of the GST is along the normal direction of (001) [(100)] surface.

These GST with different orientations can result in Te nanowires with different orientations in the growth process. As shown in Fig. 7, a freshly adsorbed atom has a high energy of 4.06 eV, which is larger than the hopping barriers of both (001) and (100) surface. It can move on the surfaces of Te crystal with a slight decrease of its energy. But when it moves on a (001) [(100)] GST, it has a rapid loss of energy induced by the GST, resulting in an energy state lower than the hopping barrier of (001) [(100)] surface. The adsorbed atoms grow mainly on the (001) [(100)] GST, leading to the formation of nanowires with (001) [(100)] orientations. We call this the growth-sharp-tip (GST) mechanism, for the special role of GST in the formation process of nanowires.

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[1] The lattice was built as follows. First a (001) surface with 1.5 lattice constant thickness was cleaved from the optimized hexagonal Te lattice of which the constants are $a = 4.436$ Å and $c = 5.924$ Å. Then a vacuum slab of 8.0 Å is used to build a 3D lattice. We then construct a $5 \times 5 \times 1$ superlattice to avoid the interaction between absorbed atom and its reproduction due to Born–von Karman boundary condition. Finally, some unimportant atoms are deleted to save computation time.

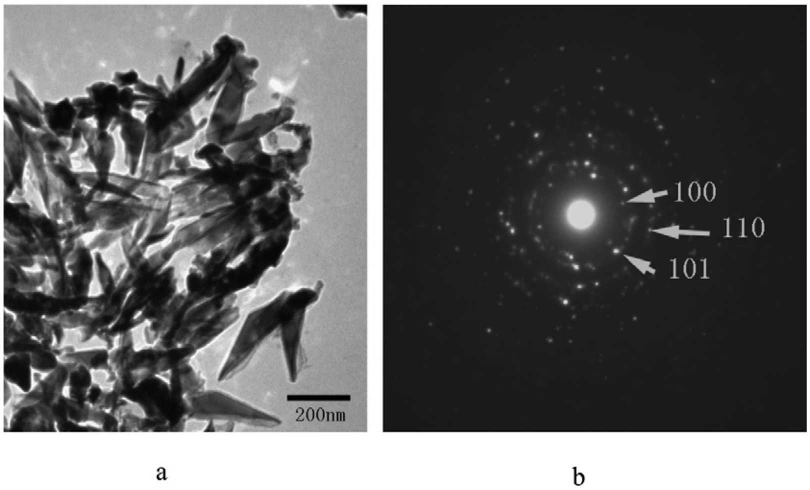

Fig. 6. (a) Te nuclei formed at high source temperature; (b) the diffraction pattern of the nuclei shown in (a).

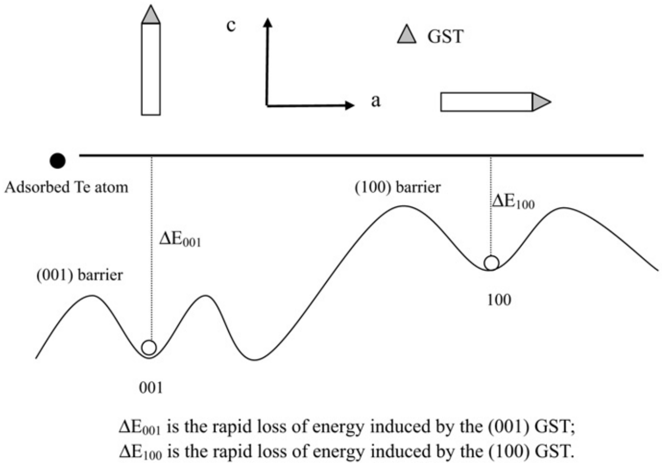

Fig. 7. The formation of Te nanowires with (001) and (100) orientations are due to the rapid loss of energy induced by the (001) and (100) GST, respectively.

5. Conclusion

In conclusion, by vapor deposition method, we fabricated Te nanowires with different orientations on a substrate of $NaNO_2$ particles with a big curvature. At a source temperature of 523 K (or 573 K), the orientation of Te nanowire is parallel (or perpendicular) to c-axis of Te. To explain our experimental results, we propose a growth-sharp-tip (GST) mechanism to describe the formation process of the Te nanowires. We suggest a scenario in which the sharp-tip can efficiently reduce the energy of adsorbed atoms, leading to favorable growth along the GST direction. Based on our computed result of the hopping barriers on Te (001) and (100) surfaces, we consider the deposition rate at various conditions and come to the conclusion that if the hopping barriers of two surfaces are different the direction of GST can vary with the growth condition. So we can expect that other 1D materials with different orientations can also be fabricated by adjusting the growth condition, for the hopping barriers of different surfaces of a crystal are often different.

Acknowledgements

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