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Large-scale Fabrication of Tellurium Nanowire Arrays by Magnetron Sputtering with Controllable Morphology

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Abstract: A convenient template-free magnetron sputtering method was employed for fabrication of highly ordered single crystalline tellurium nanowire arrays at moderate substrate temperature (200℃). The phase, morphology and microstructure of the as-prepared films were characterized by powder X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and high resolution transmission electron microscope (HRTEM). The results indicate that the produced nanowire arrays are composed of single-crystalline Te nanowires, which grow along the [101] direction with needle like morphology. These nanowires have an average diameter of 100 nm and length up to about 1 μm. Working pressure and substrate temperature are both essential for the formation of Te nanowire arrays, which balance the diffusion and growth of Te along [101] direction and (101) plane. The growth mechanism of such nanostructure is proposed, including an absorbing-combining-nucleation-growth process.

Key words: tellurium; nanowire arrays; radio frequency magnetron sputtering

Low-dimensional nanomaterials, especially one-dimensional (1D) semiconductor nanowires and nanotubes have attracted intensive interest in the last few decades[1-2]. Owing to their surface effect, small size effect and quantum confinement effect, 1D semiconductor nanowires and nanotubes exhibit superior and unique optical, electronic and thermal properties to those of their bulk counterparts[3-7]. To satisfy the increasing demand for realizing nanodevices, well aligned arrays of nanowires are desirable for practical use[8-12]. Meanwhile, the properties of nanowire array composites are strongly dependent on the size, morphology and orientation of individual wires.

Tellurium is a well-known p-type elemental semiconductor with a narrow band gap (0.35 eV) at room temperature and exhibits excellent and unique properties such as photoconductivity, non-linear optical response, thermoelectricity and high piezoelectricity, *etc*[13-14]. For these intriguing properties, tellurium nanomaterials have large potential applications in gas sensors, optical recording medias, optoelectronic devices, field emission devices, cooling devices and piezoelectric nanogenerators[15-19]. Te nanostructures are also used as template for the synthesis of different telluride based nanomaterials[20]. So far, different approaches have been developed for the synthesis of 1D tellurium nanostructures, such as physical evaporation, photolytic preparation, thermal decomposition, microwave-assisted synthesis, hydrothermal or solvothermal methods[21-26]. However, the fabrication of tellurium nanowire arrays has rarely been reported due to the difficulties in controlling the synthesis. Recently, Te nanowire arrays were prepared using the thermal evaporation technique and their field emission properties were also discussed[17]. Nevertheless, the preparation of Te nanowire arrays at low temperature having high binding force with substrate is still a challenge. Anodic alumina membranes (AAM) possess a uniform and parallel porous structure, which makes them an ideal host material for creating highly ordered nanowire arrays. Although electrochemical and electrophoretic deposition in AAM template has been demonstrated to be a feasible method for the fabrication of highly ordered Te nanowire arrays[27-28], the complex procedure and the low purity of the product impede it for large-scale practical application. A simpler and more environment-friendly method is highly desirable. Magnetron sputtering method is generally affirmed as a more

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efficient method for the production of nanostructures of inorganic materials with high purity and crystallinity, which is considered as a relatively practical alternative for industrial production.

Herein, we introduced a simple and controllable magnetron sputtering method for the fabrication of highly crystalline tellurium nanowire arrays in large scale uniform on various substrates using a pure Te target with a facile one-step process at relatively low substrate temperature (200℃) within only one hour. The effects of substrate temperature and working pressure on the morphology and microstructure of the Te films were systematically studied, and an absorbing- combining-nucleation-growth mechanism was proposed.

1 Experimental

Tellurium nanowire arrays were deposited on polished quartz glass at temperatures ranging from 200℃ to 300℃ for 1 h by radio frequency (RF) magnetron sputtering with a pure Te (99.99%) target (General Research Institute for Nonferrous Metals, China). Before deposition, substrates were cleaned in turn using acetone, alcohol and de-ionized water for 15 min in an ultrasonic bath. The distance between target and substrate was maintained at 90 mm and a fixed RF power of 40 W was retained during the sputtering. Base pressure of the deposition chamber was below 3.0×10^{-4} Pa and the working pressures were set at 0.5, 1.0, 1.5 and 2.0 Pa, respectively, flowing 25 sccm of Ar as the sputtering gas.

The X-ray diffraction (XRD) patterns of the products were collected on a Rigaku D/MAX 2200 PC automatic X-ray diffractometer with Cu Kα radiation (λ=0.154056 nm), with operation voltage and current maintained at 40 kV and 40 mA. The morphology and microstructure of the thin films were analyzed by field emission scanning electron microscope (FE-SEM, HITACHI S-4800) and high resolution transmission electron microscope (HR-TEM, FEI Tecnai G2 F20 S-Twin at 300 kV).

2 Results and discussion

Typical tellurium nanowire arrays were successfully prepared on polished quartz glass with substrate temperature 200℃ and working pressure 1.0 Pa for 1 h, as shown in Fig. 1(a, b). The nanowire arrays anchor firmly to the substrate. Fig. 1(a) reveals that the produced nanostructures are composed of ordered nanowires with an average diameter of 100 nm and length up to about 1 μm, while each nanowire has a needle like morphology. The cross-sectional view shown in the inset in Fig. 1(a) indicates that there is a thin layer of dense and continuous Te film between the deposited Te nanowire arrays and substrate. This transitional Te film acts as a buffer layer to relive the misfit stress, which is very important for the growth of high-quality and defect-free film[29]. Therefore, Te atoms nucleate on the continuous Te film and then grow to nanowires under suitable sputtering conditions. A few Te nanotubes also exist in the film as shown in the magnified SEM image Fig. 1(b). Fig. 1(c, d) show the TEM images of a single Te nanowire, revealing the sharp nature of the tip with diameter less than 10 nm. Nanoneedles are of particular interest because their tips exhibit a sharp curvature. Therefore, the needle like feature also make the Te nanowires have potential applications as probing tips with high spatial resolution in both vertical and horizontal dimensions or field-emission tips due to the increased field-enhancement factor. The microstructure of an individual Te nanowire was further investigated in detail by HRTEM as shown in the inset in Fig. 1(d). The lattice spacing as calculated is 0.33 nm, which corresponds to the (101) lattice plane of hexagonal Te. These images confirm that the hexagonal nanowires are single crystalline in nature without any defects and have [101] axis as the growth direction. This orientation preference is well confirmed in the XRD pattern.

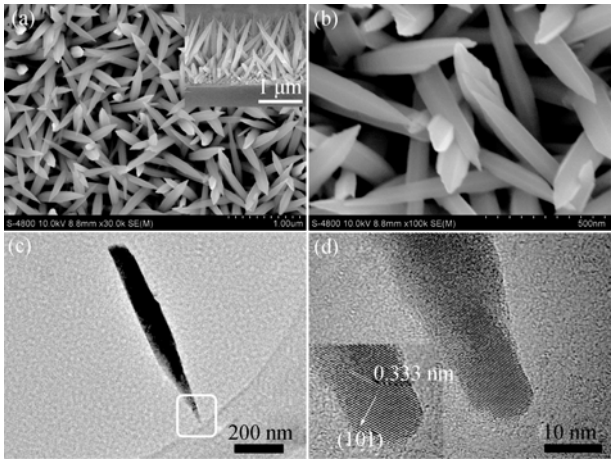

Fig. 1 (a, b) FESEM images of the tellurium nanowire arrays, (c, d) TEM images of a single tellurium nanowire
Inset in (a) shows the cross-sectional view of the nanowire arrays. Inset in (d) shows the HRTEM image on the tip

The XRD pattern of the Te nanowire arrays deposited at 200℃ and 1.0 Pa is shown in Fig. 2 together with the standard diffraction peaks of hexagonal Te (JCPDS 36-1452). Compared with the standard pattern, the (101) peak is the dominant peak and its intensity is much higher than all other peaks, revealing high [101] growth orientation of the Te nanowires with single-crystalline nature. Hexagonal Te has a highly anisotropic crystal structure consisting of helical chains of covalent bound atoms. So Te has a very high tendency to grow anisotropically. In a hexagonal lattice, Te atoms are apt to in turn bound together through van der Waals interaction to form 1D structures[30]. The suitable sputtering conditions and the intrinsic crystal structure of Te jointly being the driving force of the 1D nanostructure.

During deposition process, it was found that substrate temperature and working pressure both played important roles in determining the formation of Te nanowire arrays. Figure 3 shows the SEM images of the Te thin films deposited under different Ar pressure with a fixed substrate temperature of 200℃. The length of each nanowire decreases with the increase of Ar pressure, while the diameter remains almost unchanged. The cross-sectional view shown in the inset in Fig. 3(e) indicates that when the Ar pressure increases to 2.0 Pa, the nanowire arrays have almost disappeared and the film becomes very dense, composing of podgy nanorods. This trend would be caused by the increased scattering of Te atoms by Ar molecule at higher Ar pressure, leading to less longitudinal growth of Te. Specifically, the Te atoms sputtered from the target are scattered more severely by Ar molecule with higher pressure during deposition. Therefore, less Te atoms are deposited onto substrate, leading to less growth in [101] direction. Consequently, appropriate Ar pressure is required to balance the growth direction of each nanowire for the formation of nanowire arrays. It is clear that there is also a thin layer of dense and continuous Te film between the nanorods and substrate, which acts as a transition layer. As shown in the magnified images Fig. 3(d, f), there are some nanotubes in the films deposited under higher Ar pressure. It has been reported that the degree of supersaturation controls the morphology of the deposited nanostructures in vapor-phase synthesis[31]. As discussed above, less Te atoms are provided for the growth of wire like crystals under higher Ar pressure. This would lead to undersaturation in the central part of the growing regions and the formation of nanotubes[32]. The XRD patterns shown in Fig. 2 demonstrate that the films deposited at different Ar pressures are all composed of hexagonal Te phase with high crystallinity.

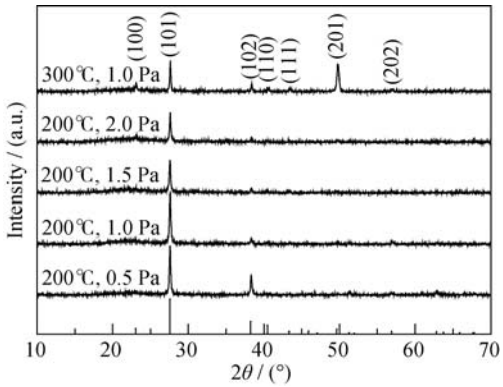

Fig. 2　XRD patterns of the tellurium nanowire arrays deposited under different Ar pressures and substrate temperatures

The effect of substrate temperature on the morphology of the Te films is shown in Fig. 4, while these films are all deposited under 1.0 Pa. As the substrate temperature is fixed at 200℃ or 250℃, well aligned Tenanowire arrays can be successfully deposited, as shown in Fig. 4(a, b). However, as the substrate temperature increases to 300℃, the nanowires change to nanorods with increased diameter and decreased length of 300 nm and 500 nm, respectively. Therefore, the film

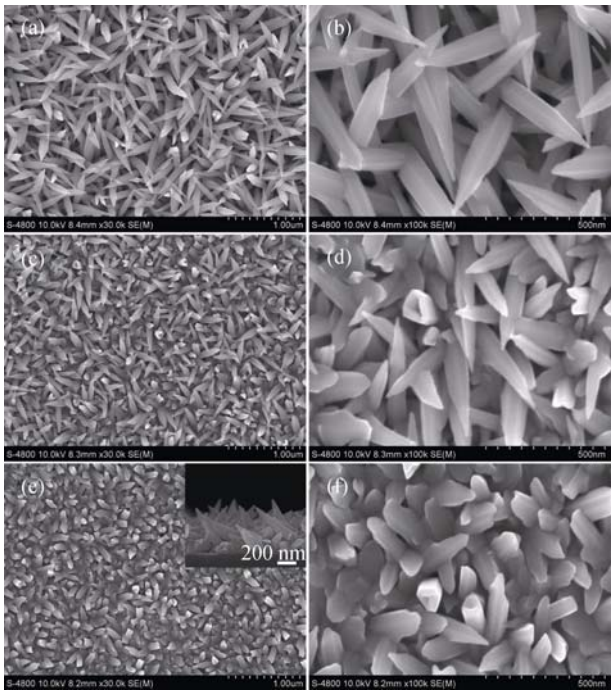

Fig. 3　FESEM images of the tellurium nanowire arrays deposited under different Ar pressures

(a, b) 0.5 Pa; (c, d) 1.5 Pa; (e, f) 2.0 Pa. Inset in (e) shows the cross-sectional view of the nanowire arrays

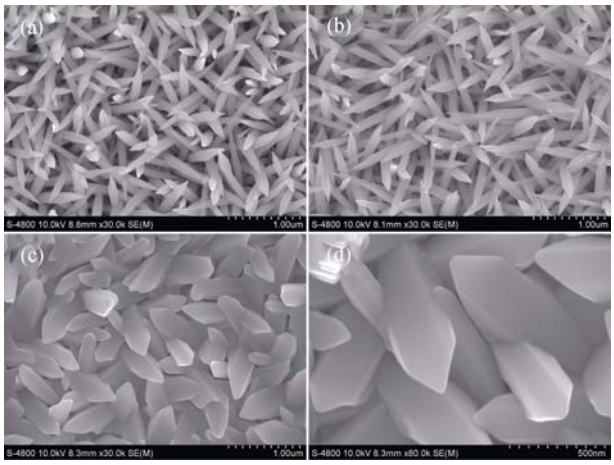

Fig. 4 FESEM images of the tellurium nanowire arrays deposited at (a) 200℃, (b) 250℃ and (c, d) 300℃

seems much denser. From the magnified image, as shown in Fig. 4(d), it can be seen that the nanorods are regular hexagonal prisms. The increased intense diffusion and growth of Te atoms along (101) plane at higher temperature may be the driving force for the formation of coarsened nanorods from nanowires. As shown in Fig. 2, the XRD pattern of the film deposited at 300℃ reveals that the (201) peak becomes as high as the (101) peak, which may be from the transitional Te film between single crystalline Te nanorods and substrate. Therefore, the competition of the diffusion and growth of Te along [101] direction and (101) plane is the key for the formation of Te nanowire arrays. Relatively lower substrate temperature is beneficial for the formation of Te nanowire arrays.

The tellurium nanowire arrays were also successfully prepared on Si(100) substrate and ITO-coated glass with the same sputtering parameters (substrate temperature 200℃ and working pressure 1.0 Pa), as shown in Fig. 5. The nanowire arrays are both composed of well aligned Te nanowires. Because there is a thin layer of dense and continuous Te film acting as a transition layer, as discussed above, the formation of Te nanowire arrays on different substrates is well-reasoned.

On the basis of the above analysis and previously reported deposition of thin films[33-34], a growth process of the nanowire arrays is illustrated in Fig. 6. Firstly, Te atoms are sputtered and absorbed on the surface of substrate to form small islands. Then, as Te atoms are deposited on-going, these small islands begin to combine and continuous film begins to form gradually to decrease the stress between film and substrate. Finally, on the surface of the continuous Te film, nucleations of

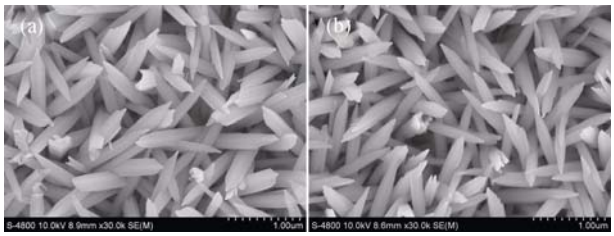

Fig. 5 FESEM images of the tellurium nanowire arrays deposited on (a) Si(100) and (b) ITO glass

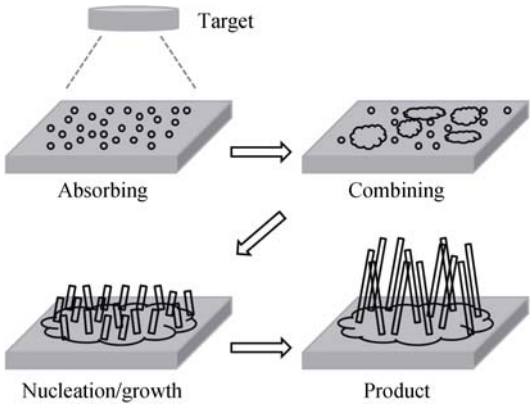

Fig. 6 Growth mechanism of tellurium nanowire arrays

Te form and gradually grow to single crystalline Te nanowires without the aid of any template under suitable temperature and working pressure because of the inherent anisotropic crystal structure.

3 Conclusions

In summary, we have successfully fabricated highly ordered arrays of single-crystalline tellurium nanowires with an average diameter of 100 nm and length up to about 1 μm by one-step RF magnetron sputtering method at relatively low substrate temperature (200℃). The nanowires have a uniform hexagonal tellurium single-crystalline structure and grow along the [101] direction with a needle like morphology. Besides the intrinsic crystal structure of Te, the exterior conditions, such as substrate temperature and working pressure are both essential for the formation of Te nanowire arrays, and they balance the diffusion and growth of Te along [101] direction and along (101) plane. An absorbing-combining-nucleation-growth mechanism was proposed for the formation of such nanostructure.

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磁控溅射法可控制备有序碲纳米线阵列

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摘 要: 采用磁控溅射法在较低基底温度下(200 ℃)制备了有序碲纳米线阵列, 并利用 X 射线衍射、扫描电镜和透射电镜对所制备薄膜进行了相、形貌和微观结构分析。结果表明, 所制备的纳米线阵列由单晶碲纳米线组成, 单根碲纳米线具有针状形貌, 并沿[101]晶向生长, 平均直径和长度分别为 100 nm 和 1 μm。氩气压力和基底温度均对碲纳米线阵列的形成具有重要影响, 以平衡碲原子沿[101]晶向和(101)晶面方向的扩散和生长。提出了碲纳米线阵列的生长机制, 包括吸附、结合、成核和生长等过程。

关 键 词: 碲; 纳米线阵列; 射频磁控溅射

中图分类号: TB34 **文献标识码:** A