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Journal of Solid State Chemistry 177 (2004) 4386–4393
JOURNAL OF SOLID STATE CHEMISTRY
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Large-scale CdX (X = S, Se) microtube arrays on glass substrate: transformation of CdOHCl microrod arrays by a simple template-sacrificing solution method

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Received 14 July 2004; received in revised form 25 August 2004; accepted 30 August 2004
Available online 11 November 2004

Abstract

Large-scale arrayed CdX (X = S, Se) microtubes have been successfully prepared on glass substrate by a simple solution route. In this process, cadmium hydroxyl chloride (CdOHCl) microrod arrays, which could be directly grown on glass surface in solution of $CdCl_2$ and methenamine, were used not only as a source of cadmium but also as a new reactive template to fabricate these highly ordered cadmium chalcogenide tube arrays, and the orientation of CdOHCl microrods on glass substrate could be easily achieved by pretreating the glass surface with appropriate concentration of NaOH aqueous solution. The transformation from arrayed CdOHCl rods to CdS and CdSe microtube arrays were conducted in thioacetamide and Na_2SeSO_3 solution, respectively. The conversion was convenient, and no CdOHCl crystallites were detected in the final products measured by X-ray powder diffraction. The hexagonal prismatic morphology and orientation of CdOHCl rods were perfectly maintained in the as-prepared cadmium chalcogenide films according to scanning electron microscopy. Transmission electron microscopy was used to further characterize these microtube structures. The effect of NaOH pretreatment on CdOHCl orientation and the formation of tubular structures were also discussed.

Keywords: Cadmium sulfides; Cadmium selenides; Arrays; Rods; Tubes

1. Introduction

One-dimension (1D) systems are the smallest dimensional structures that can be used for efficient transport of electrons and optical excitations, and are thus expected to be critical to the function and integration of nano-/microscale devices [1–4]. Recently, the aligning of 1D structures into two- or three-dimensional (2D or 3D) arrays has aroused great interest, and many metallic [5–7], oxide [8–10], chalcogenide [11–12], and groups III–V compound [13] arrays have been successfully prepared. Assembling 1D structure into large-scale arrays, especially keeping them in good orientation and arrangement as well as building them onto various substrates will probably lead a practical uses in many fields. For example, Yang et al. [14] demonstrated room temperature lasers from ZnO nanowire arrays, which could have applications in optical computing, information storage, and microanalysis. Health et al. [15] produced ultrahigh-density arrays of aligned metal and semiconductor nanowires and circuits, and a high-frequency nanomechanical resonator was also demonstrated. Besides these promising applications, fabricating 2D or 3D arrays may also give an opportunity to discovery a series of new properties that arose from those superstructures [16,17].

As one of the most important II–VI semiconductors, cadmium chalcogenides have great applications in

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doi:10.1016/j.jssc.2004.08.038

light-emitting diodes [18], solar cells [19] and as fluorescent probes in biological imaging [20]. The ability to order them into arrays may enhance the optical and photoelectric properties of these materials [17], and lead further researches to improve the efficiency of these devices [21]. Although 1D structures of cadmium chalcogenides have been successfully prepared by many methods [22–26], how to fabricate cadmium chalcogenide in 3D arrays on substrate with good orientation is still a challenge. Recently, Li et al. [27] have synthesized CdS nanowire arrays on Si substrate via a chemical vapor deposition route. Comparing with high temperature, relatively complex experimental conditions, and difficult to prepare in a large scale with uniform morphology due to the position effect of vapor process, solution chemical route has become a promising option for fabricating the large-scale film of 1D nano-/micro-scale materials due to its simple, fast, and less expensive virtues. Up to now, two major solution routes have been developed to prepare cadmium chalcogenide arrays. One method is using ordered structure as templates, such as porous anodic aluminum (AAO) [28–30], mesoporous silica [31,32], and hexagonal liquid crystals [33]. The other method is the self-assembly of nanocrystal by choosing appropriate solvents and linking molecules [34]. However, the morphologies of cadmium chalcogenides in the obtained arrays are usually limited to rod-like or wire-like in the above methods, and it is also not easy to let chalcogenide 1D entities “stand” on substrate in large scale as well as in good orientation.

In this paper, we develop a new template-sacrificing method to build highly oriented CdS and CdSe microtube arrays on glass substrate. This simple solution method involved converting CdOHCl microrod arrays into CdS or CdSe microtube arrays in sulfur or selenium resources, respectively. Although the transformation of 1D structures into different materials with similar or complementary morphologies is not a new concept [35,38,39], here we demonstrate the first fabrication of cadmium chalcogenide microtube arrays on glass substrate through a template-sacrificing reaction.

The crystal structure of CdOHCl, the template materials we used, is already known since the single crystal and powder diffraction investigated by Hoard and Grenko. The structure crystallizes in the space group $P6_3mc$ with lattice parameters $a = 366.5(1)$ pm and $c = 1025.2(2)$ pm. It is built up from neutral layer of $[\mathrm{Cd(OH)}_{3/3}\mathrm{Cl}_{3/3}]$-octahedra and apt to growth along c-axis [36,37]. Based on our experiments, the key to achieve highly ordered 1D structures pattern is the pretreatment of glass surface with appropriate concentration of NaOH aqueous solution. Furthermore, the solubility of CdOHCl is larger than those of cadmium sulfide and cadmium selenide, so it can be easily transformed to corresponding cadmium chalcogenides with the presence of sulfur or selenium resources in solution.

2. Experimental

2.1. Materials

All chemical reagents were of analytical grade, and purchased from Shanghai Chemical Reagent Corporation without further purification. Na_2SeSO_3 solution used as selenium resource was synthesized by refluxing selenium powders in sodium sulfite solution. The final concentration of Na_2SeSO_3 was 0.5 M. Amorphous glass wafers were used as substrates which were boiled by sulfuric acid (98%) for several minutes, then followed by ultrasonically cleaned in acetone and deionized water, and dried in vacuum oven.

2.2. Synthesis of arrayed CdOHCl microrods

The pretreatment of glass wafers was performed by immersing the glass substrates in a 0.1 M NaOH aqueous solution (80 °C) for 1 h, and then followed by rinsing with deionized water 3 times. The typical reaction for the synthesis of CdOHCl microrod arrays on glass substrates was carried out in a regular screw-capped bottle containing 0.1 M aqueous solution of $CdCl_2 \cdot 2.5H_2O$ and methenamine. The molar ratio of these two reagents was 1:1. A pretreated glass wafer was immersed vertically in the solution, and maintained at the desired temperature (95 °C) in oil bath. After 2 h, a white, smooth and dense film was obtained. The as-prepared film was thoroughly washed with deionized water and ethanol, and then dried in vacuum oven.

2.3. The formation of CdX (X=S, Se) microtube arrays

Well-oriented CdOHCl arrays were used to fabricate CdS and CdSe microtube arrays. In a typical preparation of CdS microtube arrays, 0.1 M aqueous solution of TAA was firstly heated to 90 °C, and then a piece of CdOHCl film was immersed in the solution. The film turned to yellow at the first seconds, and then a yellow–red, smooth and uniform film was obtained after a few minutes. After 10 min, the film was taken out and rinsed with deionized water and ethanol several times, and then dried in vacuum oven.

As for the synthesis of CdSe arrays, the reaction was carried out between CdOHCl template and Na_2SeSO_3 solution at room temperature (25 °C). The film color turned to dark red after 2.5 h, then took the film out and treated similar to that of CdS film.

2.4. Characterization

The crystal structure of the as-prepared films was analyzed by powder X-ray diffraction diffractometer (XRD, SHIMADZU XRD-6000) with a 1.54060 Å Cu Kα rotating anode point source which operated at 40 kV and 30 mA, and the scanning speed was set at 4°/min. Scanning electron microscopy (SEM, HITACHI S-2150) and transmission electron microscope (TEM, JEM-100 CX) with accelerating voltage at 100 kV were used to observe the size, orientation and morphologies of the products.

3. Results and discussion

3.1. The orientation of CdOHCl rods

When a glass wafer without pretreated with NaOH aqueous solution was used to grow CdOHCl rods, only a translucent, white and un-compact film was obtained. The XRD pattern of this film (Fig. 1a) matches the powder diffraction pattern of hexagonal CdOHCl (JCPDS card 74-1047) very well, and no impurities can be detected. However, when the glass substrate pretreated with NaOH, a white, smooth, compact, and more scratch-resistance film was achieved. The corresponding XRD pattern is shown in Fig. 1b. Comparing Fig. 1b with Fig. 1a, one can see that only (002), (004), and (006) diffraction peaks of CdOHCl crystal are presented in Fig. 1b. The dramatically enhanced (000l) peaks in Fig. 1b indicate well-oriented *c*-axis alignment of CdOHCl rods over a large substrate area.

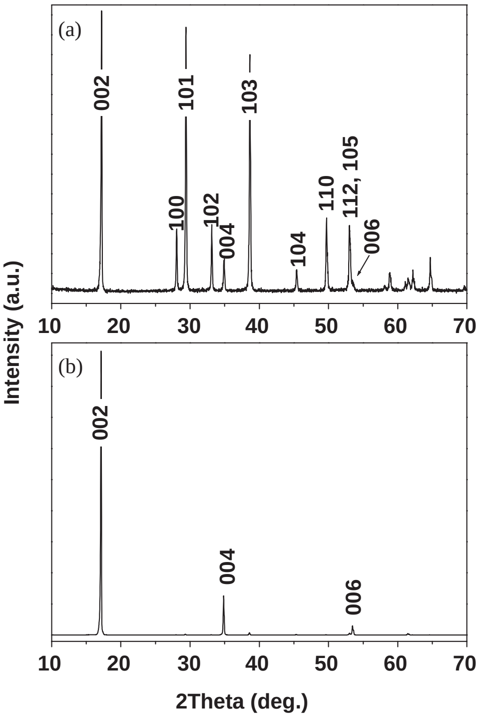

Fig. 1. XRD pattern of CdOHCl arrays: (a) grown on un-pretreated glass surface; (b) grown on glass surface pretreated with NaOH aqueous solution.

The differences in growth orientation of these two samples can be obviously observed from SEM images. Fig. 2a is the SEM image of CdOHCl grown on an un-pretreated glass surface. The CdOHCl rods are randomly aligned just like flowers. SEM image at high magnification (Fig. 2b) shows that these rods are hexagonal prism in shape and about 10 μm in length. From this figure, we can also find that the diameters of these rods are not uniform, ranging from sub-micrometers to several micrometers, and the average size is about 3 μm. However, when the substrate is pretreated with NaOH, highly ordered CdOHCl rods can be easily obtained. A low magnified SEM image (Fig. 2c) shows that the CdOHCl rods grown on a pretreated glass surface align into large-scale arrays. The hexagon end planes of the rods can be identified at high magnification (Fig. 2d), and the cross-section of this film is also shown in Fig. 2e. From these SEM images, it can be found that the CdOHCl rods are perpendicularly grown onto the substrate and arranged to very large uniform arrays. These results further indicate the good orientation of CdOHCl rods on pretreated glass substrates. The effect of NaOH pretreatment on the orientation of CdOHCl rods maybe results from the active sites that generated in the pretreatment process. First, silica is hydrolyzed with the existence of NaOH, and many silicates on the surface are formed. Then, those negatively charged silicates absorb the positively charged cadmium ions, which later become the active cites for crystal growth. We believe it is the numerous active cites that bring a space hinder effect on the CdOHCl crystal growth. That is, the growth of lateral is restricted and only the direction perpendicular to the substrate is approved. As a result, a good arrangement of CdOHCl rods is formed on the substrates. In the experiment, we further find that the pretreatment of the glass surface with NaOH solution not only improve the orientation of CdOHCl arrays, but also increase the aspect ratio of CdOHCl rods. The average diameter of the rods is reduced to 1μm according to Fig. 2d and Fig. 2e. The SAED pattern (Fig. 2f) of single CdOHCl rod (inset) reveals that the obtained CdOHCl microrods are single-crystalline.

3.2. The formation of CdS microtube arrays

In the case of fabricating CdS arrays, we performed the sulfurization process in TAA solution at 90 °C. The reaction is very fast, and only a few minutes are needed. Fig. 3 is the XRD pattern of the as-prepared film after

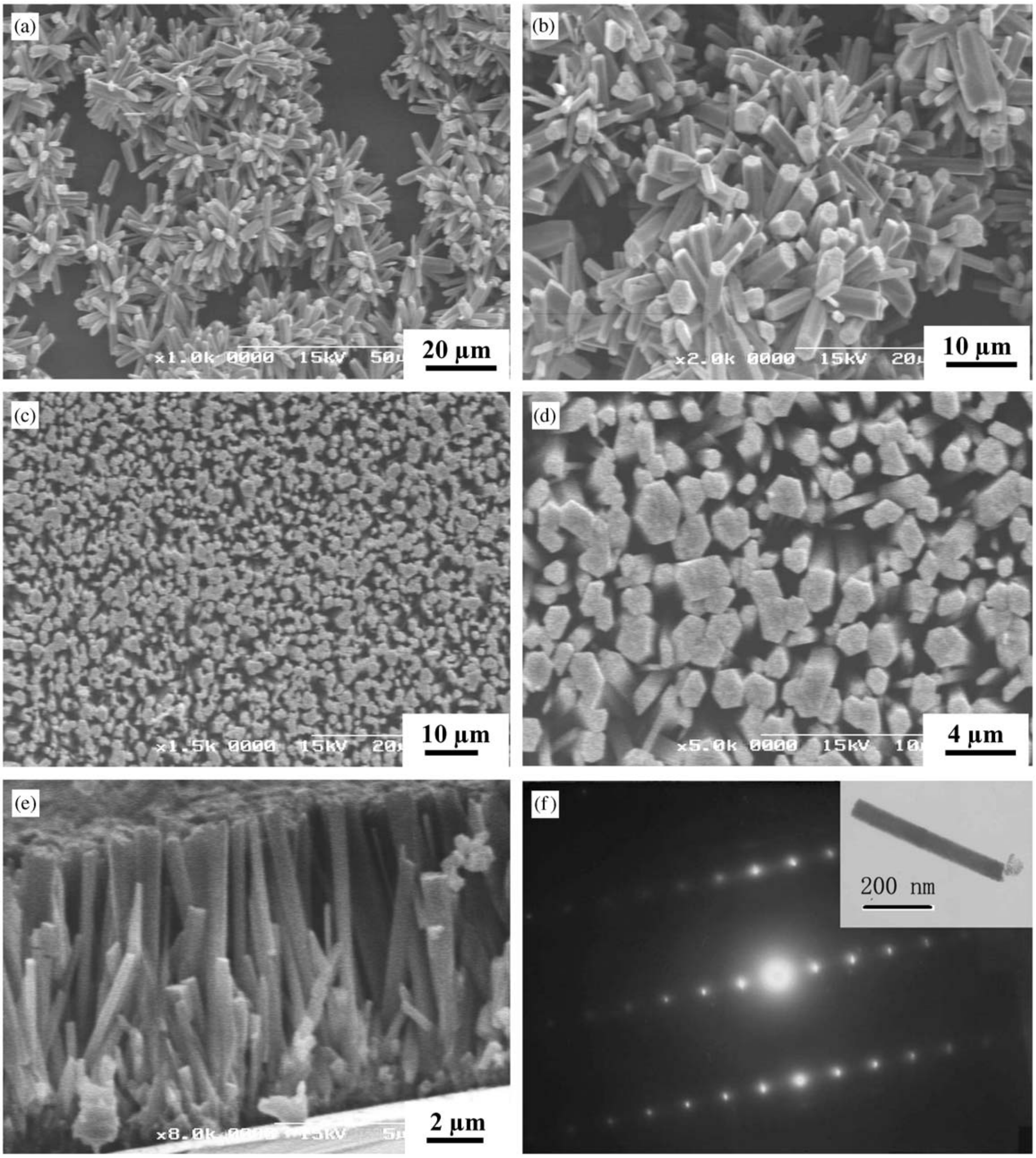

Fig. 2. SEM images of CdOHCl arrays: (a–b) grown on un-pretreated glass surface at different magnifications; (c–e) grown on glass surface pretreated with NaOH aqueous solution from top view and side view; (f) SAED pattern of single rod shown in inset (rod with small diameter was chose to permit electronic beams to permeate).

being reacted for 10 min. All the peaks can be indexed to hexagonal CdS with lattice constants comparable to the values of JCPDS card 77-2306, and no CdOHCl diffraction peaks are detected in this pattern, which indicates the full conversion of CdOHCl to CdS. Some broadening of the diffraction peaks suggests that there are some small sizes of CdS crystals in the obtained film, and the average particle size is 12 nm estimated from the Scherrer formula.

SEM images of the film from top view and side view are shown in Fig. 4a and b, respectively. As can be seen, the morphologies of original CdOHCl rods are successfully preserved, and the obtained 1D CdS rods have a prismatic morphology and align in a large scale. Further investigates show that these rod-like CdS are actually tubular structures with closed tops. Fig. 4c shows the cross-section of a damaged film, and tubular structures can be clearly observed. An SEM image at high

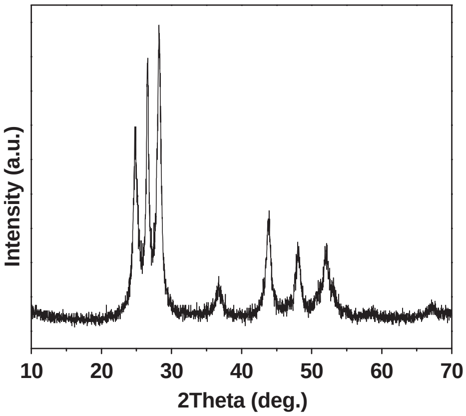

Fig. 3. XRD pattern of arrayed CdS film obtained after CdOHCl arrays being reacted with TAA solution at 90 °C for 10 min.

magnification (Fig. 4d) shows the obtained CdS tubes with smooth outer surface but with some particles adhere to their inner surfaces, which imply the growth procedure of CdS maybe via ion exchange and in-diffusion of sulfur resource into the CdOHCl crystal. According to Fig. 4d, the thickness of these tubes is estimated to be 50–100 nm, nearly a 20–10th of rod diameter. From the TEM image of CdS tubes (Fig. 4e), we can also find some particles inside the tubular structures, and the particle size estimated from Fig. 4d and Fig. 4e ranges from 50 to 200 nm, which heavily deviates from the result calculated form the XRD. A careful analysis from Fig. 4e inset reveals that particles shown in SEM or TEM are secondary particles aggregated by small CdS nanocrystals. The size of these small CdS nanocrystals is in the range of 10–15 nm, which is in agreement with the XRD result. The SAED pattern (Fig. 4F) also indicates that the tubular structures are in hexagonal phase and composed of large numbers of small single crystalline of CdS, which is compatible with the observation in TEM and the result in XRD.

The conversion of arrayed CdOHCl microrods to arrayed CdS microtubes in TAA solution may be as followed:

$$CH_3CSNH_2 \rightarrow CH_3CN + H_2S \\ (\leftrightarrow CH_3CN + 2H^+ + S^{2-}), \quad (1)$$

$$CdOHCl + S^{2-} \rightarrow CdS + Cl^- + OH^-. \quad (2)$$

Just as we mentioned above that the formation of CdS may via ion diffusion and exchange process. In this process, S^{2-} first reacted with CdOHCl through Eq. (2), and a layer of CdS is formed on the outer surface of CdOHCl rods, therefore, the morphology of CdOHCl can be maintained. As to the particles aggregating inside the tubes, we attribute them to the different diffusion speed of cadmium ion and sulfur ion as well as the different cell constants of CdS and CdOHCl. It is supposed that the in-diffusion of sulfur ion is likely to be faster than the out-diffusion of cadmium ion in our situation, which is different from the sulfurization of ZnO [38]. Owing to the larger crystal cell of CdOHCl, some irregular interstices and voids are generated in the inner part of the rods in the diffusion process. Then, the fast in-diffused sulfur ion react with the cadmium ion in these irregular cites, and CdS particles are formed inside.

3.3. *The formation of CdSe microtube arrays*

The formation of CdSe microtube arrays was performed at 25 °C with Na_2SeSO_3 as precursor, and a dark red film was obtained after 2.5 h. The diffraction peaks in the XRD pattern (Fig. 5) shows that cubic phase CdSe is obtained, which is consonant with JCPDS card 19-191, and no CdOHCl diffraction peaks are detected in this pattern, indicating CdOHCl are completely transformed into CdSe. Estimated from the Scherrer formula, the crystal size of CdSe is about 4 nm. The conversion of hexagonal phase of template to the cubic phase of CdSe indicates the growth is nonepitaxial [39], and the process is suggested to be similar to the conversion of CdS.

The SEM images of CdSe film are shown in Fig. 6a and b at different magnification. Tubular structure of CdSe can be clearly identified in these figures, and the thickness of these tubes is estimated about 100 nm. It is noted that these tubes are uncapped which is different from that of CdS. SEM image taken at the middle step of the conversion process (Fig. 6c) shows some cavities on the top of rods. At the present time, no clear answer to the formation of these cavities can be given, and the mechanism is still under researching by our group. However, we believe it is these cavities, which become larger or fuse together with reaction time that finally result the tubular structure of CdSe. The irregular outline of the inner surface (pointed by arrow) shown in Fig. 6b further supports our hypothesis. Fig. 6d shows the SAED pattern of a single CdSe microtube (inset). The CdSe tubes are polycrystalline according to this pattern which implying that the tubes consist of many tiny CdSe crystallinities.

In a control experiment, we find that the conversion from CdOHCl to CdSe is difficult to complete at approximate 100 °C. The XRD pattern of the film obtained after being reacted for 2.5 h at 100 °C still shows the strong diffraction peaks of CdOHCl, which suggests that the conversion is uncompleted at this condition. Further studies find that extending the reaction time has no help to complete this conversion process. The difficulty of conversion at high temperature

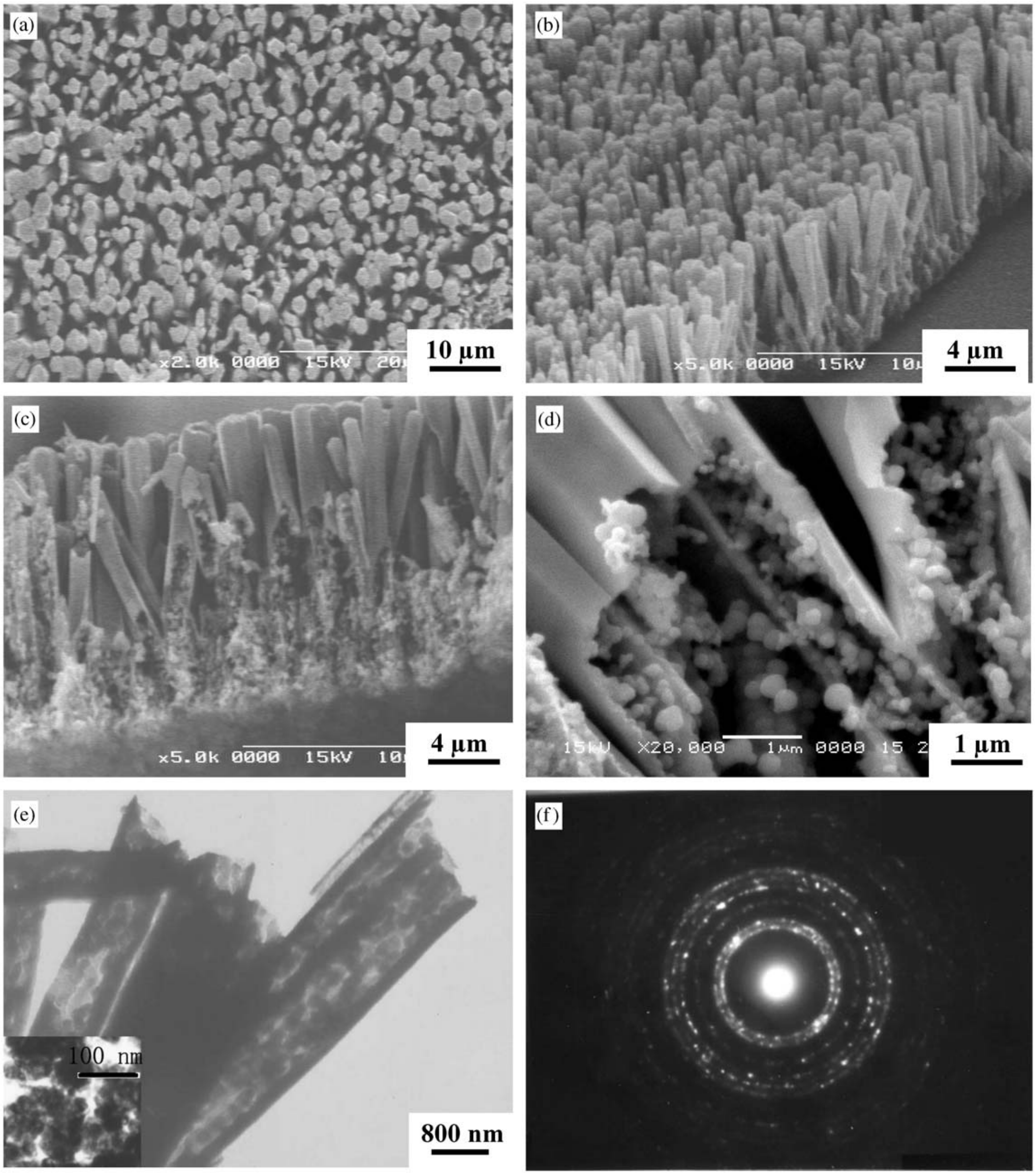

Fig. 4. SEM images of arrayed CdS film: (a) top view; (b) side view; (c) cross-section of a damaged film; (d) ruptured CdS tubes shown in C at high magnification; (e) TEM image of CdS tubes scratched from glass surface and the particles adhere to their inner surface (inset); (f) SAED pattern obtained from a CdS tube.

may be due to the dense CdSe sheath formed around CdOHCl template [35], and this sheath further inhibits the in-diffusion of selenium resource.

4. Conclusions

In summary, large-scale arrayed Cd*X* (*X* = S, Se) microtubes have been successfully prepared on glass surface with CdOHCl arrays as templates in aqueous solution. The orientation of CdOHCl microrods on glass substrates could be easily achieved by pretreating the glass surface with appropriate concentration of NaOH solution. Through the ion exchange and diffusion process, large-scale arrays of CdS microtubes with top closed, while CdSe microtubs with tops uncapped are obtained, and the morphologies of original CdOHCl template are perfectly coppied. To build such 3D arrays of cadmium chalcogenide may have promising applications in nano-/microdevices, particularly in solar cells and LEDs. The method we presented here is simple and suitable to a large-scale synthesis, and maybe useful to fabricate other cadmium salt arrays.

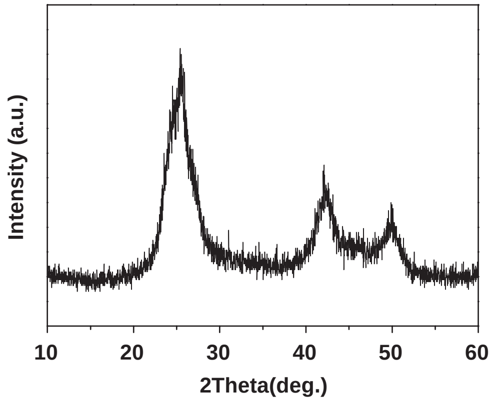

Fig. 5. XRD pattern of arrayed CdSe film obtained after CdOHCl arrays being reacted with Na_2SeSO_3 at room temperature for 2.5 h.

Acknowledgments

This work was financially supported by the National Natural Foundation of China (50103006), the Shanghai ShuGuang Project (01-SG-15) and the Shanghai Nanomaterials Project (0241nm106).

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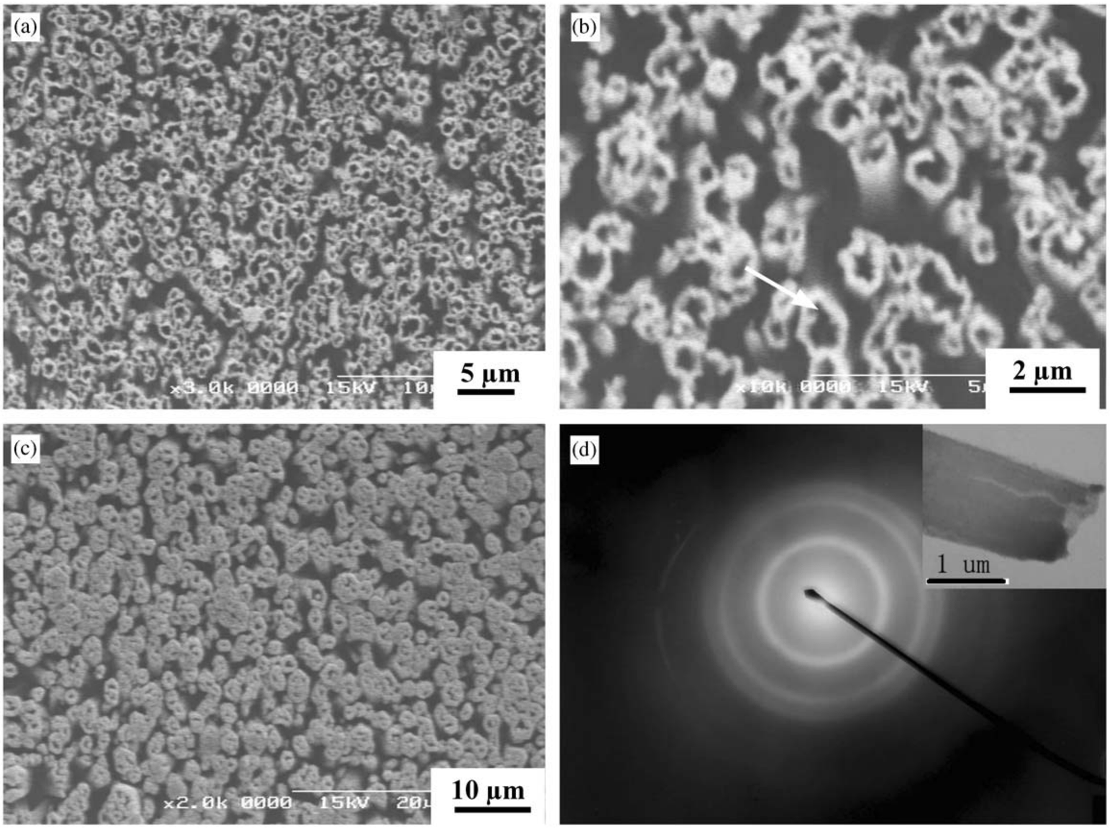

Fig. 6. (a–b) SEM images of CdSe film at different magnifications after being reacted for 2.5 h. (c) SEM image taken at the middle step of conversion process with reaction time at 1 h. (d) SAED pattern of CdSe tube shown in inset.

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