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Controllable Catalytic Growth of CdTe Nanostructures and Optical Property Studies

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Abstract

Several high crystalline CdTe nanostructures were synthesized through a simple chemical vapor deposition using silicon substrate. The morphologies of CdTe nanostructures were controlled by adjusting the flow rate of the carrier gas. A canthosphereshaped CdTe nanostructures were fabricated at the low flow rate, while branch-shaped and long CdTe nanostructures were obtained with higher flow rate. The feasible growth mechanism for these CdTe nanostructures has been proposed. Further photoluminescence measurements show the near infrared emission of the synthesized CdTe nanorods is significantly dependent on their size and shape. Our work provides a new synthetic method for growing CdTe nanomateirals through a controllable manner.

Keywords: CdTe, Nanostructure, Controllable growth, Near infraredemission.

Introduction

One-dimensional (1D) semiconductor nanostructures like nanotubes and nanowires (nanorods) have attracted much attention due to their specific geometries and distinct properties in nanoscale electronic and optoelectronic device applications [1-3]. Among these nanostructures, 1D II-VI group nanostructured materials have shown their unique properties and wide range of applications in the fields of electronic devices, photonic crystals, and biological sensors, etc [4-7]. Being a group II-VI semiconductor material, CdTe has a direct band gap of 1.5eV (300K) and a high optical absorption coefficient in the whole solar energy spectrum, which is suggested to be an ideal material for the fabrication of photovoltaic devices and solar cells[8]. Generally, CdTe nanowires are synthesized by the solution-based techniques, such as the hydrothermal method [9-10] and the aqueous synthetic approach [11-12]. However, most of these nanowires by solution-based techniques are typically polycrystalline. Additionally, Neretina et al. synthesized the vertically aligned CdTe nanowire arrays by pulsed laser deposition (PLD) using Bi or Bi, Te, as a catalyst [1314]. Importantly, based techniques such as thermalevaporation and chemical vapor deposition(CVD) are well established to synthesize the single-crystalline 1-D nanostructures with largedensity and highquality [15-16]. As previously reported, Ruiz synthesized CdTe nanorods prompted by Bi_2Te_3 droplets viathe close spaced sublimation (CSS) method [17]. Lee et al. synthesized long CdTe nanowires using a Bi catalyst on plastic by a modified CVD process [18]. However, the most of previous studies focused on the synthesis of CdTe nanowires and nanorods [19-20]. A systematic study on the controllable catalytic growth of the different CdTe nanostructures by adjusting the flow rate of the carrier gas, and the related formation mechanisms have not been addressed yet.

Experimental Details

Preparation of CdTe nanostructures

The CdTe nanostructures with the different morphologies were synthesized by a thermal evaporation method in a horizontal tube furnace. The mixed powder of CdTe (99.99%) and Bi (99.9%) (CdTe: Bi=10: 0.5 in molar ratio) was placed in a quartz boat located at the center of a quartz tube, which was then inserted into a horizontal tube furnace. Several pieces of pre-cleaned silicon wafers used as the substrates were placed on the other quartz boat which was located downstream from the furnace center about 22-26 cm. Before heating, the furnace chamber was first evacuated to a base pressure of 0.015 mTorr and then the high-purity $H_2(5\%)/Ar$ forming gas was introduced into the quartz tube with a constant flowing rate of 50 sccm (standard cubic centimeter per minute) for 60 min to purge away oxygen. The furnace was subsequently heated to 950 °C with a heating rate of 40 °C per minuteand then maintained at this temperature for 60 min. To investigate the influence of the flow rate of carrier gas on the material morphology, the four different flow rates of 50 sccm, 100 sccm, 150 sccm and 200 sccm were used in experiment. During the growth process, the pressure in the quartz tube was maintained at300 Torr by regulating the outlet

needle valve. After reaction, the system was naturally cooled to the room temperature.

Characterization

Samples collected from the silicon substrates were characterized using an X-ray diffractmeter (XRD, Philips X'pert PRO), a fieldemission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) and a transmission electron microscope (TEM, FEI Tecnai G20) equipped with an energy-dispersive X-ray spectrometer (EDS). Photoluminescence (PL) measurements were conducted at room temperature using a confocal laser Micro-Raman spectrometer (LabRAM HR800).

Results and discussion

Figure 1 shows the SEM images of four CdTe nanostructures morphology at the different flow rates of 50sccm (a)(b), 100sccm (c)(d), 150 sccm (e)(f)and 200 sccm (g)(h), respectively. The morphology of the CdTe nanostructures changed distinctly as the flow rate increases. Specifically, it shows clearly that a large amount of acanthosphere-shaped CdTe nanorods with the lengths of 1-20µm and diameters of 500-1000 nm shown in Figure 1(a)(b). The inset indicates the smooth surface of a single nanorod. At the flow rate of 100 sccm, the similar a canthosphere-shaped CdTe nanorods were obtained shown in Figure 1(c)(d), however numerous burrs are observed. Branchshaped CdTe nanorods were obtained at the flow rate of 150 sccm as seen in Figure 1(e)(f), which show obviously different morphology from the previous ones'. Additionally, those aligned branch-shaped nanorods have the diameters of 100-800nm with the catalyst droplets at the top of the nanorods. As the flow rate increases to 200sccm, the relatively long nanorods (up to 80µm) are observed with diameters of 500-2000 nm shown in Figure 1(g)(h). Note that catalyst droplets are visible at the end of the nanorods, indicating a catalyst assisted vapor-liquid-solid (VLS) mechanism of the CdTe nanorods formation. The sizes and morphologies of the CdTe nanostructures at the fourflow rates are summarized in Table 1.

And Figure 2 shows the X-ray diffraction (XRD) patterns of CdTe

nanostructures at the different flow rates of 50sccm (a), 100 sccm (b), 150 sccm (c) and 200 sccm (d), respectively. In the curve (a) and (b), it indicates that (111), (220), (311), (400) and (331) peaks can be indexed to the cubic zinc blend structure. All the patterns confirm that the acanthosphere-shaped CdTe nanostructures are mainly composed of cubic zinc blend structured CdTe (JCPDS, No. 65-8395) and small amount of Bi₂Te₃ and Bi. In curves (c) and (d), all diffraction peaks correspond to the bulk cubic zinc blend phase CdTe (JCPDS 65-1085) except for the weak peaks of Bi. No diffraction peaks from CdO, Cd, Te or other impurities are observed in the synthesized materials. It is noting that the diffraction patterns of Bi, Te, in the curves (a) and (b) are not observed any longer in the curves (c) and (d). It indicates that Bi₂Te₂ does not participate in the catalytic growth processes of the branch-shaped and long CdTe nanostructures at the relatively high flow rates of 150 and 200 sccm.

As previously reported, the possible factors that can influence the nanostructure morphology are the flow rate of carrier gas, concentrations, temperature, and intrinsic crystal structures [21-24]. It is shown that the morphologies of the CdTe nanostructures can be significantly modified by the factor of the flow rates, implying the possible reaction process shown in Figure 3. Because the pressure in the quartz tube are keptas a constant of 300 Torr in the experiment, the concentrations of Cd, Te and Bi atoms around the Si substrates are relatively high at the low flow rate of 50 sccm. Therefore, an amount of Bi atoms seeds are exposed to a flux of Cd and Te atoms atthe high temperature. It leads to the formation of the Bi, Te, droplets, which is in accordance with the measured results of Figure 2(a). According to the previous reports, the Bi₂Te₂ droplets can be used as the catalyst in the VLS process [13,14,17]. Thus, it is reasonable to speculate that the Bi₂Te₂ droplets guide the subsequent oriented VLS growth of the acanthosphere-shaped CdTe nanorods. At the flow rate of 100 sccm, many Cd, Te and Bi atoms may adhere to the surface of the formed acanthosphere-shaped nanorods. And the nanorod surface turns to be rough gradually, which agrees with the observed results from Figure 1(c)(d). At the high flow rate of 150 sccm, the Bi nanoparticles can be adhered to the trunk nanorods



Figure 1: SEM images of fourCdTenanostructuresmorphologyunderthe different flow rates of 50sccm (a, b); 100sccm (c, d); 150 sccm (e, f) and 200 sccm (g, h) respectively

The flow rate of carrier gas (sccm)	Shape	Diameter (nm)	Length (µm)
50	Acanthosphere-shaped nanorods	500-1000	1-20
100	Acanthosphere-shaped nanorods	500-1000	1-20
150	Branch-shaped nanorods	100-800	1-10
200	Long nanorods	500-2000	30-80





Figure 2: Typical XRD patterns of as-preparedCdTe nanostructures atthe flow rates of 50sccm (a); 100sccm (b); 150 sccm (c) and 200 sccm (d) respectively

as the main nanorods growth. It may guide the branch-shaped nanowires further growing on the surface of the truck nanorods shown in Figure 3(c). At the flow rate of 200 sccm, the most Bi seeds are dispersed and it leads to alow concentration of Bi seeds nearby the Si substrate. Subsequently, the further growth processes of the acanthosphere-shaped or the branch-shaped nanostructures are limited, and traditional VLS growth of long



Figure 3: Schematic illustrations for the possible reaction processes under the four flow rates of 50sccm (a); 100sccm (b); 150 sccm (c) and 200 sccm (d)

CdTenanorods becomes important. And the formation of the long nanorod is related to a Bi catalyst assisted VLS mechanism in accordance with the XRD curves (d) in Figure 2[19].

The left inset of Figure 4(a) shows a typical low magnification TEM image of the obtained CdTe nanorods at the flow rate of 50 sccm with a smooth surface. Figure 4(a) is an HRTEM image of the single CdTe nanorod. It can be observed the lattice planes along the growth direction with the spacing distances of 0.37 nm, which corresponds to the {111} lattice plane spacing of the



at the flow rate of 150 sccm

zinc blend CdTe. The corresponding selected-area electrondiffraction (SAED) pattern is shown in the right inset of Figure 4(a), indicating a single-crystal structure with a growth direction along [111]. The measured EDX data shown in Figure 4(b) reveals that it consists of Bi, Cd, Te and Cu signals and the molar ratio of Cd and Te is nearly 1:1. And the signal from Cu element is due to the TEM grid. Figure 4(c) and (d) show the typical HRTEM and low magnification TEM images of the obtained branchshaped nanorods at the flow rate of 150 sccm, respectively. It shows that the lattice plane has the spacing of 0.37 nm with the growth direction along [111]. The inset of Figure 4(d) shows the corresponding SAED pattern, indicating the cubic singlecrystalline of the branch CdTe nanorods.

Figure 5 shows the normalized photoluminescence (PL) measurementspectra of the CdTe nanorods with the excitation wavelength of 532 nm at room temperature. There is no detection of any emission commonly connected with structure defects, ionized vacancies or impurities. The PL peaks of single CdTe nanorod at the different flow rates of 50 sccm (a), 100 sccm (b), 150 sccm (c) and 200 sccm (d) are located at 814, 839, 833 and 840 nm, respectively, which corresponds to the near infrared band-edge emission of CdTe (830 nm from bulk). The full width of half-maximum (FWHM) of the PL spectra in Figure 5(a)(c) (d) and 4(b) are about 32~33 and 55 nm, which indicate strong crystallinity dependence on the morphology of CdTe nanorods. Clearly, these CdTe nanostructures fabricated at different flow rates have distinct diameters from 500 to 2000 nm and length ranges from 1 to 80 µm, which significantly modulate the corresponding near infrared emission. Both the variations of peak position and FWHM suggest the presence of quantum size effect, namely shape and size, which most likely originates from quantum-confinement effects [1]. And the relatively wider PL spectrum of CdTe nanorods in Figure 5(b) may be attributed to their inhomogeneous surface morphology which could give rise to a variety of combined emission rather than one [11].

Conclusion

In summary, CdTe nanostructures with different morphologiesare obtained using a simple Bi-assisted CVD process based on VLS mechanism. The flow rate of the carrier gas is the key to control the morphological evolutions of CdTe nanostructures by the analysis of the reaction process and the material characterization. The results indicate Bi_2Te_3 participates in the growth processes of acanthosphere-shaped CdTe nanostructures at the low flow rate of 50 sccm and 100 sccm, and the growth of the branch-shaped and long CdTe nanostructures are related to the Bi nanoparticles at the relatively high flow rates of 150 sccm and 200 sccm. The photoluminescence measurements show the near infrared emission (peak position and FWHM)of the synthesized CdTe nanorods shows strong dependence on their size and shape. This study opens up a new avenue for growing CdTe nanomateirals through a controllable manner.

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