Low-pressure thermal chemical vapour deposition of molybdenum oxide nanorods

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ARTICLE INFO

ABSTRACT

Molybdenum oxide nanorods were synthesized on different substrates in the thermal chemical vapour deposition system at low pressure, where the molybdenum trioxide and selenium powders were used as the source materials. The results of field emission scanning electron microscope, transmission electron microscope, X-ray diffractometer, energy dispersive X-ray spectrometer and micro-Raman spectroscope indicate that the molybdenum oxide nanorods have a single-crystalline structure and are mainly composed of MoO_3 with traces of MoO_2 and Mo_4O_{11}. A vapour-solid growth mechanism based on the condensation of MoO_{3-x} molecules and the diffusion of MoO_3 molecules on the substrate has been proposed to explain the formation of molybdenum oxide nanorods. Furthermore, the photoluminescence (PL) properties of molybdenum oxide nanorods have been studied in Ramalog system using a 325 nm line of He–Cd laser as the excitation source. The PL results show that the molybdenum oxide nanorods generate strong green PL bands located at about 510 and 521 nm and weak PL band located at about 654 nm, which are related to the defects in the molybdenum oxide nanorods. The outcomes can enrich our knowledge on the synthesis and optical properties of molybdenum oxide nanomaterials and contribute to the development of optoelectronic devices related to molybdenum oxide nanomaterials.

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1. Introduction

Molybdenum oxide nanomaterials have attractive catalytic, photochromic and electronic properties, and a lot of potential applications in the areas of electrochemistry and microelectronic devices [1–5]. Depending on the synthesis conditions, the molybdenum oxide nanomaterials exhibit different structures and properties such as α-MoO_3 nanorods, α-MoO_3 nanoflakes and MoO_2 nanorods [3,6,7], which can advance the applications of molybdenum oxide nanomaterials.

To date, molybdenum oxide nanomaterials were mainly synthesized by evaporation and liquid methods [1–3,5–7]. However, in these processes, it took a long time to synthesize molybdenum oxide nanomaterials or the synthesis process required a high temperature. For example, it took 2–24 h to synthesize α-MoO_3 nanorods in the HNO_3 solution by hydrothermal method [3].

Another example is the synthesis of MoO_2 nanorods by evaporation which was carried out at the growth temperature of ~ 1200 °C [7]. These examples imply that much energy is consumed for the synthesis of molybdenum oxide nanomaterials. Moreover, the effluent liquid is harmful to environment. This activates us to develop new synthesis route of molybdenum oxide nanomaterials. Chemical vapour deposition (CVD) system is a simple equipment, which can synthesize some nanomaterials at a low temperature within a short time. Can the molybdenum oxide nanomaterials be synthesized by CVD? If the molybdenum oxide nanomaterials can be synthesized by CVD using nontoxic gas, it is beneficial for saving energy source and friendly to environment. It is known that Ar is a nontoxic gas, and thus we studied the synthesis of molybdenum oxide nanomaterials by CVD using Ar as carrier gas.

In this work, we have successfully synthesized molybdenum oxide nanorods on different substrates in the thermal chemical vapour deposition system at low pressure, where the molybdenum trioxide (MoO_3) and selenium (Se) powders were used as the source materials. It is found that the nanorods are composed of MoO_3, MoO_2 and Mo_4O_{11}, which is different with the previous

works [8–11]. It has been demonstrated in the previous works that, among these molybdenum oxides, the Mo_4O_{11} phase is generally considered to be an intermediate material in the reduction process of MoO_3 [8,9] and that it should be reduced by Se into $MoSe_2$ species due to its instability [10]. We have interpreted this finding based on the low pressure used in our work and proposed a vapour-solid growth mechanism to explain the formation of molybdenum oxide nanorods. Moreover, the photoluminescence properties of molybdenum oxide nanorods were also studied in this work.

2. Experimental details

Before the molybdenum oxide nanorods were synthesized, the silicon substrates were cleaned in the individual ultrasonic solution of methylbenzene, acetone and alcohol for 15 min. Then, they were boiled in a solution composed of ammonia, hydrogen peroxide and deionized water with a volume ratio of 1:2:5 for 15 min (the temperature of mixed solution was set at 75 °C). The zinc oxide (ZnO) buffer layer with a thickness of about 50 nm was deposited on the cleaned substrate by magnetic sputtering.

The molybdenum oxide nanorods were synthesized in a thermal chemical vapour deposition (TCVD) system described in Fig. 1. As shown in Fig. 1, the TCVD tube is made of silica, and its length and interior diameter are about 100 and 5 cm, respectively. After about 0.02 g MoO_3 and 1.5 g Se powders were placed in the TCVD reactor, the TCVD reactor was evacuated to a base pressure of about 20 Pa. Then, Ar gas with a flow rate of 50 sccm was inlet into the TCVD reactor. When the pressure was increased to about 200 Pa, the TCVD reactor was heated to 700 °C in 30 min. Due to heating, the pressure gradually increased. Through adjusting the vacuum valve, the pressure was set at about 300 Pa. Under these conditions, the TCVD reactor was heated for another 15 min, and thereafter it was cooled to room temperature naturally. In this work, two samples were prepared: sample A was deposited on the silicon wafer pre-deposited with a layer of ZnO film and sample B was directly synthesized on the pure silicon wafer.

The morphology and structure of molybdenum oxide nanorods were studied using Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at 15 kV, FEI TECNAI G2 transmission electron microscope (TEM) operated at 200 kV, JEOL 2010F field emission TEM operated at 200 kV, respectively. The composition and crystal phase of molybdenum oxide nanorods were investigated using TTRAX3 X-ray diffractometer (XRD), energy dispersive X-ray (EDX) spectrometer coupled to FEI TECNAI G2 TEM, and HR 800 micro-Raman spectroscope using a 532 nm line of semiconductor laser as the excitation source, respectively. The PL properties of molybdenum oxide nanorods were measured in SPEX 1403 Ramalog system using a 325 nm line of He–Cd laser as the excitation source.

3. Results and discussion

3.1. Structure and composition of molybdenum oxide nanorods

Fig. 2 (a) and (b) shows the FESEM images of samples A and B. As
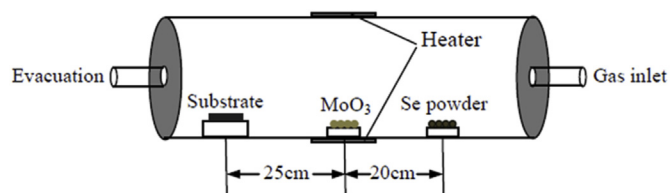

Fig. 1. Schematic of the TCVD system used in our work.

shown in Fig. 2, the nanorods can be formed on the ZnO film and the silicon substrate. According to Fig. 2, the diameters of the synthesized nanorods are in the range of about 10–28 nm for sample A and 10–33 nm for sample B. In addition, Fig. 2 indicates that the nanorods grow along the substrate surface since they are not vertical to the substrate surface. From Fig. 2, one can also see that there appear some MoO_3 nanorods with a large diameter in sample B compared with sample A, which implies that the MoO_3 nanorods grown on the ZnO film and the silicon substrate have a difference in the diameter. This difference possibly originates from the different growth rates of MoO_3 nanorods on different substrates.

Fig. 3 shows the XRD patterns of samples A and B. As shown in Fig. 3, the diffraction peaks located at about $2\theta = 29.59, 33.86, 34.43, 55.45, 56.34°$ can be assigned as the orthorhombic phase of MoO_3 (JCPDS: 35–0609). The other peaks appearing in the spectra are related to the Mo_4O_{11} and Se phases: the peaks located at about 22.17 and 33.08° originate from the diffraction of Mo_4O_{11} (211) and Mo_4O_{11} (311) planes (JCPDS: 65–0397) while the peaks located at about 16.33, 54.56 and 57.27° are attributed to the diffraction of Se particles (JCPDS: 47–1515, 65–1285), respectively.

Fig. 4 records the Raman spectra of samples A and B. For the spectrum (a), the Raman peaks located at about 104 and 438 cm^{-1} are attributed to the E_2 low- and E_2 high-frequency phonon modes of ZnO nanostructures [12,13], which is due to the pre-deposition of a layer of ZnO film on the silicon substrate. The peaks located at about 130, 139 and 149 cm^{-1} are associated with MoO_3 and Se clusters, respectively [14,15]. Because the MoO_3 and Se powders are evaporated in the heating process [10], some MoO_3 and Se molecules can deposit on the substrate so that the Raman spectrum reveals the peaks related to MoO_3 and Se. For the weak peak located at 323 cm^{-1}, the origin of this peak is unclear. It may be related to the hexagonal MoO_3 phase because it is reported that a Raman peak at about 319 cm^{-1} results from the hexagonal MoO_3 phase [16]. The rest of four Raman peaks are related to MoO_2 and Mo_4O_{11}. Among these four Raman peaks, the peaks located at about 233 and 365 cm^{-1} result from the Raman scattering of MoO_2 [7,9] and the peaks located at 306 and 343 cm^{-1} originate from the Raman scattering of Mo_4O_{11} [9,11].

For the spectrum (b), the Raman peaks are related to Se, MoO_3, MoO_2 and Mo_4O_{11}, respectively. Among these Raman peaks, the peaks at about 117 and 129 cm^{-1} are related to the Raman scattering of Se cluster [15]; the peaks at about 159, 246, 283 and 291 cm^{-1} are associated with the Raman scattering of MoO_3 [9,14]; the peaks at about 200, 220 and 365 cm^{-1} can be assigned to the Raman scattering of MoO_2 [7,9]; and the peaks at about 306, 341, 382 and 455 cm^{-1} originate from the Raman scattering of Mo_4O_{11} [9]. In the spectrum (b), the two peaks at about 246 and 283 cm^{-1} are similar to the Raman peaks of $MoSe_2$ at 243.9 and 285.9 cm^{-1} or 242.6 and 285.4 cm^{-1} observed in the previous works [10,17]. However, as shown in the spectrum (b), the peak located at about 246 cm^{-1} is much weaker than the peak located at about 283 cm^{-1}, which is opposite to the Raman results of $MoSe_2$ observed in the previous works (the intensity of the 246 cm^{-1} peak is much stronger than the intensity of 283 cm^{-1} peak) [10,17]. Thus, these two peaks can not be attributed to the Raman scattering of $MoSe_2$. Based on the Raman results, we can conclude that the nanorods are composed of molybdenum oxide consisting of MoO_3, MoO_2 and Mo_4O_{11} phases, which is consistent with the XRD result. However, Fig. 3 does not show the peak related to MoO_2, which may result from the formation of a very small amount of MoO_2.

To further investigate the structure and composition of molybdenum oxide nanorods, these two samples are studied by TEM, EDX and high resolution TEM (HRTEM) and the results are shown in Figs. 5 and 6. As shown in Fig. 5, the samples are composed of