Controlling the electronic structure of SnO_2 nanowires by Mo-doping*

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Mo-doped SnO_2 (MTO) nanowires are synthesized by an in-situ doping chemical vapour deposition method. Raman scattering spectra indicate that the lattice symmetry of MTO nanowires lowers with the increase of Mo doping, which implies that Mo ions do enter into the lattice of SnO_2 nanowire. Ultraviolet-visible diffuse reflectance spectra show that the band gap of MTO nanowires decreases with the increase of Mo concentration. The photoluminescence emission of SnO_2 nanowires around 580 nm at room temperature can also be controlled accurately by Mo-doping, and it is extremely sensitive to Mo ions and will disappear when the atomic ratio reaches 0.46%.

Keywords: doping, nanostructures, chemical vapor deposition processes, semiconducting materials

PACC: 6146, 7155F, 8115H

1. Introduction

Tin dioxide (SnO_2) is a very important n-type semiconductor with a large band gap (3.6 eV at 300 K), and it has been widely used in transparent conducting electrodes,[1] solid-state gas sensors,[2] lithium-ion batteries and solar cells.[3] The metal-doping of SnO_2 can modify its electronic structures and lead to the improvement of its physicochemical, electrical, optical and sensing properties. For example, gas sensors based on SnO_2 film doped by Mo, Ru, Pt, Pd, Al, Cu, etc. present higher selectivity towards a specific gas or can work under a lower operating temperature.[4−7] Recently, many kinds of pure SnO_2 one-dimensional (1D) nanostructures, such as nanobelts,[8,9] nanowires[10] and nanorods,[11] have been easily synthesized by many methods. In, Sb doped SnO_2 1D nanostructures have also been successfully synthesized, which excel pure SnO_2 1D nanostructures in physical and chemical properties apparently.[12,13]

In the late 1990s, the mixture of SnO_2 and MoO3 was shown experimentally to have excellent catalytic properties for the selective oxidation of methanol and other organic compounds.[14] The Mo–Sn–O system was demonstrated to possess high activity in oxidative dehydrogenation of ethanol and high selectivity in the production of acetic acid from ethanol in one single step.[15] SnO_2 thin film doped by Mo presented higher sensitivity to alcohol under a lower operating temperature.[16] However, there was no literature dealing with the preparation and the properties of Mo-doped SnO2 (MTO) 1D nanostructures. When the diameter of 1D nanostructure approaches the Debye length of its material, surface redox process will turn almost the whole nanostructure into a depletion (accumulation) zone of charge carriers. The depleted (accumulated) 1D nanostructure will have an extreme sensitivity to gas molecules absorbed on the surface. Compared with Mo-doped SnO_2 film, MTO 1D nanostructures have a large surface-to-volume ratio, which makes them stronger contenders as gas sensors.

In the present work, we synthesize monodispersed MTO nanowires in mass production by an in-situ doping chemical vapor deposition (CVD) method. The x-ray diffraction (XRD) patterns indicate that the rutile structure of SnO_2 nanowires is independent of Mo-doping. Raman scattering spectra indicate that the lattice symmetry of MTO nanowires lowers with the increase of Mo doping, which implies that Mo ions do enter into the lattice of SnO_2 nanowire. Ultraviolet-

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visible (UV-Vis) diffuse reflectance spectra show that the band gap of MTO nanowires decreases with the increase of Mo concentration. The photoluminescence (PL) emission of MTO nanowires around 580 nm at room temperature can also be controlled accurately by Mo doping, and it is extremely sensitive to Mo ions and will disappear when the atomic ratio reaches 0.46%.

2. Experiment

The experiment apparatus for chemical vapour deposition is similar to that described in our previous work.[17] A quartz tube (1200 mm in length and 25 mm in diameter) is located in a horizontal tube furnace and serves as a sample growth chamber. One end of this quartz tube is connected to the gas supply system and the other end to the vacuum system. The pressure in the growth chamber can be controlled accurately by controlling the pump speed and the flow rate of carrier gas. The source materials SnO, Sn and MoO_3 powders (purity $\geq 99.9\%$) were mixed fully and loaded into an alumina boat. An n-type (100) Si wafer (5 mm×5 mm) covered with 5 nm gold (Au) film was located 20–40 mm downstream from the source materials. The carrier gas, high-purity argon, was introduced into the quartz tube at a flow rate of 150 SCCM (Standard Cubic Centimeter per Minute) to remove the air from it. The alumina boat was then pushed into the centre of a quartz tube in a horizontal tube furnace which had been preheated up to 850 °C. And then a trace of oxygen gas was introduced into the growth chamber. The pressure in the quartz tube was kept at 5.0×10^3 Pa during the growth process. After an hour, sample was unloaded from the growth chamber immediately under the protection of Ar. A layer of wool-like product on the silicon substrate is the sample we have synthesized. The Mo-doping ratio (Mo/Sn) was controlled by changing the atomic ratio of Mo to Sn in the source material.

The morphologies, microstructures and electronic structure of the as-synthesized product were characterized by scanning electron microscopy (SEM) (JEOL-6360Lv), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD) (Aolong Y2000, Cu Kα, $\lambda = 0.15405$ nm), Raman spectroscopy (alpha SNOM 3000S, Ar^+-ion laser, 488 nm), near-field scanning optical microscopy (NSOM) (He–Cd laser, 325 nm) and ultraviolet/visible spectrophotometer equipped with a 60-mm integral sphere (PerkinElmer Lambda750).

3. Results and discussion

Figure 1 shows the typical SEM images of pure SnO_2 nanowires (a) and MTO nanowires with different nominal Mo concentrations (Mo/Sn: 1% (b), 4% (c), and 7% (d) in source material), which indicate that the as-prepared MTO nanowires are loosely entangled and have a uniform diameter of about 60 nm and lengths up to several tens of micrometers. It seems that the morphologies of MTO nanowires are independent of Mo concentration. TEM observation shows that the MTO nanowires are of single crystal (their images are not shown here).

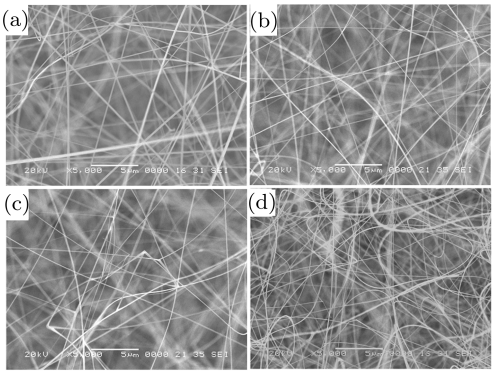


Fig. 1. Typical SEM images of pure SnO_2 nanowires (a) and MTO nanowires with different nominal Mo concentrations (Mo/Sn: 1% (b), 4% (c), and 7% (d)); The scale bars in the figure are 5 μm in length, and the magnification is 5000×.

Figure 2 gives the XRD patterns of pure SnO_2 nanowires and MTO nanowires with different nominal Mo concentrations. All the sharp diffraction peaks of pure SnO_2 nanowires (Fig. 2(a)) can be perfectly indexed as a tetragonal rutile structure with lattice constants of $a = b = 0.47420$ nm and $c = 0.31815$ nm, which are consistent with the standard values for bulk SnO_2 (JCPDS No. 41-1445). It is noticeable that no diffraction peak other than that of SnO_2 can be identified in the XRD patterns of MTO nanowires (Figs. 2(b), 2(c) and 2(d)) and there are no obvious differences among the corresponding peaks of MTO nanowires with different nominal Mo concentrations. The small peak at ∼32° in Fig. 2(b) can be assigned to the (101) peak of Sn. According to XRD data, MTO nanowires present slightly broad diffraction peaks and small lattice constants compared with pure SnO_2 nanowires (for example, $a = b =$

0.47360 nm, $c = 0.31704$ nm for MTO nanowires with the nominal Mo concentration of 10%). This decreases in the unit cell constants in MTO nanowires might be due to the substitution of Sn^{4+} ions ($r = 0.069$ nm) by Mo^{4+} ions ($r = 0.067$ nm).

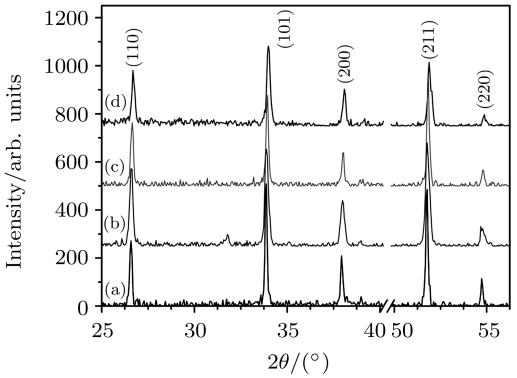


Fig. 2. XRD patterns of pure SnO_2 nanowires (a) and MTO nanowires with different nominal Mo concentrations (Mo/Sn: 4% (b), 7% (c), and 10% (d)).

Figure 3 shows Raman scattering spectra of pure SnO_2 nanowires and MTO nanowires recorded at room temperature. According to group theory,[18] the tetragonal rutile structure of SnO_2 belongs to the space group D_{4h}^{14} (P42/mnm), which has 15 lattice vibration modes, such as $A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_u + E_g + 3E_u$. Among these modes, only the A_{1g}, B_{1g}, B_{2g}, and E_g are Raman active. In the spectrum of pure SnO_2 nanowires (Fig. 3(a)), three fundamental Raman peaks at 478, 633, and 776 cm^{-1}, corresponding to E_g, A_{1g}, and B_{2g} vibration modes respectively, confirm the perfect tetragonal rutile structure of the SnO_2 nanowires.[19] With the increase of Mo concentration in the source material, the Raman peaks of the as-synthesized MTO nanowires shift toward lower frequencies and weaken gradually, and the full widths at half maximum of these Raman peaks increase noticeably (Figs. 3(b), 3(c), and 3(d)). Furthermore, there is no Raman peak other than that of SnO_2 can be identified. These phenomena might be attributed to lattice distortion or lattice symmetry lowering, induced by Mo-doping.[20]

The electronic structures of pure SnO_2 nanowires and MTO nanowires have been characterized by UV/VIS/NIR spectrophotometer equipped with a 60-mm integrating sphere. Figure 4 shows the plots of the Kubelka–Munk function, $F(R) = (1 - R)^2/2R$, versus wavelength for pure SnO_2 nanowires and MTO nanowires, where R is diffuse reflectance ratio. The band gap can be determined by extrapolating the rising part of the plots to the wavelength axis (black line in Fig. 4).[21] The band gap of pure SnO_2 nanowires is about 3.81 eV (325 nm), and is larger than the value of 3.6 eV for bulk SnO_2, which can be attributed to quantum confinement effect.[21] The band gap of MTO nanowires decreases from 3.81 eV (325 nm) to 3.60 eV (344 nm), 3.56 eV (348 nm) and 3.31 eV (375 nm) when the nominal Mo concentration increases from 0% to 4%, 7% and 10%, respectively. It seems that the continuous decrease in band gap is due to the formation of the substitutional solid solution (the band gap of MoO_3 is about 3.3 eV).

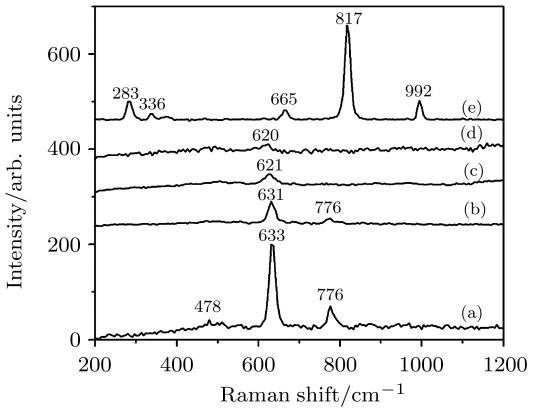


Fig. 3. Raman scattering spectra of pure SnO_2 nanowires (a), MTO nanowires with different nominal Mo concentrations (Mo/Sn: 4% (b), 7% (c), and 10% (d)), and pure MoO_3 powder (e).

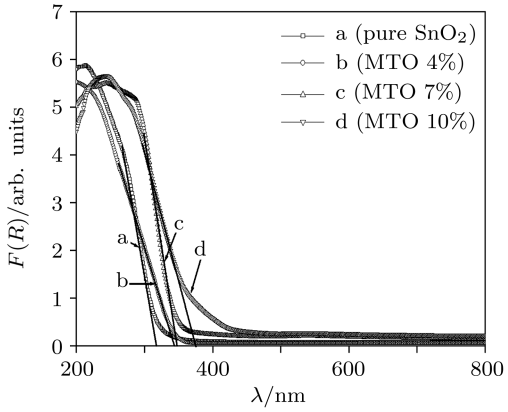


Fig. 4. Plots of $F(R) = (1 - R)^2/2R$ vs. wavelength of pure SnO_2 nanowires (a) and MTO nanowires with different nominal Mo concentrations (Mo/Sn: 4% (b), 7% (c), and 10% (d)).

Figure 5 shows the room-temperature PL spectra of pure SnO_2 nanowires and MTO nanowires with different nominal Mo concentrations by using a He–Cd laser (325 nm) as an excitation source. A yellow broad emission peak at about 580 nm was observed from pure SnO_2 nanowires, which might be related to the defect levels associated with O vacancies or Sn

interstitials as previously reported.[22,23] However, for MTO nanowires, the intensity of the emission peak at 580 nm is extremely sensitive to the addition of Mo, which decreases quickly and even to zero when the nominal Mo concentration reaches 0.5%.

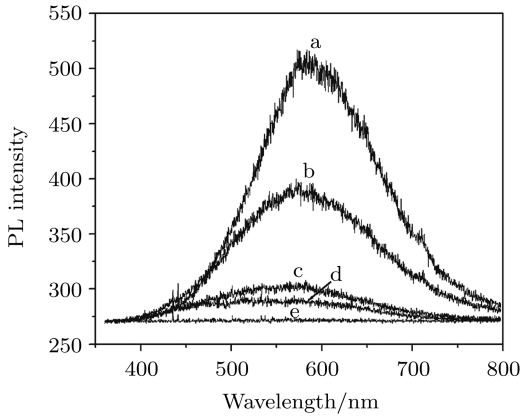


Fig. 5. Room-temperature photoluminescence spectra of pure SnO_2 nanowires (a) and MTO nanowires with different nominal Mo concentrations (Mo/Sn: 0.1% (b), 0.2% (c), 0.3% (d), and 0.5% (e)).

The EDS spectra indicate that the Mo atomic concentration in MTO nanowires increases from 0 to 0.46%, 0.69% and 2.18% when the nominal Mo concentration increases from 0 to 0.5%, 1% and 4%, respectively (Fig. 6). The EDS spectra also indicate that the atomic ratio of oxygen to tin of MTO nanowires decreases with Mo concentration increasing (Fig. 6(c)). The O/Sn atomic ratio larger than their stoichiometric ratio of pure SnO_2 nanowires might be due to oxygen adsorption on their surface from air. Therefore, we consider that the PL emission at about 580 nm is extremely sensitive to the concentration of Mo ions and can be controlled accurately by Mo doping.

MoO_3 powder evaporates mainly into $(MoO_3)_{3-5}$ molecular clusters at temperatures above 700 °C,[24] and then the Mo concentration along the direction of carrier gas decreases evidently, which might result in much lower Mo concentrations in MTO nanowires than their nominal concentrations because the Si wafer for collecting samples were located 20–40 mm downstream from the source materials. The EDS spectra do indicate that the Mo atomic concentration and the atomic ratio of oxygen to tin in MTO nanowires are different from spot to spot on the same small substrate (5 mm×5 mm). On the one hand the lattice constants of MTO nanowires do not change markedly compared with those of pure SnO_2 nanowires, and on the other hand MTO nanowires do exhibit continuous decrease in band gap. Therefore the change in the electronic structure of SnO_2 induced by Mo doping cannot be attributed simply to the formation of the substitutional solid solution. After all, the Mo concentration in the MTO nanowires is very low. Based on the experimental facts, we consider that Mo ions distribute mainly on the surface of SnO_2 nanowires in the form of Mo^{3+}, which introduces surface energy band into the band gap of SnO_2 nanowires and more O vacancies into the lattice of SnO_2 nanowires. The PL emission at about 580 nm of SnO_2 nanowires might also be attributed to surface energy levels associated with Mo^{3+}, which can be controlled accurately during the growth process.

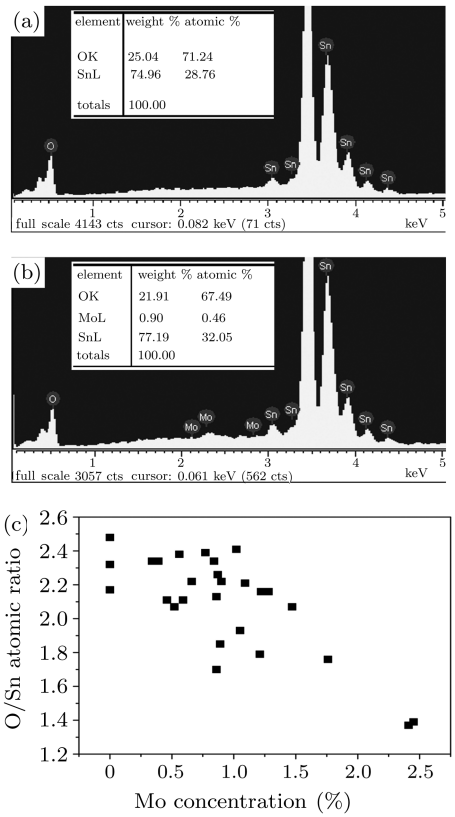


Fig. 6. EDS spectra of pure SnO_2 nanowires (a), MTO nanowires with nominal Mo concentration of 0.5% (b) and the distribution of O/Sn atomic ratio as a function of Mo concentration (c).

4. Conclusion

Monodispersed MTO nanowires are synthesized by an in-situ doping chemical vapour deposition method. Raman scattering spectra indicate that the lattice symmetry of MTO nanowires lowers with the increase of Mo doping, which implies that Mo ions

do enter into the lattice of the SnO_2 nanowire. UV-Vis diffuse reflectance spectra show that the band gap of MTO nanowires decreases with the increase of Mo concentration. The PL emission of MTO nanowires around 580 nm at room temperature can also be controlled accurately by Mo doping, which is extremely sensitive to molybdenum ions and will disappear when the concentration reaches 0.46% in atomic ratio. Due to their distinguished electrical properties, MTO nanowires will find wide applications to gas sensing with high sensitivity and a low operating temperature. A similar synthesis strategy could be used to synthesize various metal-doped 1D SnO_2 nanostructures.

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