The preparation of SnO$_2$ and SnO$_2$:Sb nanopowders by a hydrothermal method

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Abstract

Nanopowders of antimony-doped tin oxide have been prepared by a hydrothermal method with Sb dopant concentration changed from 0 to 3 at.%. The reactions of samples were investigated at room temperature. The band gap and luminescence properties of samples were investigated at room temperature. The band gap of SnO$_2$:Sb varied from 3.9 to 4.2 eV with variation of the Sb dopant concentration. The nature of the photoluminescence peaks of the SnO$_2$:Sb nanoparticles will be discussed.

Keywords: tin dioxide SnO$_2$, nanopowders, hydrothermal method

Classification numbers: 4.04, 5.01

1. Introduction

Tin dioxide (SnO$_2$), an important n-type semiconductor with a wide band gap ($E_g = 3.6$ eV), exhibits excellent optical, electrical and chemical properties and high thermal stability. Research has shown that the semiconductor SnO$_2$ material has potential applicability in gas sensors, glass electrodes, secondary lithium batteries, solar cells, transistors and catalysts. In recent years, doped SnO$_2$ and SnO$_2$-based materials, such as Sn-doped SnO$_2$, Mn-doped SnO$_2$, Zn$_2$SnO$_4$, Cd$_2$SnO$_4$ and so on, have been extensively studied due to their special optical and electrical properties. On the other hand, the chemical and physical properties of these materials also depend on the sizes and shapes of particles. During the past few years, these materials have been prepared by many techniques such as sol-gel [1], simple thermal evaporation [2], thermal CVD [3], hydrothermal methods [4–7] and other methods.

In this paper, we present our success in the synthesis of SnO$_2$ and SnO$_2$:Sb nanoparticles by a hydrothermal method with Sb dopant concentration changed from 0 to 3 at.%, and some characteristics of the material.

2. Experiment

The samples of SnO$_2$:Sb nanoparticles were prepared by a hydrothermal method from initial materials of SnCl$_4$·5H$_2$O, C$_2$H$_5$OH, NH$_3$ and SbCl$_3$. The solution was obtained by dissolving SnCl$_4$·5H$_2$O and SbCl$_3$ in distilled C$_2$H$_5$OH. The solution was stirred for 30 min and then put into a Teflon liner hydrothermal autoclave. The autoclave was put into the electrical oven Mermert-500 and kept at a constant temperature of 180, 200 and 220 °C. The hydrothermal process took 24 h. After the oven was cooled to room temperature, white powder was obtained from the bottom of the Teflon liner hydrothermal autoclave. The powder was washed several times in absolute ethanol and distilled water of the Teflon liner hydrothermal autoclave. The powder was characterized by x-ray diffraction and transmission electron microscopy (TEM). TEM images were carried out from 180 to 220 °C with Sb dopant concentration changed from 0 to 3 at.%. The crystal structure of the samples was analyzed by x-ray diffraction using a DX 5005 diffractometer and TEM images using a JEM 1010 microscope. Optical properties of the samples were investigated at room temperature.
Figure 1. XRD patterns of the SnO$_2$ and SnO$_2$:Sb (3 at.%) samples synthesized in various temperature. SnO$_2$: (a) 180°C, (b) 200°C and (c) 220°C; SnO$_2$:Sb: (d) 180°C, (e) 200°C and (f) 220°C.

Table 1. The particle size of SnO$_2$:Sb powders.

| Sample         | Size of particles (nm) |
|----------------|------------------------|
| SnO$_2$        | 4.7                    |
| SnO$_2$:1%Sb   | 5.12                   |
| SnO$_2$:1.5%Sb | 5.12                   |
| SnO$_2$:2%Sb   | 5.08                   |
| SnO$_2$:2.5%Sb | 5.05                   |
| SnO$_2$:3%Sb   | 4.83                   |

Absorption spectra of the samples were measured on a UV 2450 PC spectrometer. Photoluminescence and photoluminescence excitation spectra of the samples were measured on a Fluorolog FL3-22 spectrophotometer.

3. Results and discussion

The x-ray diffraction patterns of the SnO$_2$ and SnO$_2$:Sb (3 at.%) samples synthesized at temperature changed from 180 to 220°C are shown in figure 1. The XRD patterns clearly indicate that all the SnO$_2$:Sb nanoparticles possess a polycrystalline tetragonal rutile structure with lattice constants of $a = b = 4.74$ Å and $c = 3.19$ Å.

The average grain size of the powder was calculated using the Scherrer formula

$$d = \frac{0.9\lambda}{\beta \cos \theta},$$

where $\lambda$ is the x-ray wavelength, $\theta$ is the Bragg diffraction angle and $\beta$ is the line width at half maximum of the diffraction peak. The particle sizes of the SnO$_2$:Sb nanoparticles are presented in table 1. The average size of the nanoparticles of all the samples was about 5 nm.

The morphology of the samples was observed by TEM. Typical TEM images of the SnO$_2$:Sb samples with 1 at.% and 3 at.% Sb concentrations synthesized by the hydrothermal method are shown in figure 2, from which it can be seen that the powder consists of a large quantity of nanoparticles. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were measured at room temperature. Figure 3 shows emission spectra of the SnO$_2$ and SnO$_2$:Sb samples with excitation wavelength of 276 nm. The PL spectra of SnO$_2$ exhibit a peak at 336.7 nm (3.68 eV). In the PL spectra of the Sb-doped SnO$_2$ samples only the band of 400–475 nm with weak peaks at 397.8 nm (3.11 eV), 421.3 nm (2.94 eV), 440.9 nm (2.81 eV), 450.7 nm (2.75 eV) and 471.7 nm (2.63 eV) is observed.

To more clearly observe the fluorescent green band, these samples were excited with wavelength at 314 nm (figure 4). In all the PL spectra of the undoped SnO$_2$, the peak appearing at a wavelength of 509 nm (2.44 eV) is dominant. In particular, in the PL spectra of the undoped SnO$_2$ samples synthesized at 200°C, in addition to the peak at 509 nm, two other peaks at 416 nm (2.99 eV) and 442 nm (2.80 eV) are observed. For the Sb-doped samples, two peaks appeared at wavelengths of 390 nm (3.18 eV) and 435 nm (2.85 eV) for the samples synthesized at 220°C and 398.6 nm (3.11 eV) and 442 nm (2.8 eV) for 180°C. To interpret the nature of these emission bands, the recombination mechanism of the donor–acceptor pair [8] or radiative recombination of a conduction band electron with oxygen vacancy $V_{O}^{*}$ center can be used [1]. However, in order to clear up the origin of these broad peaks, further investigation is needed.

The PLE spectra of the samples were measured at various emission peak positions. Figure 5 and 6 illustrate the PLE spectra of the samples monitored with the peak at 421 nm for the SnO$_2$:Sb (3%) sample and 505 nm for the SnO$_2$ sample.

The PLE spectra of the samples exhibit wide bands located at 300–350 nm and at 360–410 nm for the undoped...
Figure 4. PL spectra of the SnO$_2$ and SnO$_2$:Sb 3 at.% samples synthesized in various temperature. SnO$_2$: (a) 180°C, (b) 200°C and (c) 220°C; SnO$_2$:Sb: (d) 180°C, (e) 200°C and (f) 220°C; excitation wavelength $\lambda_{ex} = 314$ nm.

Figure 5. PLE spectra of SnO$_2$ samples synthesized at different temperature. (a) 180°C, (b) 200°C, (c) 220°C, $\lambda_{em} = 505$ nm.

SnO$_2$ sample (figure 5). The PLE spectra for the SnO$_2$:Sb sample prepared at 180°C exhibit a band at 290 nm (4.27 eV), while the PLE spectra for the samples prepared at 200 and 220°C exhibit wide bands centered at 269 nm (4.61 eV). In comparison with the band gap of SnO$_2$ bulk ($E_g = 3.6$ eV), the position of the excitation bands of the samples shifted to the high energy side. The cause of this energy shift can be attributed to the quantum size effect.

In order to investigate the absorption property of the SnO$_2$:Sb nanoparticles, the powders were dispersed into absolute C$_2$H$_5$OH. Absorption spectra were measured at room temperature. For the direct transition allowed, the absorption coefficient near the fundamental absorption edge is given by

$$a h v = A (h v - E_g)^{1/2}.$$  

(2)

From the plot of $(a h v)^2$ versus $h v$ the band gap energies can be deduced. Figure 7 shows the photon energy dependence of $(a h v)^2$ for the undoped SnO$_2$ sample. The band gap energies of SnO$_2$:Sb nanoparticles synthesized with various Sb concentrations are showed in table 2.

The band gap of the SnO$_2$ nanoparticles changed in the range 3.98–4.12 eV with various Sb concentrations.

4. Conclusion

In summary, SnO$_2$:Sb nanopowders were fabricated by a hydrothermal method using SnCl$_4$·5H$_2$O, C$_2$H$_5$OH, NH$_3$ and

Table 2. Band gap energy of SnO$_2$:Sb.

| No. | Sample      | $E_g$(eV) |
|-----|-------------|-----------|
| 1   | SnO$_2$     | 4.12      |
| 2   | SnO$_2$:1%Sb| 4.01      |
| 3   | SnO$_2$:1.5%Sb| 4.00     |
| 4   | SnO$_2$:2%Sb| 3.89      |
| 5   | SnO$_2$:2.5%Sb| 3.98     |
| 6   | SnO$_2$:3%Sb| 3.98      |
SbCl$_3$ as precursor. The Sb doped concentration changed from 0 to 3 at.%. From x-ray measurements, the lattice constants were $a = b = 4.74$ Å and $c = 3.19$ Å. The average grain size of the powder was in the range 4–5 nm. The band gap energy of the SnO$_2$:Sb nanoparticles varied from 3.98 eV to 4.12 eV. The room temperature PL and PLE spectra of the powders were investigated.

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