Structure and features of SnO_2 thin films prepared by RF reactive sputtering

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SnO_2 thin films with good orientation are prepared on a glass substrate by radio frequence (RF) reactive sputtering. The phases of the thin films before and after annealing are analyzed by X-ray diffraction (XRD) spectroscopy, and the surface morphologies of the thin films before and after annealing are analyzed by atomic force microscopy (AFM). The result shows that the crystalline quality of the films markedly improved, the grains grow a little, and the orientation is more consistent after annealing in the air at 400 °C for 60 min. After modular multi-grating spectrometer measurement, the average transmittance in the air is found to be 80%. By the scanning electron microscopy (SEM), the energy spectrum shows that the ratio of Sn and O is close to 1:2.

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SnO_2 is an n-type semiconductor material. Because of its good adsorptive properties and chemical stability, it can be deposited on glass, ceramics, oxides, and substrate materials of other types[1]. It has a high melting point and good transmission, and it does not easily react with oxygen and water vapor in the air, so it has a high specific volume and good cycling performance. Gas sensors based on SnO_2 thin films are used to detect a variety of hazardous gases, combustible gases, industrial emissions, and pollution gases[2]. In addition, SnO_2 thin films are also used for film resistors, electric conversion films, heat-reflective mirror, semiconductor-insulator-semiconductor (SIS) heterojunction structure, and surface protection layer of glass. At present, its most common application is as anode material of solar cells[3].

There are many preparation methods of SnO_2 thin films, and the common methods are chemical vapor deposition (CVD), physical vapor deposition (PVD), spray pyrolysis, sol-gel, and pulsed laser deposition[4]. The PVD methods include vacuum evaporation, direct current (DC) magnetron sputtering, and radio frequence (RF) sputtering. In this paper, a RF reactive sputtering method is used. The advantages of this method are the density of the films, few pinholes, high purity, good adhesive quality, simple preparation, and low cost.

In the experiment, the transparent SnO_2 thin films were prepared by RF reactive sputtering method in multicoating systems made in China. The Sn target used was made by Beijing Science and Technology Development Center Products. The purity was 99.99%, the diameter was 100 mm, and the thickness was 6 mm. The substrate was biological glass whose specification was 25.5×75.5×1 (mm).

The glass substrate was first ultrasonically cleaned with acetone, ethanol, and pure water, in a consecutive manner, for 10 min. Sputtering targets were at 6 cm away from the substrate. The sputtering power was 200 W. The working condition involved a gas mixture of Ar and O_2 (1:4) which ran through the gas flow meter controlling their flows. When the glass substrate was being coated, it maintained uniform rotation.

The energy spectrum of the SnO_2 thin film analysis was obtained by an FEI scanning electron microscope (SEM). The X-ray diffraction (XRD) spectrum of the SnO_2 thin films was obtained by a D/max-r B X-ray diffraction equipment made in Japan (Cu Ka radiation wavelength was 0.15418 nm). The surface morphology of the film was obtained by a Nano Scope III-type atomic force microscope (AFM). The transmittance of the film was obtained by a WGD-3-type modular multi-grating spectrometer with the wavelength range from 380 to 780 nm in the ultraviolet (UV) visible region.

Samples of the SnO_2 thin films were cut into two pieces. One was annealed at 400 °C for 60 min in the air, and the other one was left unannealed. The XRD spectra of the SnO_2 thin films before and after annealing are shown in Fig. 1. The diffraction pattern of pure SnO_2 powder is shown in Fig. 2[5]. The spectra in Figs. 1 and 2 show that the (110), (101), and (211) crystal faces have obvious diffraction peaks. The rest of the diffraction peaks of the other crystal faces are absent. The face diffraction peak of the (110) crystal is the most obvious. This indicates that the SnO_2 thin films have good orientation of preferred growth. As a result of annealing in the air at 400 °C for 60 min, the thin films are found to have increased intensity, spectra wherein the diffraction angle shifted to the right, and a slight reduction of the full width at half maximum (FWHM). A qualitative analysis of the Scherrer formula was made by

$$D = \frac{0.9\lambda}{B\cos\theta}, \tag{1}$$

where D is the grain size, λ is the X-ray wavelength, B is the diffraction peak at FWHM, and θ is the diffraction peak position. The results show that the grain size increases after annealing. The grain size is calculated by the Jade 5.0 software, and the result shows that grain sizes before and after annealing are 16.9 and 18.9 nm. respectively. There is an increase of about 2 nm in grain size after annealing at 400 °C for 60 min. This shows

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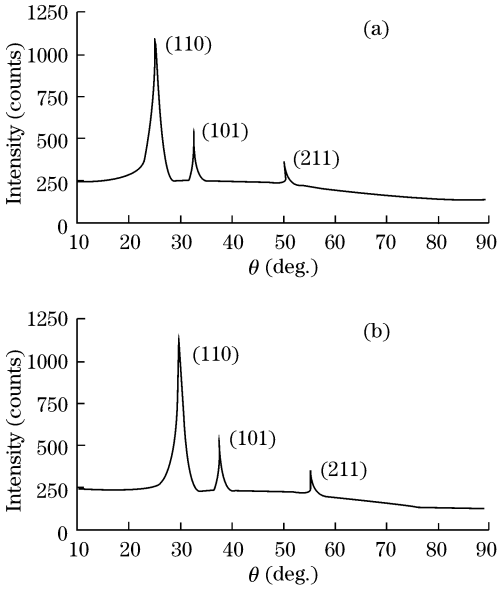

Fig. 1. XRD spectra of SnO_2 thin films (a) before and (b) after annealing.

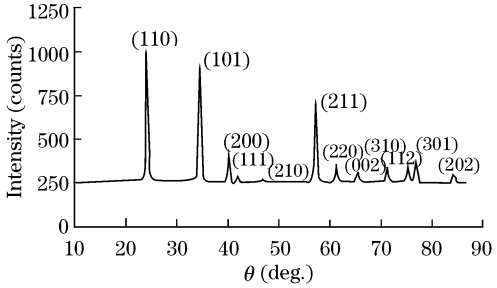

Fig. 2. XRD spectrum of pure SnO_2 powder.

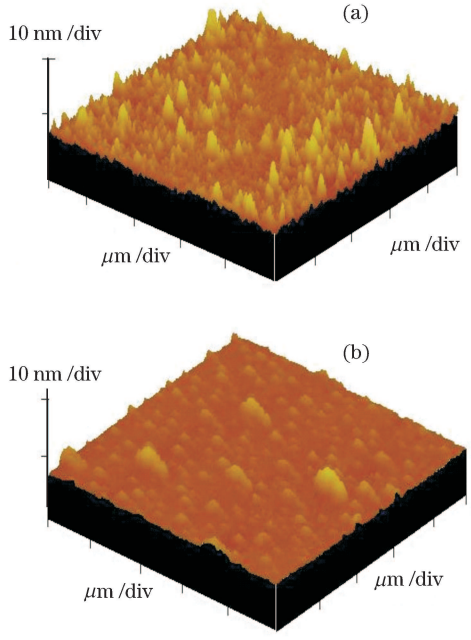

Fig. 3. AFM image of SnO_2 thin films (a) before and (b) after annealing.

that grains of SnO_2 thin films have a small growth trend under such conditions, which will lead to a more stable SnO_2 thin film gas sensor.

The AFM images of the SnO_2 thin films before and after annealing are shown in Fig. 3. We can see that after annealing, the distribution of particles become more consistent and the size is larger. During the annealing process, the atoms of the film get enough energy, so that the position of the atoms changes and recrystallization occurs. The density and homogeneity of the film improve after annealing. This is consistent with the results of the XRD.

The energy spectrum of the SnO_2 thin films is shown in Fig. 4. The ratio of Sn and O close to 1:2 indicates that the films are really SnO_2 thin films rather than other Sn oxides.

In order to estimate the size of the bandgap of the films, the transmittances of the samples are measured. A transmission spectrum of the SnO_2 thin films is shown in Fig. 5. From it, we can see that the transmittance is more than 80%. According to the relationship between the transmission and absorption, we can get the curve of the relationship between α^2 and $h\gamma$, that is

$$\alpha(h\gamma) = A(h\gamma - E_g)^{\frac{1}{2}}, \tag{2}$$

where α is the absorption coefficient, and $h\gamma$ is the photon energy. When the curve of the intersection is extended with the $h\gamma$ axis, the intersection is E_g, here E_g is 3.59 eV.

In conclusion, the SnO_2 thin films prepared by RF reactive sputtering method on biological glass substrates result in a good orientation of preferred growth, and the ratio of Sn and O is close to 1:2. The transmittance is more than 80%, and the bandgap width (E_g) is about 3.59 eV. After annealing, it is concluded that the crystalline quality and orientation improved, the film structure becomes more symmetrical and compact, the degree of crystallization tends to be perfect, and the

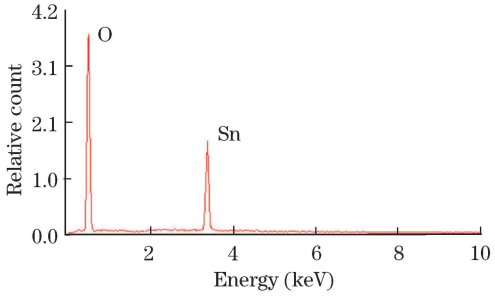

Fig. 4. Energy spectrum of SnO_2 thin films.

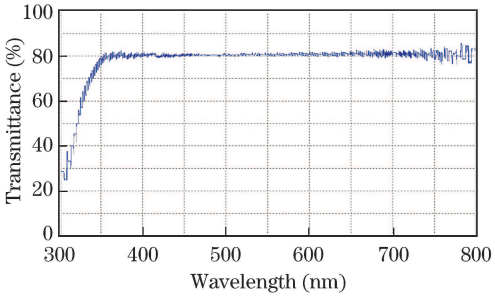

Fig. 5. Transmission spectrum of SnO_2 thin films.

grain size increases but not obviously, which will make the SnO_2 thin film gas sensor stable.

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