Research Article

Preparation and Properties of SnO₂ Film Deposited by Magnetron Sputtering

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Received 21 March 2012; Revised 15 June 2012; Accepted 15 June 2012

Academic Editor: Raghu N. Bhattacharya

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Tin oxide SnO₂ films were prepared by RF magnetron sputtering. The effects of oxygen partial pressure percentage on the SnO₂ property have been investigated to obtain relatively high-resistivity SnO₂ films which could be used as buffer layers to optimize the performance of CdTe/CdS solar cells. The oxygen partial pressure percentage varied in the range of 1%~10%. The results show that the introduction of oxygen would suppress the deposition and growth of SnO₂ films. Electrical measurement suggests that the film resistivity decreases with the increase of oxygen pressure. The SnO₂ films with resistivity of 232 Ω cm were obtained in pure Ar atmosphere. All SnO₂ films fabricated with different oxygen partial pressure percentage have almost the same optical band gap.

1. Introduction

SnO₂ is reported to be widely used in many fields owing to its good optical and electrical properties. Tin oxide SnO₂ is a kind of typical transparent n-type semiconductor with wide band gap (3.6–4.0 eV) [1]. SnO₂ thin film can be prepared by a variety of methods such as chemical vapor deposition (CVD), sputtering, sol-gel process, and spray pyrolysis. Compared with other deposition techniques, magnetron sputtering is the most attractive technique for industrial development due to its high deposition rate, competitive costs, good reproducibility, and possibility of using commercially available large-area sputtering systems [2].

In the case of intrinsic SnO₂, the density of conducting electrons has often been attributed to the presence of unintentionally introduced donor centers, usually identified as metallic interstitials (M_i) or oxygen vacancies (V_O) that produce shallow donor or impurity states located closed to the conduction band [3]. A great variety of dopants have been studied in order to improve the electrical properties of SnO₂ for certain applications [4, 5]. However, only a few researches focused on high-resistivity SnO₂ films [6–10].

As for CdTe/CdS solar cells, the window layer should be as thin as possible to improve the short-circuit current density. However, the thin window layer of CdS may lead

to the direct touch of CdTe absorption layer and the front electrode, which would degrade the device performance. Fortunately, it can be avoided by introducing a layer of high-resistivity SnO₂ film between the window layer and the front electrode. It could reduce the forward current caused by the perforation of CdS. By introducing a layer of about 50 nm SnO₂, the thickness of CdS could be reduced to 80 nm, which will cause less absorption of the incident light, and so the J_{sc} and efficiency would be improved. As a result, the performance of the CdTe solar cell would be better owing to SnO₂ buffer layer with relatively high resistivity [11].

Large variations in the electrical properties have been reported for SnO₂ films [12–16]. Oxygen plays an important role in the deposition process. In this paper, SnO₂ films with relatively high resistivity were fabricated by magnetron sputtering. And the influence of oxygen partial pressure on structural, electrical, and optical properties of SnO₂ films was studied.

2. Experimental

SnO₂ films were deposited on borosilicate glasses by RF magnetron sputtering. The target is SnO₂ ceramic disc with 5 N purity. The diameter of target is 64 mm. The substrates were placed on a substrate holder with heating block. The

distance between the substrate and target was 11 cm. The chamber was evacuated to a base pressure of 6×10^{-4} Pa and the working pressure was controlled to be 1 Pa in pure Ar gas or a mixture of Ar and O₂. The oxygen partial pressure percentage ranged from 1% to 10% and the working gases were supplied via mass-flow-controlled gas inlets. The substrate temperature was 250°C and the sputtering power was 150 W.

The structure of the films was studied by DX-2600 X-ray diffractometer with 0.15418 nm copper target K_{α} radiation. The resistivity of the film was measured using the two-probe method in our home-made instrument and film thickness was obtained by Ambios XP-2 profiler. The AFM images were obtained by CFM4000 scanning probe microscope. The transmission spectra of the films were measured by Lambda 950 UV-vis spectrometer.

3. Results and Discussion

Figure 1 illustrates the thickness of SnO₂ films deposited under the same deposition time with different oxygen partial pressures' percentage. The results show that the film thickness decreases with the increasing oxygen pressure. The maximum thickness of 148 nm was obtained in pure argon atmosphere and the minimum value was only 17 nm obtained in the film with 10% oxygen partial pressure percentage. The film thickness decreases with the increase of oxygen partial pressure. This tendency is more obvious when the percentage is lower than 3%. In order to understand this result and explore the role of oxygen in the growing process of SnO₂ films, some other films were intentionally fabricated at different deposition time and the films were measured to determine the thicknesses.

Table 1 shows the film thickness of different deposition time at different oxygen partial pressure percentage. It is out of expectation that the film thickness did not increase proportionally with the deposition time except for the sample without oxygen. For example, for samples with 5% oxygen, the film thickness with 60 min deposition time only increases 8 nm compared with the sample within 30 min. The thickness of the sample with 110 min deposition time increases no more than 50% of the sample with 30 min. This phenomenon indicates that the deposition rate of films decreased with the increase of the oxygen pressure, and in the atmosphere with oxygen, the deposition rate of SnO₂ films decreased with the increase of deposition time. This result is similar to [17], in which Suzuki and Mizunashi believed that the oxygen obstructed the deposition of SnO₂ because of the lower sputtering yield and large polarizability of the oxygen ion. And Kilic and Zunger thought the reduction in the rate deposition is attributed primarily to collisions of the ablated tin and oxygen particles with the ionized gas plasma during deposition [18]. Another explanation is as follows: in the given atmosphere, bigger oxygen partial pressure percentage means the less quantity of Ar, which leads to the increase of unionized neutral oxygen atoms. The neutral O₂ atoms impact with the sputtering particles and thus consume the energy of the sputtering particles.

Consequently, these particles diffuse to low energy positions without enough energy, resulting in low deposition rate [19].

In order to study the effect of oxygen on the surface morphology of SnO₂ films, AFM images of films deposited with different oxygen partial pressure percentage are observed as shown in Figure 2. The surface roughness (RMS) and particle size are shown in Table 1. Obviously, with same deposition time, the film particle of the sample with percentage of 0% is bigger than that of the 10%, and the surface roughness of the former was 1.2 nm while the later was 0.608 nm. With the increase of time, the particle of the film with 0% oxygen becomes bigger while the film with 10% is smaller. It seems that oxygen inhibits the growth of grain.

The XRD patterns for the samples are present in Figure 3. For SnO₂ film grown in pure argon, XRD spectrum exhibits 5 obvious diffraction peaks corresponding to (110), (101), (211), (002), and (112) plane of SnO₂ phase. No peak of other phase was observed. Among the 5 peaks, the intensity of (101) plane was much stronger. Once introduced oxygen, the intensity of (110) peak decreased sharply and (211) peak disappeared. (101) peak totally disappeared once introduced oxygen. Through the XRD data, it can be concluded that oxygen had an adverse effect on the crystallization of SnO₂ films deposited by magnetron sputtering. The effect of O₂ on film structure can be explained as follows. In the atmosphere containing oxygen, the particles that reached the substrate had not enough energy to form polycrystalline films. What's more, the oxygen might induce defects in the films, which will influence the nucleation and growth of the films. As a result, the films look more amorphous.

The relationship between electrical resistivity for SnO₂ films and oxygen partial pressure percentage is plotted in Figure 4. Similar with thickness, increasing oxygen caused the decline of resistivity. For the film deposited in pure Ar, the resistivity was the maximum with value of 232 Ω cm. Once introduced 1% oxygen, the value was less than half of the maximum. When oxygen partial pressure percentage is 3%, the resistivity decreased almost two orders of magnitude to about 1 Ω cm. With more oxygen, the value decreased continuously and reached the lowest one of 0.11 Ω cm at 10% oxygen partial pressure percentage. It is worthy to note that the resistivity curve is very similar to the thickness curve. We suppose that there is some relationship between them.

It is known that completely stoichiometric SnO₂ is an insulator or at most an ionic conductor. However, in practice this material is never stoichiometric and invariably presents defects. These defects are responsible for making free carriers available in the conduction process. For the RF magnetron-sputtered SnO₂ films, stoichiometric films cannot be acquired even though in pure Ar atmosphere. In the case of intrinsic materials, the density of conducting electrons has often been attributed to the presence of unintentionally introduced donor centers, usually identified as metallic interstitials (M_i) or oxygen vacancies (V_O) that produce shallow donor or impurity states located close to the conduction band. The excess of donor electrons is thermally ionized at room temperature and moves into the host conduction band. In SnO₂, the important role of Sn_i in populating the conduction band, in addition to the V_O , has

TABLE 1: Film thickness, surface roughness, and particle size of SnO₂ films deposited with different conditions.

Oxygen partial pressure percentage (%)	Deposition time (min)	Thickness (nm)	RMS (nm)	Particle size (nm)
0	20	62	0.612	0.8
	60	148	1.2	2.4
3	60	55	—	—
	110	87	—	—
5	30	50	—	—
	60	58	—	—
	110	70	—	—
10	60	30	0.608	1.4
	135	50	0.56	1.2

FIGURE 1: Thickness of SnO₂ films as a function of the oxygen partial pressure.

been conclusively supported by first-principle calculation of Suzuki and Mizuhashi [17]. They showed that Sn_i and V_O, which dominated the defect structure of SnO₂ due to the multivalence of Sn, explained the natural nonstoichiometry of this material and produce shallow donor levels, turning the material into an intrinsic n-type semiconductor.

The decrease of film resistivity might be attributed to V_O and Sn_i that both play positive role in film conductivity. With the increasing oxygen, the amount of Sn_i increased while V_O decreased. According to the report of Kilic and Zunger, the effect of Sn_i on film conductivity was more obvious than that of V_O due to the lower formation energy of Sn_i than V_O [18]. As a consequence, the carrier concentration increased and hence the mobility, resulting in a decrease in film resistivity. De and Ray have found amorphous phases of unknown stoichiometry with resistivity of about 33.3 Ω cm [13] and Eun-Kyung Kim and Oliver have reported the amorphous SnO₂ with resistivity of $5.6 \times 10^{(-3)}$ Ω cm [2]. As we known, the resistivity of 232 Ω cm for SnO₂ film is higher than that of other similar reports.

The optical transmittance spectra of all samples in the region of 200 nm to 900 nm are shown in Figure 5. There is no obvious change in the optical transmittance with the increase of oxygen partial pressure percentage. The

average transmittance in visible region varied from 83.18% to 88.63% with the maximum appeared at 1% sample and minimum at 10%. The optical energy band gap of SnO₂ films was calculated using (1) [20]:

$$\alpha = \frac{B(h\nu - E_g)^n}{h\nu}, \quad (1)$$

where the exponent n could have the values of 0.5, 1.5, 2, and 3 depending on the type of the electronic transition in k -space. For the allowed direct band gap transition in a crystal, $n = 0.5$. The band gap was determined by extrapolating the liner region of $(\alpha h\nu)^2 - h\nu$ plots. The bang gap E_g of the SnO₂ films deposited in 10% oxygen partial pressure percentage was 3.9 eV, and the others were 4.0 eV. That is, the oxygen content seemed to have no obvious effect on the optical band gap of films, which is discrepant with some researches. Lee reported that the band gap varied from 3.74 eV to 4.20 eV according to deposition conditions [21].

At room temperature, the band gap of SnO₂ is 3.6 eV, which is lower than what we got. According to the Brus

FIGURE 2: AFM images of samples of different oxygen pressure percentage and deposition time.

FIGURE 3: XRD patterns of SnO_2 films deposited at different oxygen concentration.

formula, the band gap change caused by small grain size can be calculated using

$$\Delta E = \frac{E^2 \pi^2}{2m^* r^2} = \frac{h^2}{8m^* r^2}, \quad (2)$$

where $m^* = m_e m_h / m_e + m_h$, $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ [22]. Considering the grain size in this paper, ΔE has been calculated to be 0.38 eV, which means the band gap will increase to 3.98 eV due to the confinement quantum effect. This result is very close to our experimental data (4.0 eV).

FIGURE 4: Electrical resistivity as a function of oxygen partial pressure percentage.

FIGURE 5: The transmittance of SnO₂ films deposited at various oxygen pressure percentages.

Because of the special features of the electronic structure of SnO₂, the formation of intrinsic defects in SnO₂ has only small effects on the optical transparency [18]. It might be caused by the combined effects of the thickness, defect density, and oxygen content. In addition, the reflection was not concerned. To find the real origin, it is necessary to do some further studies.

4. Conclusions

SnO₂ films were deposited with different oxygen partial pressure percentage by RF magnetron sputtering using SnO₂ ceramic disc. The film structure and morphology were analyzed. The results show that the oxygen would obstruct the deposition of SnO₂ and further to deteriorate the crystallization of SnO₂ film. With the increasing oxygen partial pressure, the resistivity of SnO₂ decreases while the

optical band gap was maintained at 4.0 eV. The SnO₂ film with the resistivity of 232 Ω cm was obtained in pure argon atmosphere.

Acknowledgment

The research is supported by the National 973 Project (2011CBA00708).

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