Optical characteristic and gap states distribution of amorphous SnO_2:(Zn, In) film*

Zhang Zhi-Guo(张治国)†

Institute of Functional Material, Quanzhou Normal University, Quanzhou 362000, *China*

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In this paper the fabrication technique of amorphous SnO_2:(Zn, In) film is presented. The transmittance and gap-states distribution of the film are given. The experimental results of gap-states distribution are compared with the calculated results by using the facts of short range order and lattice vacancy defect of the gap states theory. The distribution of gap state has been proved to be discontinuous due to the short-range order of amorphous structure.

Keywords: transmittance, amorphous film, gap states distribution

PACC: 7800, 7860, 7865

1. Introduction

Indium tin oxide (ITO) thin film has monopolized the entire display market and produced large commercial profits. Nowadays, new potential ITO thin films are still under investigation.[1−3] Both the SnO_2 film[4] and ZnO film[5−8] are good photoelectron information materials. They are of aciduric peculiarity and high transmittance. To take advantage of their unusual combination of high transparency and electric conductivity, they have been widely used in plate display, such as liquid crystal display, infrared hiding, amorphous silicon solar sell, electric-thermal converting, various sensors and photoconductor, etc. Although these materials are of good performance, there are some shortcomings. For example, the price of indium is very high, which results in the high cost of ITO film.

In addition, the microcrystal thin film does not have very smooth surfaces. Because light-emitting diode (LED) is increasingly applied in illumination domain, much effort has been put into making new luminescent materials.[9−13] The new luminescent device that emits various wavelengths is used in communication and automatic control in a growing manner. The aim of our study is to seek the thin film with low cost and proper evenness. In this paper a low-cost SnO_2:(Zn, In) transparent conducting thin film and their transmittance, photoluminescence (PL) characteristic and gap states are discussed.

2. Experiment

SnO_2:(Zn, In) thin film is fabricated by reaction evapouration method. The model DM450C vacuum plating film equipment is used. The substrate used is common glass with a size of 11×11 cm^2 and 21×21 cm^2. The operating order is as follows: 1) clean the substrate by water, 2) dehydrate it with absolute alcohol, 3) clean it for 5 minutes with acetone by supersonic, 4) clean it once more with absolute alcohol by supersonic for 5 minutes, 5) clean it twice with deionized water by supersonic for 5 minutes, 6) dry it and put it on sample frame to maintain the substrate at a temperature of 200 °C, 7) stannum, zinc and indium are mixed in proportion then put into quartz boat to heat with a heating power of about 150 W under a vacuum of 4×10^{-3} Pa. The oxygen partial pressure is maintained at 7.5×10^{-2} Pa in the reaction and the time of evaporation is 30 minutes. The rev of substrate is 10 r/min.

The transmittance of the film is measured with UV-4501 double beam spectrophotometer. The PL spectrum is measured with WGY-10-type fluorescence luxmeter. The crystallinity of film is measured with Y-2000 model x-ray diffractometer, and SGC-2-type elliptical polarization meter is used to measure the thickness of the film.

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†Corresponding author. E-mail: qzzzg@yahoo.com.cn

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3. Results and discussion

3.1. The characteristics of transmittance and photoluminescence of the SnO_2:(Zn, In) film

The thickness of the SnO_2:(Zn, In) film is about 110 nm, and the resistivity is about $1.5 \times 10^{-5}\ \Omega \cdot \mathrm{cm}$. Since we did not obtain legible scanning electronic microscope image for SnO_2:(Zn, In) film, to clarify further whether the structure of the film is amorphous or not, the x-ray diffraction (XRD) analysis is used. The XRD pattern is shown in Fig. 1. There is not any diffraction maximum showed in the diffraction spectrum but the white noise implying that the film is of the characteristic amorphousness of the short-range order and long distance disorder.

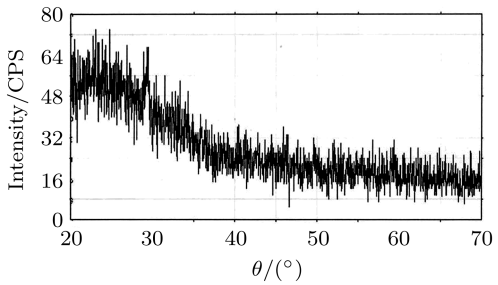


Fig. 1. The XRD of the SnO_2:(Zn, In) thin film.

The measured transmittance curve for the film on glass substrate is shown in Fig. 2 where an almost idealized characteristic can be seen clearly. The curve rises rapidly to 100% at 275 nm and keeps this high value in a wavelength interval of 3.3 nm ($\Delta\lambda = 3.3$ nm). Then drops to 77% at 283 nm where it exhibits a minimum transmittance, and followed by a rising up again with increasing wavelength to form a valley. The very high transmittance (more than 95%) exists in a wavelength range of 400–1000 nm. This is a unique transmittance curve. Furthermore, we can get hold of optics gap at the intersection of transmittance curve with the abscissa axis. The optics gap can be calculated by $E_{\mathrm{g}}^{\mathrm{opt}} = hc/\lambda$, where h is the Planck constant, c is the light velocity, λ is the wavelength. The gap-width calculated from transmittance experimental result reaches 4.43 eV.

It is worth while mentioning that this kind of thin film has a very strong fluorescence phenomenon. In order to find the distribution of fluorescence, we have measured it and the data are acquired every 10 nm. The 6-nm is chosen for both the slits of excitation light and emission light. Because the fluorescence intensity is oversized, only 30 volts is chosen for the bias of energy receiver. The distribution of measured intense fluorescence between 320 nm and 450 nm is shown in Fig. 3, there is no fluorescence in the wavelength region of 282 nm to 297 nm.

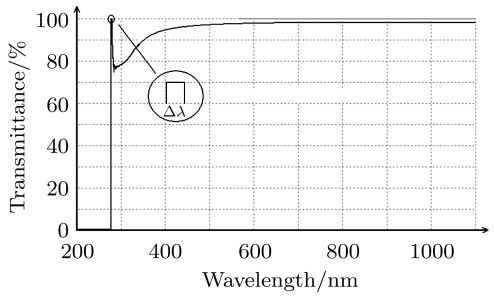


Fig. 2. The transmittance of the SnO_2:(Zn, In) thin film.

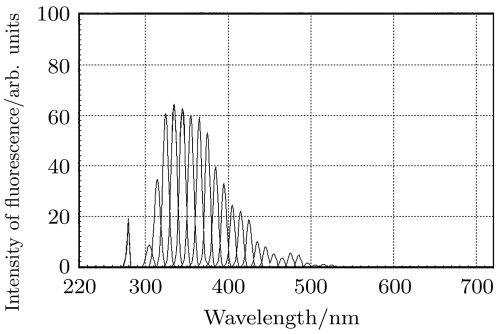


Fig. 3. Photoluminescence distribution of the SnO_2:(Zn, In) thin film.

3.2. The gap states of the film

The film is of very intense photoluminescence phenomena. If the gap states are known, photoluminescence characteristic and the added conductivity will be known. If the corresponding photoluminescence can be obtained, we can prove the presence of corresponding electronic states. Thus, we can excite it by the light with certain wavelength and measure the corresponding photoluminescence distribution, and gain continuous distribution of electronic states. Consequently, the different intensities of photoluminescence will show the distribution of density of the gap state corresponding to the wavelength. The radiation probability of photoluminescence can be calculated by the following equation:

$$W = \frac{2\pi t}{\hbar} \left|\hbar\omega_{\alpha\beta}\right|^2 \rho\left(E\right),$$

where t is the time the light acts on electronic states, $\hbar\omega_{\alpha\beta}$ is the average energy value of the photon acting on both α state and β state, and $\rho\left(E\right)$ is the density of gap state. Under definite wavelength of exciting

light, the radiation probability of photoluminescence is proportional to the density of states $\rho(E)$. The distribution of gap state of SnO_2:(Zn, In) film that we have gained is shown in Fig. 4.

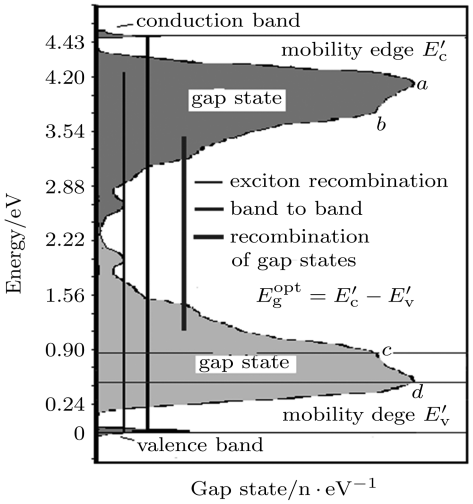


Fig. 4. Distribution of gap state of SnO_2:(Zn, In) amorphous film.

The gap width is confirmed to be $E_g^{opt} = 4.43$ eV which coincides with that from Fig. 2. It can be regarded as the distance between a mobility edge and another ($E_g^{opt} = E'_c - E'_v$). Thus, the states above mobility edge E'_c can be regarded as conduction band states; contrariwise, the states below E'_v are called valence band states. In Fig. 4, the state density in the region above E'_c is not very high. There, the higher energy is, the less state density is; and there are vacancy states on the top. In the region below E'_v, the lower the energy is, the less state density is, and there are vacancy states too at the bottom. Both kinds of distribution states are main contributors to conductivity. The fantastic thing is that there is a vacant band below E'_c, where there is no state distribution. There is a continued gap state distribution below this vacant band. The state density of the continued gap state reaches the biggest value by an energy change of 0.15 eV, then drops slowly in a small energy range followed by a dramatically falling to a minimum at 2.88 eV. After that it rises a little and turns down again, with a small tail. We call this state distribution as α state system. The lower one symmetrical state system is called β state system. The α state system is not called as band tail state of conduction band due to the fact that the α state system is not continued with conduction band. The β state system acts to be the same. By measuring the fluorescence spectrum, we have known that the contribution of fluorescence spectrum consists of three cases. The first is the transition process of band to band, the second is exciton transition process, and the third is the transition between the two gap states. Among all the third transition is the strongest. From Figs. 3 and 4, there is an empty band approximately at mobility edge (280 nm, below 4.43 eV). Consequently, the photons with this energy will not be absorbed by the thin film. In other words, the transmittance should be 100%. Therefore, a bulging appears right here on the transmittance curve shown in Fig. 2, and the transmittance reaches 100%. However the empty state belt in Fig. 4 is much wider than the bulging in Fig. 2. The empty state belt may be due to the bias of energy receiver of fluorescence spectroscope being too low (30 V) to display the states with lower density. In other words, the empty state belt may be not so wide around 280 nm in fact. But, this empty state around mobility edge can surely produce hopping conductivity.

3.3. Theoretical demonstration of gap state distribution

It was considered that the gap state of amorphous materials is continued. But the phenomena observed show that even in the case of amorphous material the gap state is not continued. For the purpose of showing the discontinuity of gap state theoretically, we did computation under the conditions as follows: first we postulate single vacancy defect, double vacancy defects, and multi-vacancy defects of amorphous film as the scattering potential barrier with same height and width; second, we use the characteristic of the short-range order to make two suppositions: the lattice point potential can be neglected in comparison with the scattering potential formed by vacancy defects and the short-range order is of the same size.

Since the amorphous film is of isotropic character, we can use the Kronig–Penney model to calculate the distribution of band tail state. Let the length of short-range order be b, c is the width of potential barrier, and $f(x) = c/b$ is the characteristic function; it is of periodicity, under these conditions, then the Schrödinger equation of this system is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2m_0}{\hbar^2}(E - V)\psi = 0. \tag{1}$$

According to Bloch theorem, the wave function can be written as

$$\psi(x) = \mathrm{e}^{\mathrm{i}kx}u(x). \tag{2}$$

Using boundary conditions, we have

$$
\begin{aligned}
&A + B - C - D = 0,\\
&\mathrm{i}(\alpha - k)A - \mathrm{i}(\alpha + k)B - (\beta - \mathrm{i}k)C + (\beta + \mathrm{i}k)D = 0,\\
&A\,\mathrm{e}^{\mathrm{i}(\alpha-k)b} + B\,\mathrm{e}^{-\mathrm{i}(\alpha+k)b} - C\,\mathrm{e}^{-(\beta-\mathrm{i}k)c} - D\,\mathrm{e}^{(\beta+\mathrm{i}k)c} = 0,\\
&A\mathrm{i}(\alpha - k)\,\mathrm{e}^{\mathrm{i}(\alpha-k)b} - B\mathrm{i}(\alpha + k)\,\mathrm{e}^{-\mathrm{i}(\alpha+k)b} - C(\beta - \mathrm{i}k)\,\mathrm{e}^{-(\beta-\mathrm{i}k)c} + D(\beta + \mathrm{i}k)\,\mathrm{e}^{(\beta+\mathrm{i}k)c} = 0,
\end{aligned}
\tag{3}
$$

where $\alpha = \sqrt{2m_0E/\hbar^2}$, $\beta = \sqrt{(2m_0/\hbar^2)(V_0 - E)}$, the Secular equation for A, B, C and D is

$$
\begin{vmatrix}
1 & 1 & -1 & -1\\
\mathrm{i}(\alpha - k) & -\mathrm{i}(\alpha + k) & -(\beta - \mathrm{i}k) & (\beta + \mathrm{i}k)\\
\mathrm{e}^{\mathrm{i}(\alpha-k)b} & \mathrm{e}^{-\mathrm{i}(\alpha+k)b} & -\mathrm{e}^{-(\beta-\mathrm{i}k)c} & -\mathrm{e}^{(\beta+\mathrm{i}k)c}\\
\dfrac{\mathrm{i}(\alpha - k)}{\mathrm{e}^{-\mathrm{i}(\alpha-k)b}} & -\dfrac{\mathrm{i}(\alpha + k)}{\mathrm{e}^{\mathrm{i}(\alpha+k)b}} & -\dfrac{(\beta - \mathrm{i}k)}{\mathrm{e}^{(\beta-\mathrm{i}k)c}} & \dfrac{(\beta + \mathrm{i}k)}{\mathrm{e}^{(\beta+\mathrm{i}k)c}}
\end{vmatrix} = 0. \tag{4}
$$

By solving Eq. (4) we can obtain

$$
\frac{V_0 - 2E}{\sqrt{(V_0 - E)\,E}}\sinh(\beta c)\sin(\alpha b) + \cosh(\beta c)\cos(\alpha b) = \cos k(b + c) = F(E). \tag{5}
$$

It can be seen from Eq. (5) that the maximum and the minimum are equal to 1 and –1 respectively.

Choose the step: $\Delta E = 0.01\ V_0$, where V_0 is the height of scattering potential barrier. The computation gives the relation $F(E) \sim E$, and by adjusting the value of characteristic function $f(x) = c/b$, we can acquire the gap state distribution of the corresponding energy.

The schematic diagram of gap state distribution is presented in Fig. 5 when $f(x) = c/b = 1/5$. It has two allowed bands and three forbidden gaps. We can see that the gap state distribution is not continuous, even in band tail state. When $f(x) = c/b$ is fixed, the allowed area of gap state distribution is fixed accordingly.

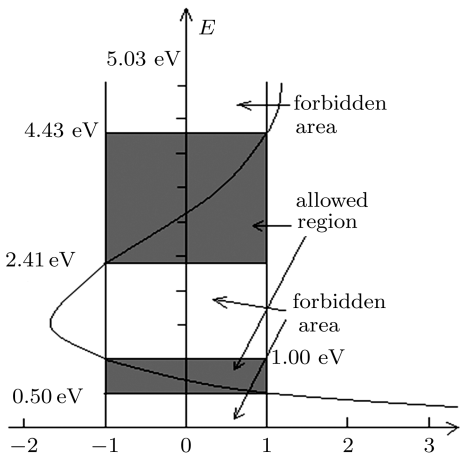


Fig. 5. The distribution of gap state $f(x) = c/b = 1/5$.

3.4. Comparison between experiment and theory

For comparison, we first consider the area of allowed bands. The theoretical calculated value for the first allowed band is between 2.41 eV and 4.43 eV. The observed value for distribution of α state system is between 2.34 eV and 4.43 eV which is slightly different from the predicted value. The reason is that we use approximate assumption when we build the theoretical model. For example, either in the case of single vacancy defect or in the case of multi-vacancy defect, we have used the same potential height and width. For the second allowed band, the distribution between 0.50 eV and 1.00 eV should be the stretch of α state system. It is corresponding to the area between points c and d in β state system in Fig. 4.

According to general theory, the top of β state system should be round and smooth, but we can see there is an indentation between points c and d as shown in Fig. 4. Whereas, this indentation just shows that the second allowed band exists in α state system. It can be found in Fig. 5, the second allowed band is between 0.50 eV and 1.00 eV, and from measured gap state curve it can be seen that the indentation appears just between 0.50 eV and 0.87 eV. It is shown that the α state system and β state system are of different properties; then, the second allowed band of α state system must compensate this part of the β state system, and forms an indentation. Contrarily, the corresponding part of β state system must compensate homologous area, and bring indentation in the

α state system. Both two pints a and b are sketched in Fig. 4. It can be seen from the hollow degree that the gap state density of second allowed band is very low. Furthermore, it is half-full, and there is no state to take it up from 0.87 eV to 1.00 eV.

4. Conclusion

From the above analyses and results, we know that the SnO_2:(Zn, In) film is of very good optical quality, and its transmittance presents excellent peculiarity in the wide range. Moreover, it is of very good electric conduction characteristic. Due to its amorphous structure, this film is of very good smoothness. The strong fluorescence phenomena prove the existence of gap states in amorphous film. Also due to the short-range order of amorphous structure, the distribution of gap state is discontinuous, and they may have allowed bands and forbidden bands. The gap state density reflects the intensity of fluorescence.

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