

Influence of doped Sb, In, P on Transparent and Conducting Characteristics of Thin Film of SnO₂ *

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Abstract: SnO₂ : (Sb, In, P) thin films were prepared by sol-gel process, in which the technique parameters of preparing were optimized and the better conditions of preparing were gained. The result of research indicates the In-doped mol proportion of 4% improves the structure of thin films effectively so as to increase its ultraviolet-visible light transmissivity remarkably; the Sb doping of 7% comes into being more free electrons to make its sheet resistance reduced; the P doping of 2% further enhances its conductance by reason of the forming of quasi-continuous doping energy band. On the basis of doped Sb, In and P, the sheet resistance and ultraviolet-visible light transmissivity of SnO₂ attain 38Ω/□ and 83% respectively.

Key words: Sol-gel technique; Doping; SnO₂; Transparent and conducting film

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0 Introduction

The transparent and conducting films are applied in many fields widely, such as solar battery, LCD, plasma display, the windows of modern fighting plane, and so on^[1]. Nowadays, the indium tin oxide (ITO) and doped thin film of SnO₂ are researched a lot^[2]. ITO thin film has better characteristic of transparence and conduction, however the resource of indium is shortage and the price is high. The thin film of doped SnO₂, rich resource and low price, is the earliest and commercial materials with the features of transparence and conduction. It has many characteristics, such as gas sensitivity, wet sensitivity, conduction, chemical stability, reflecting infrared, etc^[3]. Therefore, the thin film of SnO₂ attracts the great research interest of scientific researchers^[4].

At present, there are many methods of preparing the thin film of SnO₂, such as chemical vapor deposition (CVD) process, spray pyrolysis method and so on, and these methods based on harsh conditions that high temperature of reaction is required and the calcining procedure must be fulfilled. Usually the thin films using different methods of fabrication have different characteristics. The sol-gel process is carried out at low temperature and therefore by this technical process the doped thin films of SnO₂ are prepared

easily. Meanwhile by this method, doping process is quite accurate and well-distributed and large thin films are able to prepare easily^[5]. In this paper, SnCl₂ · H₂O is used as original materials, the SbCl₃, InCl₃ and (C₂H₅)₃PO₄ are used doping source, and the thin films and powder of SnO₂ : (Sb, In, P) are fabricated by sol-gel process. The technical parameters is optimized and the transparent and conducting characteristics are studied. The result shows that the thin films of SnO₂ have advantages of ITO, SnO₂ : Sb and SnO₂ : P. In a word, doped SnO₂ materials will be powerful potentiality in commercialization.

1 Experimental Setup

1.1 Preparation of thin films of SnO₂ : (Sb, In, P)

1.1.1 Preparation of thin films of SnO₂ : Sb^[6]

First of all, the pure quantified SnCl₂ · 2H₂O was dissolved in certain quantity ethanol, and pure water was put into. Thus, the solution with quantified density was formed. At 80 °C, the whole dispersed system was been circumfluent on magnetic blender several hours till the system took on light yellow, transparence and stability. In addition, some SbCl₃ was dissolved in ethanol, and certain quantity of the dispersed system of SbCl₃ was added into the solution of SnCl₂. During several hours at room temperature the colloid of Sn and Sb was gained. The colloid was spreaded evenly on the clean glass by facility. In order to get certain thickness, this process was fulfilled many times. At last, at different temperature and atmosphere, the glasses with dry colloid were calcined so as to get the thin films of SnO₂ : Sb.

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1.1.2 Preparation of thin films of SnO₂ : (Sb, In)^[6]

In order to acquire the thin film of SnO₂ : (Sb, In), InCl₃ was dissolved in ethanol, and certain density of In dispersed system was poured into the Sb and In colloid. After the system was churned up several hours, the colloid of Sn, Sb and In formed. Consequently, the colloid was spreaded on glass several times, and to acquire the film of SnO₂ : (Sb, In) the process of calcination was carried out.

1.1.3 Preparation of thin films of SnO₂ : (Sb, In, P)

(C₂H₅)₃PO₄ was dissolved in ethanol, and P dispersed system formed stably. According to certain proportion the dispersed system was added into the Sn, Sb and In colloid so as to form the new dispersed system of Sn, Sb, In and P. At 80°C, the whole dispersed system was been circumfluent on magnetic blender two hours till the system took on light yellow, transparence and stability. The colloid of Sn, Sb, In and P was spreaded on clean glass several times, and by calcination the thin film of SnO₂ : (Sb, In, P) was formed.

1.2 Adjustment of Resistance of SnO₂ : (Sb, In, P) Films

In order to gain the thin film of SnO₂ : (Sb, In, P) with low resistance, and on the basis of the theory of oxygenic volatilization the thin films were calcined in the atmosphere of nitrogen at certain temperature.

2 Results and Discussion

2.1 The influence of doped Sb on the conduction and transmissivity of SnO₂

The solution of Sn(OC₂H₅)₂ with the density of 0.5mol/L formed according to the technical parameters based on reference^[6]. The different mol proportion of Sb(OC₂H₅)₃ was poured into the solution of Sn(OC₂H₅)₂, which was 5%, 6%, 7%, 8%, 9% and 10% respectively. At 500°C, the acquired films were calcined two hours, and Fig. 1 is the curve of sheet resistance of Sb-doped SnO₂ films as a function of the Sb-doped amounts. According to the curve, with the increase of Sb-doped amounts, the curve lowers about to 460Ω at the point of 7%, and then it mounts up slowly. On the basis of doping theory of semiconductor, the doped Sb replaces the atom of Sn to release a free and surplus electron. Consequently, with the

enhancement of Sb-doped density, more and more Sn are replaced, and much more free electrons generates. Thus, the sheet resistance of films lower. However the rapid growth of doping must form a large number of defects of crystal lattice, and these defects cannot but drop the transferable rate of electrons down. This is the reason why the curve goes up again.

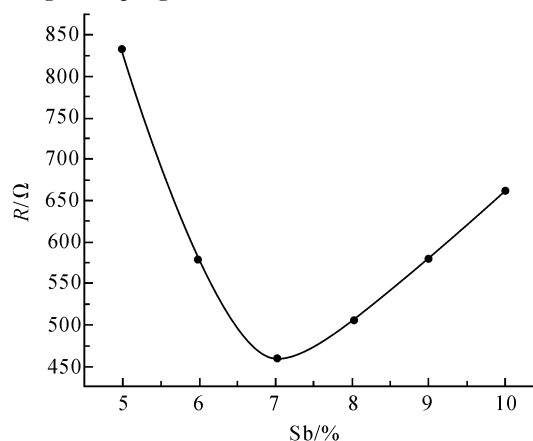


Fig. 1 Sheet resistance of sb-doped SnO₂ films as a function of thesb-doped amounts

The transmissivity of Sb-doped SnO₂ is slightly lower than pure SnO₂, and this situation is not discussed detailedly.

2.2 Influence of doped In on the conduction and transmissivity of SnO₂ : Sb

On the basis of Sb-doping by 7%, into the blended solution of Sn(OC₂H₅)₂ and Sb(OC₂H₅)₃, the In(OC₂H₅)₃ was put respectively at the mol rate: 1%, 2%, 3% and 4%. At 500°C, the acquired films were calcined two hours, and the thin film of SnO₂ : (Sb, In) was gotten. Fig. 2 is the curve of sheet resistance of (Sb, In)-doped SnO₂ films as a function of the In-doped amounts. Fig. 2 shows that with the increase of In - doped

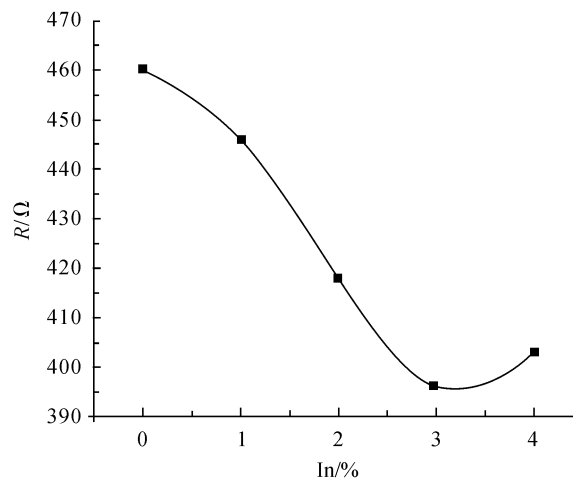


Fig. 2 Sheet Resistance of (Sb, In)-doped SnO₂ films as a function of the in-doped amounts

amounts, the sheet resistance of the thin films drop down slightly. While the curve goes up at the point of 3% (the value of sheet resistance is about 396Ω). The writer reckons the doped In improves the Sb to replace Sn further and thus some free electrons are released. When the amounts of doped In increase continuously, to certain extent, the doping of acceptor emerges, and partly the electrons are counteracted. Thus, the sheet resistance increases correspondingly.

With the increase of In-doped amounts, the transmissivity of the visible and ultraviolet light enhance remarkably, and the borderline of absorbency moves towards ultraviolet field. On the basis of analysis of Fig. 3, to large extent, doped In changes the internal structure of thin films to have the reflection declined.

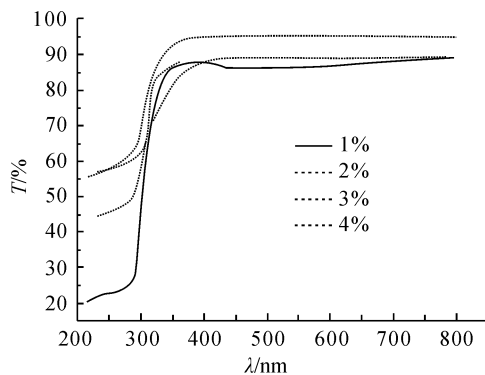


Fig. 3 Transmittance spectrum of $\text{SnO}_2 : (\text{Sb}, \text{In})$ thin film with the different in-doped amounts

2.3 The influence of doped P on the conduction and transmissivity of $\text{SnO}_2 : (\text{Sb}, \text{In})$

On the basis of the mol rates of 7% Sb doping and 4% In doping, into the blended solution of $\text{Sn}(\text{OC}_2\text{H}_5)_2$, $\text{Sb}(\text{OC}_2\text{H}_5)_3$ and $\text{In}(\text{OC}_2\text{H}_5)_3$, the solution of $(\text{C}_2\text{H}_5)_3\text{PO}_4$ in ethanol was poured respectively at the mol rate of 1%, 2%, 3%, 4%, 5% and 6%. In the same way, at 500°C , the gained films were calcined two hours, and the film of $\text{SnO}_2 : (\text{Sb}, \text{In}, \text{P})$ was gotten. Fig. 3 was the transmittance spectrum of $\text{SnO}_2 : (\text{Sb}, \text{In})$ thin film with the different in-doped amounts. Fig. 4 is the curve of sheet resistance of $(\text{Sb}, \text{In}, \text{P})$ -doped SnO_2 films as a function of the P-doped amounts. Fig. 4 indicates that the change of sheet resistance of the thin film takes on the pattern of valley. Obviously, the minimum value of the valley lies in about 3%, which is P-doped amount. With the gradual increase of P doping, the sheet resistance of the thin film rose quickly. Through analyzing above phenomena of experiments and the atomic radius and electronic configuration of doped Sb, In

and P, we drew some important conclusions: 1) the doped P replaced the position of Sb in crystal lattice of SnO_2 and became P^{5+} and thus a surplus electron came into being and participated to conduct; 2) these energy levels of local states of doped Sb, In and P lie in forbidden band, in which these energy levels of local states arrayed closely, and quasi-continuous energy band formed; 3) owing to the surplus electrons and quasi-continuous band, the sheet resistance of thin films was reduced greatly.

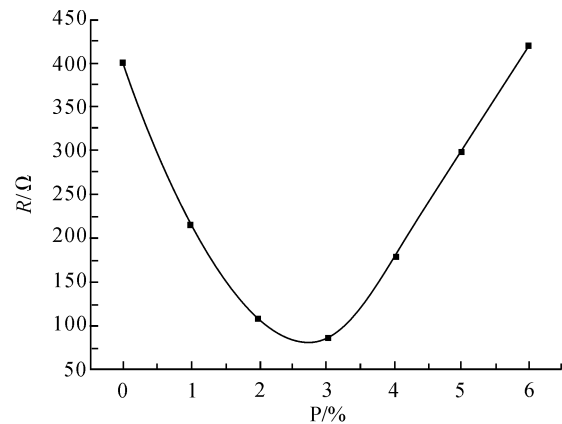


Fig. 4 Sheet resistance of $(\text{Sb}, \text{In}, \text{P})$ -doped SnO_2 films as a function of the P-doped amounts

When the P-doped amount was increased, the $(\text{Sb}, \text{In}, \text{P})$ -doped system became from transparency to white color, and transmissivity of visible and ultraviolet light dropped obviously. Fig. 5 is the transmittance spectrum of $\text{SnO}_2 : (\text{Sb}, \text{In}, \text{P})$ thin film with the different P-doped amounts. Basing on the analysis of theory on the Fig. 5, we reckoned that more and more $(\text{C}_2\text{H}_5)_3\text{PO}_4$ (namely P doping) destroyed the stabilization of dispersed system with Sb and In doping on account of the hydrolyzation of $(\text{C}_2\text{H}_5)_3\text{PO}_4$ and suspended granule came into being. Therefore, the color of the whole system

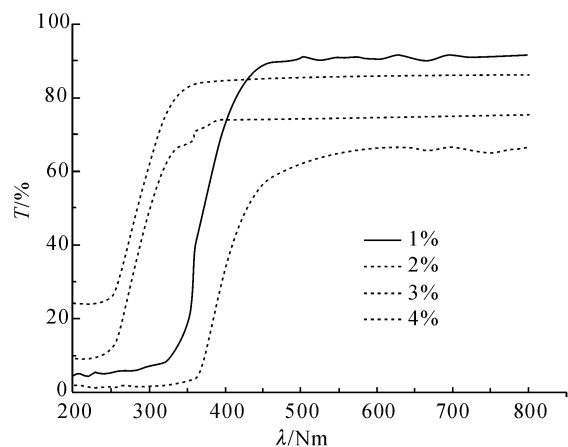


Fig. 5 Transmittance spectrum of $\text{SnO}_2 : (\text{Sb}, \text{In}, \text{P})$ thin film with the different p-doped amounts

got opacified slowly, and the transmissivity of SnO₂ : (Sb, In, P) fell in evidence.

3 Conclusion

In conclusion, by sol-gel method we prepared thin films of SnO₂ : (Sb, In, P) successfully, which had excellent characteristics of transparency and conduction. On basis of the transparent and conducting demand, when respective doping mol proportion of Sb, In and P are 7%, 4% and 2%, the quality of the thin films of SnO₂ is optimum. The sheet resistance and ultraviolet-visible light transmissivity are respectively 38Ω/□ and 83%. This simple process of technique takes on remarkable commercial value.

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Sb, In, P 掺杂对 SnO₂ 薄膜透明导电性能的影响

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摘要: 采用溶胶凝胶(Sol-Gel)技术制备了 SnO₂ : (Sb, In)透明导电薄膜, 优化了制备工艺参数, 获得了最佳制备条件. 研究表明, 4%的铟掺杂有效地改善了薄膜的内部结构, 使得紫外-可见光的透过率显著增加; 7%的锑掺杂释放出了更多的载流子, 使薄膜的方块电阻降低, 2%的磷掺杂因准连续杂质能带的形成进一步提高了薄膜的电导率. Sb, In, P的掺入使得 SnO₂ 薄膜的紫外-可见光的透过率达 83%, 方块电阻达 38Ω/□

关键词: Sol-Gel; 掺杂; 二氧化锡; 透明导电薄膜



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