

Effects of Ion Implantation on Electrical Properties of ITO Thin Film

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Abstract: $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) thin films were implanted by Sn^+ , Ag^+ and Mo^+ ions with different dose of implantation and annealed in air at 250 °C for 1 h. The as-deposited sample and implanted ones before and after annealing were characterized by Hall measurement to investigate the dependencies of the electrical properties of ITO on the metal kind and dose of ion implantation. It is indicated that various ion implantation decrease the conductivities of ITO, while heat annealing has an opposite effect. Mo^+ ion implantation supplies more carriers than Sn^+ and Ag^+ . Sn^+ ion implantation influences the mobility of ITO the least among the three kinds of ions. With a dose of $1 \times 10^{15} \text{ cm}^{-2}$, Mo^+ implantation and the following heat annealing increase the carrier concentration of ITO by 14%.

Key words: $\text{In}_2\text{O}_3:\text{Sn}$; ion implantation; heat annealing; electrical properties

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1 Introduction

As a kind of transparent conductive oxide (TCO), $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) thin film has a wide band gap, high optical transmittance in visible range, low electrical resistivity and high reflectivity to the infrared^[1]. With these outstanding characteristics especially the high electrical conductivity, ITO has been extensively used in various fields, including transparent conductive electrodes in displays, touch screens, thin film solar cells, light emitting diodes (LEDs), energy-efficient or smart coatings, and heat reflecting mirrors, *et al*^[2-4]. It is known that the low resistivity value of ITO is due to high carrier concentration caused by both oxygen vacancies and substitution tin dopants.

Numerous studies on preparation and properties of ITO films have been carried out with various methods. Researchers mainly bend

themselves to explore the deposition methods, clarify the influences of the deposition parameters, and obtain first-rank preparation conditions of ITO films^[5-7]. The present research focus still lies in the improvement of the optical and electrical properties of ITO thin films^[8].

Ion implantation technique is known as a significant method to dope conduction carriers into semiconductors^[9]. Meanwhile, it's also an important technique of surface modification^[10]. However, studies of the ion implantation effecting upon ITO thin films were rarely reported^[11,12].

As Sn itself is the doping element in ITO, while Ag is one of the most active metals, and the highest charge-state of Mo could reach 6^+ , in this paper, Sn^+ , Ag^+ and Mo^+ ions were chosen to be implanted into ITO thin films with different dose ranging from $1 \times 10^{15} \text{ cm}^{-2}$ to $1 \times 10^{16} \text{ cm}^{-2}$. All the implanted samples were

annealed in air at 250 °C for 1 h . Then, by the Hall measurement, the electrical properties, including the carrier concentration, Hall mobility and resistivity values of the samples before and after annealing are investigated and compared.

2 Experiments

A uniform piece of ITO conductive glass manufactured by Shenzhen Laibao High Technology Corporation was cut into twenty square samples with the size of each one being 25 mm×25 mm. The as-deposited samples had a film thickness of 350 nm and sheet resistivity of 4.0 Ω/□ with the errors limited within 3%. A MEVVA ion implantation instrument^[13] built by Institute of Low Energy Nuclear Physics, Beijing Normal University, was used to carry out the ion implantation experiments. The ion kinds and doses of the implantation upon each sample are listed in Table 1. The excitation voltage and ions beam are 40 keV and 0.5 mA, respectively.

Table 1 Implantation ions and dose upon different samples

Ions	Sample No.	Dose(×10 ¹⁵ cm ⁻²)
None	0 [#]	0
	1 [#]	1
	2 [#]	5
	3 [#]	10
Sn ⁺	4 [#]	1
	5 [#]	5
	6 [#]	10
Ag ⁺	7 [#]	1
	8 [#]	5
	9 [#]	10

After ion implantation, 1[#] ~ 9[#] samples were annealed. In order to avoid the deviation of the chemical components induced by high temperature, 250 °C was chosen in this work^[14]. The heat annealing was carried out in a tubular oven under air atmosphere at 250 °C for 1 h. The thickness of the films was monitored by an α-step surface profiler (Dektak IIA). Hall measurement was used to determine the resistivity,

carrier concentration and Hall mobility of the ITO samples. All the characterizations were performed at room temperature.

3 Results and Discussion

The dependencies of electrical properties of ITO thin films on the dose of Mo⁺ ion implantation are shown in Table 2 and Fig. 1, where the values of resistivity (ρ), Hall mobility (μ) and carrier concentration (N_e) are illustrated. The relationships among the three values can be expressed by ^[15]

$$R_H = \frac{1}{f \cdot N_e \cdot e} = \mu \cdot \rho \tag{1}$$

in which R_H represents the Hall coefficient of semiconductor and f is f-factor with its approximate value being 1 in this work. The last column of Table 2 lists the values of $\frac{\rho_x - \rho_0}{\rho_0} \times 100\%$ (x means the No. of the sample), indicating the variations of electrical resistivity between the processed samples and the as-deposited one. Fig. 1 shows the resistivity and carrier concentration values of the samples visually.

Table 2 Mobilities and variations of resistivity values of Mo⁺ ion implanted samples before and after heat annealing

Sample No.	Annealing State	Hall Mobility (cm ² /V · s)	Rate of ρ-Variation(%)
0 [#]	None	42.0	0
1 [#]	Before	36.0	18.7
	After	38.5	−4.9
2 [#]	Before	36.0	24.8
	After	38.0	−0.6
3 [#]	Before	37.0	58.9
	After	39.5	24.1

Evident information can be obtained from Table 2 and Fig. 1 that all the implanted samples have lower Hall mobility than the as-deposited ITO. The decrease extent reaches 6 cm²/V · s. Meanwhile, before heat annealing, the carrier concentration goes down induced by Mo⁺ ions

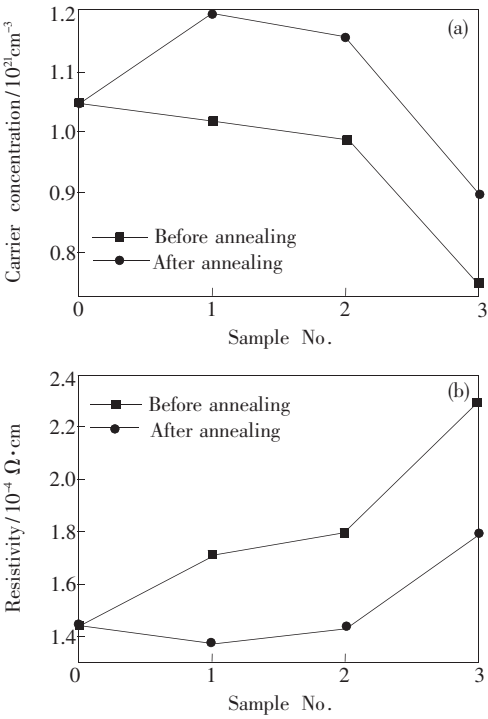


Fig. 1 Carrier concentration (a) and resistivity values (b) of ITO thin films implanted with Mo⁺ ions before and after heat annealing

implantation. As the dose of implantation increases from 0 to $1 \times 10^{16} \text{ cm}^{-2}$, the N_e value decreases from $1.049 \times 10^{21} \text{ cm}^{-3}$ to $7.490 \times 10^{20} \text{ cm}^{-3}$. On the other hand, heat annealing has opposite influences on the electrical properties. Not only the values of Hall mobility, but also those of the carrier concentration are increased by the annealing process. Although the Hall mobility could not return to $42 \text{ cm}^2/\text{V} \cdot \text{s}$, the N_e values of sample 1[#] and 2[#] exceed the un-implanted one. When the dose is $1 \times 10^{15} \text{ cm}^{-2}$, the implanted ITO sample after heat annealing obtains a carrier concentration of $1.196 \times 10^{21} \text{ cm}^{-3}$, which is 14% higher than that of the un-implanted one. According to Eq. 1, the resistivity of the sample is a result determined by μ , N_e and f values. The relatively greater increase of the N_e -value than the drop of μ -value results in the decrease of ρ -value by 4.9%.

The results can be explained as the following. Process of ion implantation will induce

damages in the structure of semiconductors and lead to a large number of defects. At the same time, the implanted ions often exist at the interval positions instead of the replacement ones, which means the implanted Mo^{x+} ($x = 1 \sim 6$)^[16] ions have not been activated or stimulated^[14]. As a result, before heat annealing, compared with the as-deposited ITO thin film, the implanted samples have a decrease in both Hall mobility and carrier concentration. However, heat annealing can partly eliminate the damages and defects in the films and activate the implanted ions. At 250 °C, Mo^{4+} , Mo^{5+} and Mo^{6+} ions can be stimulated and part of them replace In^{3+} or Sn^{4+} , supplying more electrons. Mo ions play the roles of donors. Meanwhile, the ratio of activated ions to the implanted ones will decrease as the implantation dose increases^[14]. Consequently, the top value of carrier concentration, 14% higher than that of the un-implanted sample, is obtained when the implantation dose is $1 \times 10^{15} \text{ cm}^{-2}$. Similar phenomenon can be found in the implantation effects upon GaAs and other compound semiconductors^[14].

As to Sn^{+} ion implantation, the electrical properties of ITO samples are showed in Table 3 and Fig. 2. The atomic diameter of Sn is 0.158 nm, which is the most similar to the diameter of In atom (0.167 nm). For this reason, damages caused by Sn^{+} ion implantation should be less than those brought by Mo^{+} and Ag^{+} implantation. From the Hall mobility column of Table 3, the correspondence result can be seen that the variations of mobility are in a small extent. However, after implantation and the following heat annealing, the ITO samples can't exceed the un-implanted one in the number of carrier concentration. Through simulated calculation, Fan Zhixin *et al*^[17] reported that the theoretical upper limit of the carrier concentration value of ITO is $1.475 \times 10^{21} \text{ cm}^{-3}$. No sample in this experiment reaches this limit. Therefore, the object of improving the electrical conductivity of

Table 3 Mobilities and variations of resistivity values of Sn⁺ ion implanted samples before and after heat annealing

Sample No.	Annealing State	Hall Mobility (cm ² /V · s)	Rate of ρ -Variation(%)
0 [#]	None	42.0	0
4 [#]	Before	40.0	10.6
	After	41.0	2.3
5 [#]	Before	38.5	16.2
	After	41.0	8.9
6 [#]	Before	39	20.7
	After	41.0	10.3

Table 4 Mobilities and variations of resistivity values of Ag⁺ ion implanted samples before and after heat annealing

Sample No.	Annealing State	Hall Mobility (cm ² /V · s)	Rate of ρ -Variation(%)
0 [#]	None	42	0
7 [#]	Before	37	33.4
	After	41	7.1
8 [#]	Before	38	36.8
	After	40	9.2
9 [#]	Before	37	39.7
	After	41	17.0

Table 4 and Fig. 3 show the effects of Ag⁺ ion implantation and heat annealing on the electrical properties of ITO thin film. Apparently, as to the improvement of conductivity, the contributions of Ag⁺ ions are even less than Sn⁺ ion implantation because of the average charge state (3+) of Ag ions produced by MEVVA^[16] is higher than its stable charge state(1+). On the

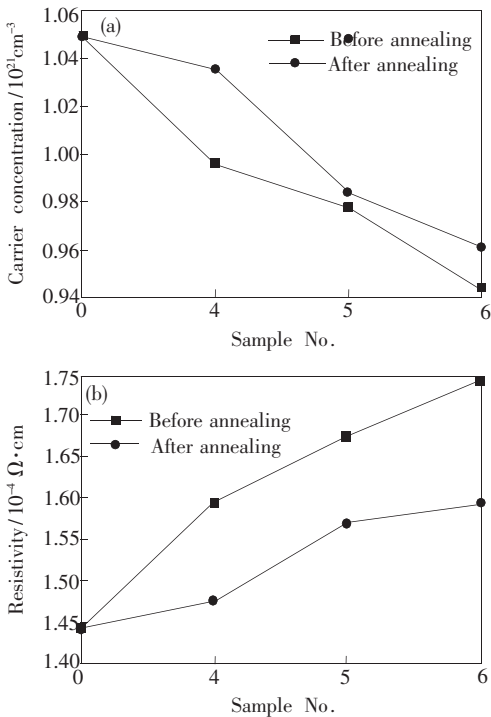


Fig. 2 Carrier concentration (a) and resistivity values (b) of ITO thin films implanted with Sn⁺ ions before and after heat annealing

ITO by Sn⁺ ion implantation is not realized here. There are probably two reasons as below. The implantation dose, 1 × 10¹⁵ cm⁻² has exceeded the saturation point of implantation dose and O²⁻ vacancy can't be influenced by Sn⁺ ion implantation. Further investigations are carried out to clarify whether lower dose of Sn⁺ ion implantation could increase the carrier concentration of ITO to approach the upper theoretic limit.

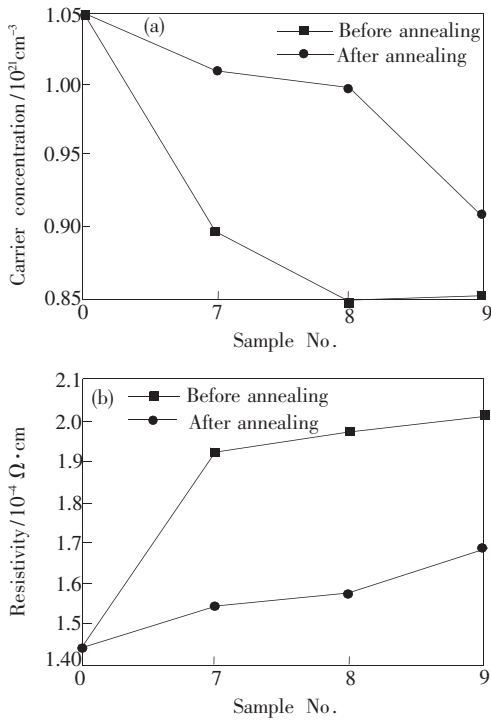


Fig. 3 Carrier concentration (a) and resistivity values (b) of ITO thin films implanted with Ag⁺ ions before and after heat annealing

other hand, although Ag itself is an active metal, the discontinuous distribution of the implanted ions in the films will obstruct the electron conduction.

4 Conclusion

Sn^+ , Ag^+ and Mo^+ ions were respectively implanted into ITO thin film samples with different dose ranging from $1 \times 10^{15} \text{ cm}^{-2}$ to $1 \times 10^{16} \text{ cm}^{-2}$. Afterwards, all the implanted samples were annealed in air at 250°C for 1 h. Then, by the Hall measurement, the electrical properties

of both processed and as-deposited samples were determined and compared. Among these three kinds of ions, only Mo^+ ion implantation with the following heat annealing can increase the carrier concentration and electrical conductivity of ITO thin film. Mo ions can play as donor in the doping process. Sn^+ ion implantation reduces the mobility least, although it can not supply more electrons with the applied dose in this work. The implantation of Ag^+ is also proved to be an inappropriate method to improve the electrical properties of ITO.

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离子注入对 ITO 薄膜电学特性的影响

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摘 要

对系列 $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) 薄膜样品分别实施了不同剂量的 Sn^+ , Ag^+ 和 Mo^+ 离子注入并将它们在 $250\text{ }^\circ\text{C}$ 下进行了热处理。利用霍尔测量研究了原始样品及注入和退火前后各样品的电学特性。研究了 ITO 薄膜的电学参数受离子注入的种类及剂量的影响。实验证明不同种类的离子注入会不同程度地降低 ITO 的导电性能, 但热处理的效应与之相反。3 种金属中, Sn^+ 离子对薄膜造成的注入损伤最小, 而高价的钼离子可以替换铟离子的位置成为施主, 当注入剂量为 $1\times 10^{15}\text{ cm}^{-2}$ 时, 经过 Mo^+ 离子注入和后续退火的 ITO 薄膜, 载流子浓度提高了 14%。

关 键 词: $\text{In}_2\text{O}_3:\text{Sn}$ (ITO); 离子注入; 热退火; 电学特性

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