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Study on fluorine-doped indium oxide films deposited by reactive evaporating in CF_4/O_2 gases

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Abstract

Fluorine doped In_2O_3 films were deposited by DC plasma enhanced evaporating in CF_4/O_2 mixture gases. The effects of F-doping and annealing on the electrical and optical properties of the films have been investigated. The film resistivity significantly decreased, but the transmittance became low due to F-doping. The film transmittance can be improved by annealing in the vacuum. The annealing at higher temperature is required for higher F-doped amorphous In_2O_3 films to be crystallized. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: ITO film; F-doping; Plasma enhanced evaporating

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1. Introduction

Sn-doped In_2O_3 (ITO) film is at present practically used as transparent electrodes in liquid crystal displays, electroluminescent displays or solar cells, due to its relative low resistivity and high visible transmittance [1,2]. Free carrier density of ITO film is known to be dominated by the following two kinds of donor sites: (1) substitutional four-valent Sn^{4+} ions at three-valent In^{3+} site; (2) oxygen vacancies. Other cation doping elements, such as Te, Zr and Hf were studied on In_2O_3. However, none of them were more effective than Sn [3–5]. On the other hand, anion doping of fluorine (F) could be worth trying, and substitution replacement of one-valent of negative ion F^- with two-valent negative ion O^{2-} is expected. A study on F-doped In_2O_3 films deposited by RF magnetron sputtering has been performed [6]. It has been reported that the F-doping of In_2O_3 was carried out by two different methods: (1) placing InF_3 pellets on the erosion area of the In_2O_3 target, and (2) introducing CF_4 gas into the sputtering chamber. In both cases, the systematic increase in carrier density was observed with F/O ratio in the films, but doping efficiency was higher in the case (1) than in case (2).

The plasma enhanced reactive evaporation is one of the most promising techniques for obtaining commercial uniform coating in large area. Sn-doped In_2O_3 films with transmittance higher than 85% and resistivity of 1.5×10^{-3} Ω cm, were deposited by using this technique [7]. In this study, F-doped In_2O_3 films were prepared by DC plasma enhanced reactive evaporation in the mixture of CF_4/O_2 gases. The changes in structure, resistivity and transmission of In_2O_3 films with F-doping and annealing have been investigated in detail.

2. Experimental

The film samples with thickness of 200 nm were deposited on soda-lime glass substrates at 100 °C with 99.99% pure indium in a vacuum evaporating apparatus. Before depositing, firstly the chamber was pumped up to 2×10^{-3} Pa, then the reactive gases of CF_4 and O_2 were fed in. Two mass flow controllers controlled their flow rates, respectively. In the experiments, the

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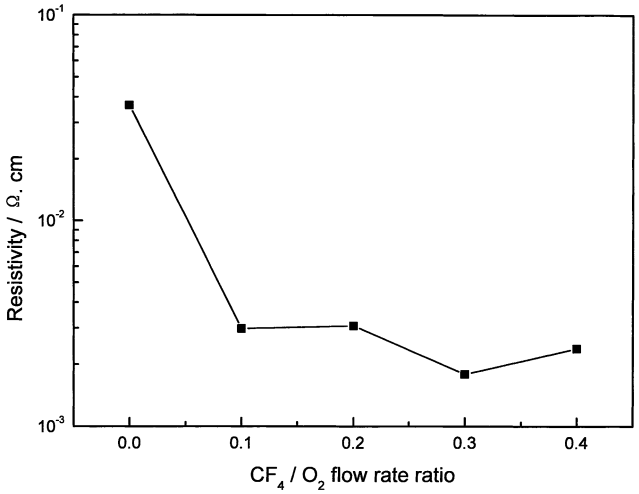

Fig. 1. Resistivities of the as deposited films at several CF_4/O_2 flow rate ratios.

flow rate of O_2 was fixed at 5 sccm and the flow rate of CF_4 was varied when CF_4/O_2 ratios were kept at 0.1, 0.2, 0.3, and 0.4 under a total pressure of 2 Pa. The low temperature plasma was formed by DC glow discharge during the depositions in order to enhance the reactions of oxidizing and F-doping.

After the depositions, the samples of F-doped and nondoped films have been annealed in the situ of the pressure of 2×10^{-3} Pa at 300, 400 and 500 °C for 30 min, respectively. The film thickness was measured with a surface profiler. The resistivity, Hall mobility and carrier density of the films were estimated by the four-point probe and Hall effect measurements. The film transmittance was obtained by an UV–VIS spectrometer. The X-ray diffraction was carried out by 40 kV, 20 mA Cu K_α radiation.

3. Results and discussion

F-doping of the films were carried out by introducing CF_4 into the chamber. Fig. 1 shows the resistivities of the films prepared with varying CF_4/O_2 ratio at substrate temperature of 100 °C. It indicates that the resistivities of F-doped films are much lower than nondoped film. For example, it decreased from 2.4×10^{-2} Ω cm for nondoped film to 2.8×10^{-3} Ω cm for F-doped film deposited at $CF_4/O_2 = 0.1$. The results also show that the film resistivity rapidly decreases by increasing CF_4, when CF_4/O_2 is lower than 0.1, then its change becomes slow. The decrease of the film resistivity is because that some of the doped F^- ions might terminate In^+ ions (such as –O–In–O–In–F), and the systematic increase in carrier density was clearly observed for doped films. For comparison, the resistivities of the F-doped films deposited using two sputtering methods reported in [6] and reactive evaporating in this paper have been shown in Table 1.

From Table 1, the resistivities of F-doped films deposited by three methods were much lower than one of nondoped films. For example, it decreased from 8.0×10^{-2} to 2.5×10^{-3} Ω cm for the films deposited by reactive sputtering at $CF_4/Ar = 0.04$, and 1.5×10^{-3} Ω cm for the film deposited by sputtering with a mixture target placing three InF_3 pellets. But the decreases of the resistivities become slow with continuous increasing F-doping (more CF_4/Ar or InF_3 pellets). These results coincide with the one obtained from this study. The resistivities of F-doped films deposited by reactive evaporation is about $1.5–3.0 \times 10^{-3}$ Ω cm. This shows that the plasma reactive evaporation is an effective method to deposit F-doped In_2O_3 films with low resistivity.

To investigate the effect of annealing on the film resistivity, the nondoped and F-doped films prepared at different CF_4/O_2 flow ratios were annealed at 300, 400 and 500 °C, respectively. Fig. 2 shows that the resistivity of the nondoped film changed much by annealing. It decreased obviously with increasing temperature, but the resistivity of F-doped film did not almost affected by heating. In addition, the resistivity of F-doped film is still much lower than nondoped, after high temperature annealing of 500 °C. This shows that F-doped film has more stable structure. It could be because that $In_2O_{3-x}F_x$ was formed in the film owing to F-doping. They are more thermal stable components under high temperature than In_2O_3.

Fig. 3 shows the Hall mobility, μ (a), carrier density, n (b), and resistivity, ρ (c) for the as deposited and post-annealed at 300 and 500 °C films prepared in the case of $CF_4/O_2 = 0–0.4$. For nondoped In_2O_3 film, the

Table 1
The resistivities of the films prepared by three methods

Reactive evaporation		Reactive sputtering		Sputtering with mixture target	
CF_4/O_2	ρ (Ω cm)	CF_4/Ar	ρ (Ω cm)	Placing InF_3 pellet	ρ (Ω cm)
0	2.4×10^{-2}	0	8.0×10^{-2}	0	8.0×10^{-2}
0.1	2.8×10^{-3}	0.03	5.0×10^{-3}	1	3.2×10^{-3}
0.2	2.9×10^{-3}	0.04	2.5×10^{-3}	2	1.5×10^{-3}
0.3	1.8×10^{-3}	0.05	5.0×10^{-3}	3	2.0×10^{-3}

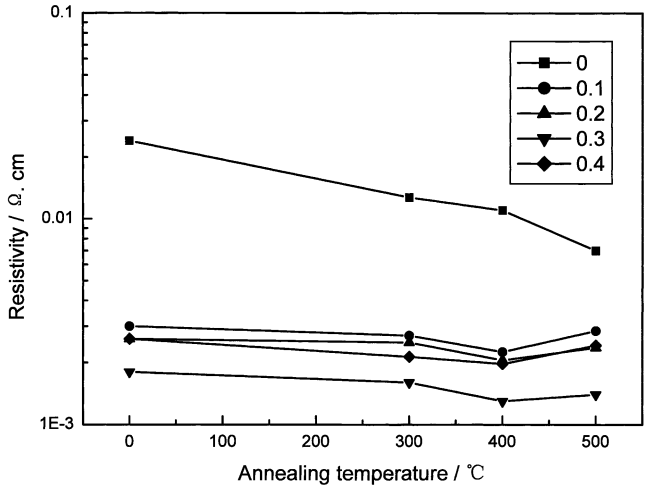

Fig. 2. Resistivities of the films prepared at several CF_4/O_2 flow rate ratios as a function of annealing temperature.

carriers are generated by the oxygen vacancies [8]. The increase in n for the post-annealed films was, therefore, attributed to an increase in oxygen vacancies caused by vacuum annealing in the absence of oxygen. The clear decrease in ρ was due to the increase in n after annealing while no notable change in μ was observed. For F-doped In_2O_3 film, a remarkable increase in n by F-doping was obtained. This result implies that F^- ions substituted for O^{2-} ions in the In_2O_3 host lattice. The μ slight decreases with increasing F-doping suggests an increase in the ionized impurity scattering center. But ρ decrease gradually with increasing CF_4 flow rate as a result of the significant increasing in n, in spite of a decrease in μ.

In the experiments, we also found that F-doping of the film affected its transmission. The transmittance spectra of the films deposited at several CF_4/O_2 ratios are shown in Fig. 3. It can be seen that the transmittances of all F-doped films are lower than nondoped films in the range of 300–800 nm, and the more F is doped in the film, the more transmittance decreased.

The effects of annealing on the film transmission have been studied. Fig. 4 shows the transmittance of nondoped films after annealing at 300, 400 and 500 °C. The film transmittance increased after annealing with increasing temperature, especially in the range of short wavelength. It also shows that the effect of annealing on F-doped film transmittance is much higher than nondoped. You can see from Fig. 4 that the transmittance of the film prepared at $CF_4/O_2 = 0.4$ increased much in the all measured wavelength range after 500 °C annealing.

To investigate the effects of F-doping and annealing on the film crystallinity, XRD analysis was carried out. It shows that all of nondoped and F-doped In_2O_3 films as deposited at 100 °C are amorphous, and their structures can transfer from amorphous to polycrystalline by annealing, but the heating temperature depends on the F-doping quantity. Fig. 5 shows that XRD patterns of nondoped film, and F-doped films obtained at $CF_4/O_2 = 0.2$, 0.3 after annealing at 300 °C. A clear (222) diffraction peak at 30° peak was observed for nondoped film. This indicated that nondoped film was crystallized by 300 °C annealing. However (222) peak for the film deposited at $CF_4/O_2 = 0.2$ was small, and higher F-doping film (deposited at $CF_4/O_2 = 0.3$) was still amorphous. This result shows that the crystallinity of the film becomes poor by F-doping. A higher temperature annealing is necessary to crystallization for higher F-doped film. Fig. 6 shows that XRD patterns of the films obtained at $CF_4/O_2 = 0.3$ after annealing at different temperatures. (222) Peak can be seen when the temperature is 400 °C. Then this peak became higher and shaper, and (400) and (440) peaks also appeared

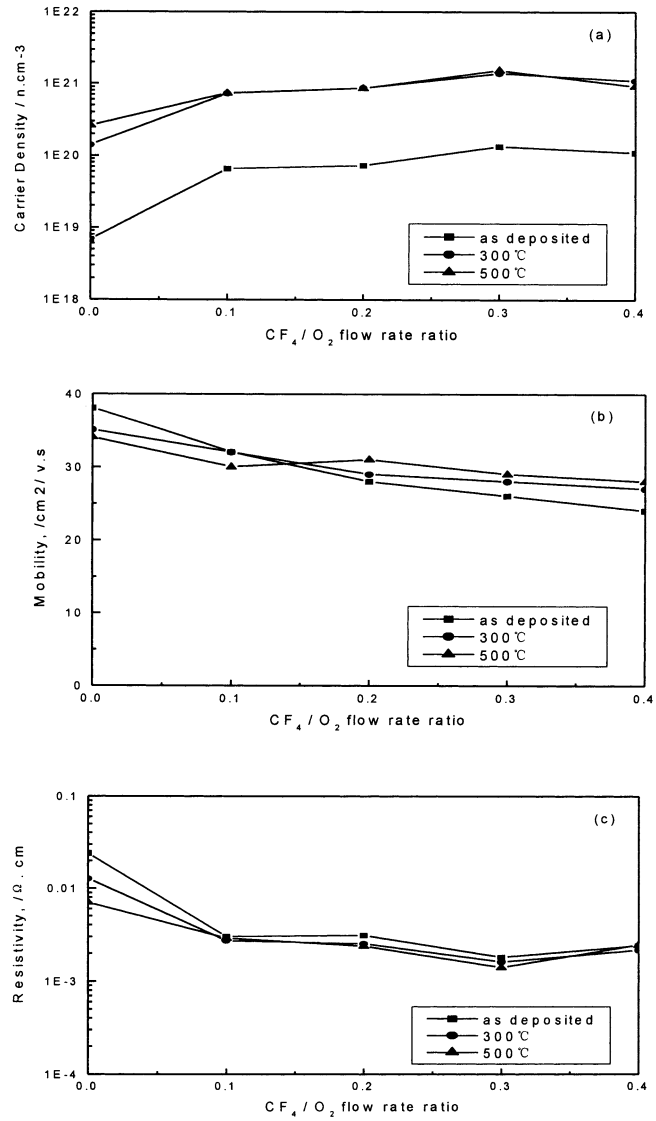

Fig. 3. (a) Carrier density; (b) Hall mobility; (c) resistivity of the as deposited and post-annealed films prepared at varying CF_4/O_2 ratio.

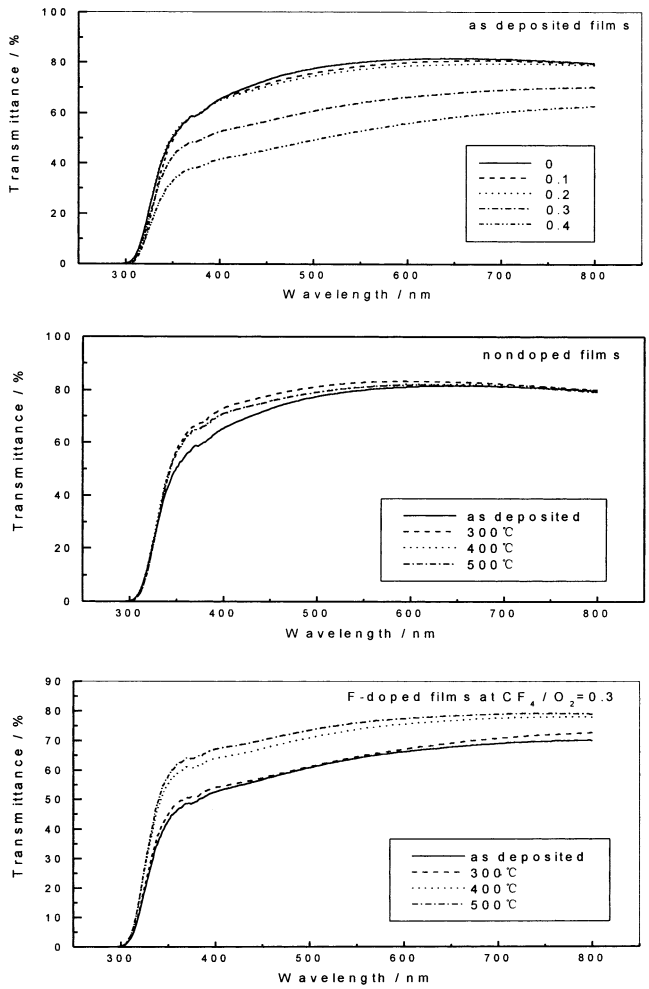

Fig. 4. The transmittances of the films (a) as deposited at several CF4/O_2; (b) nondoped, post-annealed at several temperatures; (c) F-doped, post-annealed.

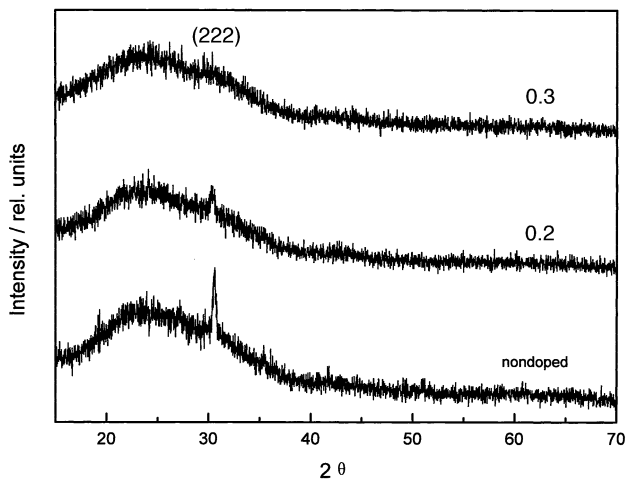

Fig. 5. The XRD patterns of the nondoped and F-doped films after 300 °C annealing.

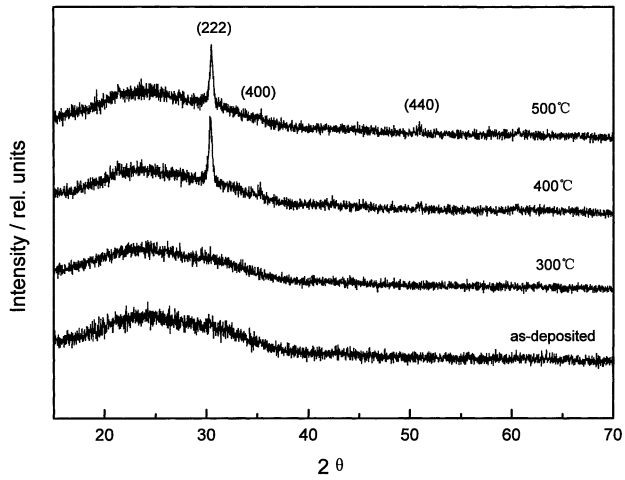

Fig. 6. The XRD patterns of the F-doped films prepared at $CF_4/O_2 = 0.3$ after annealing at several temperatures.

when the temperature goes up to 500 °C. This indicates the increasing crystallite size and upgrade of crystallinity. It is known that the transmittance of the films depends on its crystallinity. XRD analysis explained that why the transmittance of the films after F-doping degraded, and it can be improved by annealing.

4. Conclusions

The transparent and conductive F-doped In_2O_3 films with low resistivity and high transmittance were deposited by DC plasma enhanced reactive evaporating using CF_4/O_2 as the source gases. The effects of F-doping and annealing on the film resistivity and transmission have been investigated. The results show: (1) the film resistivity decreases with F-doping; (2) the change of resistivity for F-doped film by annealing is much lower than nondoped film. This indicates that F-doped In_2O_3 film has better thermal stability and (3) the transmittance of the film degraded with F-doping. It can be upgraded by annealing owing to improving the crystallinity. Higher F-doping film needs annealing at higher temperature.

Acknowledgements

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