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Fluorine-doped indium oxide thin films prepared by chemical vapor deposition

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Transparent conductive fluorine-doped indium oxide thin films were prepared by an atmospheric-pressure chemical vapor deposition method. The raw material was \([\text{C}_7\text{H}_{15}\text{C}_0\text{O}_2]\)\(_2\) In[H\((\text{CF}_2)_4\text{COO}\)]. The polycrystalline films were obtained at a reaction temperature in the range of 350-450 °C. This chemical vapor deposition method incorporates fluorine atoms into a crystalline structure and consequently leads to a high carrier concentration, yielding fluorine-doped indium oxide films of low resistivity. For the 320-nm-thick film deposited at 380 °C, the resistivity was \(4.4 \times 10^{-4}\ \Omega \cdot \text{cm}\), and the sheet resistance was 13.8 \(\Omega/\square\).

I. INTRODUCTION

Indium oxide (\(\text{In}_2\text{O}_3\)) thin films have a wide range of applications, e.g., transparent electrodes of liquid crystal and other displays, with developing preparation methods of thin films of high quality. In particular, \(\text{In}_2\text{O}_3\) films doped with tin (ITO) are widely used as transparent conductive films. Recently, fluorine-doped indium oxide (\(\text{In}_2\text{O}_3\):F) has been reported to have potential applications as a transparent conductive film.

High-quality \(\text{In}_2\text{O}_3\) film has been prepared by various physical vapor deposition methods such as vacuum evaporation, rf sputtering, dc sputtering, and rf ion plating. However, reports on the use of the chemical vapor deposition (CVD) methods are few in spite of the fact that the CVD method does not require a high vacuum and accordingly has the advantage of relative ease for large-scale application, granting the possibility of coating complicated shapes. \(\text{In}_2\text{O}_3\) film has been difficult to prepare by the thermal CVD method because of a lack of volatile, thermally stable precursor materials. In addition, the \(\text{In}_2\text{O}_3\):F film deposition processes have suffered from a lack of reproducibility because of the difficulty in doping fluorine.

In this paper, an indium 2-ethylhexanoate derivative is proposed as a precursor material for obtaining \(\text{In}_2\text{O}_3\):F films. The low-temperature CVD of this raw material, which involves bonds with fluorine atoms, yields fluorine-doped films with no need of supplying a fluorine donor. The reaction temperature for obtaining the film of the lowest resistivity will be discussed on the basis of the carrier concentration and mobility which were measured by using the Hall effect.

II. EXPERIMENT

Indium 2-ethylhexanoate derivative (\(\text{[C}_7\text{H}_{15}\text{C}_0\text{O}_2]\)\(_2\) \(\times\) \(\text{In}\ [\text{H}(\text{CF}_2)_4\text{COO}\])\), Nihon Kagaku Sangyo Co., Ltd.) of reagent grade was used as the source materials. \(\text{[C}_7\text{H}_{15}\text{C}_0\text{O}_2]\)\(_2\) In[H\((\text{CF}_2)_4\text{COO}\)] was placed in a container maintained at 280 °C. The generated gas was entrained by nitrogen carrier gas.

FIG. 1. X-ray diffraction patterns of the \(\text{In}_2\text{O}_3\):F film deposited on borosilicate glass substrate at 380 °C.
temperature. Within the range of reaction temperature, the ratio is consistently larger than that (0.33) for the nonoriented polycrystalline, indicating (400) plane texturing, which was observed in fluorine doping$^4$ and tin doping$^5,6$ for $\text{In}_2\text{O}_3$ film. Figure 3 shows the full width at half maximum (FWHM) of the (400) diffraction peak as a function of reaction temperature. The result suggests that the crystallite size in [400] direction monotonically decreases with increasing reaction temperature. From the value of the FWHM of the (400) diffraction peak, the crystallite size in [400] direction was obtained to be 43 nm at 400°C.

Figure 4 shows the electric resistivity, carrier concentration, and Hall mobility for the $\text{In}_2\text{O}_3$:F film as a function of reaction temperature. The carrier concentration shows the maximum value at about 370°C, while the Hall mobility peaks at about 430°C. As a result, the $\text{In}_2\text{O}_3$:F film give the minimum value of resistivity at 380–400°C. The lowest resistivity was obtained for the film deposited at 380°C; the resistivity was $4.4 \times 10^{-4} \ \Omega \ \text{cm}$, and the sheet resistance was 13.8 Ω/□ for the 320-nm-thick film. About the carrier concentration, the fluorine content of the film is expressed as the atomic ratio F/In, and it is shown in Fig. 5 as a function of the reaction temperature. The fluorine content is maximum at 370°C, and the content decreases with increasing temperature from 370°C. A comparison of Fig.

![Graph 1](image1.png)

**FIG. 2.** Ratio of the intensity of (400) peak to (222) peak as a function of reaction temperature.

![Graph 2](image2.png)

**FIG. 4.** Electric resistivity, carrier concentration, and Hall mobility for $\text{In}_2\text{O}_3$:F film as a function of reaction temperature.

![Graph 3](image3.png)

**FIG. 3.** Full width at half maximum (FWHM) of the diffraction peak corresponding to the (400) reflection as a function of reaction temperature.

![Graph 4](image4.png)

**FIG. 5.** The ratio F/In of $\text{In}_2\text{O}_3$:F film as a function of reaction temperature.
and Fig. 4 shows that temperature dependence of fluorine content is similar to that of carrier concentration. However, the fluorine concentration of the film is higher than that of carrier concentration. For example, at reaction temperature 400 °C the former is \(3.2 \times 10^{21} \text{ cm}^{-3}\) (F/In = 0.1), while the latter is \(4.1 \times 10^{20} \text{ cm}^{-3}\). Extra fluorine atoms are inferred to be incorporated into the film as neutral dopants.

Figure 6 shows the optical transmittances for the 98-nm-thick film deposited on a quartz glass substrate at 380 °C. The transmittance is more than 80% in the wavelength range above 400 nm. Figure 7 shows the square absorption coefficients \(\alpha^2\) as a function of photon energy. The extrapolations to the abscissa indicate that the optical energy gap of \(\text{In}_2\text{O}_3\):F for the direct transition is 3.72 eV. Thus no deviation from the value for \(\text{In}_2\text{O}_3\) by fluorine doping is observable.

**IV. CONCLUSIONS**

Transparent conductive fluorine-doped indium oxide thin films were prepared by an atmospheric-pressure chemical vapor deposition method. The raw material was \([\text{C}_3\text{H}_5\text{COO}]_2\text{In}\{\text{H}[(\text{CF}_2)_2\text{COO}]\}. The polycrystalline films were obtained at a reaction temperature in the range of 350–450 °C. This chemical vapor deposition method incorporates fluorine atoms into a crystalline structure and consequently leads to a high carrier concentration, yielding fluorine-doped indium oxide films of low resistivity. For the 320-nm-thick film deposited at 380 °C, the resistivity was \(4.4 \times 10^{-4} \Omega \text{ cm}\), and the sheet resistance was 13.8 Ω/□.

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