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The characterization of fluorine doped tin oxide films by Fourier Transformation Infrared spectrum

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ABSTRACT

SnO_2 films, both undoped and doped with fluorine were prepared by spray pyrolysis technique. The FTIR spectrum was employed to investigate the oxygen vacancy and substitution of fluorine in SnO_2 lattice. The feature of SnF_2 confirms the substitution of fluorine for oxygen. The result of substitution can be expressed as a defect model of SnO_xF_{2-4x}, which serves as the donor of free electrons. The cutoff wavelength of reflectivity is calculated and confirms the rationality of SnO_xF_{4-x} model for fluorine doped SnO_2 film. The calculation indicates that the carrier concentration is a decisive role for the reflectivity of fluorine doped SnO_2 film.

1. Introduction

Tin oxide (SnO_2) has been a promising material in technological applications due to its excellent optical and electronic properties [1–3]. Recent years have witnessed its extensive use in solar energy, low-emission glass and thermal insulation [4,5]. Its high reflectivity in infrared band makes it suitable for coatings on energy-saving window, lamp and furnace window. The SnO_2 films can be prepared by many techniques, such as chemical vapor deposition, sputtering, spray pyrolysis, etc. Among these, spray pyrolysis (SP) is the most convenient method in the industry because of its simplicity, low cost, high growth rate and mass production capability for uniform large area coatings [6].

The stoichiometric SnO_2 film has low reflectivity property. Its weak reflectivity is supposed to be due to the double ionized oxygen vacancies serving as donors. To improve its optical reflectivity, doping with Sb, Cl, Br and F has been achieved by adding a suitable compound of the dopant [7]. Fluorine (F) has been shown to be the most effective of these dopants. It has been supposed that fluorine atoms substitute oxygen in the lattice and play the role of donors. However, the experimental evidence of the substitution and oxygen vacancy is scarce. In this paper, the evidence of oxygen vacancy and substitution of fluorine for oxygen is shown and discussed. The effects of fluorine doping on the carrier concentration and mobility are also indicated. We further evaluate the decisive parameter of optical reflectivity according to the plasma response frequency of free carrier.

2. Experimental

The SnO_2 films were prepared by a spray pyrolysis coating setup. An aqueous solution of high pure stannic chloride ($SnCl_4 \cdot 5H_2O$) was used as the deposition solution. Fluorine doping was achieved by adding ammonium fluoride (NH_4F) to the solution, fixed at 15 wt.% according to previous research works [8,9]. The atomization was carried out by ultrasonic agitation and carried by the compressed air to the deposition chamber. The structure of the films was investigated by X-ray diffraction (Rigaku, Rint-2200) and a Fourier Transform Infrared (FTIR) spectrometer (Bruker, Tensor27). The carrier concentration and Hall mobility were obtained by a Hall measurement (Ecopia, HMS3000) in van der Pauw configuration at room temperature. The optical transmittance and reflectivity of the films were measured by a Uv–Vis–Nir double-beam spectrophotometer (Perkin Elmer, Lambda 950) in wavelength of 200–3000 nm.

3. Results and discussion

3.1. Structural studies

The X-ray diffraction patterns of SnO_2 and SnO_2:F films are shown in Fig. 1. Both films show a polycrystalline nature with preferred orientation along (200), which is similar with the bulk material of SnO_2. There is no feature of fluoride in the pattern of SnO_2:F film, providing experimental evidence of the incorporation of fluorine atoms into the SnO_2 lattice.

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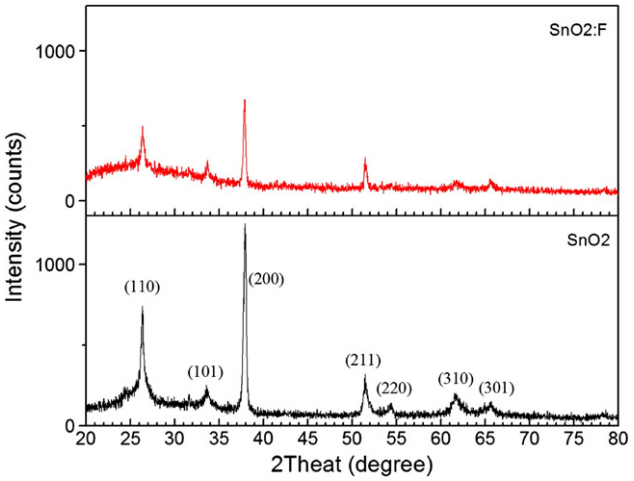

Fig. 1. The XRD patterns of SnO_2 and SnO_2:F films.

Selected regions of the recorded spectrums for SnO_2 and SnO_2:F films are shown in Fig. 2. Below 800 cm^{-1}, the spectrum contains a resonance of tin oxide stretching vibration modes. The main features of O–Sn–O and Sn–O stretching vibration are found at 466 cm^{-1} and 615 cm^{-1}, respectively [10]. Two interesting phenomena have been observed. One is the obvious feature at 516 cm^{-1} in the pattern of SnO_2 film, which disappeared in the pattern of SnO_2:F film. The other is the feature of O–Sn–O splitting into two features at 466 cm^{-1} and 484 cm^{-1} in the pattern of SnO_2:F film, which correspond to O–Sn–O and Sn–F vibration frequency respectively [11].

There are two positions for O^{2-} (u,u,0; 0.5 + u,0.5–u,0.5) in the SnO_2 lattice, which correspond to the O^{2-} in the group of O–Sn–O and Sn–O. The vibrations of these two groups are suggested in FTIR. When oxygen vacancy (V_O^{2+}) introduces into the SnO_2 lattice, it may occur on the group of O–Sn–O because of the different bond length (O–Sn–O:2.597 Å, Sn–O:2.053 Å). The presence of V_O^{2+} would deform the O–Sn–O group to the V_O^{2+}–Sn–O group, and then the repulsive force between Sn^{4+} and V_O^{2+} makes the deformed Sn–O show a shorter bond length that, in turn, leads to the vibration feature at 516 cm^{-1}. Therefore, the feature of deformed Sn–O at 516 cm^{-1} is a result of the V_O^{2+} occurring in the lattice. Its disappearance in the FTIR pattern of SnO_2:F film is consistent with the assumption of V_O^{2+}.

In SnO_2:F film, the fluorine ions are supposed to occupy the position of oxygen for the following reasons: the similar ionic size (F^-: 0.133 nm, O^{2-}: 0.132 nm), the comparable energy of bond with tin (Sn–F bond: 26.75 D°/kJ mol^{-1}, Sn–O bond 31.05 D°/kJ mol^{-1}), and Coulomb forces that bind the lattice together are reduced since the charge on F^- is only half of the charge on O^{2-}. Thus, geometrically the lattice is nearly unable to distinguish between F^- and O^{2-} [12]. This substitution is well confirmed by the feature of α-SnF_2 at 484 cm^{-1} in FTIR. Elangovan et al. [13] have predicted the SnF_4 is a possible production. But our experimental evidence suggests that SnF_2 is the production of fluorine doping. It is reasonable to suggest that the production of SnF_2 is just a result of the substitution of fluorine occurring on the group of O–Sn–O.

In the substitution of fluorine for oxygen, each fluorine ion substitutes an oxygen ion in SnO_2 lattice and the substituted oxygen ion provides one more free electron, which causes to an increase of carrier concentration in the SnO_2:F film. This is well revealed by the results of Hall measurement, in which the carrier concentration of SnO_2 and SnO_2:F are $-(0.2\sim1.3)\times10^{20}$ cm^{-3}, $-(7.0\sim8.8)\times10^{20}$ cm^{-3}) respectively. The result of substitution can be expressed as the defect model of SnO_xF_{4-2x}.

3.2. Reflectivity studies

The optical transmittance and reflectivity of SnO_2 and SnO_2:F films are described in Fig. 3. The most conspicuous characteristic is that the SnO_2:F film has a transmission window in wavelength of 400–1300 nm, whereas the undoped SnO_2 film show high transmission in near-infrared band. The reflectivity of SnO_2:F displays an increase after 1500 nm. This increase can ascribe to the variation of the free-carrier plasma resonance frequency ω_p [14]. Based on Maxwell's equations and the Drude theory of free electrons, the quantity ω_p is derived as Eq. (1) [15].

$$\omega_p = \left(\frac{ne^2}{\varepsilon_0 \varepsilon_\infty m_c^*}\right) \tag{1}$$

where n is the carrier concentration, e is the electronic charge, ε_0 is the permittivity of free space, ε_∞ is the high-frequency permittivity, and m_c^* is the conductivity effective mass. At low frequencies $\omega<\omega_p$, at which both refractive index and extinction coefficient are large, the material has near-unity reflectance, as expected from the Fresnel expression for the reflection coefficient [16]. The cutoff wavelength λ_p

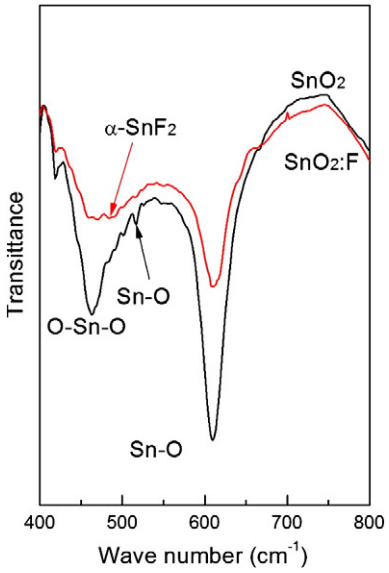

Fig. 2. The FTIR spectrum of SnO_2 and SnO_2:F films.

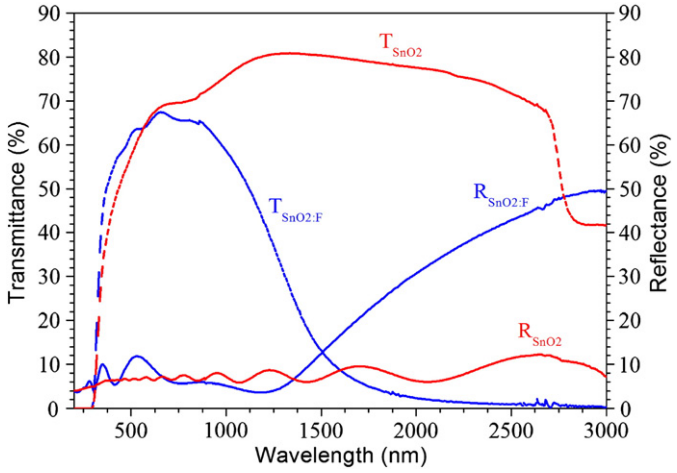

Fig. 3. The optical transmittance and reflectance spectrum of SnO_2 and SnO_2:F film.

corresponding to the plasma resonance frequency can be expressed as Eq. (2) [17].

$$\lambda_p = 2\pi c_0 \left(ne^2/\varepsilon_0 \varepsilon_\infty m_c^*\right)^{-1/2} \quad (2)$$

Assuming that ionized fluorine in the SnO_2 lattice serve as donors, the optical cutoff wavelength is calculated based on SnO_xF_{4-2x} model. The calculated cutoff wavelength is $\lambda_p \approx 1700$ nm. The result is close to our experimental value in Fig. 3. The consistency between calculated value and experimental data suggests that the model of SnO_xF_{4-2x} is suitable for SnO_2:F film. Others have reported that the λ_p of SnO_x films on glass and SiO_2 substrate are about $\lambda_p < 2500$ nm and $\lambda_p > 2500$ nm, respectively [18,19]. It is noting that the low carrier concentration in their reports may account for the redshift of cutoff wavelength.

4. Conclusion

The SnO_2 and SnO_2:F films were prepared by spray pyrolysis technique. The FTIR spectrums suggest the experimental evidence of oxygen vacancy and substitution of fluorine for oxygen. The result of substitution can be expressed as the defect model of SnO_xF_{4-2x}. At the same time, the substitution provides more free carriers, causing an increase of carrier concentration and that further improves the reflectivity of the film. The carrier concentration plays an important role for the reflectivity property of the SnO_2 film.

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