JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 1, January 2011, p. 89 - 93

The studies on the role of fluorine in SnO_2:F films prepared by spray pyrolysis with $SnCl_4$

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The SnO_2:F films with varied fluorine concentrations were prepared by spray pyrolysis method. The experimental evidence of fluorine substitution for oxygen is provided by FTIR spectrum. The FTIR and carrier concentration results suggest that the fluorine ions prefer to occupy the oxygen position in SnO_2 lattice at the low doping levels, which plays a role of donors. While beyond a certain doping level, the fluorine starts to fill the interstitial site in the lattice, which has a negative effect on carrier concentration that, in turn, affects the infrared reflectivity of SnO_2 films. The increased disorder of the SnO_2 lattice is also shown by the FTIR as the rise of fluorine concentration. The scattering of free carriers occurring in the films is also discussed in the paper.

(Received January 10, 2011; accepted January 26, 2011)

Keywords: SnO_2 film, FTIR, Defects, Infrared reflectivity, Scattering

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1. Introduction

Tin oxide(SnO_2) has attracted the researchers because of its wide applications in both industry and research. It is extensively used for a variety of applications including low emission glass, heat mirror, smart windows, solar cell and thin film photovoltaics[1,2]. Recent years have witnessed the pure and doped SnO_2 films on glass substrates are used extensively on architectural windows for energy conservation and transparent electrodes in thin film photovoltaic solar cells. Due to its excellent optical and electrical properties fluorine doped SnO_2(SnO_2:F) films have been reported in many articles. The details of the growth and properties of SnO_2:F for various deposition techniques can be found in[3-8].

Thin films of SnO_2:F can be prepared by many techniques, such as chemical vapor deposition, sputtering, sol-gel, reactive evaporation, pulsed laser ablation, screen printing technique, spray pyrolysis etc. Among these techniques, spray pyrolysis is the most convenient method because of its simpleness, low cost, easy to add doping materials and vary the film properties by changing composition of deposition solution. In addition, this method is promising for high rate and mass production capability of uniform large area coatings in industry[10].

In SnO_2:F films, the fluorine ions are supposed to substitute the oxygen ions in the lattice, and the substituted oxygen ions provide more free electrons. But the experimental details of the substitution of fluorine for oxygen in the lattice are scarce. In the paper, we use the FTIR spectrum to investigate the SnO_2:F films with different fluorine concentrations. The experimental evidence of fluorine substitution has been shown. The rule of site occupancy for the incorporated fluorine is also analyzed. We further demonstrate the varied the optical and electrical properties of SnO_2:F films with different fluorine concentrations.

2. Material and methods

The SnO_2:F films were grown on the soda-lime glass substrates by ultrasonic spray pyrolysis (USP). The details of USP are described as Fig.1. An aqueous solution of high purity tin chloride ($SnCl_4{\cdot}5H_2O$) with concentration of 0.1M was used as starting solution. A small amount of concentrated hydrochloric acid (HCl) was added to prevent hydrolysis. Fluorine doping was achieved by adding ammonium fluoride (NH_4F) to the solution with varying concentrations of 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%. The solution was atomized at a frequency of 1.7MHz by an ultrasonic nebulizer, and carried by compressed air to the deposition chamber. The substrate temperature was maintained at 350℃. The spray process was not continuous with an intermittence to keep the temperature of substrates.

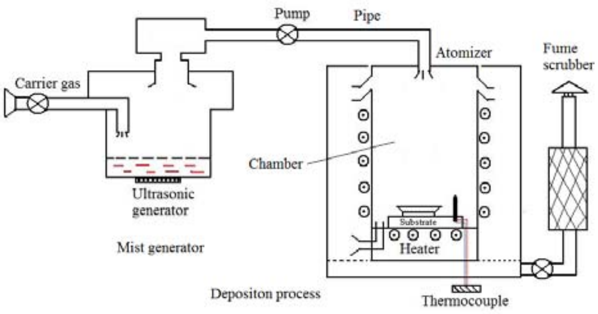


Fig. 1. The basic setup of Ultrasonic Spray Pyrolysis equipment.

The crystalline characteristic of SnO_2:F films was studied by X-ray diffraction (RINT-2200, Rigaku). The FTIR measurements were conducted in transmittance mode using a Bruker Fourier transform spectrophotometer. The SnO_2:F films were deposited on KBr for this purpose. The SnO_2:F films were also characterized by Hall effect measurement(HMS3000, Ecopia) to determine the carrier concentration and Hall mobility in van der Pauw configuration at room temperature. The optical transmission and reflectance spectra were measured by a Perkin-Elmer double beam spectrophotometer (Lambda950).

3. Results and discussion

3.1 Structural studies

The XRD patterns of SnO_2:F films with various fluorine concentrations are shown in Fig. 2. All the films are found to be tetragonal rutile structure with a polycrystalline nature. All the fluorine doped SnO_2 films show a preferred orientation of (110) irrespective of doping levels. Presence of weak reflections such as (101), (200), (211), and (310) have also been detected with lower intensities. There is no feature of fluoride in the patterns of SnO_2:F films, providing the experimental evidence of the incorporation of fluorine into the SnO_2 lattice.

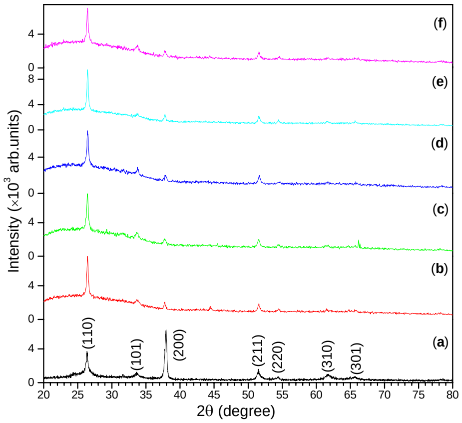


Fig. 2. The XRD patterns of SnO_2:F films: (a)0wt.%, (b)5wt.%, (c)10wt.%, (d)15wt.%, (e)20wt.%, (f)25wt.%

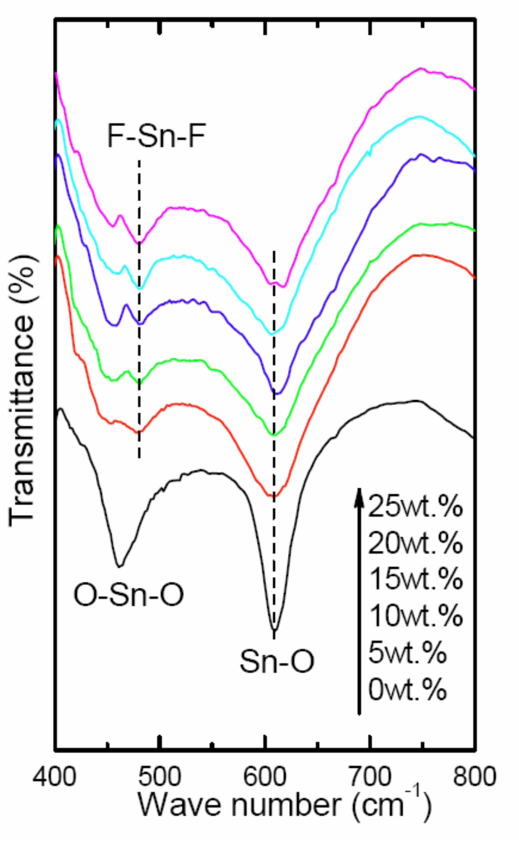


Fig. 3. The FTIR spectra of SnO_2:F films

FTIR is employed to examine more details of defects in the structure. Selected region of the recorded spectra for SnO_2:F films is shown in Fig. 3. The main IR features of SnO_2 lattice appears at 461 and 609 cm^{-1}, which assign to O-Sn-O and Sn-O stretching vibration, respectively[11]. The O-Sn-O feature splits into two features at 461 and 482cm^{-1} as the introduction of fluorine, which correspond to the vibration of O-Sn-O and Sn-F bond(α-SnF_2)[12]. The vibrational frequency of Sn-O shows an redshift from 609cm^{-1} to 619cm^{-1} after the fluorine doping of 20wt.%.

In SnO_2:F films, the fluorine ions(F^-) have been supposed to substitute oxygen ions(O^{2-}) as following reasons[13]: the similar ionic size(F^-~0.133nm, O^{2-}~0.132nm), the comparable bond energy with Sn(Sn-O bond~31.05 D°/kJ mol^{-1}, Sn-F bond~26.75 D°/kJ mol^{-1}), and Coulomb forces that bind the lattice together are reduced, since the charge on the F^- is only half of the charge on the O^{2-}. Thus, geometrically the lattice is nearly unable to distinguish between F^- and O^{2-}. In the case, the presence of Sn-F(α-SnF_2) vibration feature in FTIR provides the experimental evidence for the fluorine substitution(F_O^{+1}). The intensity of Sn-F feature reveals that the substitution becomes obvious as the rise of fluorine concentrations. The production of fluorine doping is further obtained as α-SnF_2 by the FTIR, although Elangovan et al.[13] have predicted the SnF_4 is a possible production on the basis of chemical reactions in the deposition. The possible reason can be sought from the fluorine substitution occurring on the group of O-Sn-O. The different bond length(O-Sn-O:2.597Å; Sn-O:2.053Å) can account for the fluorine substitution occurring on O-Sn-O group. The redshift of Sn-O suggests that there is a solubility limit of fluorine ions in SnO_2 lattice beyond which the excess fluorine ions would occupy the interstitial site in the lattice. The interstitial fluorine increases the disorder of the lattice remarkably, which leads to the shift of Sn-O vibrational frequency in FTIR.

3.2 Electrical studies

The carrier concentration and Hall mobility of the SnO_2:F films as a function of doping level is shown in Fig. 4. The carrier concentration increases till 20wt.%, and then decreases as the increasing of fluorine concentration. The similar results can be found in [13,14]. The increase of free carriers can be ascribed to the substituent of fluorine for oxygen, which is confirmed by the FTIR. In the substituent, each F^- substitutes an O^{2-} in the lattice and the substituted O^{2-} provides one free electrons[14]. However, when the fluorine concentration exceeds the solubility limit of fluorine in SnO_2 lattice, the excess fluorine ions do not occupy the proper lattice positions to contribute to the free electrons, but fill the octahedral interstice of tin-oxygen to form interstitial fluorine(F_i^{-1}). The interstitial fluorine can trap the free electrons in the films, which has a negative effect on the carrier concentration. This incorporation of fluorine into SnO_2 lattice at various fluorine concentrations is in consistence with the FTIR studies.

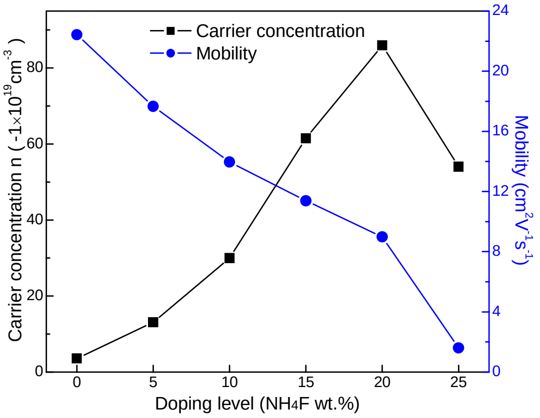
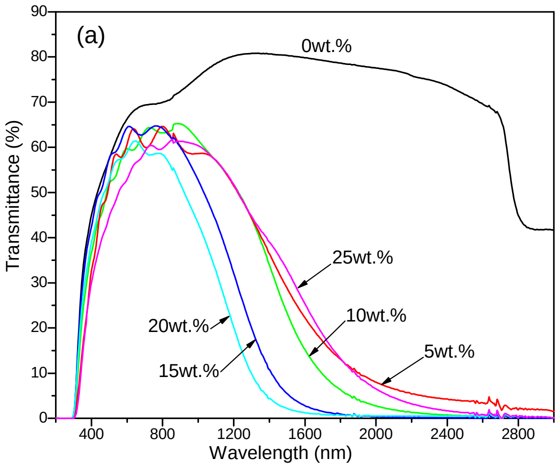


Fig. 4. The carrier concentration and Hall mobility of SnO_2:F films

The mobility of SnO_2:F films decreases monotonically from 22$cm^2V^{-1}s^{-1}$ to 2$cm^2V^{-1}s^{-1}$ as the increasing of fluorine concentration. The actual value of mobility is determined by the interaction between the various scattering centers and free carriers. In the films prepared by spray pyrolysis method, an ideal lattice cannot be expected, even if no donor atoms are present. Hence, the scattering of electrons by the thermal vibration of the lattice atoms can omitted in the case[15]. Thangaraju et al.[16] have verified grain boundary and impurity ion scattering are the possible dominant scattering mechanism in the films. The condition of grain boundary scattering to be dominant is the mean free path values should be comparable to crystallite size. In the case, we calculate the mean free path according to the high degeneracy model and find the mean free path does not exceed 6nm, which is considerable shorter than grain size. Thus, scattering due to grain boundary is not the main scattering. Gilmore et al.[17] have reported that the influence of grain boundary is in a different manner and they though the optical mobility was not impacted by grain boundary as long as the grain size was much greater than the mean free path.

3.3 Optical studies

The transmittance and reflectance spectra of SnO_2:F films are shown in Fig. 5. The SnO_2:F films have almost equal transmittance values in the visible band. The most conspicuous characteristic is that all SnO_2:F films have a transmission window in wavelength of 400-1600nm, whereas the undoped SnO_2 film shows high transmission in the whole near-infrared band. The transmission window is narrowest at the doping level of 20wt.%. The typical reflectance spectrum of SnO_2:F films with various fluorine concentrations are shown in Fig.5(b). The reflectivity of the films is almost a constant whereas it increases gradually after 1300nm for SnO_2:F films. The max reflectivity is obtained at doping of 20wt.%. More or less fluorine atoms would lead to a decrease of reflectivity.



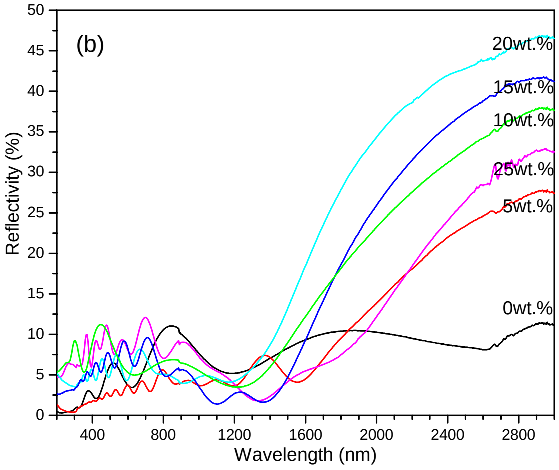


Fig. 5. The optical transmittance and reflectance spectra of SnO_2:F films: (a) Transmittance, (b) Reflectance

The characteristic of transmission window for SnO_2:F films is the result of the absorption in the films. At short wavelengths, absorption occurs due to the fundamental band gap, and thus light cannot be transmitted due to a quantum phenomenon [18]. The short-wavelength cutoff corresponds to the fundamental band gap energy of the materials. At long wavelengths, reflection occurs because of the plasma edge, and light cannot be transmitted due to a classical phenomenon. The long-wavelength edge corresponds to the free-carrier plasma resonance frequency ω_p. At high frequencies $(\omega > \omega_p)$, the SnO_2 film behaves like a perfect dielectric, whereas at sufficiently 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. According to Drude theory of free electrons, the quantity ω_p is derived as equation (1)[19].

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

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. From equation(2), it is found that the reflectivity is determined by the carrier concentration in the material, which well accounts for that the optimal value of carrier concentration and reflectivity is obtained at the same doping level. Thus, the substitution of fluorine in the SnO_2:F films changes the carrier concentration that, in turn, affects the reflectivity of the SnO_2:F films.

4. Conclusion

The SnO_2:F films with varied fluorine concentrations were prepared by ultrasonic spray pyrolysis technique. The FTIR was used to investigate the defects of the films and gave the experimental evidence of fluorine substitution for oxygen. The FTIR and carrier concentration suggest that the incorporated fluorine ions are prone to replace the oxygen in the SnO_2 lattice at low doping levels. While beyond a certain doping concentration, the fluorine ions start to occupy the interstitial site, which has a negative effect on the free carrier. The defects in the films alter the carrier concentration that, in turn, affect the reflectivity of the SnO_2:F films. The increased disorder caused by the incorporation of fluorine can also be demonstrated by FTIR. The grain boundary scattering does not play a key role for the mobility of SnO_2:F films.

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