Influences of H_2O on the Structure and Properties of Sn:F Film

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Abstract: F-doped tin oxide (Sn:F) film was prepared by atmosphere pressure chemical vapor deposition (APCVD) on float glass using monobutyltin trichloride ($C_4H_9SnCl_3$, MBTC) and trifluoro acetic acid (CF_3COOH, TFA) as the precursor and dopant, respectively. Different concentrations of H_2O were used as the activator. The prepared films were characterized by means of XRD, SEM, and UV-VIS-NIR spectroscopy. Experimental results reveal that the structures and properties of the films are greatly affected by the H_2O content. Water in a certain range of concentrations will promote the formation of SN:F film and improve the properties of the films.

Key words: low-E glass; on-line CVD; precursor; F-doped; activator

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Many glass products are coated with conductive fluorine-doped tin oxide (Sn:F) film as the functional layer, because SN:F film imparts a low emissivity. Doping of a thin tin oxide film with fluorine is commonly practiced in order to increase its conductivity and thus to decrease its emissivity[1~5]. Thin films of Sn:F can be prepared by various techniques such as chemical vapor deposition, sputtering, spray pyrolysis, etc. Among the various deposition techniques available, atmosphere pressure chemical vapor deposition is the most convenient method because this method is simple, inexpensive, and ease to add doping materials. Moreover, this method is amenable to mass production to coat a large area uniformly, which is desirable for industrial applications[6~9]. Many researchers have investigated how to make low-E glasses, but most of the studies have concentrated on off-line coating and rarely on on-line coating. For on-line coating technology, the coating process is carried out on the float glass in the manufacturing line and there are only a few changeable parameters to be adjusted.

On-line chemical vapor deposition (CVD) takes advantage of the hot surface of the float glass. Organometallic compounds are often used as precursors of oxide thin films because they readily decompose at or near the surface of the hot glass ribbon. Literature survey turned out little work on the preparation of SN:F film (SnO_2:F) thin films by on-line chemical vapor deposition. And little research was done on the effects of H_2O as the activator in the coating process[10~14].

In this paper, we prepared SN:F film by atmosphere pressure chemical vapor deposition (APCVD) on a float glass manufacturing line using monobutyltin trichloride ($C_4H_9SnCl_3$, MBTC) and trifluoro acetic acid (CF_3COOH, TFA) as the precursors and H_2O as the activator. Furthermore, we also investigated the effects of the activator H_2O on the structure, surface appearance, electric character, optical character of SN:F film.

1 Experimental

SN:F film on float glass was prepared by atmosphere pressure chemical vapor deposition (APCVD) using monobutyltin trichloride ($C_4H_9SnCl_3$, MBTC) and trifluoro acetic acid (CF_3COOH ,TFA) as the precursor and dopant. High purity N_2 was used as the carrier gas and H_2O was used as activator. The experimental conditions were as following: MBTC (99% purity) and TFA (99% purity) were gasified primarily in bubble room at 160 ℃ and 20 ℃, respectively. Their usage or flow rates were 1.05 g/min or 0.54 L/min for MBTC and 0.057 g/min or 0.092 L/min for TFA. The activator gas H_2O was carried with air and gasified at 30 ℃. Its usage or flow rate was 0.027 g/min or 0.767 L/min. The oxygen and carrier gas nitrogen flow rates were 0.12

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L/min and 3.045 L/min respectively. The temperature of glass surface was 650℃ and the drawing speed of glass ribbon was 380 m/h.

The structure of the film was investigated by X-ray diffraction (Rigaku International Corporation, D/max-2500/PC) with the wavelength of 0.15406 nm and scanning electron microscopy (SEM) (KYKY-2800). The sheet resistance of the film was measured by XX-2 square resistance tester. The thickness was tested by WVASE32TM ellipse polarization analyzer at the wavelength from 300 to 1300 nm.

2 Results and Discussion

2.1 Effects of H_2O addition on the structure of film surface

Sn:F were prepared in the presence of 0%, 0.6%, 1.2%, and 1.8% activator H_2O. Their structures were examined by X-Ray diffraction. As shown in Fig.1, their X-Ray diffraction pattern shows that all films prepared with different concentrations of H_2O were composed of multi-crystal, which have the similar structure of cubic rutile. With the increase of the H_2O content, the diffraction peaks become sharper and stronger, indicating that the crystals in the tin oxide film grow larger.

The Sn:F films made with different concentrations of H_2O were also examined by scanning electron microscope. The SEM images of the SnO_2:F film prepared at different H_2O contents are shown in Fig.2. As shown in Fig.2a, without the activator H_2O, the prepared film is not compact and contains pores. With the increase of the H_2O content, the pore sizes decrease and the film becomes more compact. Moreover, the sizes of the crystals become larger too (Fig.2b, 2c, 2d), which is consistent with the result of XRD patterns in Fig 1.

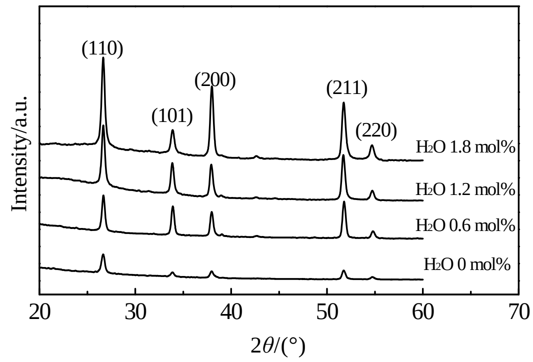

Fig.1 X-ray diffraction patterns of the Sn:F film prepared by adding different H_2O concentrations of 0 mol%, 0.6 mol%, 1.2 mol%, 1.8 mol%

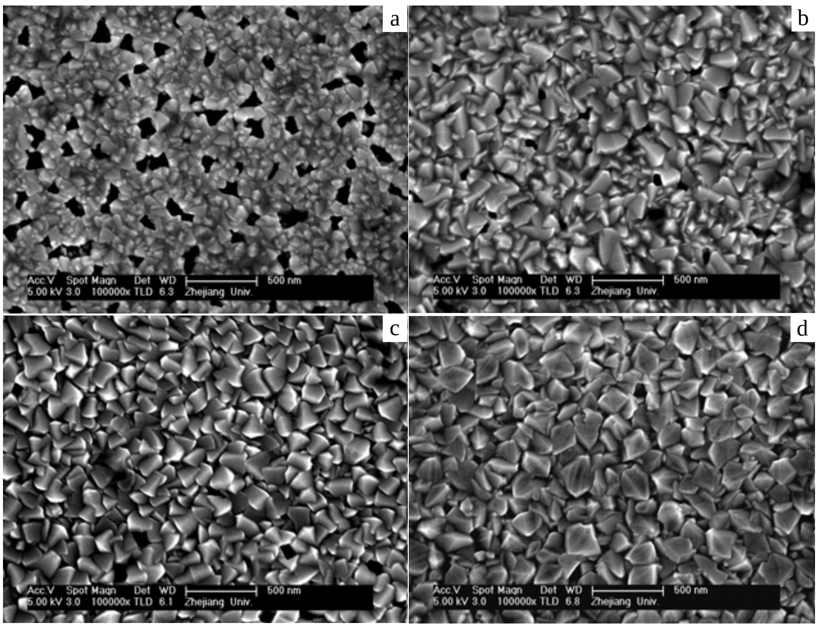

Fig.2 Morphology of Sn:F films prepared by adding different H_2O concentrations of (a) 0 mol%, (b) 0.6 mol%, (c) 1.2 mol%, and (d) 1.8 mol%

2.2 Effects of H_2O on the thickness of SN:F film

The changes of the thickness of the Sn:F film prepared at the same substrate temperature versus H_2O concentration are shown in Fig.3, indicating the film is thickened with the increase of H_2O content. The growth rate of film is faster at low H_2O concentrations and becomes slower when the H_2O concentration is higher than 1 mol%. It reaches a plateau when the concentration exceeds 2 mol%. This phenomena is related with the deposition rate of Sn:F film. With the increase of H_2O concentration, the activation energy likely decreases. Therefore, the deposition rate grows and the film is thickened. When the H_2O concentration reaches certain point, the rate of the activation energy decrease likely slows down, so does the thickness of the film.

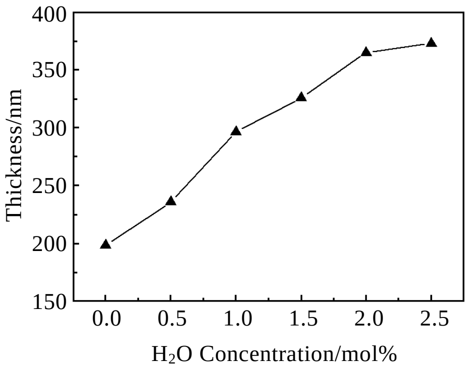

Fig.3　Dependence of thickness of Sn:F film on the H_2O concentrations

2.3　Effects of H_2O on the sheet resistance of the film

The changes of the sheet resistance of films with different concentrations of H_2O were also studied. As shown in Fig.4, the sheet resistances of the film prepare at the same substrate temperature decreased with the increase of H_2O content. But it remains the same level when the H_2O concentration is higher than 1 mol%.

Without the activator H_2O, the crystal grains in the film are small and the film contains many pores and crystal interfaces. Therefore, the mobility of the carrier in the film is low and the sheet resistance is high. With the increase of H_2O concentration, the crystal grains grow larger and the crystal interfaces are reduced. The number of the free electron restricted by the crystal interface decreased and the dispersion of the potential barrier to the carriers is lowered. As a result, the mobility of the films increases.

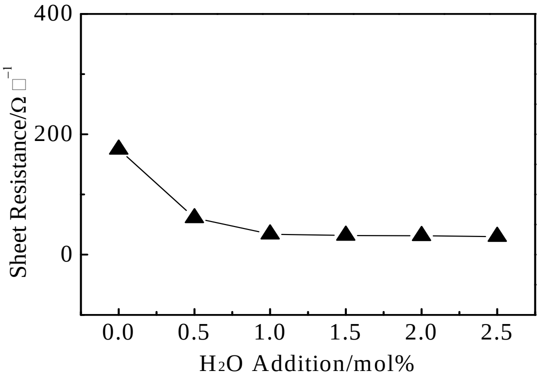

Fig.4　Dependence of sheet resistance on the H_2O concentrations

2.4　Effects of H_2O concentrations on the light transmission and reflection of films

The UV-Visual light transmission curves and the visual light reflection curves of Sn:F films with different H_2O concentrations are shown in Fig.5. The results show that with the increase of H_2O content, the visible light transmission and reflection properties of the films change only little. In the region of 380~780 nm, the average transmission and reflection rates are about 70% and 10%, respectively. Specifically, when the H_2O concentrations are 0%, 0.6%, 1.2%, and 1.8%, the related reflection rates of visible light are 66.8%, 68.9%, 69.8%, and 71.1%, respectively.

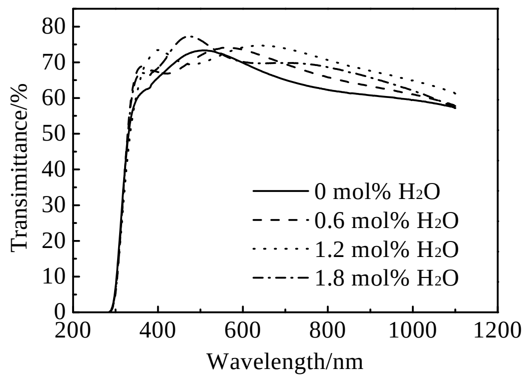

Fig.5　UV-Visual light transmission of Sn:F films prepared by adding different concentrations of H_2O

As shown in the transmission curves (Fig.5), the light at 284 nm is absorbed completely by all the films, because the ultraviolet light is absorbed by the electron transition from the valence band to the conduction band. Due to the interference of the film, the transmission and reflection curves show a fluctuation and wave-like pattern.

2.5　The mechanism of action of H_2O

Water could activate the formation of Sn:F film by two types of mechanisms.　One is that H_2O can promote the cleavage of the chemical bonds in MBTC, i.e. the vapor at high temperature facilitate the disconnection of the Sn-Cl bond and C_4H_9-Sn bond in MBTC. The break-down products are then oxidized to SnO_2, HCl, CO_2, CO etc. In this mechanism of action, water does not participate in the reaction and the oxygen in tin oxide comes from the O_2 in air. Another mechanism is that water directly participates in the hydrolysis reaction of MBTC at high temperature, i.e. H_2O combines with the MBTC to form SnO_2 and other intermediates, which are then oxidized to CO_2 and CO by the atmospheric O_2. In this mechanism of action, the oxygen in tin oxide comes from water. It is likely that both mechanisms of action appear in the preparation of tin oxide films. More research is needed to figure out which one is more important.

3　Conclusion

F-doped tin oxide film can be prepared by atmosphere pressure chemical vapor deposition (APCVD) on-line on float glass. The structures and properties of the films are greatly affected by the H_2O content. Water in a certain range of concentrations will promote the formation of tin oxide film and improve the properties of the films.

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催化剂水对掺杂氟的氧化锡膜性能与结构的影响

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摘　要：采用常压化学气相沉积法（APCVD），以有机金属化合物-单丁三氯化锡（$C_4H_9SnCl_3$，MBTC）和三氟乙烯(CF_3COOH，TFA)为前驱物和掺杂剂，以水为催化剂，在线制备了 F 掺杂的 SnO_2 膜；采用 XRD、SEM、椭偏仪等方法研究催化剂 H_2O 的用量对薄膜的结构和光电性能的影响。结果表明，H_2O 可促进反应混合气体在基板表面的热分解反应，加速薄膜沉积速率，提高薄膜结晶性能。

关键词：低辐射玻璃；在线镀膜；SnO_2 膜；H_2O

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