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Study on the growth mechanism of tin-doped indium oxide films deposited by direct current pulse magnetron sputtering

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ABSTRACT

Tin-doped indium oxide (ITO) films were deposited on Si(100) and glass substrates at different deposition time by direct current pulse magnetron sputtering. The step profiler, four-point probe measurements and atomic force microscopy were used to study the thickness, sheet resistance, as well as the nucleation and growth behavior of ITO films, respectively. The dynamic scaling of roughness evolution could be divided into three stages, which are the growth of islands, the coalescence of islands, and the homogeneous growth, respectively. Compared with the glass substrate, it needs long time to nucleate on Si(100) substrate for fewer defects on the surface. Base on the result above, the mechanisms of defect nucleation and islands coalescence could be given.

1. Introduction

Recently, transparent conducting oxides have attracted much attention, such as tin-doped indium oxide (ITO), aluminum doped zinc oxide, gallium doped zinc oxide, and antimony doped tin oxide [1–4]. ITO is a highly degenerate n-type semiconductor, which has excellent electrical conductivity and highly transparence to the visible light [5,6]. Due to these unique properties, ITO films have been utilized in devices such as flat panel displays, solar cells, lamps, and so on [5,7–9], especially as the anodes in organic light emitting diodes (OLEDs) [1,10–14]. As the anode in OLEDs, it is difficult for the rough surface of ITO films to be fully covered by the light emitting materials, which results in the short circuit between anode and cathode deposited subsequently. Therefore, there is a large demand for ITO films with smoothed surface. Various methods of post-processing are used to smooth the surface of ITO films [15–20], which increase the production costs. Then, the direct process for the preparation of smooth ITO films is desired. To provide a theoretical basis for deposition of smooth ITO films, it is necessary to research on the nucleation and growth behavior of ITO films.

Dynamic scaling theory is one of the most important theories to study the nucleation and growth behavior of films. According to dynamic scaling theory, the films surface roughness (W) is consistent with the following scaling relations: [21,22]

$$W(L,t)\propto L^{\alpha} f\left(t/L^{z}\right) \tag{1}$$

where L is the scan length, t is the deposition time, α is the roughness exponent, z is the dynamic exponent, $f(x)$ is the scaling function defined by formula (2),

$$f(x)\propto\begin{cases} x^{\beta} & x<<1, \\ constant & x>>1, \end{cases} \tag{2}$$

where β is the growth exponent, and $\beta = \alpha/z$. So, the formula (1) could be simplified as formula (3)

$$W(L,t)\propto\begin{cases} t^{\beta} & t<<L^{z}, \\ L^{\alpha} & t>>L^{z}, \end{cases} \tag{3}$$

The exponents α and β can be used to analyze the growth behavior of thin films.

In this paper, atomic force microscopy (AFM) has been applied to study the morphological evolution of ITO films on Si(100) substrates. With the dynamic scaling of films morphology at different growth stages, the nucleation and growth behavior have been studied for ITO films deposited by direct current (DC) pulse magnetron sputtering.

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2. Experimental details

ITO films were deposited on Si(100) and glass substrates by DC pulse magnetron sputtering at different sputtering times. Before the deposition, the substrates were ultrasonically pre-cleaned in ethanol and deionized water, and dried, and finally loaded into the processing chamber. The ITO target was set parallel to the substrates, which was rectangular (20×9 cm^2, ULVAC Inc.) with 10 wt. % SnO_2 and 90 wt. % In_2O_3 in composition. The target-substrate distance and the base vacuum were fixed at 13.5 cm and 5×10^{-3} Pa for all samples, respectively. The deposition was carried out after pre-sputtering for 3 min in order to clean the target surface. During the deposition, the working pressure and the sputtering power were kept at 0.6 Pa and 300 W, respectively. The substrate was heated with a home-made infrared heater and the temperature maintained at 245 ± 5 °C during the deposition process. The deposition rate was about 0.6 nm/s.

The surface morphology of samples was obtained by a SPM9500-J3 AFM system, with 2.0 Hz scanning frequency in tapping mode. The collected data consisted of the height information on square 256×256 arrays of pixels. Then the root mean square roughness (R_{rms}) of surface could be calculated by the AFM system automatically according to the following formula:

$$R_{rms} = \sqrt{\frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y}\left[z\left(x_i, y_j\right) - \frac{1}{N_x N_y}\sum_{i=1}^{N_x}\sum_{j=1}^{N_y} z\left(x_i, y_j\right)\right]^2} \quad (4)$$

where N_x, N_y are the number of pixels in X, Y direction, respectively. Z(x, y) is the height at the pixels (x, y). The thickness of ITO films was measured by a Dektak 6 M step profiler with the resolution of 1 nm. The sheet resistance was measured using MCP-T360 four-point probe measurements. The crystal structure of ITO film was investigated by a Panalytical Empyrean X-ray diffractometer (XRD) using Cu $K\alpha$ radiation (40 kV, 30 mA), which was carried out in 2θ scan mode, and the data was collected at intervals of 0.02° with a scan speed of 10°/min.

3. Results and discussion

3.1. Nucleation and growth analysis

Fig. 1 shows AFM morphology images of ITO films deposited on Si(100) substrate with various deposition times (10–300 s). From Fig. 1, it can be seen clearly that the surface morphology varies significantly with the increase of deposition time. At the initial stage, the islands are clearly observed as shown in Fig. 1a. With the increase of deposition time, the islands grow larger, just as shown in Fig. 1b. Then, the neighbor islands combine with each other to form a continuous film, as shown in Fig. 1c. The sharp islands as in Fig. 1a and b do not exist again. After continuity, the surface becomes rough obviously with the increase of deposition time, just as shown in Fig. 1c–f. The surface features in Fig. 1e and f probably correspond to the tops of the columns in the microstructure. In summary, at the first stage, the film grows following Volmer–Weber growth model or the islands growth model [23], then, after the continuity of the film, it grows following Stranski–Krastanow growth model or the island-on-wetting-layer growth model.

For a further understanding of the growth mechanisms, the cross-section images of ITO islands are presented at Fig. 2. Comparing with Fig. 2a and b, the average height and slope angle of the islands increases from 1.75 to 5.33 nm and 2.67 to 7.69° respectively, while the average diameter of the islands does not increase much. It means that the islands prefer to grow in vertical direction at the stage of Volmer–Weber growth.

The growth of the film is a competition process of absorption and desorption of deposited atoms (monomers). In order to clarify the growth phenomena mentioned above, three competition principles are presented. (a) The monomers prefer to be fixed at the defects of Si substrate [24]. Compared to the silicon substrate, the monomers are easier fixed at the growth surface of ITO film because of homo-deposition. (b) The In(Sn)-O bond is more stable than In(Sn)-In(Sn) and/or O-O bond for the higher bond energy. So monomers prefer to form the band structure of In_2O_3. (c) A growth model of the asymmetric energy barrier of diffusion at the step edge has been proposed as shown in Fig. 3a. The lower step edge is a preferential sticking site, causing a net adatom flux across the step [25].

Based on the three competition principles presented above, the growth phenomena in Figs. 1 and 2 could be explained. At the beginning of the deposition, the monomers were more easily fixed at the defects of Si substrate, which became the nucleation centers. While the monomers absorbed at other sites preferred to diffuse or desorb. Soon, the monomers gathered on the location of defects and the small size monolayers formed, as shown in Fig. 3b. The monolayers extended horizontally with the increase of deposition time. Simultaneity, the monomers preferred to absorb on the monolayers. As one monolayer extended to a large enough size, the absorbed monomers could diffuse only on the monolayer. A dimmer could be formed by the encountering of two monormers. For simplicity, we assumed that only monomers could diffuse on the surface, while the polymers with two or more monomers remained immobile. The monomers preferred to stick to the edge of the polymers, which resulted in the expanding of polymers in horizontal direction, as shown by the red circle in Fig. 3c. Then, other polymers formed on the previous ones with large enough size, which resulted in the expanding of islands in vertical direction. The expanding of the polymers and the formation of other polymers reflected growth of ITO islands in horizontal and vertical direction, respectively. The ratio of horizontal and vertical growth rates determines the gradient of ITO islands. As shown in Fig. 3d, when the islands connected each other at the bottom monolayer, the monomers adsorbed on upper monolayer preferred to transfer down and fill the valley between the islands. This would trigger a rapid decrease of surface roughness, which will be discussed in detail later.

3.2. Dynamic scaling of morphological evolution of ITO films

The exponent α is widely used to study the growth behavior of films at the late growth stage, which reflects the difference in height of the grains nearby. Fig. 4 shows R_{rms} value of ITO film deposited on Si(100) substrate for 300 s as a function of scan length. From Fig. 4, there is a crossover length $L_C = 1000$ nm, which is the minimum scan length for statistical roughness. The R_{rms} is nearly constant at large length scales until L_C is reached below which the R_{rms} increases approximately linearly. By linear fitting, the exponent α is estimated as 0.41 ± 0.03, which describes a wigglier surface of ITO film. To further study, XRD is performed. The insert figure of Fig. 4 shows the XRD pattern of ITO film deposited on Si(100) substrate for 300 s, as well as the standard XRD pattern of ITO nanopowders [26]. Compared with the standard XRD pattern, the diffraction peak intensity ratios for (400)/(222) and (211)/(222) of ITO film increased significantly. XRD result revealed that ITO film deposited on Si(100) substrate for 300 s has a mixture of (100) and (211) preferential orientations. The competition of (100) and (211) preferential orientation leads to the wigglier surface of ITO films.

The exponent β is used to study the dynamic scaling of morphological evolution of films, which describes how the vertical width of the surface scales with time. Fig. 5 shows the variation in R_{rms} of ITO films deposited on Si(100) substrates as a function of deposition time. The scan length of AFM is 8 μm, which is much larger than L_C. From Fig. 5, the dynamic scaling of roughness evolution can be divided into three stages, which the exponent β are 1.53, −0.85 and 1.25, respectively. The three experimental value of β are all incompatible with the conventional theoretical range, which can be explained as follows. At the first stage, the growth rate is not a stable value. For