

# On the initial growth of indium tin oxide on glass

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(Received 12 December 1995; accepted for publication 1 March 1996)

The initial growth mode of indium tin oxide on glass was studied. An interesting transition from a 3D island growth mode at low temperatures to 2D growth at higher temperature was observed. This transition from the Volmer-Weber mechanism to the Frank-van der Merwe mechanism occurs at about 150°C. It coincides with the transition from amorphous to polycrystalline growth of the thin films. © 1996 American Institute of Physics. [S0003-6951(96)01719-6]

The growth of thin films can generally be classified into 3 major modes: a 3D nucleated growth (Volmer-Weber), a layer-by-layer growth (Frank-van de Merwe) and a 2D growth with a transition to 3D at higher thickness (Stranski-Krastinov). These initial growth modes may determine the ultimate properties of the thin films deposited. Various microscopic techniques such as atomic force microscopy and electron microscopy have been employed to examine the dynamics of the initial film growth process.<sup>1,2</sup> Here, we report a study of the growth of indium tin oxide (ITO) on glass using the technique of *in situ* resistance measurement. ITO is a technologically important material as it is both optically transparent and electrically conductive. It is ubiquitous in all flat panel display devices and is commercially available. It is commonly made by sputtering at moderately elevated substrate temperature. Recently, we found that high quality ITO films could be deposited on glass at room temperature using pulsed laser deposition (PLD).<sup>3</sup> By depositing ITO at higher temperatures on crystalline substrates, we also found that very good quality films could be obtained.<sup>4</sup> X-ray rocking curves of less than 0.1° in width and resistivities of near 0.1 mΩ-cm were measured. This letter concentrates on studying the initial growth mechanism of ITO on glass at low temperatures.

*In situ* resistance measurement has been applied in the past to study the properties of thin metallic films.<sup>5</sup> It has also been applied by us previously to study the dynamics of oxidation of high temperature superconducting oxide films.<sup>6</sup> This technique, though quite simple, is very powerful in obtaining detailed information of the growth process. Recently, *in situ* resistance has been used by Korobov *et al.*<sup>7</sup> to show that the growth of ITO films goes through different stages of tunneling, percolation and linear ohmic growth.

There is no lattice matching for ITO growth on glass. Under this circumstance, the most likely initial growth at low temperature has to be island formation from nucleation sites.<sup>8</sup> How the islands grow and coalesce is the subject of the present study. We shall show that below a substrate temperature of 150°C, the islands grow in 3 dimensions similar to the Volmer-Weber mechanism. Above that temperature, the growth is 2 dimensional similar to the Frank-van der Merwe mechanism. Preliminary results of the *in situ* resistance measurement have been reported previously.<sup>9</sup> In this

letter, we shall show that the change in the growth characteristics is related to the crystallinity of the deposited films.

The thin films were deposited by excimer pulsed laser deposition (PLD).<sup>4-6</sup> Essentially, an ArF laser was focused onto an ITO target at a fluence of about 1 J/cm<sup>2</sup> in a vacuum chamber. The target was a sintered ceramic disk with 10% SnO<sub>2</sub> and 90% InO<sub>2</sub>. The chamber was filled with oxygen to about 10 mtorr during deposition and was filled to 1 atmosphere after deposition. For PLD of oxides, we have shown previously that the optimum ambient oxygen pressure is dependent on the substrate temperature.<sup>10</sup> The resistance of the film was measured using a 4-probe technique during deposition. A current source was used to bias the substrate, and the voltage produced across the film was measured and recorded by a computer. The laser repetition rate was typically 10 Hz, allowing ample time for the data acquisition system to digitize the results. It is estimated that our system is capable of measuring the resistance of a 1 nm thick film with a resistivity of 1 Ω-cm or less. This sensitivity is more than sufficient for studying the initial growth of ITO or other conductors.

Figure 1 shows the composite result of measurements at several substrate temperatures ranging from 20°C to 350°C. It can be seen that in all cases, there is an initial period where the film does not conduct. Then there is a sudden onset of conductivity. In our experiment, the onset of conductivity is defined to be the time when the measured resistance is 95 MΩ. This definition is predicated by the maximum resistance that we can measure, which is 100 MΩ. It is obvious that the initial region of no conductivity in Fig. 1 is due to island formation, with the islands of ITO sufficiently isolated. Reference 7 showed that the shape of the rising portion of the conductivity curve could be fitted using the theory of tunneling conduction, followed by percolation of the islands and eventually ohmic conduction. However, in this letter, we are concerned only with the earlier region before the onset of conductivity.

We can define the critical thickness as the nominal thickness of the film at the onset of conductivity. To calculate the critical thickness, we simply divide the volume of the material deposited by the area of the film. Figure 2 plots the critical thickness as a function of substrate temperature of the film. It can be seen that the critical thickness decreases monotonically as temperature increases and reaches an asymptotic value of 1.2 nm, which is approximately the lattice constant of ITO. The critical thickness is more or less constant above 200°C. The low temperature decreasing portion

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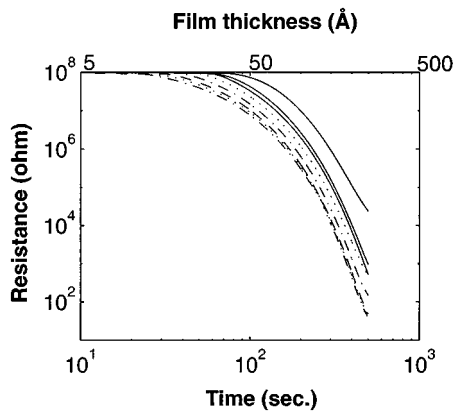


FIG. 1. Resistance of ITO films as a function of film thickness for various substrate temperatures. To avoid cluttering, the temperature values are not indicated in the figure. They are, starting from the top curve, 20 °C, 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, and 350 °C, respectively.

of the curve in Fig. 2 can be extrapolated to intercept the 1.2 nm horizontal line at 150°C. From Fig. 2, one can therefore infer that the growth characteristics of ITO are different below and above 150°C.

Figure 3 shows the x-ray diffraction curves for samples prepared at 100°C, 150°C, and 250°C, respectively. It can be seen that a weak (222) peak begins to appear at 150°C. Below that temperature, there is only a broad feature indicating amorphous films. So it can be seen that there is a transition from amorphous film growth to polycrystalline film growth at about 150°C. This result is similar to that of a previous study<sup>11</sup> where it was found that at 200°C, films thinner than 4 nm were amorphous, while films thicker than 4 nm were polycrystalline.

The interpretation of our results is as follows. In the low temperature range studied, the initial growth is always island formation on the glass substrate. These islands will grow and coalesce either via a 2D or 3D process. Below 150-200°C, these islands grow in 3D similar to the Volmer-Weber mechanism. Above 150-200°C, these islands become typically 1 unit cell thick and then grow laterally in a 2D manner according to the Frank-van der Merwe mechanism.

The argument is as follows. In the Frank-van der Merwe mechanism, the building blocks grow laterally in a 2D manner. The volume of the film therefore scales as the total area

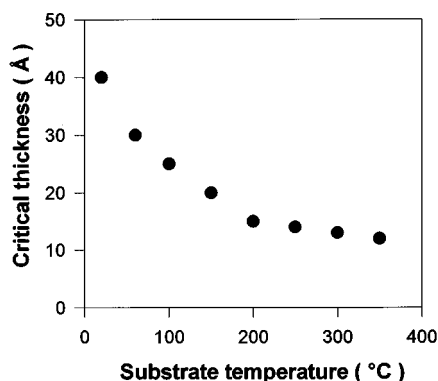


FIG. 2. Critical thickness for conductivity onset as a function of substrate temperature.

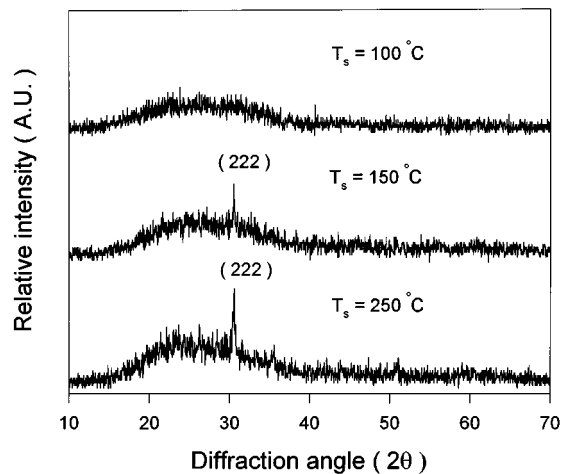


FIG. 3. X-ray diffraction curves of the ITO films deposited at 100 °C, 150 °C, and 250 °C, respectively.

of the film. Hence the critical thickness will be constant regardless of the separation of the nucleation sites. If we assume that the effect of temperature is mainly in changing the nucleation site density, then the critical thickness will therefore be independent of temperature. This is the case for temperature higher than 150°. Hence we can conclude that the growth mechanism at high temperature is Frank-van der Merwe, and the critical thickness is of the order of the thickness of the building blocks which is equal to one lattice constant. This argument from the *in situ* resistance measurement results is consistent with the x-ray results. From Fig. 3, it can be seen that above 150°, the film becomes polycrystalline. So we can infer that polycrystalline films grow in a 2D manner.

At a lower temperature, the film is amorphous, and the critical thickness depends on temperature. This is consistent with a picture of 3D growth of the islands. In 3D growth, the volume of the film scales as  $L^3$  while the area of the film scales as  $L^2$ , where  $L$  is the linear dimension of the islands. Hence the critical thickness of the film when the islands begin to touch will depend on the separation of the nucleation sites. We can use a highly simplified model to illustrate this point and extract some semiquantitative information from the data. Assume that the nucleation sites are arranged in a hexagonal manner with a separation of  $d$ , and the islands are half spheres. Then, when the islands touch, the average thickness of the film can easily be shown to be  $\pi d/6\sqrt{3}$ . Hence using this simple model, the nucleation sites are separated by 13.2 nm at 20°C and 6.6 nm at 150°C.

While the exact value of the nucleation site density may not be exactly correct, the interesting fact is that the change from a 3D to a 2D growth mechanism coincides with the onset of polycrystallinity in the ITO film. It may have to do with the wetting energy difference between amorphous and polycrystalline islands. Our results also imply that the nucleation site density is higher at high temperatures. This is consistent with thermally activated nucleation. Incidentally, true epitaxial growth corresponds to the case of extremely high nucleation site density, which is not the case here.

In summary, it is found that the growth of ITO on glass

always starts with formation of islands on activated nucleation sites. At low substrate temperatures, these islands are amorphous. They grow laterally as well as in height in a 3D manner. At higher temperatures, when the islands are polycrystalline, the islands first grow to a thickness of about one lattice parameter. They will then grow only laterally in a 2D manner. The transition temperature between the two modes occurs at 150–200°C. Interestingly, it is found that the transition in growth mode coincides approximately with the change from amorphous film to polycrystalline film formation. Similar effect may be true also for other types of films.

This research was supported by a grant from the Research Grants Council of Hong Kong.

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