ITO Thin Films Prepared by Magnetron Sputtering Method Using ITO Target
(Effects of Plasma Conditions and Substrate Temperature on ITO Film Properties)

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ITO (indium tin oxide) thin films have been prepared by the magnetron sputtering method. The effects of plasma conditions on ITO thin-film properties have been investigated by means of the Langmuir probe method. Furthermore, the effects of substrate temperature have been investigated. The following results were obtained:
(1) Polycrystal ITO thin films were prepared at 40°C substrate temperature. (2) High electron temperature ($T_e$) is necessary for ITO thin-film crystallization. (3) The magnetic field plays an important role in generating high-$T_e$ plasma.

Key Words: Plasma, Thin Film, ITO, Magnetron Sputtering, Plasma Conditions, Substrate Temperature, Langmuir Probe, Electron Density, Electron Temperature, Crystallization

1. Introduction

ITO (indium tin oxide) thin films, for their good electrical conductivity and light transparency, are now in widespread use as transparent conducting films in a variety of devices. One of the applications of ITO films is in liquid crystal displays (LCDs), which are considered as a promising candidate for large-sized flat displays. Large LCDs, on which a great deal of development effort has been expended, must attain the following four goals: (1) low electrical resistivity, (2) high light transparency, (3) high reliability (in terms of heat resistance, light resistance, humidity resistance and chemical resistance), and (4) capability to be sputtered at low temperature.

We studied optimization of sputtering conditions and improvements of experimental apparatus using a DC magnetron sputtering method in an effort to attain the above four goals. The studies showed that goals (1) and (2) were realized by controlling sputtering pressure, concentration of oxygen and substrate temperature so that appropriate oxygen vacancies were created within an ITO film (13), and that goal (3) was realized by making polycrystal ITO thin films satisfy reliability conditions (13). In connection with goal (4), the studies also showed that polycrystal ITO thin films were prepared at temperatures as low as 40°C (13), in contrast to a conventional method in which the substrate temperature needed to be raised above 150°C (13). This paper presents the results and discussion of experiments which were conducted to study possible factors which allowed us to fabricate polycrystal ITO thin films at a low temperature. The specific purpose of the experiments was to investigate how polycrystal ITO thin-film properties were affected by plasma conditions (electron density and electron temperature) and substrate temperature.

2. Experimental Details

ITO thin films were prepared by the DC magnetron sputtering method using an ITO target. Figure 1 shows a schematic diagram of the experimental...
Fig. 1 Schematic diagram of experimental apparatus

The vacuum chamber was comprised of a load lock chamber (1) and a sputtering chamber (2). The load lock chamber (1), was evacuated to 1.07 mPa using a combination of rotary pump (3) and a cryo pump (4) and substrate heating was performed by a halogen lamp (5). The sputtering chamber (2) has an ITO target (95 wt.% In$_2$O$_3$, 5 wt.% SnO$_2$) (6), with dimensions of 127 mm x 241 mm x t 5 mm. The substrate was a Corning 7059 glass with dimensions of 150 mm x 150 mm x t 1.1 mm, which was mounted on a substrate tray. Sputtering deposition onto the substrate was performed while the substrate tray was reciprocally moving in parallel with the surface of the target with a distance of 50 mm kept between the target surface and the substrate tray. To measure plasma conditions, the sputtering chamber (2) was provided with a plasma diagnostic system which employs a Langmuir probe method. Figure 2 shows the schematic diagram of the plasma diagnostic system. The Langmuir probe used was a 0.2-mm-diameter tungsten wire sealed in a 3-mm-diameter glass tube. When measuring plasma parameters, it was mounted on the substrate tray with the glass substrate immediately below the target.

3. Experimental Method and Results

3.1 Experimental method

A variety of sputtering conditions affect properties of the ITO thin film (such as electrical conductivity, light transparency and crystallization)\(^{(1)-(4)}\). Table 1 shows typical ITO thin-film sputtering conditions which were obtained from the experimental apparatus and which achieved characteristic performance levels, a specific resistance smaller than 6 x 10\(^{-4}\) Ω·cm and a light transparency \( T \) greater than 82% at 540 nm, which transparent conducting films for LCDs (color filters, in particular) require.

Both the plasma conditions and substrate temperature \( T_s \) seemed to greatly affect the crystallization of ITO thin film according to the experiment on sputtering deposition\(^{(1,2)}\). For that reason, ITO thin films were evaluated for crystallization by varying the plasma conditions and substrate temperature as described below.

Principal parameters which vary the plasma conditions (electron density \( n_e \) and electron temperature \( T_e \) were selected for analysis) are sputtering pressure \( P_{sp} \), and discharge current \( I \) and a magnetron magnetic circuit of a sputtering cathode. In this experiment, how the two parameters, sputtering pressure \( P_{sp} \) and magnetron magnetic circuit, affected the plasma conditions involved in ITO thin-film crystallization was investigated with discharge current \( I \) kept at 1.0 A, and substrate velocity \( V_s \) at 5 mm/s (resulting film thickness of ITO thin film 60 nm). Also investigated was how the above two parameters affected the plasma conditions with substrate temperature \( T_s \) set to various temperatures.

Sputtering pressure \( P_{sp} \) was set to various values within the range from 0.53 to 2.68 Pa as listed in Table 1 to meet the specific resistance condition of ITO thin film already described.

As for the magnetron magnetic circuit, distance \( D_{cm} \) between a permanent magnet and the surface of ITO target was varied to vary magnetic field intensity on the surface of the target in Fig.3. Table 2 is magnetic field intensity on the surface of the target. In Table 2, \( B_z \) represents magnetic field intensity at position 1 (the center of the target), perpendicular to the surface of the target. \( B_r \) represents magnetic
Table 2  The relationship between target–magnet distance and magnetic field intensity

<table>
<thead>
<tr>
<th>$D_{TM}$ (mm)</th>
<th>$B_\perp$ (T)</th>
<th>$B_\parallel$ (T)</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>8.0 x 10^{-2}</td>
<td>6.5 x 10^{-2}</td>
</tr>
<tr>
<td>30</td>
<td>5.1 x 10^{-2}</td>
<td>4.1 x 10^{-2}</td>
</tr>
<tr>
<td>40</td>
<td>3.0 x 10^{-2}</td>
<td>2.4 x 10^{-2}</td>
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Fig. 3  Schematic diagram of sputtering cathode

The magnetic field intensity in parallel with the surface of the target at position 2 (32 mm away along the minor axis from the center of the target: erosion region where material is mainly sputtered off the target).

Besides the magnetron magnetic circuit, sputtering pressure $P_{sp}$, and substrate temperature $T_s$, the remaining sputtering conditions were set as below. Sputtering gas was a mixture of Ar and O$_2$ (O$_2$ 1.25 vol%), with mass flow rate of 30 sccm, and discharge current $I$ = 1.0 A and substrate velocity $V_s$ = 5 mm/s.

Crystallization was evaluated by X-ray diffraction patterns and TEM (transmission electron micrograph) images.

We clarified the relationship between crystallization of film and the plasma conditions, and substrate temperature, and discussed factors which contributed to polycrystal ITO thin film were prepared at a low temperature.

3.2 Results

Figure 4 shows results of X-ray diffraction patterns of ITO thin films obtained under several sets of varied parameters of sputtering pressure $P_{sp}$, magnetron magnetic circuit (distance $D_{TM}$ between the target and magnet), and substrate temperature $T_s$. Figure 5 shows TEM images corresponding to the results of Fig. 4. Figure 6 plots grain size of crystallization based on TEM images. Figures 4(a), 5(a) and 6(a) show results obtained by varying sputtering pressure $P_{sp}$ with substrate temperature kept $T_s$ at 84°C and target–magnet distance $D_{TM}$ at 20 mm. Figures 4(b), 5(b) and 6(b) show results obtained by varying the magnetron magnetic circuit (target–magnet distance $D_{TM}$) with sputtering pressure $P_{sp}$ kept at 1.07 Pa and substrate temperature $T_s$ at 84°C. Figures 4(c), 5(c) and 6(c) show results obtained by varying substrate temperature $T_s$ with sputtering pressure $P_{sp}$ at 1.07 Pa and target–magnet distance $D_{TM}$ at 20 mm.

3.2.1 Effect of sputtering pressure $P_{sp}$  From the X-ray diffraction patterns in Fig. 4(a), it is observed that all of the test parameters tested in the sputtering pressure range from $P_{sp}$ = 0.53 Pa to $P_{sp}$ = 2.68 Pa result in a similar intensity level with respect
to the main orientation of the ITO thin film (222). This indicates that crystallization was achieved. From TEM images in Fig. 5(a), it is observed that sputtering pressure $P_{sp}$ affected grain size. Specifically, the lower the sputtering pressure, the larger the grain size of the ITO thin film. Figure 6(a) shows the relationship between the grain size measured from TEM images in Fig. 5(a) and the sputtering pressure $P_{sp}$. As seen from Fig. 6(a), it is obvious that the sputtering pressure $P_{sp}$ plays an important role in grain size. This suggests that the lower the sputtering pressure $P_{sp}$, the more the energy input during the sputtering process. Namely, the lower the sputtering pressure $P_{sp}$ the higher the energy of the sputtered particles, and this presumably accelerates the growth of grain. When sputtering pressure $P_{sp}$ was 1.07 Pa, mean grain size was approximately 60 nm.

3.2.2 Effect of the magnetron magnetic circuit (target-magnet distance $D_{TM}$) From the X-ray diffraction patterns in Fig. 4(b), it is observed that all of the test parameters tested in the target-magnet distance range from $D_{TM}=20$ mm to $D_{TM}=40$ mm resulted in the main orientation of the ITO thin film (222). This indicates that crystallization was achieved. The intensity of the main orientation (222) increases as the target-magnet distance $D_{TM}$ decreases, and crystallization is obviously accelerated. As seen from TEM images in Fig. 5(b) and the relationship between target-magnet distance $D_{TM}$ and grain size shown in Fig. 6(b), grain size of the ITO
thin film increases slightly as target–magnet distance \( D_{TM} \) decreases. The mechanism which worked under the effect of sputtering pressure \( P_{sp} \) as described above in the preceding paragraph also worked under the effect of target–magnet distance \( D_{TM} \). Namely, the energy involved in the sputtering process increases as target–magnet distance \( D_{TM} \) decreases.

3.2.2.3 Effect of substrate temperature \( T_s \)

From the X-ray diffraction patterns shown in Fig. 4 (c), it is observed that substrate temperature \( T_s \) plays an important role in crystallization. Namely, no orientation peak appears at \( T_s=22^\circ C \), suggesting an amorphous state. At 40°C and over, however, the main orientation of ITO thin films, (222) orientation, appears, suggesting crystallization. Along with the increase of the substrate temperature \( T_s \), the intensity of orientation increases, accelerating crystallization. This means that polycrystal ITO thin films are prepared at a temperature as low as 40°C and suggests a substantial lowering of temperature involved in sputtering deposition of polycrystal ITO thin films, compared with a conventional method in which sputtering is performed at a substrate temperature \( T_s \) of 150°C\(^{8,9,10}\) or another conventional method in which thin films are subjected to heat treatment at a recrystallization temperature of approximately 350°C or higher after the sputtering process. From TEM images in Fig. 5 (c) and the relationship between the substrate temperature \( T_s \) and grain size in Fig. 6 (c), grain size slightly increases along with the increase in the substrate temperature \( T_s \). This accelerates the growth of grains.

4. Discussion

Plasma affected by the sputtering pressure \( P_{sp} \) and the magnetron magnetic circuit (target–magnet distance \( D_{TM} \)) presumably plays an important role in the determination of crystallization of ITO thin films. Discussed below are measurement results of how the plasma conditions (represented by electron density \( n_e \) and electron temperature \( T_e \)) vary with sputtering pressure \( P_{sp} \) and the magnetron magnetic circuit (target–magnet distance \( D_{TM} \)).

Figure 7 shows the plasma conditions (electron density \( n_e \) and electron temperature \( T_e \)) measured in the vicinity of the substrate (10 mm above the surface of the substrate, below the erosion region), with sputtering pressure \( P_{sp} \) varied. With sputtering pressure \( P_{sp} \) decreasing, electron density \( n_e \) decreases, and electron temperature \( T_e \) increases. This shows that high-energy electrons exist in the vicinity of the substrate when sputtering pressure \( P_{sp} \) is low. A low sputtering pressure \( P_{sp} \) causes the mean free path to increase, lowering the probability of collision of atoms or molecules in a plasma. The results shown in Figs. 4(a), 5(a), 6(a) and 7 suggest that under a lower sputtering pressure \( P_{sp} \), sputtered particles in the form of atoms sputtered off the target are consumed for forming films, without loss of their energy due to collisions with other atoms (In, Sn, Ar, O) in the path toward the substrate. This allows grains to grow larger.

Figure 8 shows the plasma conditions (electron density \( n_e \) and electron temperature \( T_e \)) measured in the vicinity of the substrate (in a plane parallel to the substrate with a 10 mm separation allowed, in the direction of movement of motion away from the target center), with target–magnet distance \( D_{TM} \) set to several values as parameters. With target–magnet distance \( D_{TM} \) decreasing, electron density \( n_e \) and electron temperature \( T_e \) show broad peaks below the erosion region (within 20 to 40 mm from the center of the target) with its peak point approximately at \( D_{TM}=20 \) mm. With target–magnet distance \( D_{TM} \)
decreasing, magnetic field intensity increases in the vicinity of the substrate, allowing electrons to move in a cyclotron motion with a smaller Larmor radius. This presumably accelerates ionization and excitation due to collisions of electrons in the vicinity of the substrate. At target–magnet distance $D_{TM}=40$ mm, magnetic field intensity decreases in the vicinity of the substrate, weakening the effect of magnetic field and allowing electrons to diffuse. An increased electron density take places in the center portion of the target, presumably because there is an effect of electrons originating from the plasma which is generated centered on the erosion region which is symmetrically distributed with its center at the center of the target. The results in Figs. 4(b), 5(b), 6(b) and 7 show that electron density $n_e$ and electron temperature $T_e$ in particular are high at $D_{TM}=20$ mm, and argon (Ar) and oxygen (O) are actively ionized and excited. Ar and O thus have high energy. This allows sputtered particles in the form of atoms sputtered off the target to be consumed for forming films, without loss of their energy due to collisions with Ar or O in the path toward the substrate. This is expected to accelerate crystallization. When target–magnet distance $D_{TM}$ is 40 mm, electron temperature $T_e$ is low, and electron density $n_e$ is large. Ar and O are not sufficiently ionized and excited. Sputtered particles lose their substantial energy in the course of collisions with low-energy Ar and O, failing to accelerate crystallization.

In summary, the following two conditions are necessary for the preparation of polycrystal ITO thin films under a low-temperature environment.

1. The energy of sputtered particles must be high, and should be prevented from being consumed in the path toward the substrate.

2. Sputtered particles lose their energy due to heat capacity of the substrate when they reach the substrate. It is necessary to compensate for the energy loss to some degree by heating the substrate.

5. Conclusions

The effects of plasma conditions and substrate temperature on crystallization of ITO thin films have been investigated, and the following conclusions were reached:

1. The plasma conditions capable of forming low-temperature polycrystal ITO thin films at a temperature as low as 40°C were defined.

2. The plasma conditions played a major role in low-temperature crystallization, directly governing crystal grain size. Substrate temperature still played an important role, although the degree of its effect on crystallization was weaker than that of the plasma conditions.

3. When plasma conditions include high electron temperature, crystallization of ITO thin film was accelerated. This suggests that a high-energy plasma generated by a magnetron magnetic circuit is a major factor in low-temperature crystallization.

References


