Design of an Electromagnet for Electron Cyclotron Resonance Plasma System for Deposition of Fluorine Doped Tin Oxide

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ABSTRACT

Electromagnets suitable for large-scale electron cyclotron resonance (ECR) plasma systems consisting of linear microwaves of 2.45 GHz with a uniform electromagnetic field of 875 G were designed from simulation data. A thin film of fluorine-doped tin oxide was deposited at low temperature using the designed electromagnet to obtain the desired electromagnetic field. The simulation data and numerical analysis results for the electromagnetic field of the designed electromagnet and the formation of a large-scale ECR zone agreed well. A large-scale ECR zone with a magnetic field of 875 G was formed at 16 cm from the z-axis. The composition of the fluorine-doped tin oxide film deposited under the ECR zone of 16 cm from the z-axis was dependent on the input current of the electromagnet, which affected the deposition region and the ECR zone. Within this experimental range, the distribution of electrical resistivity of the thin film was influenced by the electromagnetic field.

Keywords: Electromagnet, Magnetic field, Electron cyclotron resonance plasma, Fluorine-doped tin oxide, Electrical resistivity

1. Introduction

Recently, the demand for portable touch-screen panels (PTSPs) in portable electronic devices has drastically increased. Therefore, transparent conducting oxides (TCOs), which possess high electrical conductivity and high optical transmission in the visible wavelength region, are being increasingly used. Indium tin oxide (ITO) is a typical TCO that is widely used for applications requiring good electrical conductivity, such as organic light-emitting devices, photovoltaic devices, and portable electronic devices [1-9]. Multi-component oxides with various dopants such as binary and ternary oxides of indium zinc oxide (IZO), aluminum zinc oxide (AZO), and fluorine-doped tin oxide (FTO) have been proposed as TCO alternatives to ITO. Some of them are also being partially commercialized [10-13]. These TCOs are expected to possess low electrical resistance and high transmission in the visible wavelength region to fabricate TSPs of outstanding image quality with a good and fast response to the input signal. Moreover, the TCOs should also be durable to facilitate operation under external impact and prolonged frigid conditions, allowing them to be employed in the manufacture of smart electronic devices with transparent heating and variable color functionality of the window. FTO is a potential candidate for a TCO because its visible transmission and electrical conductivity are comparable to those of ITO.

ITO is typically used in transparent conductive films, but there is a limit to its use for flexible solar cells or dye-sensitized solar cells because of its low resistance to acid. However, FTO has excellent resistance to acids, low electrical resistance, and high optical transmittance, making it a substitute for ITO. Further, unlike the film deposited

by the sputtering or evaporation method, the film deposited by ECR metal-organic chemical vapor deposition (MOCVD) has excellent adhesion between polyethylene terephthalate (PET) substrates and the deposited FTO layer due to anchoring. The anchoring effect was studied previously by examining the deposition of Cu film using ECR MOCVD [14]. In addition, the ECR MOCVD method can be used at temperatures below 80 °C; thus, it can be applied to polymer substrates through a low-temperature process. FTO is typically used as the electrode material in dye-sensitized solar cells (DSSCs) and smart windows due to its corrosion resistance against acid [15]. FTO exhibits a wide range of band gap energy depending on the concentration and composition of the dopant material. It also exhibits a high optical transmittance of 92 % in the visible range of 400-700nm, and a low electrical resistivity of $5.7 \times 10^{-2} \Omega \text{ cm}$ [12,16]. FTO requires a specific low-temperature process that is used for depositing a low-melting-point metal oxide on a PET film via MOCVD. For this, the ECR plasma system is the most suitable.

The deposition of a FTO film using a large-scale ECR plasma system was previously reported [17]. Large circular electromagnets were employed for use in the ECR plasma system; however, they cannot be used commercially owing to space limitations. To achieve a large-scale ECR plasma system with high energy density, it is important to induce linear microwaves in the chamber and ensure a uniform distribution of the electromagnetic field.

In this study, an ECR system was designed from simulation data with linear microwaves of frequency 2.45 GHz and an electromagnetic field distribution of 875 G, and the characteristics of the deposited FTO film were studied.

2. Experimental details

It is important to design an electromagnet that can provide a uniform electromagnetic field and microwave-induced intensity at the substrate surface to form a large-scale ECR plasma system. Therefore, we used a microwave system composed of a dual-type microwave generator and microwave guide. As shown in Fig. 1, the large-scale ECR plasma system consists of two parts, namely the dual microwave generator and the electromagnet. Microwaves of 2.45 GHz were introduced into the plasma chamber through a copper antenna of low electrical resistance in a 4 cm diameter quartz tube. The central portion of each rectangular electromagnet was hollow to facilitate the formation of a uniform electromagnetic field. The plasma chamber and reactor for ionization and decomposition of the reactants were double-walled and contained a cooling jacket of dimensions 85 cm $\times$ 17.5 cm $\times$ 51 cm. The plasma chamber was located near the central portion of the rectangular electromagnets. Ar and tetra methyl tin (TMT) were used as the flow gas and metal organic (MO) source, respectively. For FTO deposition, the base pressure was maintained at 2.0×10^{-6} Torr using three turbo-molecular pumps; the temperature of the canister with TMT was maintained at -5°C . O_2 was used as the reaction gas with a supply rate of 50 sccm. The vapor pressure of TMT in the canister was kept constant at 65 Torr for deposition of a certain thickness. CF_4 gas was supplied at a rate of 3 sccm for doping of Fluorine and was premixed with reaction gas to be supplied to the reactor. During the FTO deposition, the working pressure was maintained at 1.0×10^{-3} Torr. The uniform deposition of the FTO film is affected by the uniformity of the reaction gas supplied. In the ECR MOCVD process, the source injection affects the flow pattern of the fluid in the vacuum process, which can change the uniformity of the deposited film. The nozzle used in this experiment was tested and optimized using three previously known types of nozzles [18].

The plasma gas and reactive gas were introduced by a linear nozzle of width 62.5 cm. The nozzle had holes of diameter 0.05 cm, which were approximately 1 cm apart on the 0.64 cm tube. The nozzle was placed at a suitable distance from the main drum. PET film was used as the substrate. An FTO film was deposited on a roll of PET film of width 50 cm and length 250 m. The line speed of the main drum was 0.1 and 0.3 m/min. The main drum coiled with the PET film was located for the deposition with uniform electromagnetic field and microwave-induced intensity at the substrate surface. The PET film was designed to pass through the center of the main drum. Figure 1(b) depicts a schematic of the side view of the ECR plasma system. Three turbo-molecular pumps were installed to facilitate a uniform distribution

of the flow gas around the substrate and the exhaust gas between the ECR plasma generators.

A magnetic simulator consisting of a communications program for the transfer of data and a current controller with power supply was employed to design the large-scale electromagnet. The electromagnetic field simulations were measured by a gauss meter (Tesla Gauss meter TM701) equipped with an electromagnetic detector probe and jig for various coordinates. Electromagnetic fields were measured 0.5 cm apart up to $x = 50$ cm, $y = 12$ cm, and $z = 20$ cm from the center of the electromagnet. The measured data was written in xyz contour using Origin software. The optical and electrical properties of the FTO thin film deposited on the PET film by the large-scale ECR plasma system were analyzed with varying electromagnetic currents and line speeds for deposition. To compare the optical and electrical properties, FTO thin films were deposited under the same pressure, microwave power, flow rate of carrier gas, and metal organic source gas conditions.

The composition and surface morphology of the deposited thin films were analyzed by electron spectroscopy for chemical analysis (ESCA, PHI 5800) and scanning electron microscopy (SEM, type Hitachi S-4200). A UV-vis spectrophotometer (Konica Minolta, CM-3500d) and four-point probe (Mitsubishi Analytec., Loresta-GP, MCP-T610, ESP-type probe) were employed to measure the optical transmittance and electrical surface resistance of the FTO thin film.

3. Results and discussion

The concentration profile of active ions around the given substrate is critical for uniform deposition on a large-scale substrate. The uniform deposition of the FTO thin film depends on the concentration profile of active ions generated from the ECR plasma and the flow pattern of the reactive gas supplied to the reactor chamber. While neutral radical species and molecules are affected by the pressure distribution in the deposition chamber, active ions and electrons are affected by the electromagnetic field. Low-temperature deposition using ECR plasma is affected by active ions, whose behavior is dependent on the distribution of the electromagnetic field; hence, a uniform magnetic field is crucial.

Figure 2 shows the position with the ECR zone of 875 G from the electromagnet center, the electromagnetic planning, and the image installed. The specific position of the ECR zone with 875 G depends on the current applied to the electromagnet. When the substrate is placed in the ECR zone, etching by the ion bombardment damages the surface of the substrate. When the substrate is adequately far away from the ECR zone, deposition occurs by the reactive ion species generated from the decomposition of the reaction gas by the ions and electrons generated in the ECR zone. Therefore, the ECR zone is a key factor in determining the etching and deposition conditions on the substrate surface. The distance of the substrate from the ECR zone of 875 G along the electromagnetic width (x-axis) at an input magnet current of 292 A was in the range of 15–18 cm. The ECR zone at the plasma chamber position of -20 to 20 cm (on the x-axis) and -12 to 12 cm (on the y-axis) showed homogeneous broadening.

Figure 3 shows the magnetic field (Gauss) distribution contour obtained from the theoretical and experimental values at ECR plasma reactor dimensions of 85 cm $\times$ 17.5 cm $\times$ 51 cm. It was simulated by varying the input current when the ECR plasma magnet dimension was from the center of the plasma chamber ($x = y = z = 0$) to $x = 50$ cm, $y = 12$ cm, and $z = 20$ cm to obtain the uniform magnetic field.

Figure 1. (a) 3D image and (b) side view of the large-scale ECR MOCVD plasma system with linear microwave and electromagnet.

Figure 2. ECR zone of 875 G along the electromagnet width (x-axis) at an input magnet current of 292 A and image of an electromagnet with dimensions of 143.1 cm x 63.4 cm.

Figure 3. Comparison of (a), (b) simulated and (c), (d) measured total magnetic field (Gauss) distribution contour in the xz-plane, $y = 0$.

The electromagnet is designed based on the simulation data. The magnetic field (Gauss) distribution contour shows a symmetrical size range of $x = 50$ cm, $y = 12$ cm, and $z = 20$ cm from the center of the plasma chamber ($x = y = z = 0$). Figures 3(a) and 3(b) show the simulated magnetic field (Gauss) distribution contour in the xz-plane and xy-plane, respectively. Figures 3(c) and 3(d) show the magnetic field (Gauss) distribution contour in the xz-plane and xy-plane from the designed electromagnet based on the simulation data in Figs. 3(a) and 3(b), respectively. These results are in good agreement with the theoretical data. The ECR region of 875 G is formed in the range of -16 to -17 cm along the z-axis. The results illustrated in Fig. 3(a) are consistent with those in Fig. 2. The magnetic field is much higher at the center compared to lower side of the electromagnetic z-axis. The magnetic field at the 500 mm of the x-axis with a dense coil of electromagnet is more than 2000 G. The magnetic field contour in the xy-plane at the center of the electromagnetic z-axis has an elliptical orbit.

Figure 4 shows the simulated magnetic field distribution by moving the y-axis 10 cm away from the z-axis from the center of the electromagnet. As shown in Fig. 4(a), the magnetic field increases around the edge of the electromagnet but decreases at the center of the electromagnet. The magnetic field of 875 G meets the condition for ECR formation in the range of 0-25 cm on the x-axis.

Figure 4(b) shows the magnetic field distribution by changing the z-coordinate at each position of the x-axis. The magnetic field

Figure 4. Magnetic field distribution with (a) y-axis (electromagnetic width) and (b) z-axis.

Figure 5. Comparison of magnetic field along the z-axis and ECR zone in the designed electromagnet 1, 2.

decreased dramatically as we moved further from the center of the z-axis. The ECR region with a magnetic field of 875 G on the z-axis is the point corresponding to 16 cm from the center. Therefore, the points beyond 16 cm would be appropriate for the deposition process when using this electromagnet.

As shown in Figs. 3 and 4, based on the simulation data of the electromagnetic field, an electromagnet with a magnetic field of 875 G that satisfies the ECR condition was designed for the experiment. The electromagnet is formed of 14 layers with a small rectangular bandage copper tube, and cooling water flowing through the copper tube. The maximum input current and electrical potential are 300 A and 50 V, respectively. A pressure drop of 800 kPa and a flow rate of 0.0083

Figure 6. (a) XPS spectra and (b) mole ratio of deposited FTO film with input electromagnetic current.

m³/min were set in the rectangular copper tube. Figure 5 shows the simulated data and the actual measured electromagnetic field along the z-axis. The measured electromagnetic field is well consistent with the simulation data, and the ECR zone having a magnetic field of 875 G was formed at 16 cm along the z-axis, as shown in Fig. 4(b).

FTO was deposited on the PET film by the ECR system configured by the dual microwave generator and designed a electromagnet. XPS analysis was performed to investigate the chemical composition of the deposited film. The properties of the deposited films, such as composition, changed because the input current of the electromagnet affected the deposition region and ECR zone. Figure 6 shows the narrow scan XPS spectra and the molar ratio of the deposited FTO films at a roll speed 0.1 m/min and input currents of 200, 250, and 300 A. Figure 6(a) shows the intensity of the inter-molecular bonds from the peak separation of C1s at a binding energy of 280–290 eV, and O1s in the range 525 to 535 eV for the deposited FTO thin film at different values of currents. The C1s peak shows the three peaks due to the C-C bond at 284.8 eV, C-O bond at 286.51 eV, and C = O bond at 288.9 eV. The O 1s peak also shows four peaks due

Figure 7. Optical transmittance and reflectance of the deposited FTO film with the electromagnetic input current.

to the O-Sn-O bond at 529.7 eV, O-C bond at 530.4 eV, C = O bond at 531.2 eV, and C-OH bond at 532.7 eV. In the case of the carbon peak in the range 280–290 eV, the increase in electromagnetic current leads to an increase in the area of the C-O peak at 286.51 eV and a decrease in the area of the C = O peak at 288.9 eV. The areas under the O-C peak at 530.4 eV and C-OH peak at 531.2 eV increased and the area under the C = O peak at 531.2 eV decreased. The position of the PET film substrate and ECR plasma zone depends on the electromagnetic current. Therefore, the electromagnetic current can affect the electrical and optical properties due to compositional changes in the deposited FTO film. To reveal the impact of the electromagnetic current on the compositional changes in the deposited FTO film, the atomic mole ratio was calculated from the peak separation in Fig. 6(a). Figure 6(b) shows the mole ratio of O/Sn, C/Sn, and O/C. The mole ratio of O/Sn and C/Sn decreases as the electromagnetic current increased. That is, the mole of Sn atoms in the deposited FTO films increased, and the mole ratios of C and O decreased. The mole ratios of O/C did not change much with the electromagnetic current, but the mole of O atom increased at the current value of 300 A. This is because the surface reaction to form the FTO film is efficiently conducted by the transfer of oxygen ions from the gas phase to the substrate as the current through the electromagnet increases.

Figure 7 shows a comparison between raw PET and the optical transmittance of the FTO film at conditions where the current of the electromagnet is 200, 250, and 300 A. The raw PET used an optical film with an optical transmittance of 90.10 % at a wavelength of 550 nm. The transmittance of films deposited at 200, 250, and 300 A was 88.56, 87.42, and 84.32 %, respectively, and reflectivity was within the range of 10–20 %. The optical transmittance tends to decrease slightly with increasing the current in the electromagnet, which is believed to be influenced by the formation of dense film and by electrons with high energy as the ECR zone near the substrate.

Figure 8 shows the thickness of the FTO film deposited under 250 and 300 A conditions and the SEM image of the surface. An ionized ion is formed by the resonance of an electron cyclotron of an O₂ gas supplied to the ECR area at a distance of more than 15 cm from the substrate under conditions of 250–300 A. Oxygen ions activated by the gas phase decomposition with reaction gas TMT from the nozzle and Sn ions formed FTO film. The thickness of the film decreased at the same deposition time as the current flowing through the

Figure 8. SEM images of cross-section and surface morphology at the electromagnetic input current (a) 250 A and (b) 300 A.

Figure 9. Deposition thickness and grain size from surface morphology of the deposited FTO film with the electromagnetic input current.

electromagnet increased due to the formation of the dense film. Surface morphology looked similar from the shape of grains present on the surface for synthesis condition of currents of 250 and 300 A, but grain appeared to be smaller for that deposited at 300 A. This is thought to be caused by the slight movement of the ECR zone towards the substrates by high current and the high energy of the active species by plasma density.

Figure 9 shows the film thickness and grain size on either edge of the deposited FTO film with the electromagnetic input current at line speed 0.1 and 0.3 m/min. In the case of the films deposited at the electromagnetic current of 200 A, the film thickness on either edge was in the range of 90-100 nm and the thickness difference was approximately 10 nm. For deposition conditions with current values of 250 and 300 A, the thicknesses were 50-60 and 40 nm, respectively. The film thickness on either edge of the deposited FTO film deposited at the current of 300 A was uniform. The grain sizes on the two edges of the deposited FTO films were 8.5 and 6.5 nm at 200 A, 7 and 10.5 nm at 250 A, and 8.5 nm at 300 A. The grain size of the deposited FTO film at a high electromagnetic current had more uniform distribution. A possible explanation could be that the FTO films deposited at a low

Figure 10. Surface resistance distribution with film width (x-axis) as a function of the input power magnetic field and SEM images of the cross-section and surface.

electromagnetic current were affected by the flow pattern of the active radicals due to the high deviance of the electromagnetic field. The FTO film deposited at a high electromagnetic current, however, was affected by the electromagnetic field rather than the flow pattern. That is, the reactive ions produced by the electromagnetic field at a high current were important for uniform film deposition on either edge of the deposited FTO film.

Figure 10 shows the surface electrical resistivity distribution and SEM images of the cross-section and the surface morphology of the deposited films. The thickness of the film deposited at the current value of 250 A was 60 nm, and the surface morphology shows uniformly distributed fine grains with nano-scale sizes. The electrical resistivity was high. The electrical resistivity distribution of the film deposited at 200 A had high deviance in the range of 1.2×10^{-2} to $9.0 \times 10^{-3} \Omega\text{-cm}$ depending on the deposition position. At 250 A, the surface electrical resistivity was much lower in the range of 5.5×10^{-3} to $4.90 \times 10^{-3} \Omega\text{-cm}$ on both edges of the deposited FTO film. The electrical resistivity distribution was higher at the center and lower parts at both the edges. This electrical resistivity distribution tendency is similar to the specific locations of the ECR zone with 875 G in Fig. 2. This is attributed to the electrical resistivity distribution affecting the concentration of generated active ions from the decomposition of the reactive gas in the ECR zone. In the case of 300 A condition, the electrical resistivity showed a uniform distribution in the range of 4.8×10^{-3} – $3.8 \times 10^{-3} \Omega\text{-cm}$ influenced by the electromagnetic field more than that at 250 A. As a result of this, the surface electrical resistivity improved and the electromagnetic field distribution became uniform in the ECR zone.

4. Conclusions

We designed an electromagnet for large-scale FTO film deposition using ECR plasma with a linear microwave of 2.45 GHz. The electromagnet having a uniform electromagnetic field distribution was simulated and it was specially produced based on the simulation data. The properties of the FTO film deposited at different applied currents were compared. The electromagnetic field at the designed electromagnet zone was found to be consistent with the numerical analysis results, and an ECR zone having a magnetic field of 875 G was formed at 16 cm from the z-axis. The concentration of O, Sn, F, and C in the

fluorine-doped tin oxide film depended on the input electromagnetic current affecting the deposition region. The electrical resistivity of the deposited FTO film was dependent on the ECR zone.

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