Mol. Cryst. Liq. Cryst., Vol. 532: pp. 141/[557]–147/[563], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.497060

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Fabrication of Transparent Semiconducting Indium Zinc Tin Oxide Thin Films and Its Wet Chemical Etching Characteristics in Hydrochloric Acid

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We have fabricated the transparent semiconducting indium zinc tin oxide (IZTO) thin films on polymeric substrates at room temperature by RF-magnetron sputtering method, and investigated their wet chemical etching behavior in HCl solution. The study has revealed that the control of O_2 flow rate during deposition attribute to the variation of resistivity for IZTO films, resulting in the conductor–semiconductor conductivity transition. The increasing etchant molarity and temperature of etching solution lead to the increase in etching rate of IZTO films according to the chemical dissolution reaction. As a result, the IZTO active channel is defined successfully, suggesting sufficient possibility for the application to flexible transparent thin film transistors.

Keywords Flexible transparent thin film transistor; HCL etchant; indium zinc tin oxide (IZTO); transparent semiconductor; wet chemical etching

Introduction

Recently, transparent thin film transistors (TTFTs) fabricated on polymer substrates using oxide semiconductor have attracted much attention for the application of flexible displays due to high mobility, good uniformity and low process temperature [1–3].

In flexible TTFT device, the amorphous semiconducting oxides, indium-rich oxides such as In-Zn-O, In-Ga-Zn-O, and In-Ga-O, are suitable for the plastic

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substrate under low process temperature, because of being provided more uniform structure and smoother channel interface to the gate insulators, compared to polycrystalline semiconductor such as ZnO-based oxides [4].

It has been reported that amorphous transparent conducting oxides (TCOs) can be adjusted to the channel material in the TTFT by the control of conductivity, originating from the conductivity transition between conductor and semiconductor [5]. Among TCOs, a promising material is indium zinc tin oxide (IZTO) because of their possibility for use as TCO films with excellent chemical and thermal stability, as well as high electrical conductivity and optical transparency [6,7].

On the other hands, in general, the wet chemical etching process is simpler than the dry method, and provides a high throughput and low cost. Therefore, wet etching is used to pattern TCO films in display manufacturing [8]. For the application of IZTO semiconductor to flexible TTFT devices, the wet etching behavior must be investigated to evaluate its chemical stability and to explore etchants for use in wet etching, which is an essential subject for the device fabrication using this material. This work is motivated from the fact that wet chemical etching characteristics of IZTO thin films in the aqueous etching solutions conventionally used in TFT industry is yet to be reported. In wet etching process, hydrochloric acid (HCl) has been widely used as one of the conventional etchants for patterning of TCO films [9–11].

Hence, in this study, we have prepared transparent semiconducting IZTO thin film on polyethylene naphthalate (PEN) substrate by RF-magnetron sputtering method, and investigated their wet chemical etching characteristics in HCl solutions.

Experimental

The IZTO thin films were deposited on the PEN (Teijin Dupont Films) substrate covered with hard coating layer, using a RF-magnetron sputtering method, at room temperature with varying O_2 fraction in the mixture of Ar and O_2. Prior to deposition, the substrates were cleaned with acetone, methanol and de-ionized water for 10 min in an ultrasonic bath. The base pressure in the chamber was adjusted to 1.0×10^{-6} Torr and the pressure during the deposition was maintained at 3 mTorr regardless of O_2 fraction in Ar and O_2 gas mixture. The composition of 3 inch sputtering target used in the experiment was In_2O_3: ZnO: $SnO_2 = 90$: 7: 3 in weight ratio with purity of 99.99%.

The semiconducting IZTO films were patterned using a conventional photolithographic method. The etching was carried out in hydrochloric acid solutions as a function of etchant concentration and etching temperature. After etching process, the samples were rinsed in deionized water, the photoresist was stripped using acetone and then the films were dried in N_2 flow.

The thickness and etching rates of the films were determined by a surface profiler (KLA Tencor, Alpha-Step IQ). In order to examine the crystallinity of IZTO thin films, x-ray diffraction (XRD, Rigaku, D/MAX-2500) measurement was performed. The XRD diffraction patterns of the films did not contain any peaks attributable to crystal, indicating amorphous state. The electrical properties of IZTO thin films were obtained from the Hall Effect measurement (Ecopia, HMS-3000) by the Van der Pauw technique. Optical transmittance characteristics of the films were measured by means of an ultraviolet-visible spectrophotometer (Otsuka, MCPD-7000) in the visible region. Optical microscope (Olympus,

BX51 M) and field emission scanning electron microscope (FE-SEM, JEOL, JSM-7000 F) were used to observe the pattern images and etching profiles, respectively.

Results and Discussion

Figure 1 shows the influence of O_2 flow rate in the sputtering deposition on the deposition rate of the IZTO thin films. It is observed that when oxygen flow rate increases, deposition rate of the films decreases gradually. The decrease in the deposition rate with O_2 flow rate is caused by the relative reduction of Ar fraction under constant pressure, resulting in lower sputtering yield of the target material. Although the deposition rate is varied with O_2 flow rate, by the control of sputtering time, the thickness of the deposited IZTO films is fixed at about 100 nm, which is confirmed by the cross section images of a FE-SEM.

Figure 2 indicates the dependence of electrical properties of IZTO thin films on the oxygen flow rate. It is seen from Figure 2 that with an increasing oxygen flow rate, the resistivity of the films increases while the Hall mobility and carrier concentration decrease. It is known that the variation in the resistivity of the TCO thin film is attributed to the combined effect of changes in carrier concentration and Hall mobility, which in turn is associated with the oxygen vacancies [12]. As oxygen flow rate increases, due to the fact that the concentration of oxygen vacancies is decreased as a result of the incorporation of oxygen into the films, the amount of free carriers arising from the doubly charged oxygen vacancies is reduced, in addition that the creation of electron scattering centers such as the neutral defects and the negatively charged oxygen gives rise to interrupt electron transport, resulting in the decrease of Hall mobility [13]. Accordingly, the increases in electrical resistivity with oxygen flow rates are originated in the elimination of the oxygen vacancies in the films. In a viewpoint of TTFT application, it is interesting that the resistivity of IZTO

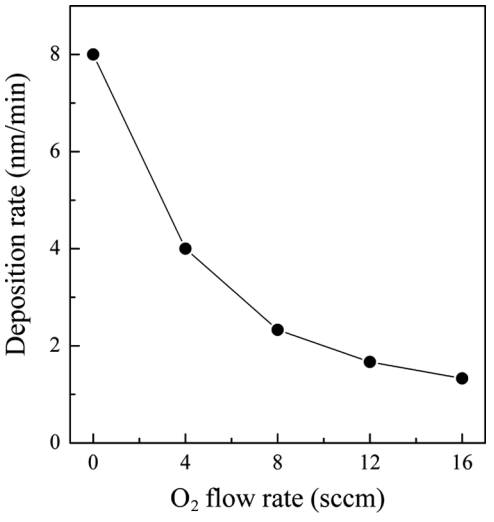


Figure 1. Deposition rate of IZTO thin films deposited with varying O_2 flow rate.

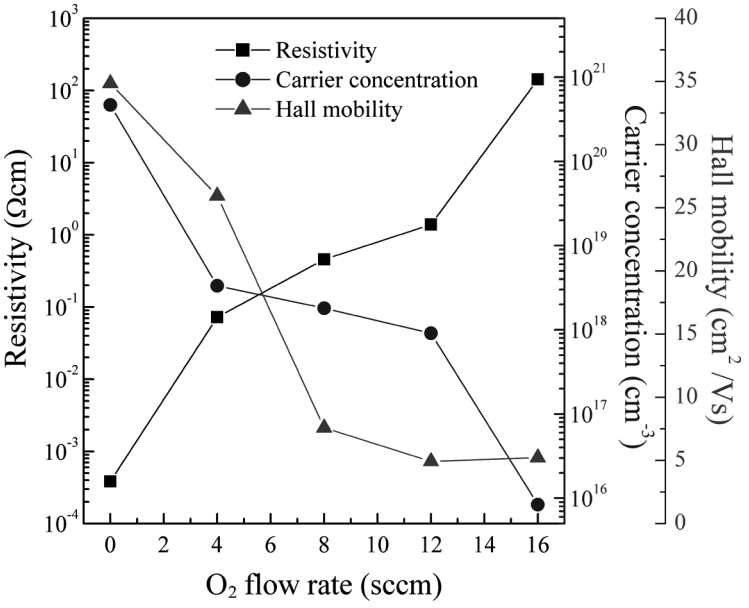


Figure 2. Electrical properties of IZTO thin films deposited with varying O_2 flow rate.

thin films, which is inversely proportional to the conductivity, can be controlled by introduction of O_2 gas during deposition, occurring in the metal–semiconductor conductivity transition. The similar phenomenon has been observed in a recent work on In-Zn-O thin films by E. Fortunato, *et al.* [14]. Hence, it is worth noting that the IZTO films deposited in pure Ar ambient shows the resistivity of about $3.5 \times 10^{-4}\,\Omega$cm, which can be used as the source, drain and gate electrodes in TTFT devices. In particular, because resistivity within the order of $1\,\Omega$cm can serve well as active channel in TTFT applications [5], the IZTO film grown at 12 sccm oxygen flow rate is a semiconductor showing the resistivity of about $1.4\,\Omega$cm, which corresponds to carrier concentration of about $9.1 \times 10^{17}/\text{cm}^3$ and Hall mobility of about $4.9\,\text{cm}^2/\text{Vs}$. Also, it cannot be ruled out that a channel material for TTFT must be fabricated with low carrier density and high carrier mobility [4]. The carrier concentration and mobility of IZTO semiconducting film are superior to those of sputtered In-Ga-Zn-O film [15], which can be a good candidate for the channel in flexible TTFT device.

The optical transmission spectrum of the semiconducting IZTO films in the wavelength range between 350 and 800 nm is shown in Figure 3. For comparison, transmittance of the PEN substrate is also indicated. The optical transmittances of ~86.5% and ~86% at 550 nm wavelength are obtained for the PEN substrate and the IZTO films on the PEN, respectively. This result indicates that a semiconducting IZTO films is transparent in the visible region.

Based on the above results, it can be concluded that the IZTO thin film deposited at 12 sccm oxygen flow rate is an amorphous semiconductor with high optical transparency, which can be applied to the channel layer in TTFT devices, and the subsequent investigation on characteristics of wet chemical etching is conducted.

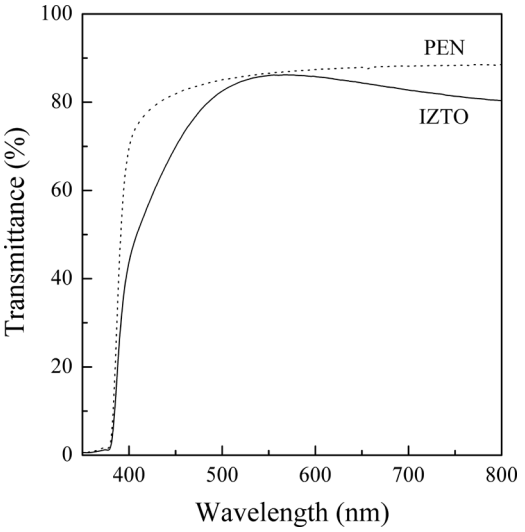


Figure 3. Optical transmittance of semiconducting IZTO films deposited on PEN substrate in visible region.

Figure 4(a) and (b) represent the effect of reaction temperature on the etching rate of the IZTO semiconductor under different HCl molarity and the corresponding logarithm plots as a function of reciprocal temperature, respectively. As seen in Figure 4(a), it can be easily found that the etching rate increases with the increase of etching temperature and etchant concentration. It has been known that the wet etching reaction rate can be controlled by changing the solution concentration and

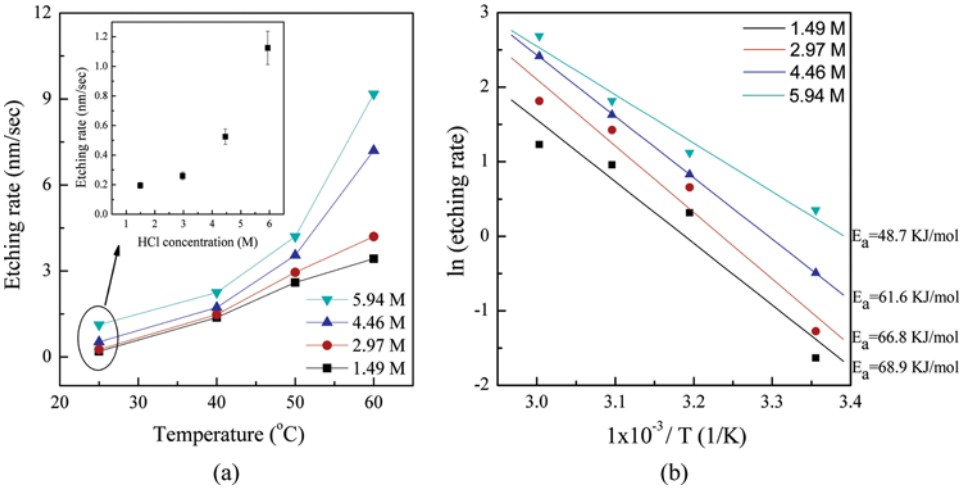


Figure 4. Effect of reaction temperature on the etching rate of the IZTO semiconductor under different HCl molarity (a) and the corresponding logarithm plots as a function of reciprocal temperature (b). The inserted figure in Figure 4(a) represent the etching rate of semiconducting IZTO films with varying HCl conentration at 25°C.

reaction temperature [16]. Also, from the inserted figure in Figure 4(a), under reaction temperature of 25°C, the IZTO etching rate is about 0.3 nm/sec at 2.97 M HCl concentration, which is satisfactory as to the requirements [11] on the industrial process. The variation of the etching rate as a function of temperature has a relation with the chemical etching activation energy. The linear plots for the logarithm of etching rate demonstrates that the Arrhenius relationship is obeyed in the reactions between 25 and 60°C. The activation energy is then calculated from the slopes of these plots. As indicated in Figure 4(b), the calculated activation energies of etching IZTO films with HCl acid are found to be from 48.7 to 68.9 kJ/mol. These high values can be explained by the chemical dissolution reaction [17] rather than electrochemical reaction. The chemical dissolution reaction of the IZTO film in HCl solutions can be described by the following reactions from (1) to (3)

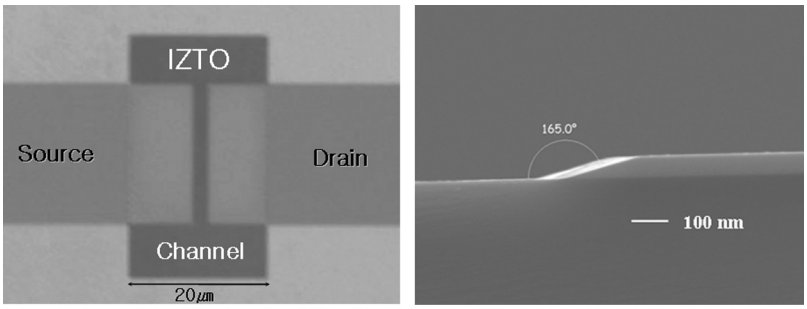
$$In_2O_3 + 6HCl \rightarrow 2InCl_3 + 3H_2O \quad (1)$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad (2)$$

$$SnO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O \quad (3)$$

These chemical reactions indicate that by actions of HCl, In, Zn, and Sn in the IZTO films effectively removed from the surface as the etch product of respective $InCl_3$, $ZnCl_2$, and $SnCl_4$. Accordingly, the increase of HCl mole concentration and solution temperature can accelerate the etching activity and the chemical reaction rate, respectively. However, a noticeable point is that dilute HCl solutions are desired to be used in order to achieve controllable etching rate at room temperature, as previously mentioned.

Figure 5 illustrates the pattern image (a) and etch profile (b) of semiconducting IZTO films after wet chemical etching with 2.97 M HCl concentration at 25°C. In Figure 5(a), it is obvious that the IZTO film is removed by dissolution along with stripping, showing the well defined channel. Also, the occurrences of surface residual byproduct and undercut pattern cannot be observed, which is attributed to relatively low etching rate and adequate thickness of photoresist to protect the pattern.



(a) (b)

Figure 5. The pattern image (a) and etch profile (b) of semiconducting IZTO films etched by HCl solution.

But, steep sidewall slop of the etched pattern is difficulty to be obtained, originating in isotropic etching characteristic of wet chemical etching for amorphous semiconductor, as shown in Figure 5(b).

Conclusions

In summary, transparent amorphous IZTO thin films were prepared by RF-magnetron sputtering techniques. The resistivity of IZTO films can be controlled by varying O_2 fraction in sputtering gas during deposition, resulting in the conductor-semiconductor conductivity transition. With increasing HCl mole concentrations and etching solution temperature, etching rate of semiconducting IZTO films are increased following the mechanism of chemical dissolution reaction. In addition, with dilute HCl solution at room temperature, the excellent pattern of IZTO channel is obtained. On the basis of this work, therefore, we suggest that fabrication of semiconducting IZTO film by the RF-magnetron sputtering method and subsequent wet chemical etching in HCl solution are suitable processes for the preparation of active channel in flexible TTFT. Accordingly, the systematic studies on the performance of flexible IZTO-based TTFT devices are also needed to investigate and determine the optimized conditions for flexible transparent display.

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