A Study on Wet Etch Behavior of Zinc Oxide Semiconductor in Acid Solutions

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Abstract

A significant progress has been made in the characterization of zinc oxide (ZnO) semiconductor as a new semiconductor layer instead of amorphous Si semiconductor used in thin film transistor due to its high electron mobility at low deposition temperature which is quite suitable for flexible display and OLED devices. The wet pattering of ZnO is another important issue with regard to mass production of ZnO thin film transistor device. However, the wet behavior of ZnO thin film in aqueous wet etching solutions conventionally used un TFT industry has not been reported yet, in this work, wet corrosion behavior of RF magnetron sputtered ZnO thin film in various wet solutions such as phosphoric and nitric acid solutions was studied using by electrochemical analysis. The effects of deposition parameters such as RF power and oxygen partial pressure on corrosion rate are also examined.

1. Introduction

Amorphous-silicon (a-Si:H) thin-film transistors (TFTs) are widely used as switching elements of active-matrix liquid crystal display (AMLCDs). Recently ZnO thin films have been studied as an active layer in the thin film transistor (TFT) instead of amorphous silicon (a-Si:H) because of their low cost, low photo sensitivity, no environmental concerns, and especially high mobility. In addition, low temperature fabrication of ZnO makes it possible to be fabricated on plastic films.

Application targeted more compatible with OLED and flexible displays. During wet pattering and photolithography process, the increasing demand for the fundamental electrochemical study on the film in LCD etchant solutions, however, little is known about corrosion behavior of the ZnO thin film etchant solutions such as nitric and phosphoric acid.

In the present study, wet corrosion behavior of RF magnetron sputtered ZnO thin films on the glass substrate has been examined. The dependency of stress and corrosion of the ZnO thin films on the deposition parameters such as RF power and O_2 partial pressure were also studied.

2. Experimental

The zinc oxide thin films were deposited on glass substrate using RF magnetron sputtering system. The thicknesses of the thin films deposited were measured immediately after the deposition. The thickness was measured with a Tencor profilometer. The residual stress measurements were carried out by recording the curvature of the Si substrate before and after the deposition. The stress of the film was obtained from the stoney formula. [1] Resistivity was obtained after metal films were deposited on ZnO thin films using transmission line methods by a probe station Agilent 4155C.

After immersion in the acid solutions including nitric acid (0.1M), phosphoric acid (0.1M), hydrochloric acid (0.1M), and acetic acid (0.1M)) for 5 seconds, dissolution rates of the films were measured from gradient of thickness via time with a

Tencor profilometer.

3. Results and discussion

ZnO thin films are fabricated by the sputtering method, which allows good control of the film thickness, uniformity, and composition. The structure and property of a sputter-deposited film are strongly affected by the sputtering parameter, such as the gas, pressure, power, substrate temperature, bias voltage and ion acceleration energy [2]. It has been known that the corrosion behavior of the thin film is strongly dependent on the structures of the film. The growth rates and resistivities of ZnO thin films increased with increasing RF power and oxygen pressure (Fig. 1). The higher RF power, deposition rates of ZnO thin films increased. As the RF power increased, sputtered zinc atoms or ions were increased by enhanced Argon ion collsion with a ZnO target. The degradation of the conductivity of the film at high RF power results from the increase in the probability of the oxygen anion bombardments into the ZnO surface. On the other hand, the resistivities of the films approached a saturation value with increasing oxygen partial content. It means that the ZnO film changed from a semiconductor into an insulator with increasing oxygen partial pressure. It was found from this work that such semiconductor/insulator transition of the film strongly affects the electrochemical process on the ZnO surface in the aqua solutions.

The X-ray diffraction spectra of ZnO thin films grown at different RF power are shown in the (a) of figure 2. The 2θ peak was observed at 34.5°, indicating that the films were grown with a preferred orientation along the (0002) plane. A preferred orientation (0002) peak was broadly shown in RF power 50~150W, but the peak was obviously shown in the film grown at 200W.

From the variation of the Full Width at Half Maximum (FWHM) of (0002) peak, it is concluded that films sputtered at high RF power have higher

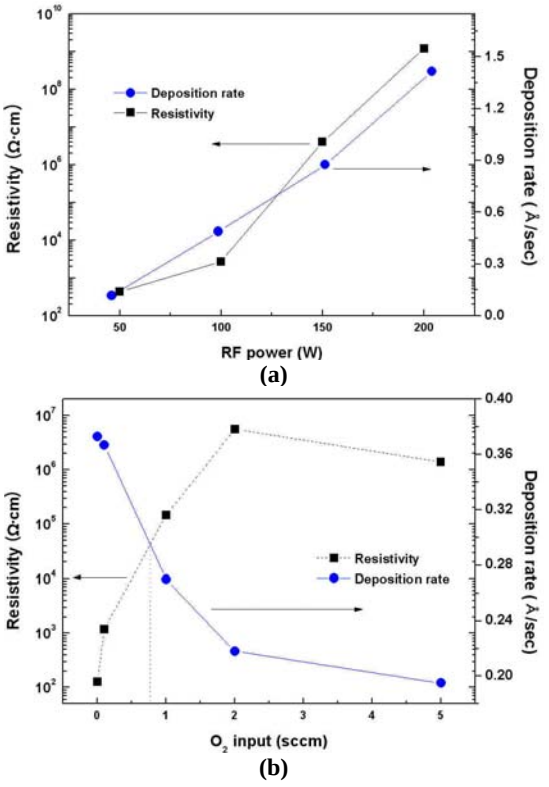


Fig. 1. Change of the resistivities and deposition rates of zinc oxide thin films on the glass substrates as functions of (a) the RF power, at 10 mTorr with the substrate temperature of 150 °C and (b) the O_2 partial pressure, at 100W and 10mTorr with 50 °C.

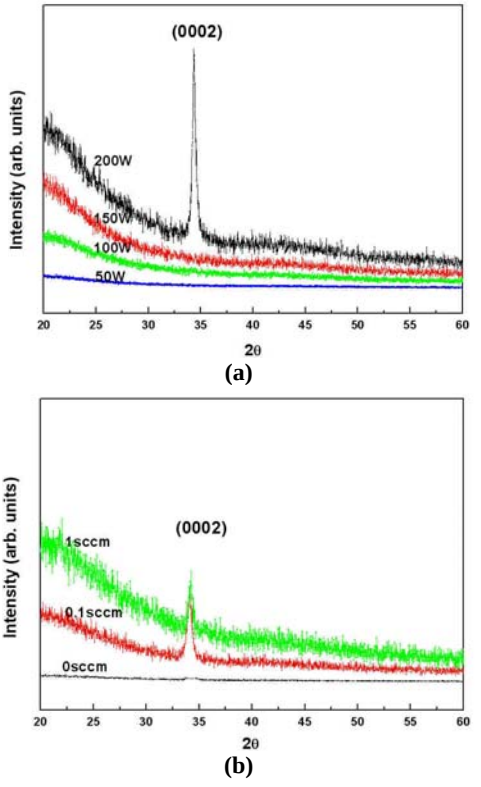
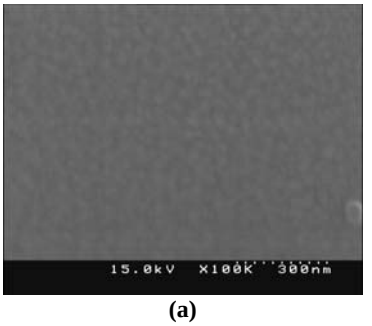


Fig. 2. X-ray diffraction peak intensities of ZnO films with a preferred orientation along the (0002) plane as functions of (a) the RF power at 10mTorr with the substrate temperature of 50°C and (b) O_2 partial pressure at 100W, 10mTorr and 50°C.

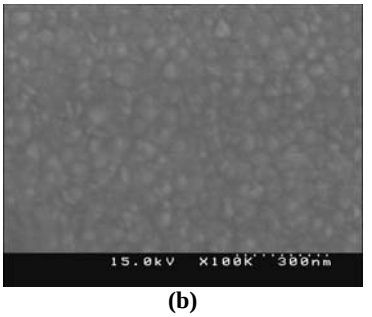
crystallinity than that of the films deposited at low RF power. The surface morphologies of the sputtered ZnO thin films are shown in Fig. 3. The grain size of the film at 300W is much larger than that of the film deposited at 50W. Similar to RF power, the films grown with high O_2 partial pressure have higher crystalline than that of the films deposited with low O_2 partial pressure. In addition, the grain size of the film grown with O_2 partial pressure of 0.5 sccm is much larger than the film with 0 sccm. It was reported that sputtered ZnO thin films have mostly compressive stress [3].

The corrosion rates of the films decreased with increasing the RF power and the oxygen partial pressure (Fig. 5). The corrosion rate of the film is strongly affected by the degree of the crystallinity of the film. As the crystallinity in the film increases, the dissolution of the film is more favorable.

Potentio-dynamic curves shows that electrochemical process is recessed as the film have a lower conductivity (Fig. 4). The film grown with 0 sccm oxygen partial pressure have a lowest resistivity value in the order of 10^2 Ω·cm.



(a)



(b)

Fig. 3. SEM plane view images showing the grain size of ZnO thin films growth at RF power of (a) 50W and (b) 300W.

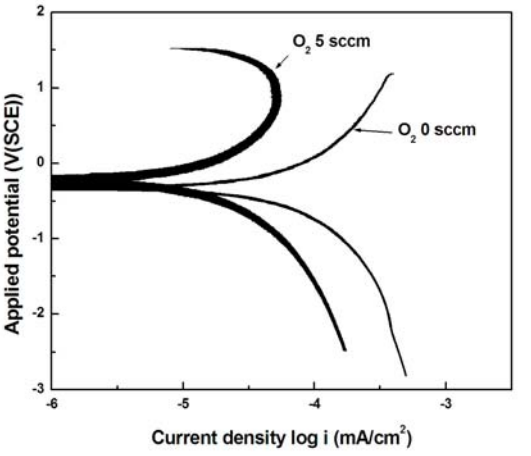


Fig. 4. Potentio-dynamic curves for the ZnO films grown with different oxygen pressures in 0.01M HCl solution.

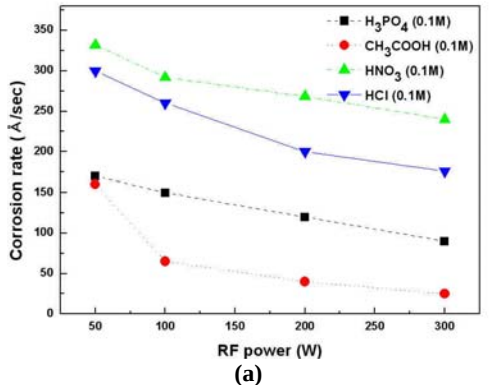
It means that the relatively large number of electrons in the conduction band of the film can bring about the electrochemical reaction. The film grown at high O_2 partial pressure can be considered like a insulator which have little free electron needed for the occurrence of the electrochemical reaction. Therefore, the electrochemical process is remarkably recessed with respect to the film grown at low oxygen pressure. In the case of high oxygen pressure, the chemical dissolution process predominates in the dissolution of the ZnO film in the HCl solution.

Figure 5 shows the dependency of corrosion rate of the ZnO thin films on various acid solutions. From the above results, it turned out that the etch rate is fastest in nitric acid (0.1M) and slowest in acetic acid (0.1M). It is well known that the dissolution of the crystalline indium tin oxide film is closely related to the halogen ions in the solution [6]. However, the dissolution tendency of the ZnO is quite different from that of the ITO films.

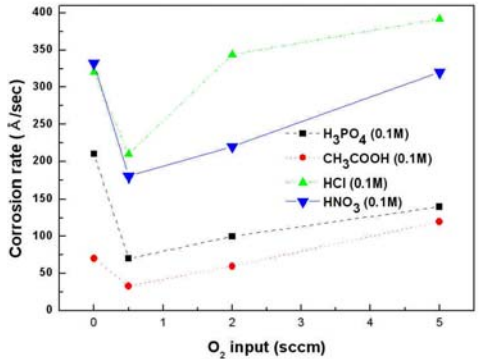
In the case of oxygen pressure, corrosion rate of the film has the minimum value at the 0.5 sccm. Above the 0.5 sccm, the dissolution rate increased with increasing oxygen pressure.

4. Summary

Wet dissolution behavior of RF magnetron sputtered ZnO thin films on the glass substrate has been examined. The dissolution rate increased with increasing the RF power and showed minimum value at the 0.5 sccm oxygen partial pressure. Such behavior is strongly related to the degree of the crystallinity of



(a)



(b)

Fig. 5. Dependency of dissolusion rates of zinc oxide thin films on various acid solutions; as functions of (a) the RF power and (b) O_2 partial pressure.

the ZnO films. The film dissolves fastest in the nitric acid and slowest in the acetic acid.

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