Fabrication of the ZnO thin films using wet-chemical etching processes on application for organic light emitting diode (OLED) devices


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We deposited ZnO thin films at room temperature by RF magnetron sputtering method with home-made targets, and for application tests using these films as transparent conductive oxide (TCO) anodes, wet-chemical etching behaviors of ZnO films were also investigated using various chemicals. In order to fabricate ZnO-based OLED devices, various etchants such as HCl, HNO3, H2SO4 and H3PO4 have been studies for the wet etching of ZnO thin film. In this experiment, we introduced two new different chemicals as etchants, ferric chloride (FeCl3$\cdot$6H2O) and oxalic acid (C2H2O4) which were controlled with various concentrations in ZnO etching process and showed an anisotropy etching shape of ZnO films.

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1. Introduction

Transparent conductive oxide films (TCO) have been comprehensively used in solar cells, touch panels, heat mirrors, organic electro-luminescence devices (OLED) and liquid crystal displays (LCD) [1–3]. This is because TCO films have wide band gaps, low specific resistances and high transparencies in the visible and near infrared wavelength range. TCO films are also key components for transparent electrodes in display and opto-electronic devices. Indium tin oxide (ITO), for example, has been commercially used in OLEDs. However, because of the cost and the scarcity of indium, researchers have been making effort to access other alternative materials for replacing ITO such as zinc oxide. It is a non-toxic, chemically stable, inexpensive and abundant material [4]. ZnO films could be formed by electron-beam evaporation, chemical vapor deposition (CVD), pulsed laser deposition (PLD) and sputtering method [3]. Among these techniques, sputtering method offered much more advantages: it is safe and simply technique, performs high deposition rate at room temperature, emits non-toxic gas, and can be extended easily to large scale glass substrate. Therefore, most researchers used sputtering techniques to prepare ZnO films [5].

For OLED manufacturing, fine delineation of films to micron/submicron scale has become increasingly important. So, dry and wet etching processes are extremely important techniques for films patterning. The wet process involves one or more chemical reactions that consume the original reactants and produce new species. Wet-chemical etching has great advantages such as low cost and anisotropic/isotropic etching. Generally, etchants such as HCl, HNO3, H2SO4 and H3PO4 have...
been used for etching ZnO thin films [7,8]. Anisotropic shapes could be generally obtained using low concentrations of these chemicals. Etching rate can be significantly increased using higher concentrations; however, control of the surface shape becomes more difficult in this case.

Recently, attempts have been made to find new etchants for more efficient etching and better shape control of ZnO films.

2. Experimental

Zinc oxide films were deposited on glass substrates by using 13.56 MHz radio frequency (RF) magnetron sputtering system. The ZnO targets were prepared from ZnO (purity, 99.99%) powder. The powder was mixed in a mechanical shaker for 24 h, pressed into a pellet 2 in. in diameters at high pressure, and then sintered at 1200 °C for 1 h in air. After pre-sputtering of the targets with Ar plasma for 5 min, ZnO films were deposited on the substrates locating on a rotating sample stage at room temperature. Gases in the sputtering system were mainly consisted of high-purity Ar (99.99%). The glass substrates (glass slides of 76 mm × 26 mm × 1 mm) were cleaned in an ultrasonic cleaner for 5 min in acetone, alcohol and alkaline solution, and then rinsed in distilled water. All substrates were blown out by nitrogen gas. The structural and electrical properties of the sputtered ZnO films were characterized by X-ray diffraction (XRD), Field Emission-Scanning Electron Microscopy (FE-SEM), and atomic force microscopy (AFM), respectively.

Photolithographic patterning was followed using positive photoresist (PR) mask (AZ 7220) on the sputtered ZnO films. The profile angle of the patterned photoresist (PR) was about 50°, due to the limitation in the photolithographic systems used in this experiment, where the PR thickness was about 1.5 µm. During etching process, the working temperature was kept at 25 °C using thermostat (DAHAN Scientific, WB-22). To acquire patterned ZnO films, the wet etching was carried out in diluted \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) and \( \text{C}_2\text{H}_2\text{O}_4 \) as a function of etching time and etchants concentrations. Then the etched ZnO films were cleaned in distilled water before characterization. The etching rates of the patterned ZnO thin films and etching shape were measured by FE-SEM using an acceleration voltage of 10.0 kV.

3. Results and discussion

3.1. ZnO film deposition

High transmittance and low resistivity are required for ZnO film to be used as OLED anode. The opto-electronic properties of magnetron sputtered ZnO films strongly depend on the deposition conditions such as RF power, target to substrate distance (D), substrate
temperature and working pressure [5,6]. Deposition conditions for high transmittance and low resistivity were optimized in our previous studies [2]. Under the deposition conditions with the RF power of 200 W, D of 45 mm and working pressure of 1.4 mTorr, highly conductive and transparent ZnO films were prepared. The detailed information was already submitted in the reference [9]. It is well-known that sputtered ZnO films are highly textured, and the c-axis lies perpendicular to the substrate surface. The X-ray measurement of a ZnO thin film shows a single peak at a 2θ value of 35°, corresponding to the (002) plane. The inset of Fig. 1 shows the high resolution XRD patterns between 33.0 and 36.0°. The mean grain size can be evaluated by using the Debye Scherrer relation: [2]

\[ B = \frac{0.94 \lambda}{t \cos \theta} \]  

(1)

where \( B \) = FWHM (full width at half maximum) of the broadened diffraction line on the 2θ scale (radians), \( t \) = diameter of the crystallites, \( \lambda \) = the wavelength of the X-ray radiation and \( \theta \) = the Bragg angle [10]. From this analysis, the mean grain size of the film was estimated to be about 30 nm. Surface morphology and cross-section of ZnO films are shown in Fig. 2. Chang et al. [5] stated that at the initial stage of deposition, a large amount of small grains was distributed at arbitrary sites and in the subsequent growth, the grains became larger and finally, large grains with columnar structure are formed. Similar to their results of Chang et al., a columnar structure can also be observed in our sample by using field emission-scanning electron microscopy (FE-SEM). Using atomic force microscopy (AFM), the RMS value of the film was estimated to be about 0.676 nm.

3.2. ZnO etching characteristics

It is well established that ZnO was dissolved in acid solution by the aqueous proton ions attacking the oxygen, forming water, and then producing soluble salt [7,8].

\[
\text{ZnO(s) + 2H}^+ (aq) \rightarrow \text{Zn}^{2+} (aq) + \text{H}_2\text{O(l)}
\]

(2)

In this experiment, we introduced two new different chemicals as etchants, ferric chloride (FeCl₃·6H₂O) and oxalic acid (C₂H₂O₄). Fig. 3 shows variation of the shape of a ZnO film as a function of the etchant concentration at 25 °C. For the surface characterization, FE-SEM was employed (Fig. 3). Comparing the images taken after etching using 0.01 and 0.001 M of C₂H₂O₄, the etching slope was decreased with increasing etchant concentration (Fig. 3a). In contrast, no clear relationship between the etchant concentration and the etching slope could be observed, when FeCl₃·6H₂O was used.

Upon increasing the concentration of C₂H₂O₄ to 0.05 M, formation of ZnO film, which cannot be observed for lower etchant concentrations, could be found on the film surface, and the surface etching did not take place (Fig. 3a): the range of the C₂H₂O₄ concentration for etching is limited, which can be regarded as a disadvantage of C₂H₂O₄ etchant. Using FeCl₃·6H₂O, etching of the subsurface regime could be found before the etching of the topmost layer was completed, resulting in formation of a porous surface structure.

The etching rates were calculated by the thickness of remnant and the etching time. We compare the etching behavior in the etchant concentration such as strong acid (H₂SO₄), weak acid (CH₃COOH), ferric chloride (FeCl₃·6H₂O) and oxalic acid (C₂H₂O₄). The etching rates and etchant concentrations in the different etching solutions are shown in Fig. 4. H₂SO₄ was shown to be the most efficient etchant: using 0.1 M of H₂SO₄, an etching rate of 2300 nm/min was obtained. The etching rate using 0.1 M for FeCl₃·6H₂O, the etch rate of 2100 nm/ min is almost comparable to that for H₂SO₄.

Strong acids generate more H⁺ ions compared to weak acid at the same mole concentration and ZnO films were dissociated quickly because H⁺ ions attack the oxygen site on the ZnO structure.

Therefore, the etching rate increased under strong acidic environment. We measured pH of the etchants which are prepared with various mole concentrations. Fig. 5 shows the etching rate of the ZnO films depending on pH of etchant. Previously, it was shown that the etching rate decreases exponentially with increasing pH value, and the etching rate depends only on the pH value regardless of a kind of etchant. In contrast to the previous results, the etching rate vs pH curve of FeCl₃·6H₂O strongly deviates from the respective curves of the hitherto investigated etchants. For obtaining a better understanding of the reason of the dissimilar etching behaviors of FeCl₃·6H₂O compared to other etchants, further studies are required.

4. Conclusion

The experiments revealed that the etching slope was decreased with increasing etching concentration of oxalic acid while a diffused etching surface was appeared on the ZnO films when ferric chloride etchant was used. Those increased under strong acid environment and showed an exponential decay with pH value.

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References