Metal-doped ZnO films with various metal contents (Al, Ag and Li of 0–10 wt.%) were prepared by RF magnetron sputtering system with specially designed ZnO targets. The structural, optical and electrical properties of MZO films depended on the type and content of doping in target. Electrical resistivity of LZO thin films increased with increasing Li doping amounts between 0 and 4 wt.%, suggesting that an epitaxial LZO film has high resistivity. We observed morphology in pure ZnO films by using different etchant. In addition, etching rate were contrasted with the etchant concentration and pH. The etching rate is proportional exponentially to pH value. These data will be the technical basis for TCO application. Also, the dry etching rate decreased with increasing the Cl\textsubscript{2} concentration in CH\textsubscript{4}/H\textsubscript{2}/Ar + additive Cl\textsubscript{2} gas mixture but metal dopants were etched effectively.

Keywords: Metal-doped ZnO thin films; optical and electrical property; etching; organic light emitting diode.

1. Introduction

Transparent and conductive oxide (TCO) films are wide band gap semiconductors with low specific resistance and high transparency in the visible and near infrared wavelength range. So, TCO such as indium–tin oxide (ITO), Al-doped zinc oxide (AZO), tin oxide (SnO\textsubscript{2}) and Zn-doped indium oxide (IZO) have attracted much interest in the applications of optoelectronic devices such as solar cells, touch panel, heat mirrors, organic light emitting diode (OLED) and liquid crystal displays (LCD).

A zinc oxide (ZnO) has attracted much attention because of excellent properties such as a large melting point of 2248K, a wide band gap (3.37 eV) and a large exciton binding energy (60 mV). Doped and undoped ZnO thin films have been prepared by physical deposition methods such as laser deposition, different sputtering methods, atomic
layer deposition\(^7\) and chemical deposition methods such as chemical vapor deposition,\(^7\) spray pyrolysis,\(^8\) chemical bath deposition\(^9\) and the sol-gel process.\(^10\)

In order to apply to TCO, fine delineation of films to micron/submicron scale has become increasingly important. So, dry/wet etching processes are extremely important techniques for films patterning. About the dry etching process, several researchers reported the ICP (inductively coupled plasma) etching of ZnO with various plasma parameters, such as ICP power,\(^11\) self-bias\(^12\) and plasma chemical elements (CH\(_3\)/H\(_2\)/Ar,\(^13\) BCl\(_3\)/Cl\(_2\)/Ar\(^14\) and Cl\(_2\)/Ar\(^15\)). Among them, the etching rate increased because active CH radicals could be formed by highly volatile Zn(CH\(_3\))\(_2\) during dry etching processes in using CH\(_3\)/H\(_2\) and Ar chemical elements. But dry etching of ZnO has a disadvantage: the photoresist (PR) is dissolved by influence of the plasma or producing carbon residues. About the wet etching process, several researchers reported that various etchants such as HCl, HNO\(_3\), H\(_3\)PO\(_4\) or H\(_2\)PO\(_4\)/HAc/H\(_2\)O have been used for the wet chemical etching of ZnO.\(^16\)-\(^18\) The mechanism is that the reaction of ZnO in acid solution produces zinc salt dissolved in water to make the etched pattern.

In this paper, we investigated the effect of dopant on the structural, optical and electrical properties of MZO thin films. The dry etching characterization of MZO thin film was studied by ICP etching process by CH\(_3\)/H\(_2\)/Ar and additive Cl\(_2\) chemistries. Also, wet chemical etching behavior of MZO films was investigated using various acid solutions such as sulfuric acid (H\(_2\)SO\(_4\)), nitric acid (HNO\(_3\)) and phosphoric acid (H\(_3\)PO\(_4\)).

2. Experiment

2.1. Metal-doped ZnO films

The three targets were prepared with different weight percent of dopant such as AgNO\(_3\), LiCl and Al(OH)\(_3\) in the targets. ZnO films were deposited on the glass substrates at room temperature, target-to-substrate distance (Dts) of 45 mm and RF power of 150 W by RF magnetron sputtering system. The MZO film thickness was about 1000 nm. The crystal structure, microstructure and thickness of MZO films were measured using X-ray diffraction (XRD) and field-emission scanning electron microscope (FE-SEM) respectively. The optical transmittance measurements were performed with an UV-visible spectrophotometer. The electrical resistivity was measured by four-point probe technique.

2.2. Wet chemical etching process

ZnO films were followed by the photolithographic patterning of a positive photoresist (PR) mask (AZ 7220) on the sputtered ZnO films. The profile angle of the patterned photoresist (PR) was about 50\(^\circ\), due to the limitation in the photolithographic systems used in this experiment, and the PR thickness was about 1.5. The wet chemical etching of the ZnO thin films was investigated by varying the etchant such as sulfuric acid (H\(_2\)SO\(_4\)), nitric acid (HNO\(_3\)) and phosphoric acid (H\(_3\)PO\(_4\)). During etching and throughout the experiments, the working temperature was kept at 25\(^\circ\)C using thermostat (DAIHAN Scientific, WB-22). To acquire patterned ZnO films, the wet etching was carried out in diluted HCl, CH\(_3\)COOH and C\(_6\)H\(_5\)O\(_2\) as a function of etching time. ZnO films were etched with different etchant concentrations and etching times, and then they were cleaned with distilled water.

The etch rates of the patterned ZnO thin films and etch shape were measured by field-emission scanning electron microscopy (FE-SEM) using an acceleration voltage of 10.0 kV.

2.3. Dry chemical etching process

A modified commercial 8-inch ICP etcher was used in this experiment.\(^19\) An RF power of 13.56 MHz was applied to the top electrode coil to induce ICP. Bottom bias electrode power of 13.56 MHz was applied to the substrate holder to induce a bias voltage to the wafer. MZO films with different metal (Ag, Li and Al) doping concentrations were prepared by RF magnetron sputtering and photolithographic patterning of a positive photoresist (PR) mask (AZ 7220) on MZO/substrates was followed. The backside temperature of the wafer chuck during etching was held at 18\(^\circ\)C. Etching conditions, such as the gas flow ratio and bottom electrode power, were controlled. Etching rates of patterned MZO films and deposition of a-C:H layers were measured by the FE-SEM. XPS investigated the species of the etched MZO surface.
3. Results and Discussion

3.1. Characteristic of MZO films

Figure 1 shows the variation of doping content and electrical resistivity as a function of Ag dopant content in the SZO films.

Figure 1(a) showed that the percentages of Ag content were 0, 3.04, 7.07, 9.65, 13.21, and 13.47% when Ag dopants increased from 0 to 10 wt.% by 2 wt.%, respectively. It seemed that the Ag dopant had strong influence on the electrical properties of SZO films because metal dopants act as donors. With increasing Ag content from 0 to 10 wt.% by 2 wt.%, the resistivity of the SZO film in Fig. 1(a) was decreased from $5 \times 10^{-1} \Omega \text{cm}$ to $1.4 \times 10^{-2} \Omega \text{cm}$. The decreased resistivity produced metallic characteristic of a silver which is aggregated. Figure 1(b) shows the resistivities of the AZO films dependence on Al concentration. Increasing the Al concentration in the target decreases the electrical resistivity and had a minimum value of 98 m$\Omega$cm for 4 wt.% Al(OH)$_3$ doped zinc oxide target. In summary, the doped Al impurity changed the structural, optical, and electrical properties. Among them, the substituted Al to zinc site was influenced on the electrical resistivity, whereas the aggregated Al in the grain boundary was not. Figure 1(c) shows the changes of the electrical resistivity (solid circle) and dopant content (open circle) in the LZO films according to the LiCl contents in the target. Between 0 and 4 wt.% Li-contents, the electrical resistivity of LZO films is increased up to 40 M$\Omega$cm and then dropped to above 4 wt.% Li-contents. Generally, ZnO thin films were n-type semiconductive metal-oxide thin films since the excess Zn or defect O were performed as a part of donor. These were induced that the carrier was contributed to conductivity. But, resistivity only in small doped LZO thin films increases because of Li was operated to reduce carrier by acceptor. Therefore, we found that the resistivity increased until the formation of 4 wt.% Li-doped ZnO thin film ($10^7 \Omega \text{cm}$). As Li doping amounts were increased unduly (above 6 wt.%) resistivity increases because the excess of Li were employed as carrier.

3.2. Wet chemical etching process

The ZnO film dissolves as the aqueous proton ions attacking the oxygen, forming water, and then producing soluble salt

$$\text{ZnO(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2\text{O}. \quad (1)$$

As shown in Fig. 2, we see the etched ZnO film images of difference etchant concentrations from the FE-SEM. The crater-shape surface is formed in the higher concentration solution (0.1 M). In the high concentration solution, the etchant molecules stay long on the ZnO surface and aggregated etchant molecule etched a part of ZnO surface and then making crater-shape. On the other hand, the crater size became smaller in the low concentration solution. On the surface of etched ZnO film in the 0.01 M etchant solution, we observed the small cavity which is the evidence of etchant diffusion. The mobility of etchant molecules was high on the ZnO surface in the low concentration solution. The dilute etchant molecules diffused in the ZnO film, consumed the etchant molecules which could not be resupplied quickly. The dissolved ZnO may be reformed on the surface. Therefore, the void of the ZnO film is largely created with increasing the etching time in Fig. 2. Usually, the surface change of the ZnO film is observed to be the same in all the etched samples. It seems that etchant diffusion appear in the ZnO structure applying for TCO because the chemical etching.
Fig. 2. SEM images show etched ZnO films morphology of various HNO$_3$ concentrations (a) and different etching times of HNO$_3$ 0.001 M (b).

on the O-terminated ZnO face or on the defect surface is rapidly more than that on the perfect surface. The edge etching occurred first under HCl, H$_2$SO$_4$ and HNO$_3$ which are generally known as strong acid and the diffused etching is observed under low concentration of H$_3$PO$_4$ (not shown here).

The etching rates and etchant concentrations of the different etching solutions are shown in Fig. 3(a). The strong acids generate more hydronium ions on the same mole concentration, and dissociate ZnO films quickly because these H$_3$O$^+$ ions attack the oxygen site of the ZnO structure. Therefore, the etching rate is quick using strong acid solution because the consumed etchant can be resupplied rapidly in the strong acid. However, the etching rates of the strong acid with high density such as H$_2$SO$_4$, HNO$_3$ are higher than those of the strong acid with low density such as HCl. It seems that the etching rates are influenced by dissociation constants as well as by the density of etchants. We measured pH value of the etchants which are prepared with various mole concentrations. Figure 3(b) shows the etching rate of the ZnO films depending on pH of etchant. On the whole, the etching rate depends on the pH value regardless of a kind of etchant. The etching rate is inversely proportional to pH value. The etching rate on pH value is calculated mathematically by non-linear fitting. The proper function is exponential decay curve such as, $y = a \times \exp(-x/t) + y_0$. In detail, some fitting curve shift to high value, compared with optimum fitting curve, it is the fitting curve of etching rate which are etched in strong acid with high density. We assume, therefore, that “a” and “t” are dependent on film quality and density respectively.

3.3. ICP dry etching process

XPS analysis measured the surface of etched 4 wt.% AZO (4AZO) films without photoresist mask, to study chemical binding states and atomic compositions during ICP etch process. The etched 4AZO films were prepared at the Q of 0.4, top ICP electrode power at 750W, and V$_{dc}$ at -150V by varying the additive Cl$_2$ gas ratio from 0 to 20sccm. The Al 2p, Zn 2p and O 1s spectra are shown in Figs. 4(a), 4(b) and 4(c), respectively.

The Al 2p XPS narrow scan spectra of the 4AZO etched films according to Cl$_2$ partial pressure are shown in Fig. 4(a). When CH$_4$/H$_2$/Ar gas mixture was introduced to additive Cl$_2$ gas, Al dopants were removed clearly. Figure 4(b) shows the Zn 2p spectra for the 4AZO etched films. The positions of both Zn 2p$_{3/2}$ and 2p$_{1/2}$ of as-deposited 4AZO films are 1022.18 and 1045.48eV respectively, and they correspond to the position of Zn 2p in pure ZnO. The peak
Fig. 3. (a) The relationship between the etching rate and various etchant concentrations. (b) The relationship between the etching rate and pH value. Color online.

FIG. 4. XP spectra obtained from the as-deposited and etched AZO film surface: (a) Al 2p, (b) Zn 2p, and O 1s peak.
4. Conclusions

MZO films with various metal contents (Al, Ag and Li of 0–10 wt.%) were prepared by RF magnetron sputtering system with specially designed ZnO targets. The structural, optical and electrical properties of MZO films depended on the type and content of dopant in target. The electrical properties of MZO films depended on a type of and a content of dopant in target. The electrical resistivities decreased with increasing metal dopants. Electrical resistivity of LZO thin films is also increased with increasing Li doping amounts between 0 and 4 wt.%, suggesting that an epitaxial LZO film has high resistivity.

Wet etching characterization of the sputtered ZnO films were mainly studied using various etchants such as HCl, CH$_3$COOH, HNO$_3$, H$_2$SO$_4$ and H$_3$PO$_4$. We observed morphology in pure ZnO films by using different etchants. In addition, etching rates were in contrast to the etchant concentration and pH. The etching rate is proportional exponentially to pH value. These data will be the technical basis for TCO application.

The dry etching of MZO films is investigated using a gas mixture of CH$_4$, H$_2$, Ar, and Cl$_2$. At a fixed CH$_4$/H$_2$/Ar gas flow rate, Cl$_2$ gas flows were added to determine the effect of Cl$_2$ gas on the MZO etching rate. The etching rate of ZnO decreased when a Cl$_2$ gas was added to the CH$_4$/H$_2$/Ar gas chemistry. The vapor pressure of the Zn(CH$_3$)$_2$, etching by-product is higher than that of ZnCl$_2$. The etching rate decreased with increasing the Cl$_2$ concentration in CH$_4$/H$_2$/Ar + additive Cl$_2$ gas mixture but metal dopants were etched effectively.

Acknowledgments

This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (20090094025).

References


