Physical properties and etching characteristics of metal (Al, Ag, Li) doped ZnO films grown by RF magnetron sputtering


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Abstract

Metal doped ZnO (MZO, metal = Al, Ag, Li) films were deposited by RF magnetron sputtering system. We investigated the physical properties and the etching characteristics of the MZO films. All MZO films have shown a preferred orientation in the [001] direction. As amounts and a kind of dopant in the target were changed, the crystallinity and the transmittance as well as the optical band gap were changed. The electrical resistivity was also changed according to the metal doping amounts and a kind of dopant. The chemical dry etching of as-grown MZO thin films was investigated by varying gas mixing ratio of CH4/(CH4 + H2 + Ar) and additive Cl2 chemistries. We could effectively etch not only a zinc oxide but also metal dopant using methane, hydrogen, argon, as well as chlorine gas. Changes of the structural, optical electrical properties, etch rate, and chemical states of etched surface for the MZO films were also explained with the data obtained by SEM, XRD, UV, 4-point-probe and XPS analyses.

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1. Introduction

A zinc oxide (ZnO) has attracted much attention because of excellent properties such as a wide band gap (3.37 eV), a large melting point of 1975 °C, and a large exciton binding energy (60 meV). The structural, physical and electrical properties of ZnO films were governed by dopants, deposition parameters [1] and post treatment [2]. In addition, the physical properties of ZnO films were changed by extrinsic impurities. Many different methods such as RF/DC sputtering [3], sol–gel method [4], metal organic chemical vapor deposition [5], and pursed laser deposition [6] have been used for the preparation of ZnO thin films. However, there are not many reports on the systematic study of metal dopant effect in the metal doped ZnO (MZO) film’s properties. Therefore, the effect of dopant on the structural, optical and electrical properties of MZO films has to be investigated.

ZnO has been applied to various fields such as transparent conducting oxide (TCO), photodetectors, and light emitting diodes [7,8]. So the fabrication of the ZnO-based optoelectronic devices requires an etching technique in the manufacturing process. Therefore, the dry etching characteristics of MZO films need to be investigated. About the dry etching process, several researchers reported the ICP etching of ZnO with various plasma parameters, such as plasma chemistry (CH4/H2/Ar [9], BCl3/Cl2/Ar [10], Cl2/Ar [11]), self-bias [12], and ICP power [13]. Among them, the etching rate increased because active CH radicals could be formed into highly volatile Zn(CH4)2 (boiling point, 44–46 °C) during dry etching processes using CH4/H2/Ar chemistry. But the etching rate is drastically decreased by chlorine chemistry (etching product, the vapor pressure of ZnCl2 is 1 mm Hg at 428 °C). Previously, we found that MZO films decreased the etching rates significantly due to lower volatility of reaction by-products of doping metal in CH4/H2/Ar plasma. When MZO films are etched, not only ZnO but also metal impurities can be effectively etched. Generally, the chlorine based etch gases presumably produce by-product of metal chloride in the metal etch process. Therefore, dry etch process of MZO films has been carried out using ICP of CH4/H2/Ar and additive Cl2.
In this paper, we investigated the effect of dopant on the structural, optical and electrical properties of metal doped ZnO (metal = Al, Ag, Li, so called AZO, SZO and LZO, respectively) thin films. Moreover, the etching characterization of as-grown MZO thin film was studied by the dry etching process using CH_{4}/H_{2}/Ar/Cl_{2} gas mixture.

2. Experimental

2.1. MZO films

Different targets were prepared with different weight percent (wt.%) of dopant (AgNO_{3}, Al(OH)_{3}, LiCl) in the targets (0 ∼ 10 wt.% MZO). ZnO films were deposited on the Si (001) and glass substrates at room temperature (RT), RF power of 150 W and target-to-substrate distance (D_{bs}) of 45 mm by RF magnetron sputtering system. The thickness of MZO films was from 150 to 1000 nm. The crystal structure, microstructure, and the thickness were observed using X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM), respectively. X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX) were also utilized to analyze the chemical ratio of MZO films. Especially, the XPS measurements were carried out using ESCA2000 with Mg Ka radiation. Individual region scans (Al 2p, Zn 2p, O 1s, C 1s and Cl 2p) were performed in hybrid mode using both electrostatic and magnetic lenses, with an energy step of 0.05 eV. Binding energy was calibrated with respect to C 1s at 284.6 eV. The optical transmittance measurements were performed with an UV/visible spectrophotometer. The electrical resistivity was measured by a four-point-probe method.

2.2. Dry etching process

A modified commercial 8-inch inductively coupled plasma (ICP) conductor etcher was used in this experiment [9]. 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 (Al, Ag and Li) 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 °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 was used to investigate the species of the etched MZO surface.

3. Results and discussion

3.1. Characteristics of MZO films

Typical X-ray diffraction patterns of MZO films showed that only (002) peaks were observed at 2 theta = 34° for all samples. The average transmittance in the range of 400–800 nm is measured by UV–visible spectroscopy. The optical band gap (E_{g}) could be obtained by the extrapolating method using the \( \alpha \nu^{2} \) vs. \( \nu \) plot (\( \alpha \) is the absorption coefficient and \( \nu \) is the photon energy). The surface compositions in the MZO films were calculated by using high resolution XP spectra. The electrical resistivity was measured according to the dopant contents in the target. As mentioned above, the change of the physical properties in MZO films was investigated corresponding to the quantity and species of dopants. Summarized figures (Figs. 1–3) show the variation of 2 theta_{(002)}, full width half maximum (FWHM), doping content, electrical resistivity, average transmittance and optical band gap as function of doping concentration.

Fig. 1 illustrates the various characterizations of AZO films by Al dopant of various ratios. Fig. 1(c) shows that the diffusion angle shifted to the higher angle slightly (until 4 wt.%) with increasing Al quantity, and the intensity of these peaks became weaker (until 8 wt.%) and broader (until 6 wt.%). The lowest FWHM value was 0.24° on deposited ZnO film using 6 wt.% AZO target. The broaden peak means the existence of the defect site such as oxygen vacancy or interstitial zinc in the lattice. The doped aluminum was replacing zinc site in the hexagonal lattice (Al_{Zn}) or the aluminum dopant aggregates to the non-crystalline region in the grain boundary (Al_{Boundary}) [15]. The excess aluminum did not influence the resistivity of AZO thin film. With increasing the Al concentration, the average transmittance decreased (see Fig. 1(a)). Perhaps, the substituted Al instead of Zn might be attributed to the effect in the free-carrier concentration. As shown in Fig. 1(a), the optical band gaps of 3.27 eV at pure ZnO film and of 3.31–3.35 eV at AZO films were obtained, respectively. The Eg of the AZO film is larger than that of pure ZnO, the reason for this was explained.
by the Burstein shift [6]. The changes of band gap according to Al concentration might be due to the increasing of the carrier density. Fig. 1(b) shows the resistivities of the AZO films dependence of Al concentration. As Al concentration in the target increased, the electrical resistivity decreased and have a minimum value of 98 mΩ 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.

Fig. 2(b) shows that the percentages of Ag content are 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 was strongly influenced on the electrical properties of SZO films because metal dopants acted as donors. With increasing the Ag contents from 0 to 10 wt.% by 2 wt.%, the resistivity of the SZO film in Fig. 2(b) was decreased from $5.0 \times 10^{-1}$ Ω cm to $1.4 \times 10^{-2}$ Ω cm. The result of resistivity decreasing produced metallic characteristic of a silver which is aggregated.

As the amount of doped Li increased, the angle of (002) diffraction peaks shifted to higher value in Fig. 3(c). These results indicate that the lattice constants of ZnO crystals are gradually decreased due to Li substitution. In detail, with increasing Li contents, asymmetric (002) diffraction peak that is attributed to LZO thin film formation appeared and the diffraction angle is also shifted towards high degree from 34.21° to 34.34°. Researchers reported that most of Zn site was substituted by a doping ion larger size than Zn ion [16,17].

Fig. 3(b) 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 MΩ 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. They induced that the carrier was contributed to conductivity. But, resistivity only in a little doped LZO thin films increases because Li was operated to reduce carrier by
acceptor [17]. 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 are increased unduly (above 6 wt. %), resistivity increases because the excess of Li acts as carrier.

### 3.2. ICP dry etch process of MZO films

As shown in the Fig. 4 which already appeared in our previous paper [14], the etching rates of MZO films were varied by the flow ratio ($Q$) of CH$_4$/(CH$_4$+H$_2$+Ar) flow ratio, $Q$, from 0.2 to 0.6 at a fixed Ar flow rate of 20 sccm and a total flow rate of 100 sccm. The top electrode power and $V_{dc}$ were fixed at 750 W and $-150 \, \text{V}$, respectively. The fixed $V_{dc}$ value was obtained by adjusting the bottom bias electrode power. The etching rates of MZO films depended on the gas flow ratio as shown in Fig. 4. In particular, the etching selectivity of MZO films showed infinite values because a-C:H layers are deposited on the top of the PR surface while the MZO films were continuously being etched, but a-C:H layers are deposited on the MZO surface at $Q$ over 0.6. On the whole, the etching rates of the MZO films were decreased with increasing doping concentration.

During the MZO etch using CH$_4$ containing plasma, the formation of etching by-products is possibly related to the formation of CH radicals in the plasma [13]. Below $Q$ of 0.5 in the CH$_4$/H$_2$/Ar mixture ambient, the CH radicals make the organic compound including zinc atom such as dialkyl zinc (alkyl=$C_nH_{2n+1}$) to react with Zn atom in the ZnO crystal. However, the high generation rate of the CH radicals over specific critical ratio ($Q_c>0.6$) can lead to a-C:H layer deposition, which results in an etch-stop of MZO films.

XPS analysis measured the surface of etched 4 wt.% Al doped-ZnO (4AZO) films without PR mask, in order to study chemical binding states and atomic compositions during plasma etch process. The etched 4AZO films were prepared at the $Q$ of 0.4, top ICP electrode power at 750 W, and $V_{dc}$ at $-150 \, \text{V}$ by Fig. 5. XPS spectra obtained from the as-deposited and etched AZO film surface; (a) Al 2p, (b) Zn 2p, (c) O 1s, (d) C 1s and (e) Cl 2p peaks (etch conditions; top electrode power: 750 W, dc self-bias voltage: $-150 \, \text{V}$, and total gas flow rate: 100 sccm).
the varying additive Cl₂ gas ratio from 0 to 20 sccm. The Al 2p, Zn 2p, O 1s, C 1s and Cl 2p spectra are shown in Fig. 5(a)–(e), respectively.

The Al 2p XPS narrow scan spectra of the 4AZO etched films according to Cl₂ partial pressure are shown in Fig. 5(a). When CH₄/H₂/Ar gas mixture introduced additive Cl₂ gas, Al dopants were removed clearly. Fig. 5(b) shows the Zn 2p spectra for the 4AZO etched films. The positions of both Zn 2p3/2 and 2p1/2 of as-deposited 4AZO films are respectively 1022.18 eV and 1045.48 eV, and they correspond with the position of Zn 2p in pure ZnO. The peak positions of both Zn 2p3/2 (1023.58 eV) and 2p1/2 (1046.78 eV) from the etched 4AZO surface over 10 sccm of additive Cl₂ gas were shifted by 1.4 eV toward the higher binding energy compared with those of as-deposited 4AZO films. The shift of binding energy indicates the formation of ZnCl₂ on the etched surface. The O 1s spectra are also shown in Fig. 5(c) that the low binding peak (530.78 eV) corresponds to the Zn–O bonds while the high binding peak (532.93 eV) corresponds to the adsorbed species such as hydrocarbon, hydroxide and carbonate. After etching, the bonding of Zn–O disappeared and the bonding of adsorbed species remained. Fig. 5(d) shows the C 1s spectra of etched 4AZO films. The peaks of carboxyl (289.18 eV) or hydrocarbon (285.03 eV) group peak observable from C 1s peak indicate a formation of a-C:H layer or dialkyl zinc on the etched film surface. As the additive Cl₂ gas flow ratio increased, Cl 2p peaks increased as shown in Fig. 5(e). These peaks were identified as signals from ZnCl₂, ZnO, and ClCl₂. The intensities of the Cl₂ peaks in the as-deposited 4AZO were quite small, but the Cl 2p intensities dramatically increased with increasing additive Cl₂ gas flow ratio. This indicates a chemical reaction between ZnO and Cl radicals with increasing Cl₂ flow ratio. The intensity of ZnO peak is negligible, which demonstrates a dramatic increase in the ZnCl₂ concentration as a result of the increased chlorination of the etched surface.

At a fixed CH₄ (40 sccm)/H₂ (40 sccm)/Ar (20 sccm) gas flow rates, Cl₂ gas flows of between 5 and 20 sccm were added to determine the effect of Cl₂ gas on the MZO etching rate. The resulting etching rate is shown in Fig. 6. The etching rate of ZnO decreased when a Cl₂ gas was added to the CH₄/H₂/Ar gas chemistry. This indicates that the addition of Cl₂ to the CH₄/H₂/Ar plasma did not enhance the ZnO etching rate effectively. The etching by-products formed for the MZO dry etching process with CH₄/H₂/Ar+ additive Cl₂ gas mixture are Zn(CH₃)₂x, ZnCl₂, and MC₁ (M = metal), presumably. The vapor pressure of the Zn(CH₃)₂x etching by-product is higher than that of ZnCl₂. The etching rate decreased with increasing the Cl₂ concentration in CH₄/H₂/Ar+ additive Cl₂ gas mixture but metal dopants were etched effectively.

4. Conclusions

MZO films with various metal contents (Al, Ag and Li of 0–10 wt.%) were prepared by RF magnetron sputtering system with especially designed ZnO targets. The structural, optical and electrical properties of MZO films depended on a type of and a content of dopant in target. To implant the metal impurity, the various properties of ZnO film are properly changed into follows. The deposited MZO films have a preferred crystalline orientation of [001] direction. As amounts of the Al dopant in the target were increased, the angles of (002) peaks were shifted to higher angle, while peaks of [001] direction were shifted to lower with increasing Ag dopant in the target, suggesting different doping mechanism. These results indicated that the lattice parameters of MZO film were changed in the c-axis with doping metal dopant. The optical band gap and electrical resistivities were 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. As mentioned above, the MZO films can be available to a variety of fields. For example, the AZO film can be applied to TCO electrode, some optoelectric device need to have SZO film and the piezoelectric devices are requiring the LZO film which has a high resistivity and a highly oriented structure.

MZO film has needed for the etching processes for manufacturing. In here, the dry etching of MZO film is investigated using a gas mixture of CH₂, H₂, Ar, and Cl₂. The etching rates of the MZO films decrease significantly to more than one of pure ZnO film in CH₂/H₂/Ar plasma. At a fixed CH₄/H₂/Ar gas flow rates, Cl₂ gas flows were added to determine the effect of Cl₂ gas on the MZO etching rate. The etching rate of ZnO decreased when a Cl₂ gas was added to the CH₄/H₂/Ar gas chemistry. The vapor pressure of the Zn(CH₃)₂x etching by-product is higher than that of ZnCl₂, the etching rate decreased with increasing the Cl₂ concentration in CH₄/H₂/Ar+ additive Cl₂ gas mixture but metal dopants were etched effectively.

Fig. 6. Etching rates of MZO films at an ICP top power of 750 W, and a dc self-bias voltage of ~150 V as a function of the additive Cl₂ flow ratio in the 0.4 of CH₄/(CH₄+H₂+Ar) plasma.
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