The effects of the post-annealing with a Zn cap on the structural and electrical properties of sol-gel derived MgxZn1−xO films

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Abstract
Structural and electrical properties of Al-doped MgxZn1−xO films were improved by post-annealing with supplying Zn vapor. The Al-doped MgxZn1−xO films were deposited on glass substrates by a sol-gel method. The substrates were dip-coated with a precursor solution and were dried on a hotplate at 270 °C for 10 min. This dip-coating and drying process was repeated 10 times, and the Al-doped MgxZn1−xO films were obtained after calcination in air at 500 °C for 1 h. The as-grown films were post-annealed in H2 at 400 °C for 20 min. To supply zinc vapor, a glass slide with a thermally evaporated Zn layer (Zn cap) was put on the sample surface during the post-annealing. The as-grown films had the wurtzite structure with the c-axis perpendicular to the substrate surface, but the intensity of the (002) diffraction peak decreased with increasing Mg content (x). The crystallinity of the films was improved after the post-annealing with a Zn cap, which was observed when x was below 0.1. The resistivity and carrier concentration of the film (x = 0.1) after the post-annealing with a Zn cap was 6.0 × 10−3 Ω cm and 5.7 × 1019 cm−3, respectively. On the other hand, the resistivity of the film (x = 0.1) after the post-annealing without a Zn cap was 6.6 × 105 Ω cm. Transmittance spectra in the visible range were not affected by the post-annealing. The optical bandgap of the film (x = 0.1) after the post-annealing with a Zn cap was 3.41 eV.

1. Introduction

Transparent conductive oxide (TCO) films are used in the field of optoelectronic devices such as liquid crystal displays and solar cells. Although indium tin oxide (ITO) is known as a typical TCO film, much attention has been focused on zinc oxide (ZnO) [1–4]. ZnO can be alloyed with MgO, and MgxZn1−xO films are considered as an attractive TCO film due to its tunable bandgap energy (3.4–7.8 eV) [5, 6]. Wide bandgap TCO films are important in ultraviolet photodetector and solar cell applications [7–9]. Impurities such as Al, Ga, and In work as donors in MgxZn1−xO films [10–12]. However, MgxZn1−xO films show relatively poor electrical properties. Electron concentration and mobility decrease with increasing Mg content [13–15]. Liu et al. reported that self-compensation by zinc vacancy acceptors, of which formation enthalpy decreases with increasing Mg content, is responsible for the deteriorated conductivity of MgxZn1−xO films [14].

MgxZn1−xO films can be formed by various techniques including chemical vapor deposition (CVD), radio frequency (RF) magnetron sputtering, and pulsed laser deposition [16–21]. Sol-gel deposition is a low-cost solution-based method, and the bandgap of MgxZn1−xO films is tuned by changing Mg concentration in a precursor solution [22–24]. However, the electrical properties of sol-gel derived MgxZn1−xO films are inferior to those deposited by vacuum processes. The typical resistivity values of MgxZn1−xO films deposited by non-vacuum processes are about 10−2–10−1 Ω cm [25, 26]. To overcome this drawback, several types of post-annealing processes are used. It is known that post-annealing in a reducing atmosphere is an effective method to improve properties of sol-gel derived TCO films [7, 26, 27].
In this study, the effects of the post-annealing with a Zn cap on the structural and electrical properties of the sol-gel derived Al-doped MgxZn1−xO films are reported. To supply zinc vapor, a glass slide with a thermally deposited Zn layer (Zn cap) was put on the film surface during the post-annealing. The structural and electrical properties of the Al-doped MgxZn1−xO films were improved after the post-annealing with a Zn cap.

2. Experimental procedures

The Al-doped MgxZn1−xO (x = 0–0.3) films were deposited on glass substrates (soda-lime glass) by a sol-gel method. Prior to the sol-gel deposition, the substrates were cleaned with acetone (ultrasonic bath), piranha solution (H2SO4/H2O2), and deionized water. The precursor solution for the sol-gel deposition was prepared by mixing zinc acetate dihydrate, magnesium acetate tetrahydrate, aluminum nitrate nonahydrate (Al/(Zn + Mg) = 3at%), monoethanolamine (0.50 mol l−1), and ethanol. The sum of the zinc and magnesium concentrations in the precursor solution was 0.25 mol l−1. Firstly, the substrates were dip-coated with the precursor solution and were dried on a hotplate at 270 °C for 10 min. This dip-coating and drying process was repeated 10 times, and the Al-doped MgxZn1−xO films were obtained after calcination in air at 500 °C for 1 h. The as-grown films were post-annealed in H2 at 400 °C for 20 min. To supply zinc vapor, a glass slide with a thermally deposited Zn layer (Zn cap) was put on the sample surface during the post-annealing. The thickness of the films was about 300 nm, regardless of the post-annealing condition. Film thickness was determined by a stylus profilometer (Accretech SURFCOM 1400G). Structural properties and surface morphologies were characterized by x-ray diffraction (XRD, Rigaku SmartLab SE) and scanning electron microscope (SEM, JEOL JSM-7001F), respectively. Electrical properties were measured at room temperature by using van der Pauw configuration. Surface composition was estimated from x-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe) measurements. The XPS spectra were calibrated to the C 1s peak at 284.8 eV.

3. Results and discussion

Figure 1 shows the surface and cross-sectional SEM images of the Al-doped MgxZn1−xO (x = 0) films. Round-shaped particles are seen in the surface and cross-sectional SEM images of the as-grown film. The as-grown film had a porous structure. The surface and cross-sectional SEM images of the film after the post-annealing with a Zn cap are shown in figures 1(c) and (d). The porous structure of the as-grown film was not seen in these SEM images. It was found that the continuity of the film was improved by the post-annealing with a Zn cap. The thickness of the film was not significantly changed by the post-annealing with a Zn cap.

The XRD patterns of the Al-doped MgxZn1−xO films are shown in figure 2. The films have the wurtzite structure with the c-axis perpendicular to the substrate surface, but the intensity of the (002) diffraction peak decreases with increasing Mg content. The Al-doped MgxZn1−xO film (x = 0.3) shows no diffraction peaks, indicating that the addition of magnesium acetate tetrahydrate to the precursor solution deteriorates the
crystallinity of the films. The XRD patterns of the films after the post-annealing with a Zn cap are shown in figure 2(b). The intensity of the (002) diffraction peak is increased after the post-annealing with a Zn cap, and the full width at half maximum (FWHM) value of the peak is decreased. The improvement depended on the crystallinity of the as-grown films. For $x = 0$, the FWHM value of the (002) diffraction peak for the as-grown film was 0.34° and that for the film after the post-annealing was 0.23°. For $x = 0.1$, the FWHM value was 0.25° after the post-annealing. The improvement of the crystallinity was observed when $x$ was below 0.1. However, further studies are needed to improve the properties of the Al-doped Mg$_x$Zn$_{1-x}$O films with high Mg content.

Many researchers have reported that electrical properties of ZnO films are improved after post-annealing in a reducing atmosphere [28–30]. The resistivity of the Al-doped Mg$_x$Zn$_{1-x}$O films was also decreased after the post-annealing without a Zn cap (conventional post-annealing in H$_2$). However, the conventional post-annealing was not effective for the Al-doped Mg$_x$Zn$_{1-x}$O films. The resistivity and electron concentration of the film ($x = 0$) after the conventional post-annealing were $7.6 \times 10^{-2}$ Ωcm and $1.9 \times 10^{19}$ cm$^{-3}$, respectively. The resistivity of the film ($x = 0.1$) after the conventional post-annealing was $6.6 \times 10^{2}$ Ωcm. We could not measure

Figure 2. XRD patterns of the as-grown films and the films after the post-annealing with a Zn cap: (a) as-grown films and (b) as-grown films and the films after the post-annealing with a Zn cap.
the electron concentration of the film \((x = 0.1)\) after the conventional post-annealing because of its high resistivity. In contrast, the electrical properties of the Al-doped \(\text{Mg}_x\text{Zn}_{1-x}\text{O}\) films were much improved after the post-annealing with a Zn cap. The resistivity of the films after the post-annealing with a Zn cap was \(3.7 \times 10^{-3}\ \Omega\text{cm}\) for \(x = 0\) and \(6.0 \times 10^{-3}\ \Omega\text{cm}\) for \(x = 0.1\). The electron concentration was \(2.1 \times 10^{20}\ \text{cm}^{-3}\) for \(x = 0\) and \(5.7 \times 10^{19}\ \text{cm}^{-3}\) for \(x = 0.1\). It should be noted that the post-annealing with a Zn cap is very effective to improve the electrical properties of the Al-doped \(\text{Mg}_x\text{Zn}_{1-x}\text{O}\) films.

The transmittance spectra of the Al-doped \(\text{Mg}_x\text{Zn}_{1-x}\text{O}\) films are shown in figure 3(a). The as-grown films showed a sharp absorption edge, and the absorption edge decreased with increasing Mg content. The transmittance spectra in the visible range were not affected by the post-annealing with a Zn cap. The optical bandgap of the films was estimated from the Tauc plot, \((\alpha h\nu)^2\) versus \(h\nu\), by extrapolating the linear portion of the plot to \((\alpha h\nu)^2 = 0\) (figure 3(b)). The optical bandgap of the as-grown films was 3.28 eV \((x = 0)\) and 3.43 eV \((x = 0.1)\). These values are consistent with the reported optical bandgap of \(\text{Mg}_x\text{Zn}_{1-x}\text{O}\) films [6, 19]. The optical bandgap of the films after the post-annealing with a Zn cap was 3.23 eV \((x = 0)\) and 3.41 eV \((x = 0.1)\). The optical bandgap of the films was decreased slightly after the post-annealing with a Zn cap, but still depended on the Mg content.
It was found that no additional ZnO layer was grown although Zn vapor was supplied during the post-annealing with a Zn cap.

XPS measurements were performed to evaluate the surface composition of the Al-doped MgₓZn₁₋ₓO films (x = 0.1). Zinc, oxygen, magnesium, carbon, and chlorine were observed from the as-grown film and the film after the post-annealing with a Zn cap. The origin of chlorine may be hydrochloric acid used to clean the back side of the substrate after the sol-gel process. The Mg/Zn ratio of the as-grown film (x = 0.1) was 0.09, which was consistent with the Mg content in the precursor solution. As the result of Zn supply, the Mg/Zn ratio was decreased after the post-annealing with a Zn cap. Therefore, the (Zn+Mg)/O ratio was increased from 0.96 to 1.05. It was found that the film after the post-annealing with a Zn cap was slightly Zn-rich. Zinc vacancies are known as dominant compensation acceptors in n-type ZnO [31]. The decrease in zinc vacancy concentration is possibly related to the increase in electron concentration after the post-annealing with a Zn cap.

Figure 4 shows XPS spectra of the Al-doped MgₓZn₁₋ₓO films (x = 0.1). The Zn 2p₁/₂ (~1044.5 eV) and Zn 2p₃/₂ (~1021.5 eV) XPS spectra were not changed by the post-annealing with a Zn cap. Figure 4(b) shows the O 1s XPS spectra of the films. The asymmetric peaks were deconvoluted into three components. The O₁ component (~530.2 eV) and the O₂ component (~531.3 eV) are attributed to the O²⁻ ions in ZnO and the O²− ions in oxygen-deficient ZnO, respectively [32–35]. The O₃ (~532.3 eV) component is related to adsorbed hydroxides and contaminants [32–35]. The O₂/O₁ ratio was decreased after the post-annealing with a Zn cap. It was suggested that crystallinity of the Al-doped MgₓZn₁₋ₓO films were improved after the post-annealing with a Zn cap.

4. Conclusion

Al-doped MgₓZn₁₋ₓO films were deposited by a sol-gel method and post-annealed in H₂. Structural and electrical properties of the films were improved by the post-annealing with a Zn cap when x was below 0.1. The film (x = 0.1) after the post-annealing with a Zn cap had resistivity of 6.0 × 10⁻³ Ωcm and electron concentration of 5.7 × 10¹⁹ cm⁻³. The film (x = 0.1) after the post-annealing without a Zn cap had resistivity of 6.6 × 10² Ωcm. The electrical properties were improved after the post-annealing with a Zn cap, while the optical bandgap was not significantly changed. These results suggest that H₂ post-annealing with a Zn cap can be used to form low-resistivity MgₓZn₁₋ₓO films.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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