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Fabrication and Characteristics of Li-doped ZnO Thin Films for SAW Filter Applications

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Li-doped ZnO films were prepared on Corning 1737 glass substrate by an rf magnetron sputtering technique using ZnO targets with various Li_2CO_3 contents ranging from 0 to 10 mol%. The effects of Li doping on the crystallinity and electrical properties of ZnO films were studied for their SAW filter applications. The film resistivity largely increased without suppressing the c-axis orientation and crystallinity with a small addition of Li. Heat treatment of the film at 400°C induced that the film resistivity, c-axis orientation and crystallinity slightly increased. However, heat treatment of the film at 500°C resulted in much lower resistivity than that of as-deposited film due to the increase of electron concentration caused by the evaporation of Li atoms from the ZnO film. Large addition of Li into the ZnO film rather diminished the film resistivity and suppressed the c-axis growth. It was concluded that a small doping of Li into the ZnO film and heat treatment at 400°C caused the film resistivity to be high enough for SAW filter applications without suppression of the c-axis orientation and crystallinity.

Key words : Zinc oxide film, Li-doping, Electrical properties, C-axis orientation

I. Introduction

Zinc oxide (ZnO) is a wide band gap n-type semiconductor (E_g=3.2 eV) with a hexagonal wurtzite structure. It has been used in many practical applications such as liquid crystal displays, solar cells, and gas sensors.[1-3] Recently, much attention has been directed to its potential use as surface acoustic wave (SAW) devices,[4-6] because of its high piezoelectricity and strong electromechanical coupling property.

For surface acoustic wave applications, it is highly important to grow ZnO films with a high electrical resistivity and excellent c-axis orientation perpendicular to the substrate.[4,7] Pure ZnO films have been prepared by various methods such as chemical vapor deposition,[8-11] dc,[12] and rf[6,13-15] sputtering, and spray pyrolysis.[2,16,17] The investigation[2,3,5,9-15,17,18] about crystallinity and electrical properties showed that ZnO films had good c-axis orientation but low resistivity unsuitable for SAW filter applications. It has been reported that the low resistivity resulted from interstitial Zn atoms and/or oxygen vacancies.[1,5] In order to obtain high resistivity required for SAW filter applications, it is necessary to dope foreign Li atoms into the ZnO films. The maximum value of resistivity reported by T.Shiosaki was 10^{14} Ωcm using Li-doped ZnO target,[19] but no report is available for the crystallinity and c-axis orientation of Li-doped ZnO film. Therefore, there is abundant interest and motivation in investigating Li doping effects on the crystallinity and electrical properties of Li-doped ZnO film.

In this paper we investigated the crystallinity and electrical properties of Li-doped ZnO films for SAW filter applications and studied on the Li doping effects on their properties.

II. Experimental Procedure

Li-doped ZnO films were deposited on Corning Glass by an rf magnetron sputtering technique. A schematic diagram of the rf magnetron sputtering system used in the study is depicted in Fig. 1. Sintered disk composed of a mixture of ZnO powder (Aldrich, 99.99%) and various amounts of Li_2CO_3 powder (Aldrich, 99.997%) was used as the target (2 inches in diameter). The contents of Li_2CO_3 in targets were 0 (undoped), 0.5, 1, 2, 5, and 10 mol%, respectively. The substrate was Corning Glass 1737 (non-alkali substrate) with much improved properties over Corning Glass 7059.[20] The distance between target and substrate was fixed at 50 mm. The surface temperature of the substrate was monitored by a thermocouple and controlled during the deposition. After pumping down to a background pressure of 5×10^{-6} torr in the sputtering chamber, high-purity argon (5N) and oxygen were used as the sputtering gas. The Ar and O_2 flow rates were separately controlled by mass flow controllers and the gas pressure was monitored with a precision Pirani gauge. Presputter etching of target was carried out to obtain a target with a clean surface.

In order to find the optimum sputtering condition for SAW filter application, the effects of deposition parameters, such as rf power, $O_2/(Ar+O_2)$ gas ratio, and substrate temperature, on the crystallinity and electrical pro-

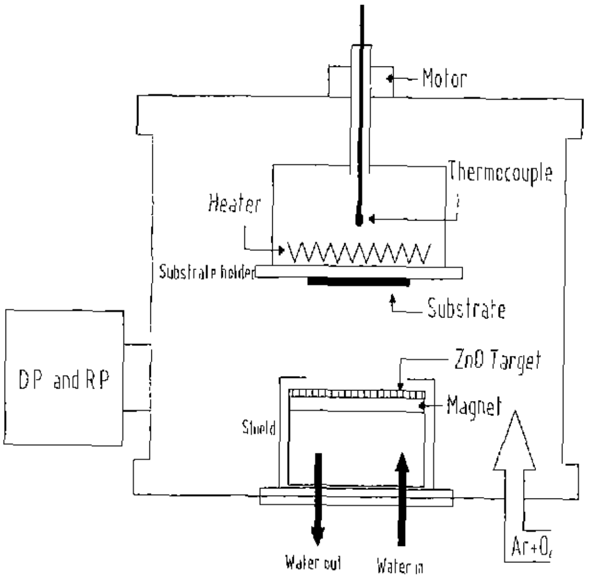

Fig. 1: *Schematic diagram of the rf magnetron sputtering system.*

Table 1. Typical Deposition Condition for ZnO Film Preparation

Target Composition	0 to 10 mol% Li_2CO_3 in ZnO
Gas pressure	6 mtorr
Target-Substrate distance	5 cm
Substrate	Corning 1737 glass
Sputtering Gas	$Ar/O_2=50/50$
Substrate temperature	350°C
RF power	75 W

perties of pure ZnO films had been precedently studied. From the precedent study, the optimum sputtering condition of Table 1 was obtained.

The film thickness was measured with a stylus (α-STEP), and the thickness was maintained at about 1 μm for all specimens. X-ray diffraction (XRD) analysis was performed in order to investigate the crystallinity and c-axis orientation of Li-doped ZnO films. The electrical resistivity of the film at room temperature was obtained from the current-voltage (I-V) measurement. For the current-voltage measurement, Pt electrodes were fabricated on ZnO films. The chemical bonding state of Li in the ZnO film was analyzed by x-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5400).

III. Results and Discussion

1. Crystallographic characteristics of Li-doped ZnO films

Fig. 2(a) shows XRD patterns of as-deposited films prepared from the targets with various Li_2CO_3 contents. The film thickness was fixed at about 1 μm for all samples. As-deposited films prepared from the targets with Li_2CO_3 content below 2 mol% had strong c-axis orientation perpendicular to the substrate. The c-axis growth and crystallinity of the films were relatively independent of the Li_2CO_3 contents in the range 0~1 mol%. However, as the Li_2CO_3 content in target increased above 2 mol%, the crystallinity evaluated from the intensity of (002) diffraction peak largely decreased, though (002) preferred orientation of the films was still unchanged. This result indicates that excess Li atoms in ZnO films inhibited c-axis growth and crystallinity. Fig. 2(b) and (c) show XRD patterns of the ZnO films heat-treated at 400°C and 500°C for 2 hrs in air, respectively. In comparison with as-deposited films, the crystallinity of the films heat-treated at 400°C increased as evaluated from the intensity in Fig. 2 and the full width at half maximum (FWHM) of the (002) diffraction peak in Fig. 3. However, the heat treatment at 400°C caused the (002) preferred orientation to be reduced and changed it to mixture orientation of (002) and (100) for the films prepared from targets with Li_2CO_3 content above 5 mol%. The ZnO films heat-treated at higher temperature of 500°C exhibited better crystallinity than that of the films heat-

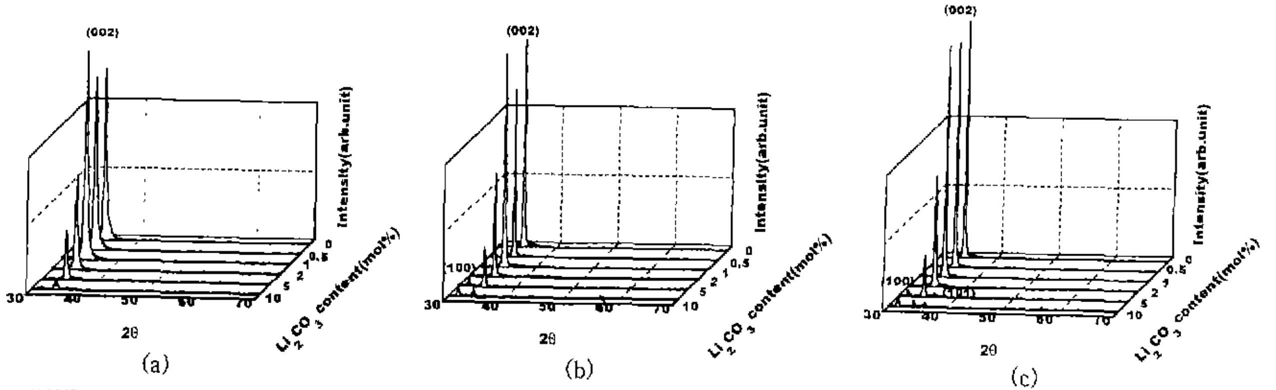

Fig. 2. XRD patterns of ZnO films deposited from the targets of various Li_2CO_3 contents; (a) as-deposited, (b) heat-treated at 400°C, (c) heat-treated at 500°C.

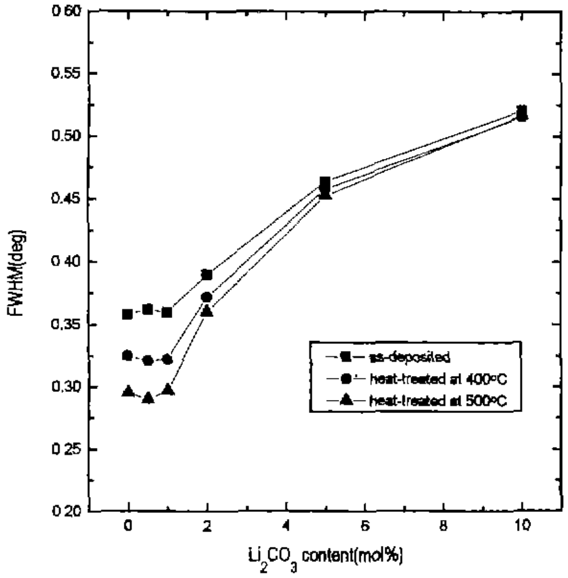

Fig. 3. FWHM of ZnO films as a function Li_2CO_3 content in target.

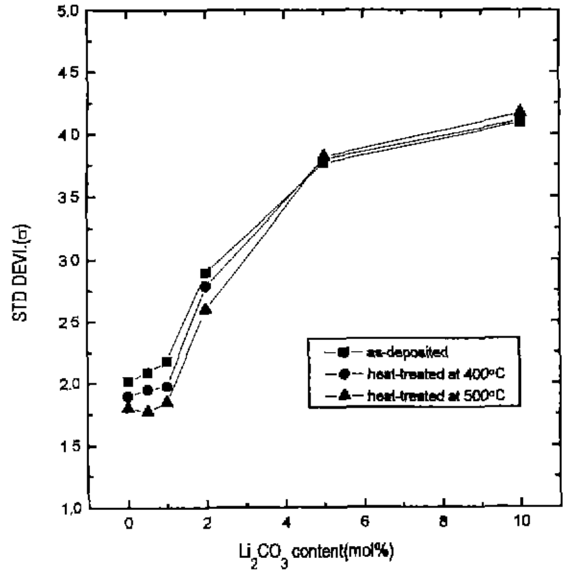

Fig. 4. Standard deviation of (002) rocking curve as a function of Li_2CO_3 content in target.

treated at 400°C as evaluated from the intensity in Fig. 2 and the full width at half maximum (FWHM) of the (002) diffraction peak in Fig. 3. However, the heat treatment at 500°C changed the (002) preferred orientation to multiple orientation of (002), (100), and (101) for the films prepared from targets with Li_2CO_3 content above 5 mol% as shown in Fig. 2(c).

In order to evaluate the degree of c-axis orientation of the films, X-ray rocking curves of these films were adopted.[5] These rocking curves were measured in the following way: first, adjust separately the θ and 2θ axis of the diffractometer to the angles where the x-ray detector gives the maximum output for the (002) peak. Then, fix the 2θ axis of the detector arm and scan the θ axis of the specimen arm. The value of standard deviation angle (σ) of the rocking curve was calculated from the Gaussian distribution. Fig. 4 shows Li_2CO_3 content dependence of standard deviation angle (σ) for ZnO films. As shown in Fig. 4, the value of σ slightly increased with increasing Li_2CO_3 content up to 1 mol%, and largely increased with a further increase of Li_2CO_3 content. Small value of standard deviation angle (σ) indicates the excellent c-axis orientation.[13] Our ZnO films prepared from the targets with Li_2CO_3 contents in the range of 0~1 mol% had σ values less than 2.25°.

The ZnO films prepared from the targets with Li_2CO_3 contents in the range 0~1 mol% were concluded to be suitable for SAW filter applications because those films had strong c-axis orientation and exhibited high crystallinity.

2. *Electrical properties of Li-doped ZnO films*

Electrical resistivity of our pure ZnO films is shown in Fig. 5 as a function of the $O_2/(Ar+O_2)$ gas ratio. As the $O_2/(Ar+O_2)$ ratio increased, the resistivity first increased, and then reached a limit with increasing the oxygen partial pressure above 50%. It is well known that ZnO is an n-type semiconductor owing to donors which result from interstitial Zn atoms and/or oxygen vacancies.[18] The film resistivity, therefore, depends on the degree of nonstoichiometry of ZnO thin films. The nonstoichiometry may be altered by changing the ratio of argon and oxygen gases.[15] However, our pure ZnO films were concluded to be not suitable for SAW filter applications because the films showed the low resistivity below 10^6 Ωcm over whole range of $O_2/(Ar+O_2)$ gas ratio.

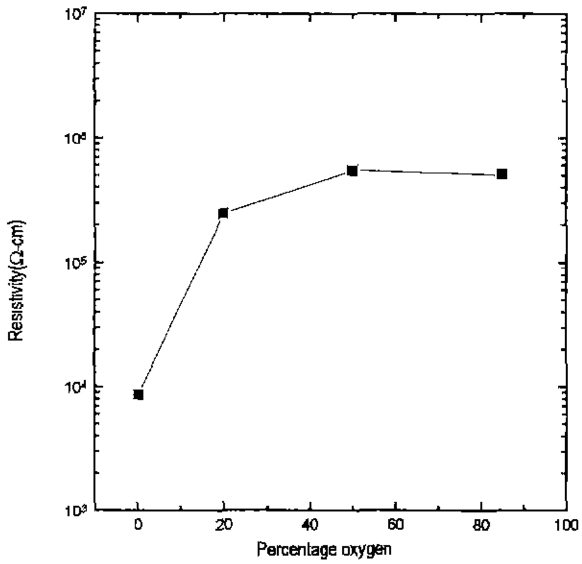

Fig. 5. Electrical resistivity of pure ZnO films as a function of the $O_2/(Ar+O_2)$ gas ratio.

The variation of film resistivity with concentration of Li_2CO_3 in target is shown in Fig. 6. The resistivity of as-deposited film increased sharply with increasing the

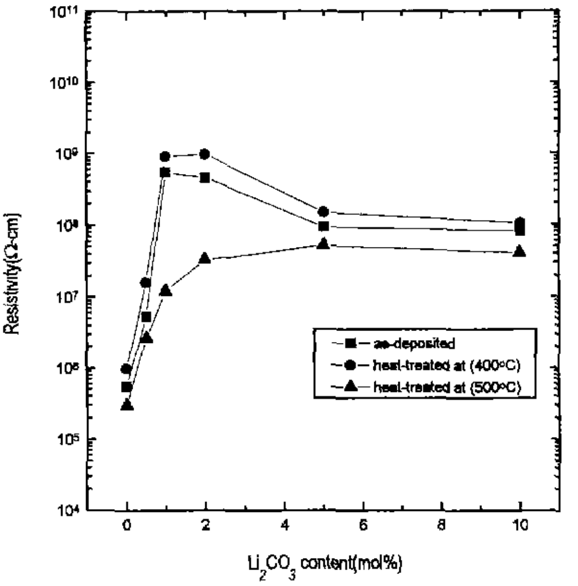

Fig. 6. Variation of film resistivity with Li_2CO_3 content in target.

Li_2CO_3 content up to 1 mol%, and then decreased with a further increase of the Li_2CO_3 content. It has been reported that the resistivity increase of ZnO film was caused by doping of Li atoms.[4,7] When Zn atoms are replaced by small substitutional Li atoms, these Li atoms act as acceptors which compensate the donors caused by excess Zn atoms. The electron density, therefore, decreases with increase of Li concentration. However, it was found from our experimental results that the resistivity of as-deposited film decreased with increase of Li_2CO_3 content in target beyond 1 mol%. It was thought that the decrease of resistivity at high Li_2CO_3 content was caused by the excess Li atoms, which were not substituted completely for Zn atoms, and thus, the Li atoms acted rather as donors than as acceptors. As shown in Fig. 6, the as-deposited film sputtered from the 1 mol% Li_2CO_3 target showed high resistivity of about 10^9 Ωcm. This value was considered to be sufficiently high for SAW filter applications.

The film resistivity slightly increased after heat treatment at 400°C for 2 hrs in air in Fig. 6. The increase in resistivity was considered to be attributed to the decrease in electron concentration due to oxygen ions adsorbed on surface and grain boundaries of the film during heat treatment.[15] On the other hand, the heat treatment at 500°C for 2 hrs in air resulted in much lower resistivity than that of the as-deposited film. This may be explained partly by the increase in mobility which is related to the improvement of crystallinity (shown in Fig. 2(c)). However, considering that film resistivity considerably decreased after heat treatment at 500°C, the above explanation is not sufficient. Supposing that evaporation of Li atoms from the ZnO film occurs at 500°C, the considerable decrease of resistivity can be adequately explained by the increase of electron concentration due to the absence of acceptors.

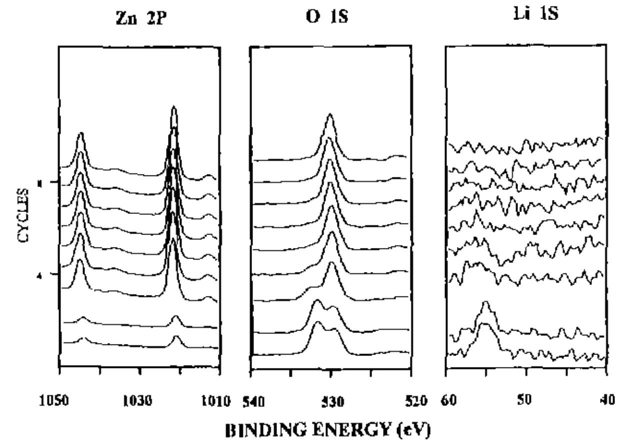

Fig. 7. XPS depth profiles of various elements for ZnO film prepared from the 2 mol% Li_2CO_3 target.

To investigate the chemical bonding state of Li in the ZnO film, XPS analyses were performed. Quantitative analysis for Li content in ZnO film was difficult because Li element had a very small ASF (atomic sensitivity factors) value.[21] Fig. 7 and Fig. 8 show XPS depth profiles of various elements for ZnO films prepared from targets with the Li_2CO_3 contents of 2 mol% and 10 mol%, respectively. The intensities of Zn 2p, O 1s and Li 1s peaks[21,22] were plotted. Vertical axis indicates the sputtered depth below the sample surface and horizontal axis does electron binding energy. In Fig. 7, O 1s peak (530.4 eV) and Zn $2p_{1/2,3/2}$ peaks (1044.8, 1021.7 eV) by ZnO bond, O 1s peak (531.3 eV) and Li 1s peak (55.6 eV) by Li_2O bond were observed at surface region. A charging effect was corrected using the position of carbon peak. The separate O 1s peaks by ZnO and Li_2O bond were merged into the single O 1s peak by only ZnO bond in inner part of the film. This means that Li-O bond existed only near the surface of the film and did not appear in inner part. For ZnO film sputtered from 10 mol% Li_2CO_3 target (in Fig. 8), large intensities of O 1s peak and Li 1s peak by Li_2O bond were observed at surface region, whereas small intensity of Zn $2p_{1/2,3/2}$ peaks was observed. This is thought to be caused by outward diffusion of Li atoms due to excess Li doping. In inner part of the film, doublet of Li 1s peak by Li_2O bond and Li 1s peak (54.7 eV) by metal Li were observed. This result suggests that Li atoms doped into ZnO film existed partly as metallic interstitialcy, and thus, resulted in the gradual decrease in resistivity (shown in Fig. 6) with increasing Li_2CO_3 content above 2 mol%. Fig. 9 shows XPS depth profiles for the ZnO film sputtered from the 2 mol% Li_2CO_3 target after heat treatment at 500°C for 2 hrs in air. From the surface to the inner part of sample, Zn $2p_{1/2,3/2}$ peaks and O 1s peak by ZnO bond were observed, whereas Li 1s peak was negligible in intensity. This result indicates that large amount of Li atoms were evaporated from the film with

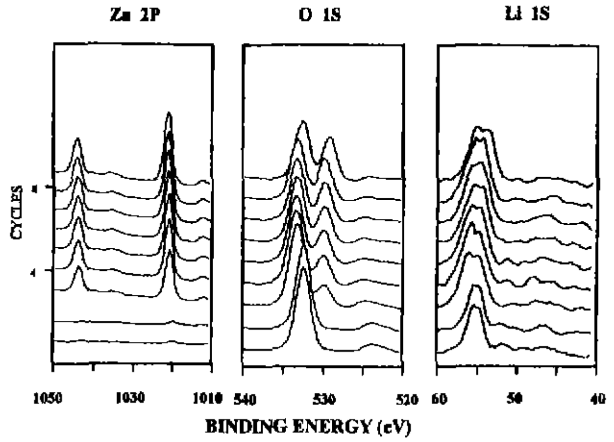

Fig. 8. XPS depth profiles of various elements for ZnO film prepared from the 10 mol% Li_2CO_3 target.

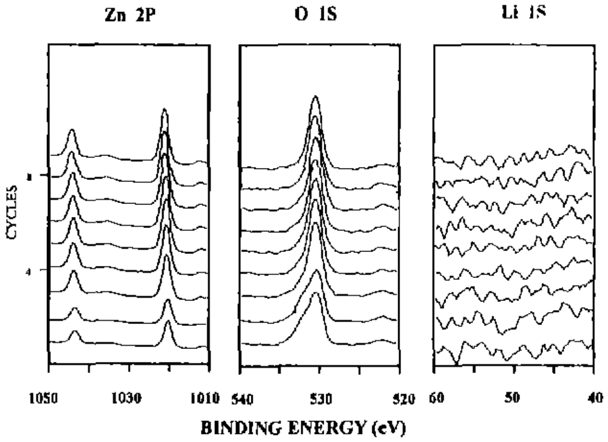

Fig. 9. XPS depth profiles of various elements for ZnO film prepared from the 2 mol% Li_2CO_3 target after heat treatment at 500°C for 2 hrs in air.

heat treatment at 500°C. The outstanding decrease in resistivity (shown in Fig. 6) for the film heat-treated at 500°C was attributed mainly to the increase of electron concentration caused by the evaporation of Li atoms from the ZnO film.

IV. Conclusion

Based on the investigation of c-axis orientation, crystallinity, and electrical properties of Li-doped ZnO films for SAW filter applications, the following conclusions were obtained.

1. As-deposited ZnO films prepared from targets with the Li_2CO_3 contents of 0 to 1 mol% showed the excellent c-axis orientation with σ value below 2.25° and high crystallinity. Heat treatment at the temperature above 400°C improved the c-axis growth and crystallinity. However, large addition of Li atoms caused the c-axis growth to be suppressive.
2. Pure ZnO films were not suitable for SAW filter applications because of their low resistivities below 10^6 Ωcm. However, the resistivity of as-deposited films highly increased with a small addition of Li atoms, and the film sputtered from the 1 mol% Li_2CO_3 target had resistivity as high as 10^9 Ωcm. The film resistivity slightly increased after heat treatment at 400°C. On the other hand, the heat treatment at 500°C resulted in much lower resistivity than that of the as-deposited film. This resulted from the increase of electron concentration, which was caused by evaporation of Li atoms. Thus, we could conclude that a small doping of Li into the ZnO film and heat treatment at 400°C increased the film resistivity high enough for SAW filter applications without suppressing the c-axis orientation and crystallinity.

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