Study on the doping effect of Li-doped ZnO film

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Available online 14 July 2007

Abstract

Zinc oxide (ZnO) is an excellent piezoelectric material with simple composition. ZnO film is applied to the piezoelectric devices because it has high resistivity and highly oriented direction at c-axis. Structural and electrical properties in ZnO films are influenced by deposition conditions. Lithium-doped ZnO (LZO) films were deposited by RF magnetron sputtering method using Li-doped ZnO ceramic target with various ratios (0 to 10 wt.% LiCl dopant). LZO films revealed high resistivity of above $10^7 \ \Omega \cdot \text{cm}$ with smooth surface when they were deposited with 4% LiCl-doped ZnO target under room temperature. However, their c-axis orientation was worse than the c-axis orientation of pure ZnO films. We have also studied on structural, optical and electrical properties of the ZnO films by XRD, AFM, SEM, XPS, and 4-point probe analyses. We concluded that LZO films were deposited with 4 wt.% LiCl-doped ZnO target and were apposite for piezoelectrical application.

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Keywords: Li-doped ZnO films; RF magnetron sputtering; Structural and electrical properties

1. Introduction

Zinc oxide (ZnO), a typical n-type compound semiconductor, wide band gap, photoconducting, piezoelectric and optical waveguide material, is applied to various applications such as optical and magnetic memory devices, light emitting diodes, solar cells (transparent conducting electrodes), transducer, surface-acoustic-wave (SAW) device and chemical sensors [1,2]. Among them, piezoelectric devices have been increasingly used. Required characteristics of ZnO films are not only a strong c-axis oriented crystalline structure but also a high resistivity of above $10^6 \ \Omega \cdot \text{cm}$ for the piezoelectric device applications. The crystal structure of ZnO is hexagonal wurtzite, which is proper to the fabrication of either a high-quality oriented or an epitaxial thin film [3]. In the case of the II–VI oxide semiconductor, oxygen defect, chemical composition and impurities have importantly influenced on physical properties such as electrical resistivity, piezoelectricity and structure. The change of property in ZnO had been reported on deposition condition and doping [4–6]. W. Water et al. reported that doped Li atoms in ZnO films were involved in their substitution for Zn atom; they acted as acceptors that compensate the donors (excess Zn atoms) [1].

ZnO thin film can be deposited by various physical vapor deposition (PVD) methods such as molecular beam deposition (MBE) [7], ion beam [8], sputtering [9] and PLD [10], etc. Among them, the sputtering method can generate an extra orientation and uniform surface close to single-crystal morphology even on amorphous substrate or low substrate temperature.

In this paper, lithium-doped ZnO (LZO) films have been deposited by RF magnetron sputtering method in low temperature. We mainly studied effects of Li doping on structural and electrical properties of ZnO films for piezoelectric devices.

2. Experimental

LZO thin films were deposited on glass and silicon substrates using an RF magnetron sputtering method. Sputtering targets were prepared by high-purity zinc oxide (ZnO, 99.99% purity) and lithium chloride (LiCl, 99.99% purity) powders where the ratio of LiCl was increased from 0 to 10 wt.% by 2 wt.% The pressure was pumped down to $3 \times 10^{-6} \ \text{Torr}$ using a turbo molecular pump and working pressure which was mainly controlled with high-purity Ar (99.99%) gas was lasted in the range of 32–36 mTorr. LZO thin films were deposited on the substrates at the room temperature (RT) with RF power of...
150 W at several target-to-substrate distance ($D_{ts}$) (45–70 mm) after pre-sputtering with Ar plasma for 5 min. All samples were analyzed in the same thickness of about 700 nm.

The crystal structures and the surface morphologies were observed by using X-ray diffraction (XRD, Rigaku, D/MAX2200+ Ultima) and plan-view scanning electron microscope (SEM, JEOL, JSM7000F). The growth rate and the film thickness were determined by cross-sectional SEM. Atomic force microscopy (AFM, ThermoMicroscope, AP0100) was used to examine the surface roughness of the films. X-ray photoelectron spectroscopy (XPS, VG, ESCA2000) was also utilized to analyze the composition change of the LZO films. The electrical resistivity was measured by a four-point probe method (Chang Min Co., LTD CMTR 1000N).

3. Results and discussion

Growth conditions of ZnO films were explained in a previous paper [11]. In summary, growth behavior and electrical resistivity of ZnO thin films were changed with target-to-substrate distance ($D_{ts}$) and other sputtering conditions. Especially, it was established that a highly oriented ZnO thin film in the direction of (002) plane with high resistivity was deposited at 70 mm of $D_{ts}$. Therefore, in this experiment, we had investigated the LZO thin films grown by various dopant (LiCl) contents at $D_{ts}$ (70 mm).

XRD patterns of pure ZnO target (a) and 10 wt.% Li-doped ZnO target (b) are shown in Fig. 1(a) and (b), respectively. LiCl (Li source) is oxidized on high temperature by annealing (see Fig. 1(b)), and because of this, we can observe only t-Li$_2$O phase. Fig. 1(c) shows XRD patterns of pure ZnO and LZO thin films that are grown with both pure ZnO and LZO targets. Noticeable thing of Fig. 1(c) is that all films were grown in the (002) direction, indicating highly oriented film formation.

High resolution X-ray (002) diffraction peaks in both pure ZnO and Li-doped ZnO thin films were obtained (Fig. 2). As the amount of doped Li increased, the intensity and angle of (002) diffraction peak are also decreased and increased, respectively. These results indicate that the lattice constants of ZnO crystals are gradually decreased due to substitution of smaller Li atom than Zn atom. In detail, with increasing Li...
contents, asymmetric (002) diffraction peak that is attributed to LZO thin film formation is appeared and the diffraction angle is also shifted toward high degree from 34.15° to 34.35°. We index the lower angle (about 34.15°) peak (I) as pure ZnO (002) peak and the higher angle (above 34.30°) peak (II) as Li-doped ZnO (002) peak, respectively. In Fig. 2, the shapes of ZnO (002) peaks are asymmetric and they are gradually shifted toward higher angle as Li doping amounts increase. This suggests that the lattice constants in the c-axis of ZnO crystal (or films) decrease with a substitution of Li ion into Zn sites. It is known generally that dopants can be substituted or inserted, depending on the doping ions size. Yamamoto and co-workers [12] reported that most doping ions (larger size than Zn ion) substituted for Zn ion sites in the doping case. Moreover, it can also cause the dopants to be inserted to between zinc ion and oxygen ion because of the small size ion. Of the two cases, the former is in good agreement with our data. As Li-doped amounts increase, the intensities of ZnO (002) peaks decrease and their FWHM values (see inset of Fig. 2) increased up to 0.444°. The maximum FWHM value is obtained from a LZO film with 10 wt.% Li content.

Fig. 3 shows that field emission SEM images in both (a) stoichiometric and (b) non-stoichiometric pure ZnO thin films, and (c) the as-deposited LZO thin films were grown on glass substrates. The crystallinity with hexagonal type above 100 nm size can be detected in Fig. 3(a) whereas crystallinity with longish type in 30–100 nm size is observed in Fig. 3(b). As shown in Fig. 3(c), the LZO film is a small broken hexagonal

![AFM images of LZO thin films according to Li doping amount including rms roughness.](image-url)
crystal which was caused by Li doping on the film. The roughness of LZO film can be made smooth by Li doping. 

Fig. 4 shows that AFM images in Li-doped ZnO thin film have different Li-doped amounts. The morphologies of undoped ZnO thin films consisted of big grains. However, the morphologies in Li-doped ZnO thin films with 2–8 wt.% Li contents display mixed large and small grains. The most uniform morphology is obtained from a LZO film’s surface with 4 wt.% Li content. To find film uniformity, we measured the surface rms (root mean square) roughness. The results show that the surface rms roughness decreased from 10.86 nm to 2.743 nm with increasing the Li contents from 0 to 4 wt.% The surface rms roughness is also retained regularly (about 6.4 nm) in the Li content range 4–10 wt.%. The most smooth film is obtained from a LZO film with 4 wt.% Li content.

Fig. 5 shows a typical XPS survey spectrum as well as high resolution Li 1s XPS spectrum (see inset) of the LZO film with 10 wt.% Li content. In survey spectrum, only zinc, oxygen and lithium peaks are observed and carbon contaminated peak is not found. And the surface compositions in both pure ZnO and LZO thin films were calculated by using each high resolution XPS such as Zn 2p3/2, O1s and Li 1s. The Li contents in LZO thin films are shown in Fig. 6 (open circle) and those are linearly increased with the Li amounts in the LZO ceramic targets.

LZO thin films are required to have high electrical resistivity for piezoelectric device application. Fig. 6 shows that the electrical resistivity (solid square) and dopant content (open circle) are changed in the LZO films according to the LiCl contents in the target. In Fig. 6, 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 are n-type semiconductive metal-oxide thin films since the excess Zn or defect O is performed a part of donor. These are induced so that the carriers contributed to conductivity. But, resistivity only in a little doped LZO thin films increases because Li is operated to reduce carrier by acceptor [13]. Therefore, we found that the resistivity increased until the formation of 4 wt.% Li-doped ZnO thin film (10^7 Ω cm). However, as Li doping amounts were increased (above 6 wt.%), resistivity decreases because the excess of Li was employed as carrier.

4. Conclusions

LZO thin films are fabricated by using home-made LZO ceramic targets by RF magnetron sputtering method. Highly oriented LZO thin films with 0–10 wt.% Li contents can be grown, and among them the most crystalline LZO film with very smooth surface and high resistivity is observed from 4 wt.% LZO target. It will be the most optimum conditions which can be used for the piezoelectric devices.

Acknowledgments

This paper was supported by Faculty Research Fund, Sungkyunkwan University, 2005. Support of this research by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, KRF-2005-005-J11902) and by the SAIT/SAINT joint project.

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