Influence of Li$^+$ dopants on the properties of the ZnO piezoelectric films

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ZnO piezoelectric films with the preferred 002-orientation were prepared by sol-gel method. The annealing temperature was 600°C and the resistivity of the ZnO film was 1×10^6 Ω·cm. Li$_2$CO$_3$ and LiCl were added respectively into ZnO precursor as source of Li$^+$-ion. The molar ratio of [Li$^+$]/[Zn^{2+}] was 0.05. It is observed that the annealing temperature for forming preferred 002-orientation of ZnO films decreases from 660 to 550°C after Li$_2$CO$_3$ being doped. When Li$_2$CO$_3$ and LiCl are doped, the resistivity of ZnO films increases to 10^8 Ω·cm and 10^9 Ω·cm, respectively, with an annealing temperature of 550°C. When annealing temperature is 600°C, the resistivity of the ZnO film with LiCl dopant increases to 10^7 Ω cm. The influence mechanism of the two dopants on the properties of the ZnO films is analyzed. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Zinc oxide (ZnO) is widely used as high-power density, large-scale micro-actuator and high-sensitive micro-sensor in microelectromechanical systems (MEMS) due to its strong piezoelectric effect [1–4]. ZnO piezoelectric thin films are usually prepared by sputtering method, but there are some problems such as micro-crack, asymmetrical thickness, and high residual stress, which is hard to solve by optimizing the technology parameters of sputtering [5–7]. Recently, sol-gel method is widely used to fabricate transparent conducting electrodes [8], nonlinear piezovaristor [9] and gas sensor [10, 11]. Compared with sputtering method, sol-gel method has one of the attractive processes due to simple facilities, low cost, good uniformity of thickness, and controllability of micro-crack and residual stress by optimizing the technology parameters of the process. The deposition of ZnO piezoelectric thin film by sol-gel method has attracted more and more attention [12–14]. The high quality ZnO piezoelectric film should possess large piezoelectric coefficient, preferred 002-orientation and high resistivity (over 10^8 Ω·cm), etc. One of the effective methods to increases the resistivity of the ZnO film is to add some dopants during the preparation of the films [15, 16].

The ZnO piezoelectric thin films we prepared are used in MEMS. We found two main problems during the preparation. First, the resistivity ranges from 10^{-1} to 10^6 Ω·cm, which are too low to be used in MEMS. The second problem is high annealing temperature. The annealing temperature for forming preferred 002-orientation on Si/SiO$_2$/Ti/Pt substrate is above 600°C. This is higher than the melting point of aluminum in MEMS devices, and will influence the electrical function of the devices. In this paper, the dopants of Li$_2$CO$_3$ and LiCl are added into ZnO precursor. Investigated is the influence of the two dopants on the decrease of the annealing temperature for forming preferred 002-orientation and on the increase of the resistivity of ZnO film.

2. Experimental

At room temperature, zinc acetate dihydrate (Zn(C$_2$H$_5$)$_2$·2H$_2$O) was dissolved into isopropanol. A suitable amount of diethanolamine (DEA) was added
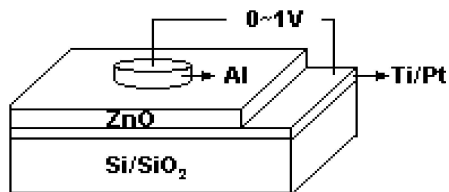
Figure 1 The structure for the measurement of the resistivity of ZnO thin films.

to increase the stability and solubility. After stirred at 65°C for 60 min, a clear and homogeneous ZnO precursor sol was obtained. The Zn^{2+} concentration is 0.3 mol/l. Then, a certain amount of Li_2CO_3 or $LiCl \cdot H_2O$ was added into the ZnO precursor sol as the Li^+ source. After stirred at 90°C for 1 h, the Li_2CO_3 or $LiCl \cdot H_2O$-doped ZnO precursor sol was yielded as coating solution, in which the molar ratio of $[Li^+]/[Zn^{2+}]$ was 0.05. The precursor sol was spin-coated with a speed of 3000 rpm onto the $Si/SiO_2/Ti/Pt$ substrate. The coating films were dried at 450°C for 10 min immediately after coating. After the coating procedure was repeated six times, the films were finally annealed at 550, 600, 700 and 800°C, respectively. The thickness of ZnO films is about 350 nm.

The crystalline orientation of the ZnO films was confirmed by X-ray diffraction (XRD-6000, Shimadzu, Japan). The thickness of ZnO films was measured by using a Surface Profiler (Surfcorder ET 4000M, Kosaka Laboratory. Ltd, Japan). The resistivity-voltage (R-V) characteristics of ZnO thin films were measured by a semiconductor characterization system (System 4200, Micromampulator Co. Inc, USA). The sketch of measurement of R-V characteristics is shown in Fig. 1. The top layer is a 0.5 μm-thick aluminum as top electrode. The middle layer is the ZnO layer prepared by sol-gel method. The low layer is a 0.2 μm-thick Pt/Ti as bottom electrode. The voltage applied between top and bottom electrodes varies from 0 to 1 V.

3. Results and discussion
3.1. Preferred crystalline orientation
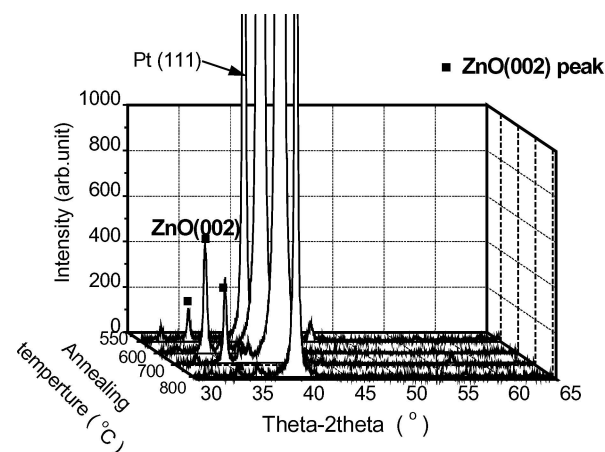Fig. 2 shows the XRD patterns of ZnO thin films annealed at 550, 600, 700 and 800°C for 30 min, respec-

tively. The strongest peaks in the figure are the ones of Pt. It is seen from Fig. 2 that the ZnO thin film annealed at 550°C cannot form preferred 002-orientation yet. When the annealing temperature increases to 600°C, the ZnO thin films shows obviously preferred orientation along 002-axis. The 002-orientation becomes weak and even disappears as the annealing temperature rises to 700 and 800°C. So 600°C is a better annealing temperature for forming a 002-orientation of ZnO film.

Fig. 3 shows the XRD patterns of Li_2CO_3–doped ZnO thin films annealed at 550, 600, 700 and 800°C for 30 min, respectively. It is found that Li_2CO_3–doped ZnO films annealed at 550°C show preferred 002-orientation. As the annealing temperature rises to 600, 700 and 800°C, the 002-orientation decreases gradually and even disappears.

Fig. 4 shows the XRD patterns of LiCl -doped ZnO thin films annealed at 550, 600, 700 and 800°C for 30 min, respectively. It can be seen from Fig. 4 that LiCl-doped ZnO films annealed at 600°C shows preferred 002-orientation. When annealed at 550, 700 and 800°C, LiCl-doped ZnO films cannot show up preferred 002-orientation. From Figs 2–4, it can be concluded that the doping of Li_2CO_3 decreases the annealing temperature for forming 002-orientation from 600 to 550°C. The annealing temperature is below the melting point
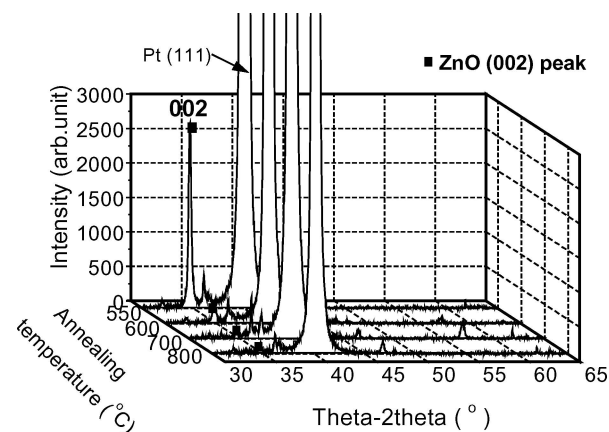

Figure 3 The XRD patterns of Li_2CO_3-doped ZnO thin film annealed at 550, 600, 700 and 800°C.
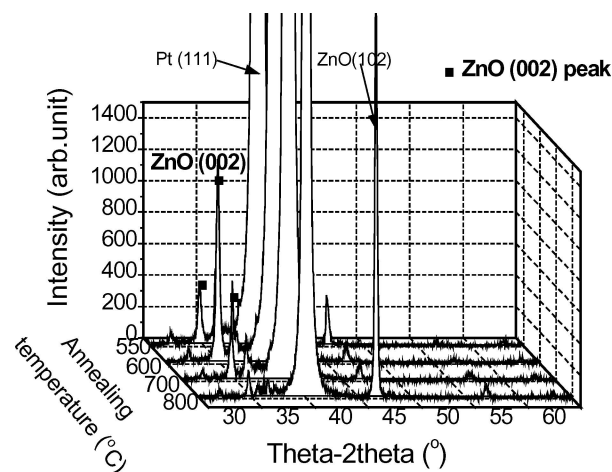

Figure 2 The XRD patterns of ZnO thin film annealed at 550, 600, 700 and 800°C.

Figure 4 The XRD patterns of LiCl-doped ZnO thin film annealed at 550, 600, 700 and 800°C.

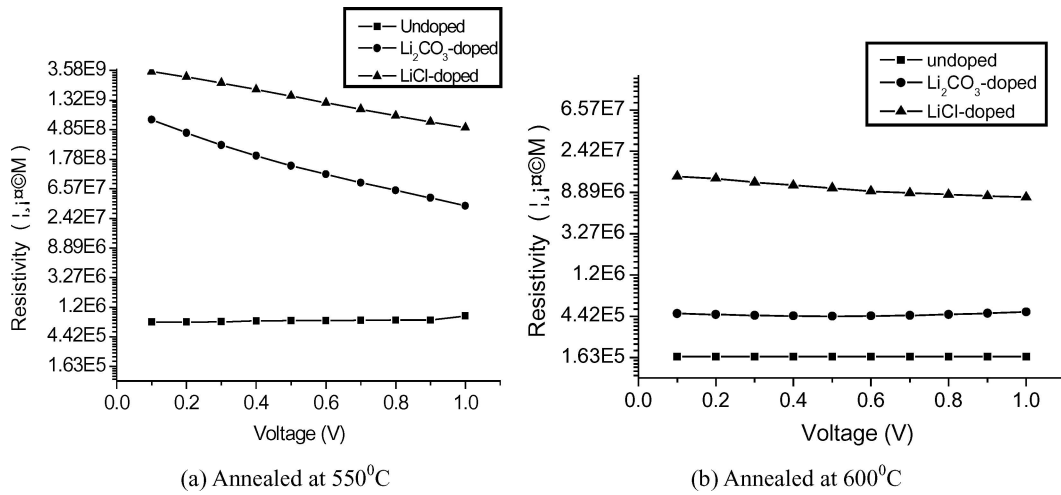(a) Annealed at 550^0C   (b) Annealed at 600^0C

Figure 5 The R-V characteristic of the doped and undoped ZnO thin films.

of aluminum in MEMS devices. It is meaningful to improve the post-CMOS integration of ZnO thin films prepared by sol-gel with standard CMOS processing in MEMS devices. The doping of LiCl cannot decrease the annealing temperature for forming preferred 002-orientation. The reasons for these phenomena may be the following. Different bonds are formed when CO_3^{2+} or Cl^- are added to ZnO precursor sol. These bonds have different binding energies, and have different influences on the annealing temperature. Further investigations are needed in this direction.

3.2. Resistivity

The resistivities of undoped ZnO films prepared by sol-gel method with the annealing temperature $550°C$ or $600°C$ are less than 1×10^6 Ω·cm, and hardly change with the measuring voltage in the voltage range of 0 to 1 V. Fig. 5a shows the resistivity-voltage (R-V) characteristics of the undoped and doped ZnO thin film annealed at $550°C$. It is seen that the doping of Li_2CO_3 and LiCl increases the resistivity of ZnO films to 10^8 Ω·cm and 10^9 Ω·cm, respectively, which are the desirable values for the ZnO films used in MEMS. We can also see from the figure that the resistivities of both Li_2CO_3 and LiCl doped ZnO thin films noticeably decrease as the measuring voltage increases from 0 to 1 V. So the high resistivity of the film can be obtained with a low measuring voltage.

When Li^+ was doped into ZnO, some Li^+ ions will occupy the lattice site of Zn^+ and form some substitutive impurities with negative charges Li'_{Zn}. The ionization equation is as follows:

$$Li^+ + Zn_{Zn} + e^- \rightarrow Li'_{Zn} + Zn^+ \qquad (1)$$

where, Zn_{Zn} represents zinc on the zinc lattice site, Li'_{Zn} represents lithium on the zinc lattice site, and e^- is the free electron with a negative charge. When Zn^{2+} is replaced by Li^+ to form Li'_{Zn}, a free electron in the N-type ZnO is used. The concentration of the free electron decreases and the resistivity increases. On the other hand, the ionic radius of Li^+ (0.060 nm) is smaller than that of Zn^{2+} (0.074 nm), and hence a part of Li^+ will be in the interstice of the ZnO lattice to form the defect of

Li_i^+. The impurity in the interstice place might result in a lattice distortion, which will increase the resistivity of the ZnO sample. The defect potential barriers are formed by the charged defects of Li_{Zn}' and Li_i^+. When the measuring voltage increases, the electric field intensity increases in the doped ZnO films. As a result, the defect barriers will be lower, and then the electrons will increase and the resistivity will decrease.

Fig. 5b shows the R-V characteristics of the undoped and doped ZnO thin films prepared by preheating at $450°C$ and annealing at $600°C$. It is found that the resistivities of ZnO films annealed at $600°C$ are smaller than the ones annealed at $550°C$ for both doped and undoped films. This is because that the oxygen vacancy $V_O^{\cdot\cdot}$ in the ZnO films increases as the annealing temperature rises. The free electrons will appear due to the oxygen vacancy ionisation, and the concentration of N-type carriers will increase, so the resistivity will decrease. The defect equation is as follows:

$$ZnO \rightarrow Zn_{Zn} + V_O^{\bullet\bullet} + 2e^- + \frac{1}{2}O_2 \qquad (2)$$
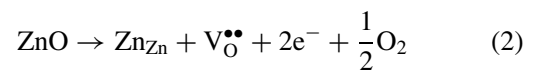
We can also see from Fig. 5b that the resistivity of Li_2CO_3-doped ZnO thin films increases a little bit, and the resisitvity of LiCl-doped film increases to 10^7 Ω·cm. The result indicates that LiCl is more effective than Li_2CO_3 as Li^+-dopant for increasing the resistivity of ZnO films when annealed at $600°C$. Both LiCl and Li_2CO_3 behave better at annealing temperature $550°C$ than $600°C$ in increasing the resistivity of ZnO films.

4. Conclusion

The ZnO piezoelectric films with preferred 002-orientation were prepared by sol-gel method. The annealing temperature was $600°C$ and the resistivity of the ZnO film was 1×10^6 Ω·cm. The annealing temperature for forming preferred 002-orientation ZnO films decreases from 600 to $550°C$ when Li_2CO_3 are doped into the films. When the Li^+-doped ZnO thin films are annealed at $550°C$, the resistivity increases from 10^6 to 10^8 Ω·cm and 10^9 Ω·cm with the addition of Li_2CO_3 and LiCl, respectively. When the annealing temperature

is 600°C, the resistiviy of the LiCl-doped ZnO films increases to 10^7 Ω·cm.

Free electrons are used when defects of Li'_{Zn} (Zn^{2+} is replaced by Li^+) form. And the concentration of the free electron decreases in N-type ZnO film. The interstice impurity Li_i^+ may result in lattice distortion. Therefore, the resistivity of the ZnO sample will increase. If the annealing temperature is high, the oxygen vacancy increases, which produces more electrons, and hence the resistivity of the Li^+-doped ZnO films decreases. The existence of defect potential barriers may be the reason for the change of the resistivity with the measuring voltage.

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