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Dielectric anomaly in Li-doped zinc oxide thin films grown by sol–gel route

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ABSTRACT Sol–gel route was employed to grow polycrystalline thin films of Li-doped ZnO thin films ($Zn_{1-x}Li_xO$, $x = 0.15$). Polycrystalline films were obtained at a growth temperature of 400–500 °C. Ferroelectricity in $Zn_{0.85}Li_{0.15}O$ was verified by examining the temperature variation of the real and imaginary parts of dielectric constant, and from the C–V measurements. The phase transition temperature was found to be 330 K. The room-temperature dielectric constant and dissipation factor were 15.5 and 0.09 respectively, at a frequency of 100 kHz. The films exhibited well-defined hysteresis loop, and the values of spontaneous polarization (P_s) and coercive field were 0.15 μC/cm^2 and 20 kV/cm, respectively, confirming the presence of ferroelectricity.

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1 Introduction

The II–VI group wide band gap semiconductors, one of which is zinc oxide, have been the subjects of recent experimental studies. ZnO is a wide band gap oxide semiconductor with hexagonal crystal structure ($P6_3mc$). ZnO has been used in various applications such as ultrasonic transducers, surface acoustic wave (SAW) devices and sensors, due to its high piezoelectricity and electromechanical coupling property [1]. While the Al doping increases the conductivity [2], Li doping increases its resistivity [3]. In order to study the structural, electronic and piezoelectric properties of ZnO, first principle calculations were carried out by the earlier groups [4, 5]. Binary alloys with off-centered ions were found to exhibit ferroelectricity at low temperatures [6]. A. Onodera et al. [7] studied the ferroelectric properties and the effect of Li^+ and Mg^{2+} dopants in zinc oxide bulk samples. They have observed a ferroelectric transition at 330 K for Li-doped ZnO bulk samples. We report here the existence of ferroelectricity in Li doped ZnO thin films. It belongs to a group of mixed materials in which neither of the binary constituents is known to be ferroelectric. It is believed that the off-centered Li ions play an important role in the existence of ferroelectricity. Earlier, similar ferroelectric behavior has been reported in other II–VI systems, such as $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$ [8]. The required condition for the existence of ferroelectricity is that the substitutional atoms should be of appreciably different size as that of the host atoms they replace. The ionic radii of the host and dopant atoms differ by 0.47 and 0.2 Å in $Pb_{1-x}Ge_xTe$ and $Cd_{1-x}Zn_xTe$, respectively [9]. In the case of $Zn_{1-x}Li_xO$, due to large difference in ionic radii between host Zn (0.74 Å) and the dopant Li (0.6 Å), Li atoms can occupy off-centered positions, forming permanent electric dipoles, and thereby resulting in ferroelectric behavior. In this letter, we report the growth and characterization of polycrystalline Li-doped ZnO thin films grown by sol–gel route.

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2 Experimental

For the majority of metal-ferroelectric-semiconductor field-effect-transistor (MFS-FET) devices, ferroelectric films are generally grown on Si substrates. Therefore, (100) oriented highly doped (10^{16}–10^{17} cm^{-3}) *p*-type Si substrates with resistivity 1–5 Ωcm, were used to deposit the films by sol–gel route. Sol–gel method is widely used to obtain various kinds of functional oxide films, including ZnO and doped ZnO thin films with preferred *c*-axis orientation. In this method, zinc acetate ($Zn(CH_3COO)_2$, 99.99%, Aldrich) and lithium acetate dihydrate ($(CH_3COO)_2Li \cdot 2H_2O$, 99.999%, Aldrich) were selected as precursors. They were dissolved in methanol to form a mixed clear solution with a designed doping ion concentration. Diethanolamine ($HN(CH_2CH_2OH)_2$, Randaxy) was added into the mixed clear solution as a stabilizer in a diethanolamine/zinc acetate molar ratio of 1 : 1. This mixed solution was used for thin films deposition. Prior to the deposition, the Si substrates were etched using 1 : 1 HF solution to remove the native SiO_2 layer. Liquid film on Si substrate was deposition by a spinning-coater (Laurell Tech WS400A-6NPP/LITE) at a spinning speed of 4000 rpm for 30 s. The liquid film was dried at 200 °C for 20 min, and the coating procedure was repeated twice and at the end, this dried film was annealed at different temperatures ranging from 400–500 °C for 30 min. Structural phase determination was carried out using X-ray diffractometer using a Cu K_α radiation. Silver dots of 1.96×10^{-3} cm^2 area were deposited by thermal evaporation onto $Zn_{0.85}Li_{0.15}O$ films as top electrodes in order to study the electrical prop-

erties of the films. The thickness of the film was measured using a Dektak thickness profilometer. Polarization hysteresis behavior was studied using an RT-66A standardized ferroelectric test system in Sawyer Tower mode. Capacitance was measured at different bias voltages with an LCZ meter (Keithley 3330). The capacitance-frequency studies were carried out in the frequency range of 0.1–100 kHz over the temperature range of 200–393 K.

3 Results and discussion

The X-ray diffraction pattern of sol–gel grown $Zn_{0.85}Li_{0.15}O$ thin film grown in the temperature range of 400–500 °C is shown in Fig. 1. All the films were polycrystalline in nature. It is found that there is an increase in 2θ for Li doped ZnO films. This will in turn decrease d spacing, in accordance with the bond-length theory. The computed value of the c-axis lengths for the undoped and $Zn_{0.85}Li_{0.15}O$ thin films were 5.21 Å and 5.138 Å, respectively. This slight decrease in lattice constant with increased Li content could lead to slight structural distortion along the polar c-axis. This could be considered as the origin of ferroelectric phase transition.

It is well known that in the phase transition region the transport coefficients of IV–VI and II–VI semiconductors such as electrical conductivity show anomalies as a result of critical scattering of carriers, due to the order parameter fluctuations [10, 11]. The measurement of dc conductivity in the temperature range 258–398 K is shown in Fig. 2. The dc activation energy in the paraelectric and ferroelectric phase is 0.28 and 0.05 eV, respectively. Such activation energy is close to the values reported for the LiZ samples and are attributed to the Li_{Zn} acceptors. The activation energy obtained is in good agreement with that reported by earlier researchers [12, 13]. The discontinuity in the dc conductivity with temperature correlates well with observations made on other ferroelectric materials [14] and thin films [15].

The dielectric measurements were carried out on ferroelectric Li-doped ZnO thin films in metal-ferroelectric-semiconductor (MFS) configuration over frequency range of 0.1–100 kHz with a Keithley 3330 LCZ meter. The samples were transferred to a low temperature cryostat and cooled to 260 K. The dielectric response with temperature was recorded during heating process. Figures 3 and 4 show the variation of dielectric constant (ε'), as well as dissipation factor ($\tan\delta$) with ambient temperature at different frequencies. The room temperature dielectric constant and dissipation factor were 15.5 and 0.09, respectively, at a frequency of 100 kHz. The data presented clearly shows a dielectric phase transition between ferroelectric phase and paraelectric phase at 330 K. The observed transition temperature was found to be in good agreement with the earlier reported values [16]. The origin of this behavior could be explained as follows: When Li ions replace the host Zn ions, there will be a small structural distortion induced along the polar c-axis. The large ionic size mismatch between Zn and Li ions, lead Li to occupy off-center position, thereby inducing permanent electric dipoles. Moreover, from the first principle studies, it was found that Li atom contains no 3d-electron [17]. When replacing Zn, it will enhance the ionic character and affect the Zn–O bond length along the polar c-axis resulting in a small structural distortion. The dispersive nature of the dielectric constant (Fig. 3) above the anomaly at 330 K may well be attributed to the space charge related blocking effect and was observed in many dielectric materials [18].

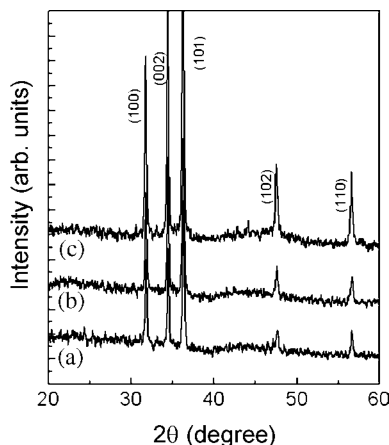

FIGURE 1 X-ray diffraction pattern of $Zn_{0.85}Li_{0.15}O$ thin films grown at different temperatures (**a**) 400 °C, (**b**) 450 °C and (**c**) 500 °C

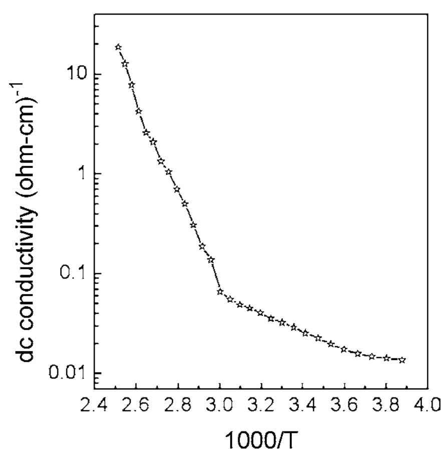

FIGURE 2 Arrhenius plot of the dc conductivity

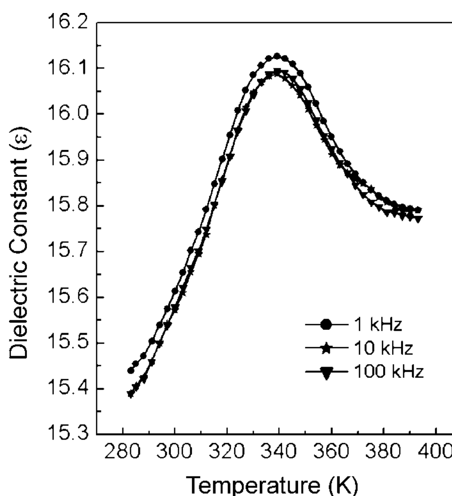

FIGURE 3 Variation of dielectric constant with temperatures at different frequencies for $Zn_{0.85}Li_{0.15}O$ thin films

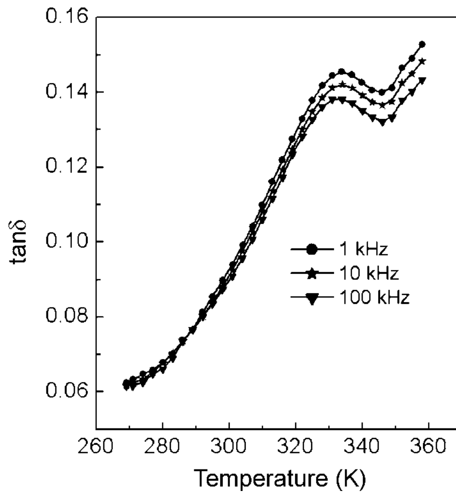

FIGURE 4 Variation of tan δ with temperatures at different frequencies for $Zn_{0.85}Li_{0.15}O$ thin films

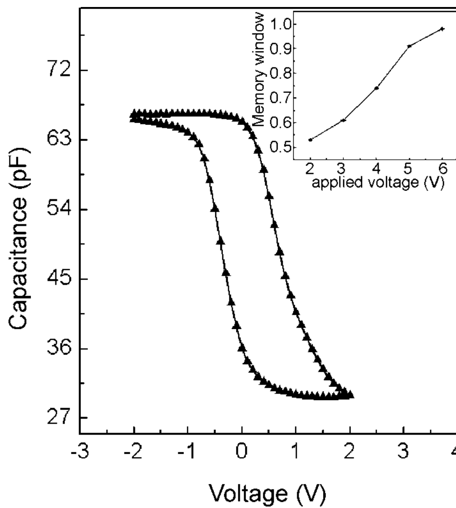

FIGURE 5 C–V characteristics of $Ag/Zn_{0.85}Li_{0.15}O/p$-Si capacitor (*inset*: variation of memory window with applied gate voltage)

The capacitance–voltage (C–V) characteristics of $Ag/Zn_{0.85}Li_{0.15}O/Si$ (p-type) capacitor is shown in Fig. 5. The external dc voltage was swept from the accumulation to inversion region, while keeping ac signal frequency at 10 kHz with the amplitude of 50 mV. The thickness of the films was 0.3 μm. A clockwise rotation in the C–V characteristics of a ferroelectric film on p-type Si is expected when charge compensation on the Si surface is induced by the ferroelectric polarization present in the film. In order to ensure that the memory window effects arise from a typical hysteresis property, C–V measurements were taken with increasing applied voltages. It may be seen that the width of the memory window increased with applied voltage and is consistent with the behavior that is normally observed for a ferroelectric polarization hysteresis behavior in a typical MFS configuration. The observed memory window is a highly attractive property in the area of MFS-FETs [19, 20]. The memory window is related to the coercive field of the ferroelectric film by a relation [21]

$$\Delta V_{\mathrm{window}} = 2 d_{\mathrm{f}} E_{\mathrm{c}} \,,$$

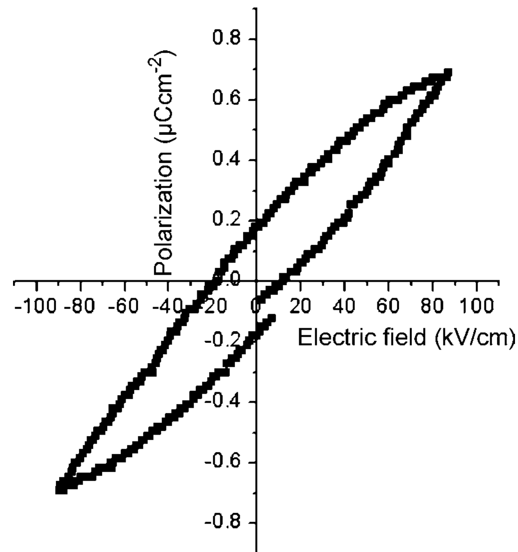

FIGURE 6 Polarization hysteresis behavior of $Zn_{0.85}Li_{0.15}O$ thin films

where $\Delta V_{\mathrm{window}}$ is the memory window, d_{f} and E_{c} are thickness and coercive field of the ferroelectric film, respectively. The measured memory window of the $Ag/Zn_{0.85}Li_{0.15}O/Si$ (p-type) structure were lower than the values estimated using above relation. This might be caused by the native SiO_2 layer present on the Si substrate. The shift of the flatband bias voltage towards the positive voltage axis indicates that the films contain a negative fixed oxide charge, likely to be originating from compensating oxygen ions and interface traps [22].

The ferroelectric nature of the $Zn_{0.85}Li_{0.15}O$ thin films was further confirmed from the polarization hysteresis measurements, as shown in Fig. 6. The curve is typical of those measured in ferroelectric materials. The measured values of spontaneous polarization and coercive field were 0.15 $\mu C/cm^2$ and 20 kV/cm at room temperature respectively. Corso et al. [23] estimated the value of spontaneous polarization based on first-principles and the values obtained were 5 $\mu C/cm^2$, which is one order larger than the present observed value. However, the value of coercive field was found to be larger. This may be associated with the space charge layer in the silicon. The space charge layer may reduce the electric field within the ferroelectric films. It is worth mentioning that the width of space charge layer varies with the direction of polarization, and could be one of the contributors for the asymmetric shape. Moreover, the off-centered polarization curve may also arise due to the asymmetric electrodes Ag and p-type Si [24].

4 Conclusions

In summary, polycrystalline $Zn_{0.85}Li_{0.15}O$ thin films were grown on p-type Si(100) substrates by sol–gel route. The ferroelectric phase transition was observed at 330 K. A clockwise C–V hysteresis curve with excellent memory window was observed. Ferroelectric P–E hysteresis loops were observed at room temperature. The observed bend in the temperature dependent dc conductivity, dielectric and ferroelectric hysteresis behavior clearly establish the onset of ferroelectric phase in Li-doped ZnO thin films. The ease of fabrication of high-quality thin films together with appear-

ance of ferroelectricity in these films makes it a promising candidate for integrated ferroelectric devices.

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