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Journal of the European Ceramic Society 23 (2003) 1593–1598
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Influence of postdeposition annealing on the properties of ZnO films prepared by RF magnetron sputtering

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Received 20 June 2002; received in revised form 10 October 2002; accepted 20 October 2002

Abstract

ZnO films were prepared on unheated silicon substrate by RF magnetron sputtering technique. Postdeposition annealing of ZnO films in vacuum were found to improve film structure and electrical characteristics, such as dense structure, smooth surface, stress relief and increasing resistivity. Suitable annealing temperature also reduced loss factor. The correlation between annealing conditions and the physical structure of the films (crystalline structure and microstructure) was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The preferred annealing condition has been found to improve ZnO film characteristics for piezoelectric applications. An over-mode acoustic resonator using the ZnO film after annealing at 400 °C in vacuum circumstance for 1 h showed a large return loss of 42 dB at the center frequency of 1.957 GHz.

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Keywords: Annealing; Films; Resonator; Sputtering; ZnO

1. Introduction

Zinc oxide (ZnO), a semiconducting, photoconducting, piezoelectric, and optical waveguide material, shows a wide range of scientific and technological applications.[1] It belongs to a group of the hexagonal wurtzite, 6-mm symmetry; it is an n-type wide-bandgap semiconductor material and has a variety of potential applications.[2,3] ZnO films also have widely been used as surface acoustic wave devices and bulk acoustic devices due to their strong piezoelectric effect.[4,5] ZnO films can be deposited by variety of deposition techniques, such as sol-gel process,[6] spray pyrolysis,[7] molecular beam deposition (MBE),[8] chemical vapor deposition (CVD)[9] and sputtering.[10–14,24] The most commonly used technique is sputtering because it is possible to obtain good orientation and uniform films close to single-crystal morphology even on amorphous substrate or at low substrate temperature.

For film bulk acoustic device applications, it is necessary for ZnO films to deposit with some specific characteristics. The first one is high resistivity. For an acoustic amplifier single-crystal piezoelectric semiconductors with resistivity from 10^3 to 10^6 ohm-cm are required.[15] ZnO has a small oxygen deficiency under ordinary circumstances. The lack of chemical stoichiometry makes ZnO an n-type semiconductor with a typical resistivity of 1–100 ohm-cm.[16] For piezoelectric applications, it is very important to raise resistivity of ZnO film. X-ray diffraction analysis is a very quick and nondestructive method of examining the quality of the sputtered films. The examination of piezoelectric films has been a major tool for determining the uniformity of crystalline structure.[17] Only *c*-axis (002) diffraction peaks were observed in the grown ZnO films using our sputtering parameters. With low dielectric constant and low loss factor of ZnO films for acoustic resonator filter applications can decrease response time and increase quality value. In this research, the experimental results of resistivity, crystalline structure, dielectric constant, loss factor and stress of ZnO films after postdeposition annealing process have been investigated, and we expect to find out the optimum annealing condition to obtain the excellent ZnO films for piezoelectric devices applications.

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PII: S0955-2219(02)00404-1

2. Experimental procedure

ZnO films were deposited by r.f. magnetron sputtering system using a ZnO target (99.9%). Li-doped ZnO target was prepared by adding 1.5 mol% Li_2CO_3 (99.99%) and firing at 900 °C for 3 h. Li-atom doping of ZnO involves their substitution for Zn atoms; they act as acceptors that compensate the donors (excess Zn atoms) to increase resistivity of ZnO films. Substrate is n-type silicon with (100) orientation and the resistivity is 8–10 ohm-cm. The substrates were thoroughly cleaned with organic solvents and dried before loading in the sputtering system. In order to measure the resistivity of films; thickness about 1500 Å titanium was grown on silicon for bottom electrode because of its nice adhesion. The chamber was down to 6×10^{-6} torr using a diffusion pump before introducing the premixed Ar and O_2 sputtering gases into the chamber through a precision leak valve and controlled by the main valve of the diffusion pump. Throughout all experiments, the target was pre-sputtered for 15 mins under 150 W r.f. power before the actual deposition began to delete any contamination on the target surface to make the system stable and reach optimum condition. The ratios of argon to oxygen were controlled by the electronic mass flow controller. The substrate temperature was monitored utilizing a thermo-coupler attached near the substrate. The ZnO films were annealed in vacuum (10^{-5} torr) for 1 h at different temperatures. The heating rate is 20 °C/min from room temperature to annealing temperature and the cooling rate is 10 °C/min from annealing temperature to 100 °C. The dependence between annealing conditions and the physical structure of the films (crystalline structure and microstructure) was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The structure for resistivity, dielectric constant, loss factor and acoustic measurement was substrate/Ti/ZnO/Al type. The thickness of top electrode (aluminium) was about 2000 Å.

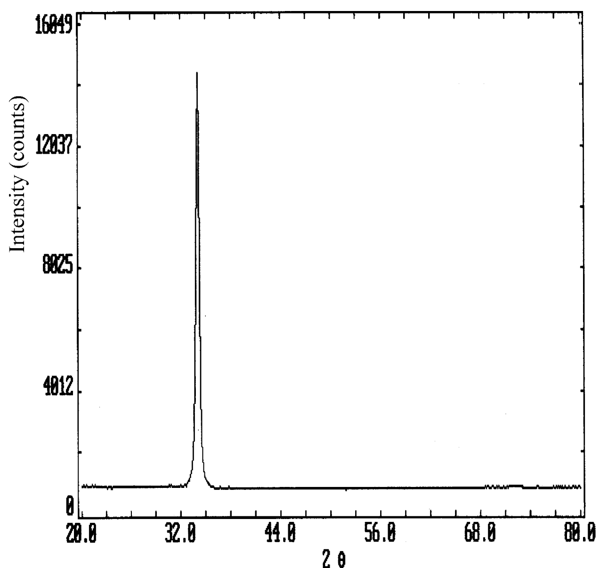


Fig. 1. X-ray pattern of (002) orientation ZnO film.

3. Results and discussions

3.1. X-ray diffraction and stress of ZnO film

The crystalline structure and orientation of the ZnO films were investigated by X-ray diffraction (XRD Rigaku D/max 2.B). The power of the XRD (Cu Kα radiation) was fixed at 25 kV and 5 mA and the XRD diffraction angles (2θ) were measured from 20 to 80°. Major peak identified and compared with JCPDS file 36-1451 (International Center for Diffraction Data) for Zinc Oxide samples are seen at 34.421 corresponding to (002) plane reflections from hexagonal type ZnO with $a=0.32498$ and $c=0.52066$ nm. Fig. 1 shows the X-ray diffraction pattern of ZnO film with strong *c*-axis (002) orientation. In our experiments, we found that it is necessary to keep the substrate temperature and sputtering power lower to obtain stronger *c*-axis oriented ZnO films. The sputtering conditions are listed in

Table 1
Sputtering conditions of ZnO films deposition

Target composition	ZnO target with 1.5 mol% Li_2CO_3
Target–substrate distance (mm)	50
Substrate temperature (°C)	100
Sputtering gas	Ar(50%) + O_2(50)%
RF power (W)	70
Deposition time (h)	3
Deposition rate (μm/h)	0.45
Deposition pressure (Torr)	10 m
Film thickness (μm)	1.35

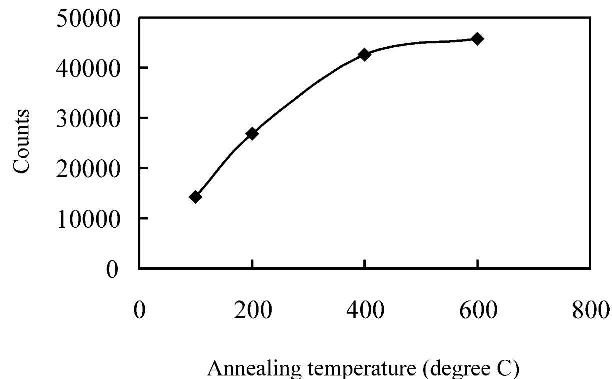


Fig. 2. (002) orientation intensity of ZnO films as a function of annealing temperature.

Table 1. Fig. 2 shows the *c*-axis (002) orientation intensity as a function of annealing temperature, higher annealing temperature greatly improved the intensity of (002) orientation. High annealing temperature provided energy of film atoms to enhance mobility that could improve porous and quality of films.

The angular peak position of ZnO powder with (002) orientation is $2\theta=34.42°$ (1997 JCPDS- International Center for Diffraction Data). However, in ZnO film, the deviation of the position of the diffraction peak from its powder value is mainly due to a uniform state of stress with compressive components parallel to substrate. The stress in sputtered ZnO films investigated by various workers has been found to be associated with sputtering atoms impacting and interstitial oxygen.[18–21]

Fig. 3 shows the X-ray diffraction peak angles of ZnO films with (002) orientation as a function of annealing temperature. The peak angles increase as annealing temperature increase, which means the compressive stress has been relieved at about 400 °C. During the annealing process, the atoms of ZnO films have energy to arrange again and will reduce the compressive stress. On the other hand, the thermal expansion coefficient of ZnO is higher than that of Si, the thermal expansion coefficient α value of silicon being $2.5\times10^{-6}/°C$ at room temperature. ZnO crystal is hexagonal and its α_{11} and α_{33} values are, respectively, 6.05 and $3.53\times10^{-6}/°C$.[20] A tensile stress will be generated by silicon when substrate temperature drops from high temperature down to room temperature. The tensile stress of silicon and compressive stress of ZnO film will cancel out each other. However, for the annealing temperature that is too high (>400 °C), the tensile stress will be stronger than compressive stress, and the peak angles increase over 34.42 degrees.

3.2. SEM and AFM

Surface morphology of ZnO films was investigated by scanning electron microscopy and atomic force microscopy techniques. Fig. 4 shows the SEM top views of ZnO films annealed at different temperatures. In Fig. 4a, the annealing temperature was 100 °C (the same as deposition temperature), which looks to have much porosity. Fig. 4b shows the ZnO film annealed at 400 °C, and looks more dense and uniform than Fig. 4a. In AFM analysis as shown in Fig. 5, the average roughness of films annealed at 100 and 400 °C 1 h were 188.0 and 92.2 Å, respectively.

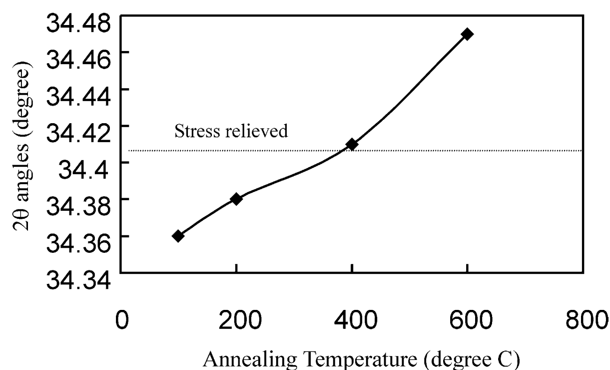
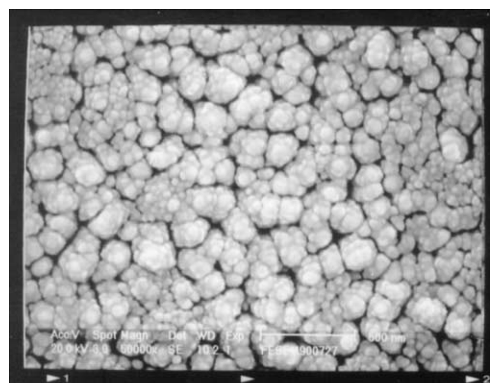


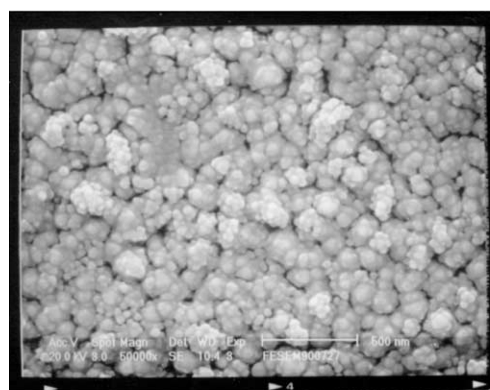
Fig. 3. X-ray diffraction 2θ angle of ZnO films with (002) orientation as a function of annealing temperature.

3.3. Resistivity

D. H. Zhang reported that ZnO film annealing in air could raise resistivity about nine orders (10^{-3}–10^{6} ohm-cm),[22] and T. Mitsuyu reported that the resistivity increased about two–three order (10^{3} –10^{6} ohm-cm) due to oxygen reactions with ZnO.[23] Fig. 6 shows the resistivity of ZnO films as a function of annealing temperature in vacuum. Postdeposition annealing of ZnO films in vacuum are to avoid the base electrode oxidation. The resistivity of ZnO films increase as annealing temperature rises. High annealing temperature will improve the quality of ZnO films.,[13] although in a vacuum circumstance, the resistivity still increases about one order after annealing 1 h at 400 °C. As annealing temperature is too high (over 400 °C), the resistivity has a little



(a)



(b)

Fig. 4. Top views of ZnO films annealed at (a) 100 °C and (b) 400 °C.

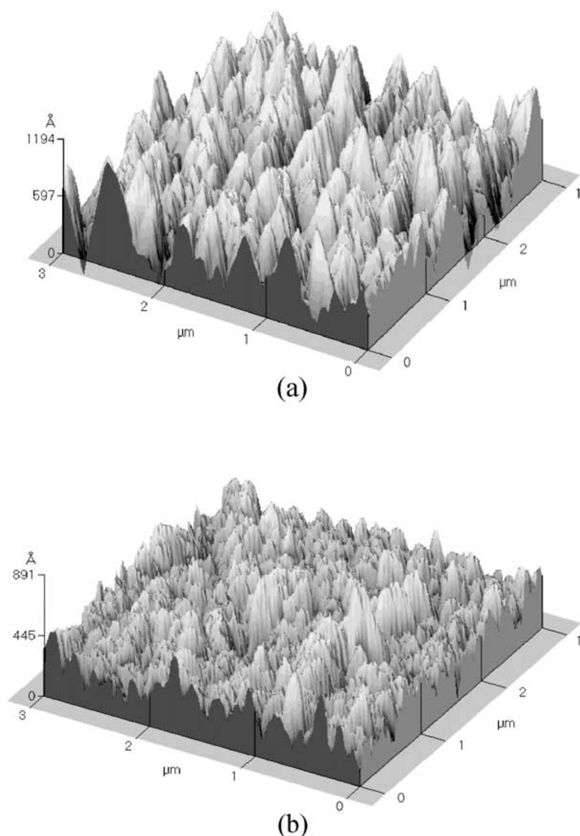


Fig. 5. AFM photographs of ZnO films (a) annealed at 100 °C, (b) annealed at 400 °C 1 h.

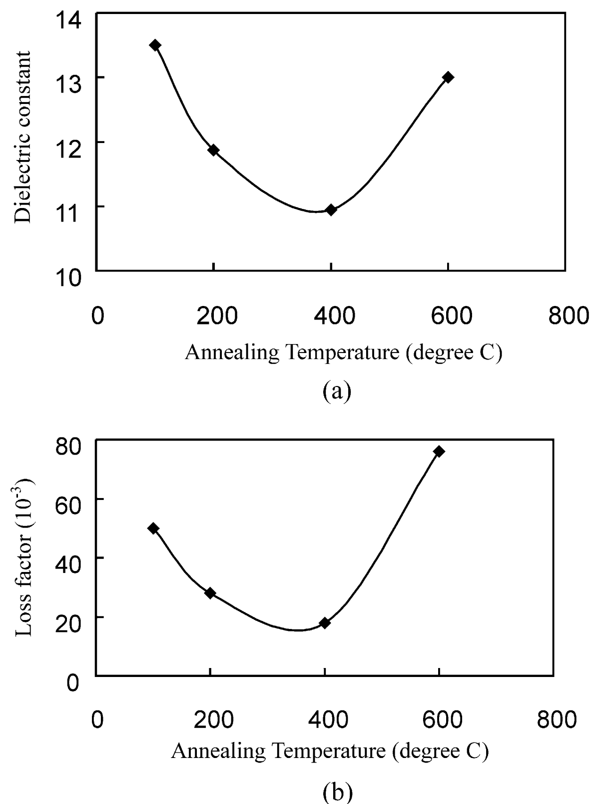


Fig. 7. (a) Dielectric constant (b) loss factor of ZnO films as a function of annealing temperature.

decrease may be due to the oxygen out-diffusion from ZnO.[14]

3.4. Dielectric constant and loss factor

The dielectric constants and loss factors were measured by HP 4194A impedance/gain-phase analyzer at 1 KHz. Dielectric constants of pure single crystal are about 10.9 (ϵ_{33}) and 8.5 (ϵ_{11}).[25] Fig. 7(a) shows the dielectric constant as a function of annealing temperature. As annealing temperature increases, the dielectric constant decreases. The minimum dielectric constant (10.94) was obtained at annealing 400 °C for 1 h, which is very close to single crystal value ϵ_{33}. Fig. 7(b) shows the loss factor as a function of annealing temperature, and the results were similar to those of dielectric constant. The dielectric behavior of ZnO was controlled by grain boundary.[26] Increasing annealing temperature will help grain growth and decrease in grain boundary. Suitable annealing temperature can improve the film density and quality, but too high annealing temperature will make the grain overgrow and break the films structure.[18] ZnO films with lower dielectric constant and loss factor value help to reduce the response time for resonator filter and obtain higher quality value.

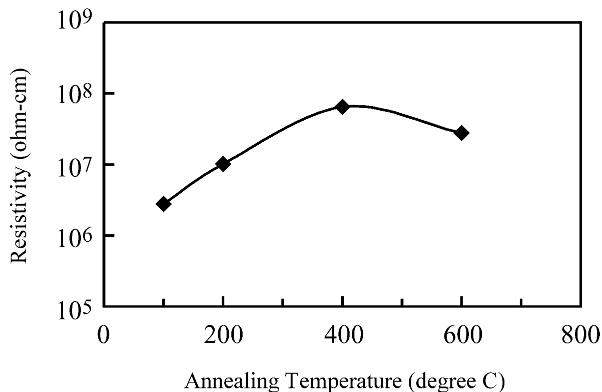


Fig. 6. Resistivity of ZnO films as a function of annealing temperature.

3.5. Acoustic measurement

The piezoelectric characteristic of the deposited ZnO films was investigated by making an over-mode resonator. Fig. 8(a) and 8(b) show the return loss versus frequency as of the over-mode resonators by different annealing conditions. Fig. 8(a) was without annealing and 8(b) was annealed at 400 °C in vacuum

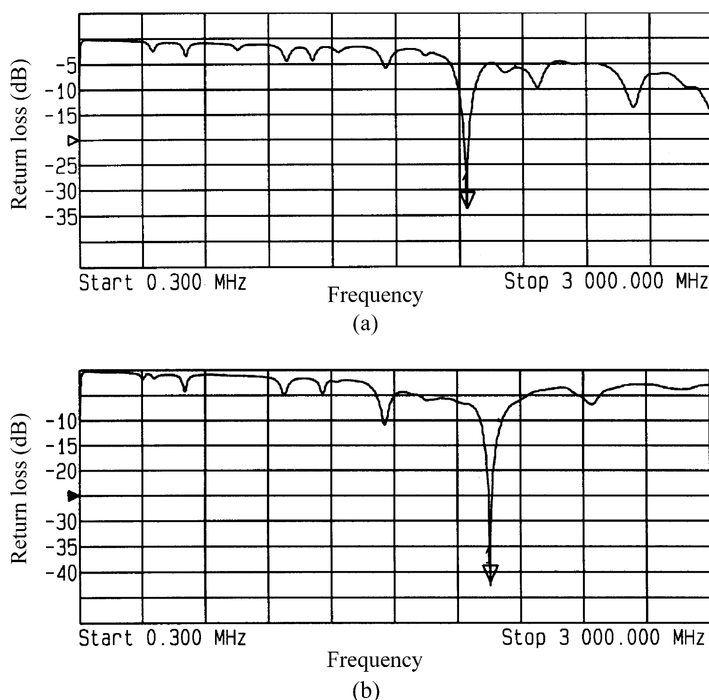


Fig. 8. Frequency responses of the over-mode resonators after impedance matching. The center frequencies and return losses are (a) 1.833 GHz and 33.629 dB (b) 1.957 GHz and 42.069 dB.

circumstance for one hour. The sputtering conditions of Fig. 8(a) and 8(b) are the same and showed in Table 1. The frequency responses were measured by HP-8714ES network analyzer, and the return losses of devices without annealing and annealed at 400 °C in vacuum circumstance of 1 h were 33.629 and 42.069 dB obtained at the center frequency of 1.833 and 1.957 GHz after impedance matching. The difference of center frequencies is due to a series of different inductances by impedance matching.

4. Conclusions

ZnO films with high resistivity and *c*-axis (002) orientation structure were deposited on silicon by r.f. sputtering technique. Postdeposition annealing at 400 °C makes ZnO films more suitable for piezoelectric applications, it makes ZnO films with higher resistivity, stronger *c*-axis (002) orientation, denser structure, smoother surface and relieved stress. However, annealing at too high temperature at 600 °C will increase loss factor and stress. Annealing 1 h at 400 °C in vacuum, the stress will be relieved; resistivity increases about one order and keeps the minimum loss factor. The good characteristic of an over-mode resonator is mainly due to the strongly preferred orientation and reduced the surface roughness of the ZnO films with postdeposition annealing process.

Acknowledgements

This research was supported by the National Science Council of Republic of China, under grant NSC-89-2213E-006-209.

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