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Annealing Effect on Structural and Optical Properties of ZnO Thin Films Sputtered on $LiNbO_3$ Substrate

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Abstract: Zinc was sputtered on $LiNbO_3$ (LN) substrate and zinc oxide (ZnO) thin films produced by thermal oxidation of the metallic zinc (Zn). The influence of the annealing temperature (400-800°C) and heating time (15-120 min), on the optical properties of the ZnO thin films was investigated. The transmittance of the ZnO thin film decreases as the temperature rises and at 800°C, when diffusion of Zn into LN takes place, transmittance and optical band-gap start to increase with heating time. Magnetron sputtering, increased substrate temperature (450k) and appropriate choice of ZnO film thickness combined with immediate oxidation produced films of good optical quality. Optical, x-ray diffraction (XRD) and scanning electron microscope (SEM) results show crystals which maintain their transparency and high surface quality after Zn has diffused into LN.

Key words: Annealing · $LiNbO_3$ Optical properties · Diffusion · Sputtering · ZnO thin film

INTRODUCTION

Zinc oxide is an n-type semiconductor and its wide optical band gap of 3.3eV leads to applications in ultraviolet (UV) light emitting diodes and laser diodes, for example, [1-3]. Zinc oxide is also an outstanding piezoelectric material for surface acoustic waves (SAW) and bulk acoustic wave device, [4,5]. $LiNbO_3$ (LN) is an excellent material for waveguide devices because of the wide wavelength range over which it is transparent. For $LiNbO_3$, the two most widely used waveguide fabrication techniques are Ti-diffusion and annealing/proton exchange (APE) processes. But however, they have some drawbacks as Ti-diffused waveguides often suffer from photorefractive damage and APE waveguides support only extraordinary polarized guided modes, [6, 7].

Although Ti-diffused waveguides have adequate performance for some applications such as propagation of light in the infra-red (IR) region, they are not suitable for operation in the visible part of the spectrum. Zn has also been employed as a diffusion material for $LiNbO_3$ and $LiTaO_3$. Zn-diffused waveguides support both ordinary and extraordinary modes and also have relatively high photorefractive damage resistance, [8,9]. Another feature of Zn-diffused waveguides is that they may be fabricated at temperatures much lower than for Ti-diffused wave guides and therefore out-diffusion of Li can be avoided.

Nevado and Lifante [9] fabricated waveguides with LN using Zn vapor to perform the diffusion, but this method faces the problem of the formation of a surface Zn-rich phase, which gives rise to scattering by the presence of inhomogenities and high propagation losses. Furthermore, some results showed severe pitting and surface damage from this technique [9].

Young *et al.* [10], reported the fabrication of planar waveguides by diffusion of ZnO films into LN crystals in a Li-rich atmosphere at temperatures of 1000-1100°C. They found that using ZnO instead of metallic Zn as a source for diffusion greatly reduces secondary phase precipitation and produces better waveguides. The ZnO film thickness is important for controlling precipitation.

To produce low scattering loss waveguides it is crucial that the surface quality is not degraded by the diffusion process. Yoon *et al.* [11] reported surface degradation resulting from diffusion of metallic Zn into LN, and chose ZnO instead of metallic Zn to limit this. Suhara *et al.* [12], claimed that pressure control is crucial to ensure modest in-diffusion and maintain surface quality with suppressed out-diffusion.

ZnO thin films for UV light emitting devices have often been grown on sapphire substrates despite the 18% lattice mismatch , but because the lattice mismatch between ZnO and $LiNbO_3$ is only about 9.3%, [13], one would expect better quality epitaxial ZnO films and therefore improved optical properties on these substrates.

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For ZnO films on LN substrates although some authors have studied the ZnO optical properties, in most cases only the films photoluminescence (PL) was investigated, [14-17]. Also, some reports have only considered the diffusion of Zn into $LiNbO_3$, [10-19]. Here, in contrast, we consider optical properties of both the ZnO and the LN crystal before and after diffusion of Zn.

To our knowledge there is no previous report on the variation of reflectance and optical band gap energy after diffusion of Zn into $LiNbO_3$.

In this work we have used magnetron sputtering to deposit pure Zn and thermal oxidation of the metallic Zn to produce ZnO films. This is an unusual approach in spite of the advantages of magnetron sputtering, including easy control of texture, uniform film thickness, high coating rate, high packing density and very good adhesion of the film to the substrate due to the high energy of the depositing particles. Important optical parameters such as the transmittance, reflectance and band gap energy, as well as their variation with temperature and annealing time were investigated. Sample structure was analyzed by XRD, SEM and Rutherford back scattering (RBS).

Experimental Details: To produce ZnO thin films, Zn was sputtered on LN substrates, followed by thermal oxidation of the Zn using a conventional oven in open air with average humidity of 60%. For deposition of the Zn, a vacuum system with base pressure of 10^{-6} *mbar* was employed, (Hind High Vacuum, H.H.V.12"MSPT) and a circular flat disc (thickness 3mm and diameter 125mm) of pure Zn (99/9%,MERCK) was used as the sputtering target. For plasma formation, research grade argon (purity 99/99%, Saman Gas Company) was used at pressures of 10^{-2}-10^{-1} *mbar*. To vary the coating rate, the discharge current was varied from 200 to 1200mA and the distance between Zn target and substrate (LN) changed from 5 to 15 cm. Conditions were optimized to obtain good, densely-packed, continuous and uniform films with a coating rate of 1.5 nm/s. All the samples in this work were deposited under these conditions.

X-cut commercial congruent $LiNbO_3$ supplied by Focktek with dimensions of $20\times10\times0.5$ mm^3 and very good optical quality polished surfaces were employed as the substrate for deposition. Before using a LN substrate, a 3-step ultrasonic cleaning process (acetone, methanol and deionized H_2O) was carried out. The substrate temperature could be changed from 300K to 600K and measured accurately by means of a digital thermocouple. Before Zn deposition, the plasma discharge was run for a few minutes and to ensure a high purity coating, the produced plasma was checked by a spectrometer with high resolving power. Only when Zn and Ar (atoms and ions) were the only lines present was deposition of Zn on LN started. ZnO thin films with 150 nm thickness (measured by RBS) were produced, since the critical ZnO film thickness for diffusion of Zn into LN is 70-200nm, [10,16,18]. Deposition of Zn on LN was carried out at 400K substrate temperature and this improved the adhesion of the Zn films to the $LiNbO_3$ substrate.

To investigate the effect of annealing on the optical properties of the ZnO, the temperature was increased up to 800°C and the heating time varied from 15 to 120 min at 800°C.

For optical measurements a double beam spectrophotometer (Camspec, model M350) with wavelength range of 200-1100 nm was employed. Structural characterization of the produced samples was performed by X-ray diffraction, using a Philips diffractometer (X'pert PW 3373) and *Cu* K_α (λ=1.544°) radiation. To observe the sample surface morphology, scanning electron microscopy (SEM, model Cambridge S360) of the samples was carried out. To investigate the diffusion of Zn into $LiNbO_3$ and also the quality of the LN crystal before and after diffusion, RBS experiments were performed with 1.5 and 2 MeV H^+ beams from a 3 MeV Van der Graaf accelerator. These revealed that all the deposited Zn diffused into the LN with a good gradient after annealing, as presented in our previous report [20].

RESULTS AND DISCUSSION

Figure 1 shows the transmittance (T) as a function of Wavelength (λ) for the virgin LN substrate and LN with ZnO coatings annealed at different temperatures. The transmittance of $LiNbO_3$ starts to rise sharply at λ=320nm and then reaches 70%, afterwards remaining roughly constant in the visible and near-IR region. The transmittance of LN with ZnO thin film starts to rise at λ=378nm (near the optical band-gap of ZnO) and as the annealing temperature increases, the transmittance of the sample reduces. When heating ZnO at temperatures higher than 500-550°C, evaporation of oxygen may occur and this produces an oxygen vacancy which is immediately ionized, releasing two electrons to the conduction band and Zn also acts as a donor. Also desorption of oxygen molecules from the grain boundaries may occur, for higher temperatures (T>600°C), which approach the decomposition temperature of ZnO, the band-gap energy (E_g) may show a reduction [17] Fig. (1).

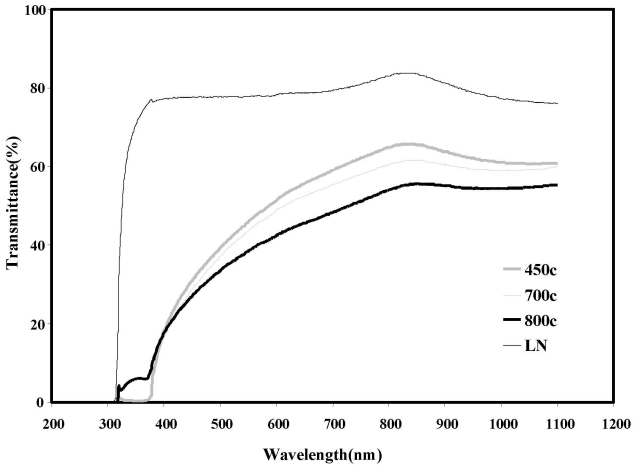

Fig. 1: Variation of transmittance of ZnO at various temperatures

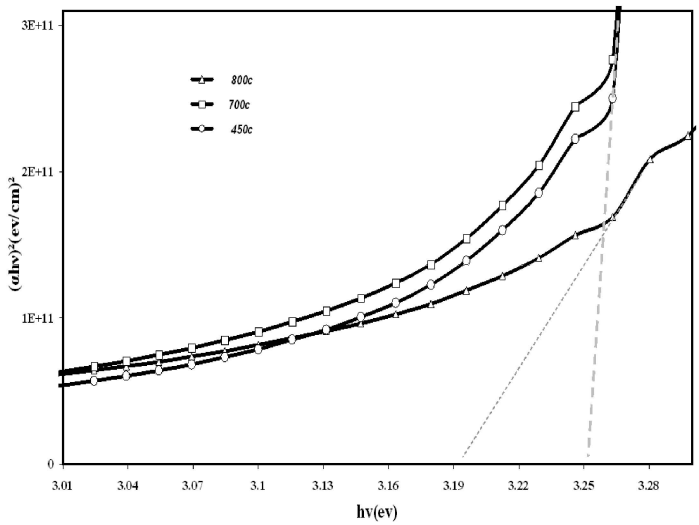

Fig. 2: Plot of $(\alpha h\nu)^2$ against photon energy for ZnO thin films at different temperature.

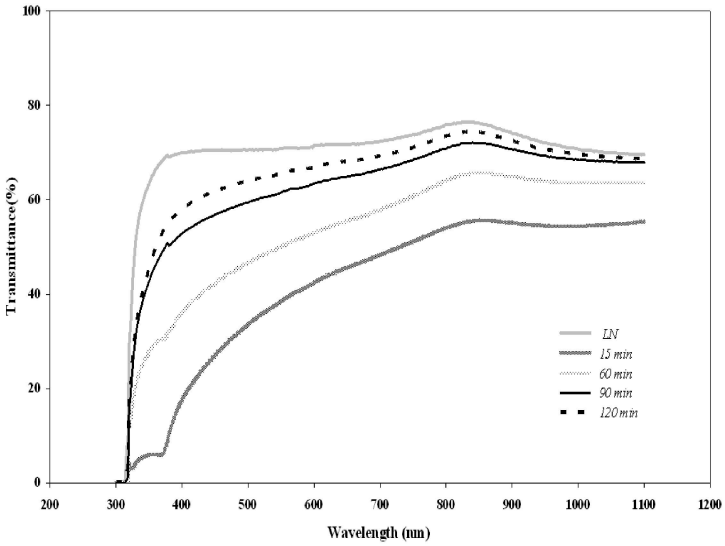

Fig. 3: Transmittance of ZnO on LN at 800°C for different period of heating

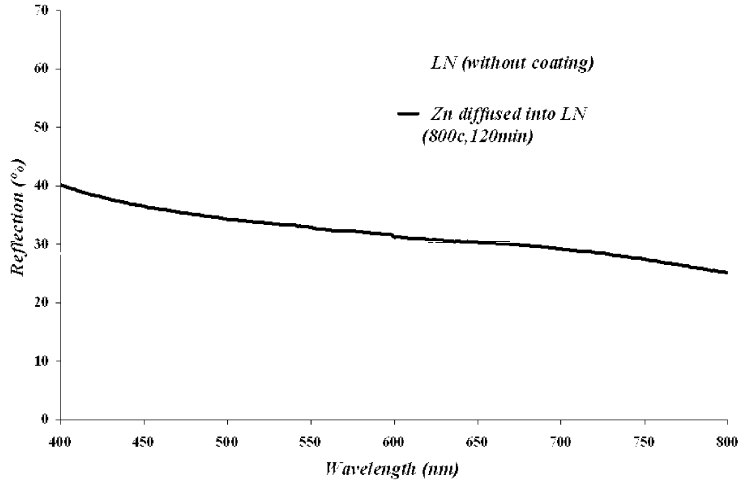

Fig. 4: Variation of reflection power of LN and Zn diffused into LN

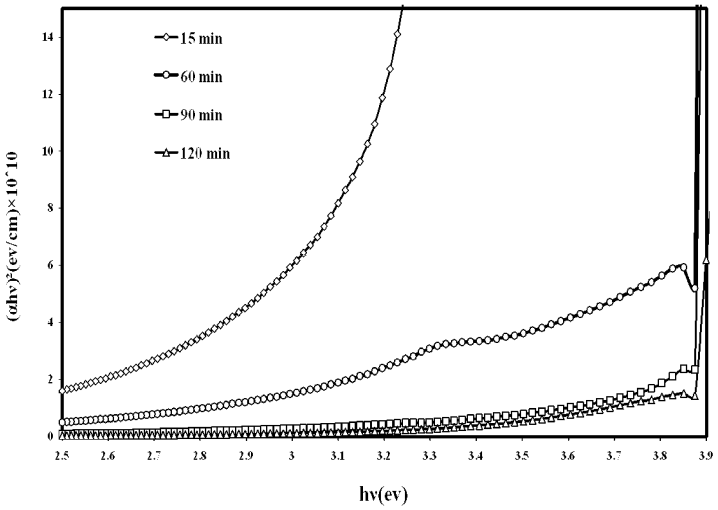

Fig. 5: Plot of $(\alpha h\nu)^2$ versus photon energy for ZnO thin films at 800°C for various periods of heating

Tabata *et al.* [21], reported that when LN is heated in vacuum, desorption of Li and O is observed for temperatures higher than 400°C and the rate of desorption increases rapidly above 500°C. According to Fujihara et al [22] and Bonasewicz *et al.* [23], Li diffusion into the ZnO film can take place, increasing the number of Zn in interstitial sites or oxygen vacancies. This could enhance the intensity of deep level emission related to interstitial Zn and oxygen vacancies.

The absorption coefficient (α) can be calculated using equation (1), [4].

$$\alpha = \frac{1}{t}\ln\left(\frac{T_0}{T}\right) \quad (1)$$

Where T and T_0 are the transmittance of the sample with ZnO thin film and the substrate (LN) without coating respectively and t is the film thickness. The optical band-gap energy assuming direct inter-band transitions (Tauc's relationship), is: [24]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

Where A is a constant, $h\upsilon$ is the energy of the incident photon and E_g is the band gap energy. To calculate E_g a graph of $(\alpha h\nu)^2$ versus $h\nu$ was plotted. Extrapolating the straight linear portion of this plot to the energy $(\alpha h\nu)^2$ axis gives the optical band-gap. Figure 2 shows the variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$), for different temperatures. E_g was founded to be roughly constant (~ 3.25 ev).For stoichiometric ZnO films the band gap is known to be 3.24ev [13], so that obtained value of E_g demonstrates the high crystallinity of the ZnO thin films on LN substrates.

Table1: Values of E_g for different temperature and various periods of heating

Temperature (°c)	450	600	700	800	800	800	800	LN without coating at room temperature
Time (min.)	15	15	15	15	60	90	120	
E_g (ev)	3.25	3.25	3.25	3.19	3.870	3.875	3.875	3.995

To observe the effect of heating time on the optical properties of ZnO, the produced samples were annealed at 800°C for various periods. Figure 3 shows the sample transmittance against wavelength for the different heating times. Longer times cause a blue shift and increase in transmittance and after 120 minutes of heating, the sample transmittance was very close to the transmittance of pure LN (without ZnO coating). In the low wavelength region of the spectrum, the optical transmittance of the produced sample is a few percent less than the pure LN substrate, which could be due to the presence of Zn in $LiNbO_3$ after diffusion.

The variation of reflectance (R) with wavelength for a LN crystal (before and after diffusion of Zn) is given in Fig. 4. When Zn has been diffused into LN, the reflectance of the sample is more than the as-received $LiNbO_3$, due to the presence of Zn in the LN crystal. This higher reflectivity may be the reason for the lower transmittance after diffusion.

Figure 5 gives a plot of against $(\alpha hv)^2$ photon energy for different annealing times at 800°C. Values of the band gap (E_g) for different temperatures and heating times are given in Table 1. The band gap energy remains constant up to 700°C-750°C, then at higher temperatures (when diffusion occurs) it shows reduction, then the band gap increases when the heating time increases and finally reaches the value of E_g for pure LN (~ 4ev) [25].

In our previous work, complete diffusion of Zn into $LiNbO_3$ took place at 800°C and a longer period of heating (180min) was required [20], while in this work the diffusion of Zn starts at a lower temperature (750°C) and a shorter heating time (120min) was needed. This is due to the increase of substrate temperature during growth, combined with an immediate oxidation step followed by annealing at suitable heating (10°C/min) and cooling (4°C/min) rates. These rates are very important to avoid stress and strain in the film [15].

The obtained results show that the method used in this work is a promising route for fabricating waveguides and active optical devices. Our procedure has the advantage that it is possible to incorporate a high doping level of Zn ions in the LN matrix, preserving a good crystallinity. Using a lower temperature helps to avoid Li out-diffusion, (since a Li-deficient surface produces an unwanted planar waveguide,[20])

Figure 6 shows the XRD pattern of the sample after initial ZnO thin film formation on LN at 450°C, while Figi 7 shows the XRD of the sample after diffusion of Zn into LN. In both XRD spectra a log scale was used for the intensity axis to be able to observe the ZnO peaks. When diffusion of Zn starts, a $ZnNb_2O_6$ peak is obtained, but when diffusion is completed this phase disappears.

SEM pictures of ZnO thin films at temperatures of 450°C (oxidation temperature) and 800°C (after diffusion of Zn), are given in Fig. 8. A very smooth, transparent (as revealed by optical microscopy) and uniform surface is obtained and no pitting is observed.

Summary and Conclusion: Use of high energy sputtered Zn particles together with a higher substrate temperature during growth leads to a shorter time and lower temperature being required for diffusion of Zn into a LN crystal. The transmittance showed a reduction with increasing annealing temperature and then at a critical temperature (~750°C, when diffusion of Zn can take place), the transmittance increases with annealing time. This reduction of T with annealing temperature could be due to desorption, re-evaporation and absorption of oxygen. After complete diffusion, the reflectance (R) of the sample is greater than that of the pure LN crystal. E_g remains roughly constant with increasing temperature and after diffusion of Zn into LN, it increases and nearly reaches the value of E_g for $LiNbO_3$. As long as a ZnO thin film is present on the surface of the LN crystal, the optical properties of the sample are very close to those of ZnO, but when diffusion of Zn takes place, the optical characteristics of the sample return to those of the LN crystal (E_g, T), with small differences due to the presence of Zn in the LN. Before complete diffusion of Zn, the XRD results showed that some new phases are present, but after complete diffusion, these peaks disappeared. SEM showed very uniform, smooth surfaces for the samples which are very important for the fabrication of waveguides.

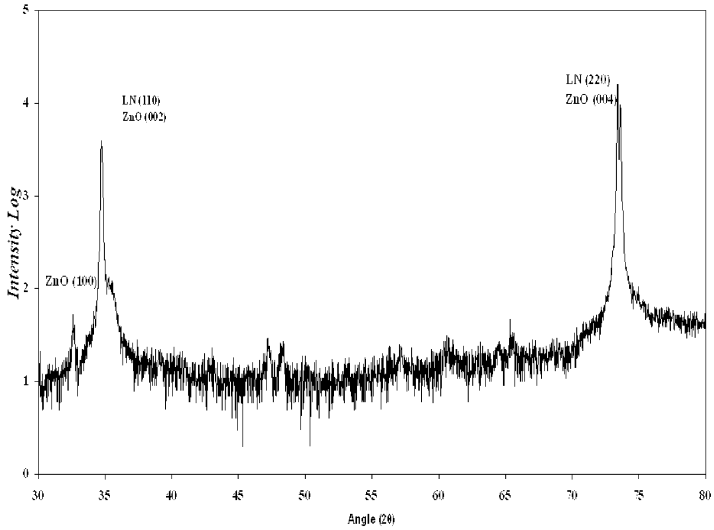

Fig. 6: XRD pattern of ZnO film heated at 450°C for 15 min

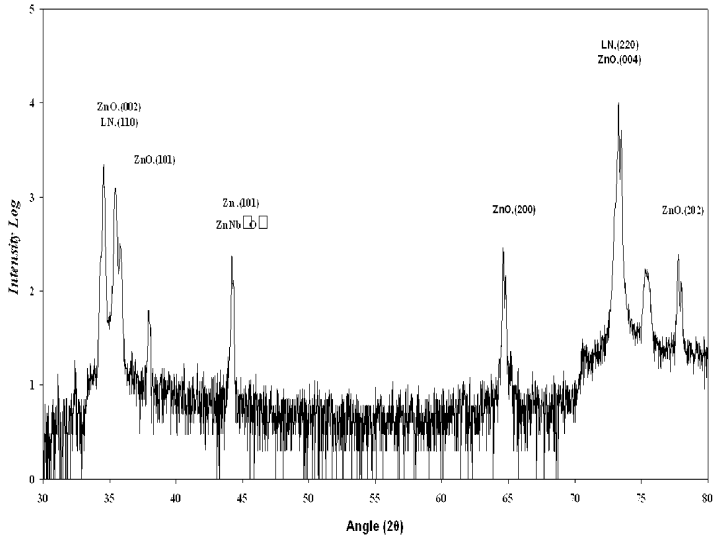

Fig. 7: XRD pattern of ZnO film heated at 750°C for 180 min

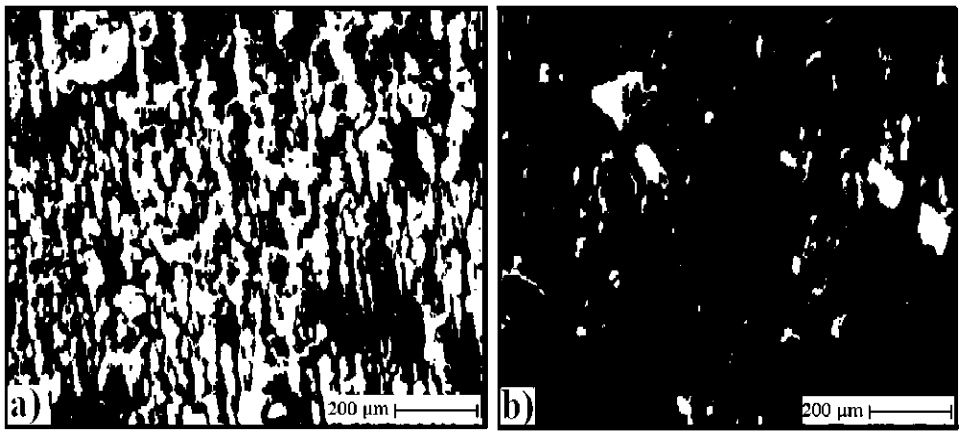

Fig. 8: SEM pictures of ZnO thin films a) heated at 450°C for 15 min. b) heated at 750°C for 120 min

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