Tailoring the optical properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films by nitrogen doping

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Abstract Thin films of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ doped with nitrogen were deposited by Radio Frequency plasma beam assisted Pulsed Laser Deposition (RF-PLD) in oxygen or oxygen-nitrogen discharge with different nitrogen/oxygen ratios. A Nd:YAG laser working at a wavelength of 266 nm, having a 10 Hz repetition rate was used for the depositions. The energy density of the incident beam was 3 J/cm$^2$ and the RF power was set to 100 W for all the samples. X-ray Diffraction (XRD) and Spectroscopic Ellipsometry (SE) were employed to investigate the samples. The degree of crystallinity is found to decrease with increasing the Mg concentration, while the solubility of Mg in ZnO increases by 30% in the N-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films grown by RF-PLD. Segregation of MgO phase at a Mg concentration of 30% for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin film is detected both by XRD and SE. The band gap of the samples increases from 3.37 to 3.57 eV with increasing the Mg concentration and the nitrogen/oxygen ratio for each Mg concentration. A dependence of the dielectric function (refractive index) on both stoichiometry and degree of crystallinity is also found, the refractive index having values between 1.7 and 2 in visible spectral range.

1 Introduction

The interest in ZnO thin films is permanently growing due to numerous applications in which it can be used [1]. Its multifunctional character and, in particular, its remarkable optical properties make ZnO one of the most investigated material. ZnO is transparent for visible light and absorbs UV radiation due to band-to-band transitions. ZnO based materials can be used to fabricate transparent electrodes for solar cells and flat panel displays [2]. ZnO layers are mechanically resistant and have high degradation threshold when exposed to high power electromagnetic radiation. Thus, ZnO is commonly used for antireflective coatings, optical filters or gratings. Furthermore ZnO can be used as semiconductor gas sensor [3] due to conductivity changes when exposed to oxidizing gases. Zinc oxide exhibits extremely stable exciton properties at room temperature due to its exciton binding energy of 60 meV [4, 5], exceeding that of GaN—25 meV and can be used in semiconductor devices. The band gap and consequently the emission spectra and the refractive indices can be tuned by alloying with Zn isovalent elements such Mg or Cd [6]. These properties recommend ZnO as the most suitable material for future optical devices. Design and control of the properties of ZnO based thin films is very important and should be done with good precision. In this case, radiofrequency (RF) plasma beam assisted pulsed laser deposition (PLD) was employed for the growth of the samples. Tuning the optical properties of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin-film alloys is usually achieved by using targets with different controlled compositions, as well as by adjusting the deposition conditions. However, controlling the composition of the targets is a time consuming and expensive procedure. In this paper we propose a faster and less expensive method to control the optical properties of the thin films by nitrogen doping of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films.
2 Experimental

The experimental setup (Fig. 1) comprises a Nd:YAG laser having a repetition rate of 10 Hz, having a pulse duration of τ = 5 ns and working at the forth harmonic (λ = 266 nm). The addition of a RF (13.56 MHz) plasma source working in O₂ and/or N₂ is an improvement with respect to a conventional PLD setup. The RF plasma expands from the discharge source into the deposition chamber as a directional beam through an aperture (nozzle) due to the differential pressure between the two chambers. This way the substrate is simultaneously exposed to the laser plasma and oxygen and nitrogen plasma beam. Three MgₓZn_{1−x}O targets with different Mg:Zn ratios (x = 0.05, 0.10 and 0.30 w/w) were used. The targets were fabricated by mixing ZnO and MgO powders and then sintering the mixtures at 1000°C. Quartz-glass substrates were used for the deposition and the substrate temperature was kept at 400°C. The pressure of oxygen or oxygen-nitrogen mixture, respectively, was kept constant at 10⁻¹ mbar, whereas the nitrogen pressure was set according to the N₂/O₂ ratios of 0.33 and 1. The RF power was 100 W and the gas flow was controlled by mass flow controllers. The distance between the target and the substrate was 4 cm, the laser fluence 3 J/cm² and 36000 laser pulses were shot for each sample.

The structural characterization was done by X-Ray Diffraction (XRD). The XRD patterns were collected using a PANalytical X’Pert MRD diffractometer equipped with a point sensitive fast detector (PIXcel) in a continuous scanning mode (counting 25 s per 0.02 2θ). The diffractograms were recorded in Bragg-Brentano geometry.

The optical properties of the samples were investigated by Spectroscopic Ellipsometry (SE) using a Woollam Variable Angle Spectroscopic Ellipsometer (VASE), equipped with a high pressure Xe discharge lamp incorporated in an HS-190 monochromator. Measurements were performed in the 0.7–5 eV spectral range. Transmittance (T) through the sample at 0° angle of incidence (AOI) was acquired by conventional spectroscopy. SE measurements were performed in reflection mode at an AOI of 60° and 70°, respectively. To avoid the unwanted backside reflection, a back covering was done with a milky tape [7].

3 Results and discussions

The XRD patterns of the targets (Fig. 2a) depict the formation of a mixture between a major ZnO phase (wurtzite structure JCPDF file 36-1451) and a minor MgO phase (JCPDF file 45-0946). The XRD spectra of the MgₓZn_{1−x}O and N-doped MgₓZn_{1−x}O thin films are presented in Figs. 2(b)–2(d). The spectra reveal the formation of a single wurtzite–ZnO structure with no by-products containing Mg, except for the highest Mg concentration (x = 0.30) for which only a small peak assigned to MgO (200) could be detected.

The structural data, the a and c lattice constants and the Scherrer crystallite sizes corresponding to the (002) and (101) peak broadenings, respectively, are gathered in Table 1. The utilization of glass-quartz substrates and the Mg incorporation effect favored the growth of polycrystalline thin films. The orientation of the MgₓZn_{1−x}O and N-doped thin films along c-axis is largely influenced by the Mg content: the (002) peak is dominant in the sample with a low amount of Mg, while it is absent for the thin films with the highest Mg concentration (samples GE08 and GE09) suggesting that Mg atoms may act as obstacles for the growth of ZnO along (002). It has been reported that the pseudobinary MgₓZn_{1−x}O alloy manifests an a-axis shortening and a c-axis shortening with increasing Mg composition while remaining in the wurtzite structure [8]. According to Vegard’s law, this is to be expected due to the difference between the ionic radii of Mg and Zn (Mg²⁺/Zn²⁺ = 0.57/0.60). As indicated in Table 1 the a-axis lattice constant shows no significant change whereas the c-axis lattice constant was found to slightly decrease by increasing Mg content.

Regarding the effect of oxygen, samples grown in oxygen-rich atmosphere exhibit poor crystalline quality with lower grain sizes (GE02, GE04) or segregates toward cubic-MgO (GE07). Apparently, an excess of oxygen might induce defects in the films which influence the nucleation and growth of the films.

It is more complicated to discern the effect of nitrogen. In our previous study [9] we observe that using only nitrogen as ZnO dopant, N₂/O₂ ratios in the 0.3–0.5 range favored higher crystallinity and larger grain sizes whereas high amounts of nitrogen or oxygen lead to low crystallinity and smaller grain sizes. An increase of the crystallites coherent length along the c-axis, which is the growth direction by...