Effect of nitrogen doping on structural and optical properties of Mg$_x$Zn$_{1-x}$O ternary alloys

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**A R T I C L E  I N F O**

**ABSTRACT**

We deposited nitrogen doped MgZnO ternary alloys by using Pulsed Laser Deposition technique assisted Radio Frequency plasma beam (RF-PLD) of varied nitrogen/oxygen ratios. We used a Nd:YAG laser operating at 266 nm wavelength and a repetition rate of 10 Hz. The RF incident beam that was used for all deposited samples had a power and an energy density of 100 W and 3 J/cm$^2$, respectively. The structural and optical properties of deposited colloids were investigated by using X-ray Diffraction (XRD) and Spectroscopic Ellipsometry (SE) techniques. As Mg concentration increases, the crystalline quality of the compounds is found to decrease. Furthermore, the band gap increases from 3.37 up to 3.57 eV while increasing the nitrogen/oxygen ratio. The Mg solubility is also shown to increase by 30% in nitrogen doped Mg$_x$Zn$_{1-x}$O nanostructures. Segregation of MgO phase in Mg$_{0.5}$Zn$_{0.5}$O nanostructures was detected by both XRD and SE. The optical refractive index had values between 1.7 and 2 in visible spectral range, it shows high dependence on both stoichiometry and degree of crystallinity of the compounds.

1. Introduction

Solar cells are showing great potential for renewable energy technologies due to their high stability, high efficiency, low-cost processing, and compatibility with flexible substrates [1,2]. Quantum dot solar cells (QDSCs) first came at a 4% energy conversion efficiency and are achieving energy efficiency as high as 13.4% recently [3]. Commercial silicon panels (QDSCs) offer efficiency above 20% however, QDSCs sound promising as they are inexpensive and efficient. They can be cost effectively mass produced by using a continuous roll-to-roll processing technique [4,5]. However, as of yet flexible QDSCs show lower solar efficiency when compared to their silicon counterparts because of the difficulty in finding an efficient electron transport layer (ETL), a key component in solar cell design, that can be manufactured at temperatures below 150 °C [5].

Zin oxides (ZnO) are routinely applied as ETL in QDSCs. However, when operating a solar cell, the charge recombination occurring within QDSCs [6] compete largely with the charge carrier collection. Ternary magnesium zinc oxide (MZO) with tailored energy levels, under different Mg concentration, was very effective against interfacial recombination between solar absorber layer and charge-collecting electrode and therefore improve photovoltaics performance [7]. The addition of Mg to ZnO makes it highly transparent, which enable the solar absorber such as lead sulphide or perovskites to receive a maximum amount of light. Because these oxides are inexpensive and abundant materials they are very useful in solar cell research. They can be deposited by printing methods, which makes the manufacturing costs low while maintaining high solar cell performance. MZO can be deposited by various techniques including sol-gel method [8], metal organic vapor phase epitaxy [9], and spray pyrolysis [10]. Meanwhile, a lot of efforts were devoted to doping ZnO and tailor its properties by using elements such as N, P, and As [11]. Among these three dopants, nitrogen is considered as best choice because it is characterized by its low toxicity and low ionization energy, and it is abundant. However, we believe that research focused on N-doping MZO is still very limited.

We report on nitrogen doped Mg$_x$Zn$_{1-x}$O ternary alloys by Pulsed Laser Deposition technique assisted Radio Frequency (RF-PLD) plasma beam of varied nitrogen/oxygen ratios. The structural and optical
Fig. 1. Schematic of experimental setup.

Fig. 2. XRD spectra of MgZnO ternary alloys grown in atmosphere with N$_2$/O$_2$ ratio of (a) as grown, (b) 0, (c) 0.33 and (d) 1.
The properties of deposited colloids were investigated by using X-ray Diffraction (XRD) and Spectroscopic Ellipsometry (SE) techniques. This work is presented as follows: section 2 shows details on the experimental process. The results and discussion are given in section 3, while section 4 summarizes conclusions.

2. Experimental process

Fig. 1 shows the experimental setup for our experiments. Nd:YAG laser has been used including λ = 266 nm, 10 Hz and τ = 5 ns (pulse duration). We also customized our classical PLD setup by adding an RF (13.56 MHz) plasma source operating under O₂ and N₂ gases mixture. Discharge source has been extended in deposition chamber of PLD. Differential pressure of two chambers is attributed to nozzle that creates directional beam. Quartz-glass substrate is simultaneously exposed to plasma of oxygen/nitrogen and beams of laser. Three targets of MgₓZn₁₋ₓO were utilized with different composition (x = 0.30, 0.10, and 0.05 w/w). MgO and ZnO powders were first mixed and then sintered at 1000 °C to form the MgZnO targets. We used substrates made of quartz-glass for deposition and we kept the substrate temperature at 400 °C. The pressure for O₂ or O₂/N₂ gas mixture, was fixed at 75 mTorr, according to O₂/N₂ ratios of 3 and 1.

A mass flow controllers was used to monitor the amount of gas flow while RF power was kept at 100 W and the distance from the target to the substrate was about 4 cm. Each sample was shot by 36000 laser pulses under a laser fluence of 3 J/cm². X-Ray Diffraction technique was used to determine the structural properties of the samples where XRD patterns were extracted using XPERT-3, powder X-ray Diffractometer using CuKα radiation (1.5 Å) with continuous scan from 30 to 70° with scan rate of 0.03/sec. The optical studies are fulfilled through Spectroscopic Ellipsometry (SE, Woollam Variable Angle Spectroscopic Ellipsometer (VASE), Germany), the spectral range is 0.7–5 eV [12]. This nondestructive technique is widely used to investigate the optical response of semiconductors, dielectrics, metals, and other materials.

3. Results and discussion

The XRD patterns depicted in Fig. 2(a) show the formation of a mixture between minor MgO phase and major ZnO phase (wurtzite structure) of the targets. Fig. 2(b)–(d) present the XRD spectra of MgZnO and N-doped MgZnO nanostructures. We identified from spectra the formation of pure ZnO without Mg content. However, a small peak assigned to MgO (200) could be seen at higher Mg concentration (x = 0.30). Table 1 presents structural parameters, nitrogen doping percentage, lattice constants a and c as well as Scherrer crystallite sizes which correspond to (002) and (101) peak broadenings, respectively. The growth of polycrystalline nanostructures seems favored by Mg incorporation when using quartz-glass substrates. The orientation of as grown and N-doped MgₓZn₁₋ₓO nanostructures along c-axis is highly dependent on Mg content: the (002) peak is absent for nanostructures with highest Mg concentration, while it is dominant with low amount of Mg. This suggests that Mg atom play the role of a barrier for ZnO growth along (002) direction. The pseudo-binary MgₓZn₁₋ₓO alloy is reported to manifest a c-axis shortening with increasing Mg concentration and c-axis lengthening, while remaining in wurtzite structure [13]. As per Vegard’s law, we expect this to happen because of the difference in ionic radii of Mg and Zn (Zn²⁺ / Mg²⁺ = 0.60/0.57). Table 1 indicates that c-axis lattice constant slightly decreases, whereas a-axis lattice constant shows no significant change by increasing Mg concentration. The oxygen content has direct influence on the structural properties of elaborated nanostructure. The samples tend to segregate toward cubic-MgO or exhibit poor crystalline quality with smaller grain sizes when deposited under oxygen-rich atmosphere. Consequently, defects in the films are induced due to oxygen excess, which affect the crystal growth nucleation of the films. As of the effect of nitrogen, high amount of nitrogen leads to low crystallinity and smaller grain sizes [14]. However, O₂/N₂ ratios in the 2–3 range favored larger grain sizes with higher crystallinity quality.

It is observed that as N₂/O₂ ratio increases, the corresponding concentration of Mg has led to increasing of crystallinity for the c-axis, which is equivalent to band gap increasing. Combinational pressures of lower O₂ and proper N₂, concentration of Mg inhibits defects formation that is appeared in good texture, big size of crystallite and high quality of crystallinity. The change in polarization is represented as an amplitude ratio, Ψ, and phase difference, Δ, which completely describe the elliptical polarization of light at the reflecting surface [15]. The thickness of the thin film and its dielectric parameters can be determined using an adequate optical model. As the change in dielectric function is sensitive to any change in physical parameters, such as stoichiometry, grain size, or phase structure, the optical analysis can be very useful in obtaining information about the ternary alloys. In this study, the transparency dependent of Eg and refractive index in terms of deposition parameters and targets is elaborated. Values of Eg are concluded from transmittance as a direct transition from valence to conduction bands. The absorption coefficient or Absorbance, a and Abs, respectively is:

\[\text{Abs}(E_g) = -\ln T(E_g) = d \alpha = d C (E - E_g)^{1/2}\]

where thickness denotes d and C is constant. As the substrate is considered optically transparent, it does not affect the above functions. We performed a linear fit through E (Abs₃) experimental data points to...
extract the band-gaps. The graphics in Fig. 3 presents the obtained values and associated fitting error bars. Using targets with low Mg concentration, band gap varies a little with ratio of N2/O2. In the case of higher Mg concentrations, \( E_g \) increases, with the exception for samples grown in the absence of N2 using Mg0.3Zn0.7O target. Overall, the band gap increases when N2 gas is introduced into the system.

Doping with Mg an isovalent impurity or N2 in ZnO increases the optical band gap. MgZnO alloy will have an energy band-gap ranging from the optical band gap of ZnO (3.2–3.4 eV) \([16–19]\) to the one corresponding to MgO (\( \sim 7.8 \) eV) \([20,21]\). This is evidenced in Fig. 3 where the increase in the band gap is a result of a high solubility of Mg in ZnO. However, because of the difference in both ZnO and MgO structures (hexagonal wurzite versus cubic rock salt), we expect a limited solubility of Mg. When using nitrogen free Mg0.3Zn0.7O target, obtained ternary alloys consist of MgO entrained in ZnO matrix. In this case, the optical band gap shown in Fig. 3 is mainly due to the ZnO matrix, because of its quasi-amorphous nature, it gives a value less than those of previous report. The results obtained from XRD measurements validated the two segregated phases. N2 impurity plays a role of an acceptor in ZnO. However, experiments have shown that p-type properties of as-grown material vanish during subsequent electrical experiments, resulting in low electrical conductivity N/ZnO material \([19,22]\). Moreover, nitrogen doping of ZnO may lead to structural changes, thus generating local structural defects such as zinc or oxygen vacancies or interstitials. Fig. 3 shows an increase in the optical band gap following the introduction of nitrogen gas in the system. The observed increment of band-gap or Burstein-Moss shift after doping manifests in doped semiconductors \([23,24]\), where the apparent increasing of \( E_g \) shows a linear relationship with \( N^{0.3} \), with \( N \) represents the free carrier concentration. In fact, a crystalline material will always have a larger band gap than its amorphous counterpart, due to the absence of significant interatomic scattering, while polycrystalline band gap for intermediate phases lies in between. The band gap increases as nitrogen is introduced to the growth system which may be interpreted as higher degree of crystallinity during growth. As for higher Mg concentration, we believe that adding nitrogen gas species increases the solubility limit of Mg in ZnO as the nitrogen solubility index remains high. There is very little experimental research on N, Mg co-doped ZnO. Dong-hua Li et al. have reported on XRD structural characterization of MgZnO samples deposited using oxygen plasma-assisted molecular beam epitaxy. It is suggested that Mg promotes the growth quality of N-doped ZnO films with a smoother morphology \([25]\). In this case, there is a possibility that Mg may generate Mg–N bonds, which leads to the favorable increase of Mg solubility in ternary mixture.

In order to investigate the ellipsometry spectra of the ternary alloys, we used an optical model consisting of three-layer. The structural model was used for the fitting of the MgZnO films on quartz-glass. The bottom layer of the model contains well-known optical constants of quartz-glass. The top layer contains the thickness and optical functions of the MgZnO film. The intermediate layer, between the MgZnO and glass, is a transitional layer referred to here as an “intermix” layer. This intermix represents a 50/50 mixture of the adjoining materials and is modeled mathematically on the effective medium approximation (EMA) \([26]\). The outer layer in the model is a surface roughness layer to account for diffuse scattering as a result of the slightly non-planar surface of the film. Mathematically, the roughness layer is an EMA consisting of a variable mixture of the MgZnO and the ambient and, as such, represents only a qualitative measure of the actual physical roughness.

We modeled the ternary alloys in the transparent region of the optical spectrum, where extinction coefficient \( k = 0 \) by a Cauchy layer \([27]\). In our modeling we did not consider the weak optical biaxial anisotropy \( \delta_n(\text{Vis}) < 0.1 \) \([28,29]\) which is present in ZnO crystal. In fact, polycrystalline nature and associated grain boundaries will substantially lower the birefringence. The thickness of the film and roughness layers were varied between 150–240 nm and 5–21 nm, respectively. The thickness measurement has been carried out using the

**Fig. 4.** Dispersion of refractive index. The dotted lines correspond to \( \text{N}_2/\text{O}_2 \) ratio = 1, the dashed lines = 0.33, while the solid line = 0. The refractive index decreases versus Mg concentration.

weight method by:

\[
t = \Delta m / (A \rho)
\]

where \( t \) is thickness, \( \Delta m \) is difference of substrate weight (substrate after deposition – substrate before deposition), \( A \) is area of sample and \( \rho \) is the density of deposited material.

The index of refraction and dispersions are plotted in Fig. 4. The index of refraction depend on both atomic mass and atomic density. We obtained ternary alloys with lower index of refraction than ZnO by inserting Mg in ZnO matrix, a lighter element than Zn, as shown in Fig. 4. We used Bruggeman medium approximation to model the combination of indexes of refraction for the two components \([30]\). When using nitrogen free ternary alloys Mg0.3Zn0.7O target, which compared to other composition, obtained film has the lowest atomic density and thus has the lowest index of refraction. Materials of high crystalline quality usually possess a higher index of refraction than amorphous counterparts. This is because the atomic density of each element is usually lower in the amorphous state as a result of higher average interatomic distances. Fig. 4 indicates an increase of index of refraction as nitrogen gas plays a role in the growth system, which is in agreement with XRD data. Such increase is a sign of higher degree of crystallinity means larger grain size with less point defects and grain boundaries, making elaborated materials suitable for optoelectronics applications \([31]\).

4. Conclusions

We deposited nitrogen doped Mg0.3Zn0.7O ternary alloys by Pulsed Laser Deposition assisted Radio Frequency plasma beam (RF-PLD) technique under varied nitrogen/oxygen ratios. Doping Mg3Zn1-xO nanostructures with nitrogen is very effective in tailoring their optical properties. When Mg concentration is less than 5% w, which is within the thermodynamic solubility limits of ZnO matrix, doping with nitrogen produces nanostructures with larger band gap and better crystallinity. As Mg concentration increases, the degree of crystallinity is found to decrease. The band gap is found to increase from 3.37 up to 3.57 eV while increasing the nitrogen/oxygen ratio for Mg concentrations above 10%. The Mg solubility is also shown to increase by 30% in nitrogen doped Mg0.3Zn0.7O nanostructures. Segregation of MgO phase in Mg0.3Zn0.7O nanostructures was detected by both XRD and SE. The optical refractive index has values between 1.7 and 2 in visible spectral range, it shows high dependence on both stoichiometry and degree of crystallinity of the compounds. With nitrogen doping, it is also possible
to increase of the Mg solubility even when using amorphous substrates. Therefore, increasing nitrogen doping is an effective method for band-gap engineering of Mg$_x$Zn$_{1-x}$O alloys.

Conflicts of interest

The authors declare that they have no conflict of interest.

Authors’ contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. N.B and Y.D. planned equally this study, carried out structural and optical characterizations and data analysis, and wrote the manuscript. S.K. prepared all figures and plotting and commented on the manuscript.

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