Effects of stabilizer ratio on photoluminescence properties of sol-gel ZnO nano-structured thin films

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Abstract

Nanostructured ZnO thin films with different molar ratios of MEA to zinc acetate (0.5, 1.0, 1.5 and 2.0) have been deposited on glass substrates by a sol–gel dip coating technique. X-ray diffraction, Scanning Electron Microscopy, UV–visible spectrophotometry and photoluminescence spectroscopy have been employed to investigate the effect of MEA stabilizer ratio on structural, morphological, absorbance and emission properties of the ZnO thin films. Diffraction patterns have shown that all the films are polycrystalline and exhibit a wurtzite hexagonal structure. The c axis orientation has been enhanced with increasing stabilizer ratio. SEM micrographs have revealed that the morphology of the ZnO films depend on stabilizer ratio. The UV–visible absorption spectra have demonstrated that the optical absorption is affected by stabilizer ratio. The photoluminescence spectra have indicated one ultraviolet and two visible emission bands (green and red), while band intensities are found to be dependent on stabilizer ratio. ZnO thin films deposited at MEA ratio of 1.0 show the highest UV emission while the minimum UV emission intensity is observed in thin films deposited at ratio of 0.5 and the maximum green has been recorded for films deposited at MEA ratio of 2.0.

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1. Introduction

Zinc oxide (ZnO) is considered as a promising semiconductor owing to its interesting properties including the stable wurtzite structure, wide and direct band gap (3.37 eV), large exciton binding energy (60 meV) and high thermal and chemical stability. These properties made ZnO thin films an excellent candidate for various technological applications such as transparent electrodes [1], light-emitting diodes in the blue and UV regions [2,3], thin films transistor [4], ultraviolet photoconductive detectors [5], solar cells [6–9], piezoelectric transducers [10] and gas sensors [11].

ZnO thin films have been prepared using numerous methods such as molecular beam epitaxy (MBE) [12], pulsed laser deposition (PLD) [13], metal-organic chemical vapor deposition (MOCVD) [14], magnetron sputtering [15], electron beam evaporation [16], spray pyrolysis [17], electrochemical deposition [18,19], hydrothermal method [20] and sol–gel process [21–25]. The sol–gel route is the most widely used for its simplicity, low cost and capability to produce thin, transparent and homogenous films of different compositions on silicon and glass substrates. However, the properties of the films prepared by the sol–gel process might be affected by a number of factors including sol aging time [26,27], nature and concentration of the precursor [28,29], type of solvent [30], preheating and post-annealing temperature [31,32].

The use of additives in thin films preparation promotes the dissolution of the precursor, controls the rate of sol–gel and supports film formation during the coating process. Furthermore, the nature of the stabilizer has different effects on structural, morphological and optical properties of ZnO thin films. Few works have been reported in the literature regarding the influence of amino-alcohols on ZnO nanostructures properties [33–37]. For example, Yahia et al. [35] have reported the dependence of ZnO thin films optical constants on MEA to Zn ratio (r) and Thongsuriwong et al. [37] have studied the influence of MEA ratio on morphological properties of ZnO powder. However, to the best of our knowledge, the effect of MEA ratio on the photoluminescence (PL) properties of ZnO thin films has not yet been reported.

In this paper, ZnO thin films were prepared by the sol–gel method and deposited on glass substrates by the dip-coating technique. The influences of stabilizer molar ratio on the structural, morphological...
and photoluminescence properties of the prepared ZnO thin films are investigated.

2. Experiments

ZnO thin films were prepared by the sol–gel process. As a starting material, zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) was dissolved in a mixture of ethanol and mono-ethanolamine (MEA, C₂H₇NO). The MEA to Zn ratios (r) were varied between 0.5 and 2.0. The final concentration of Zinc acetate in the solution was kept at 0.75 M. All prepared ZnO sols were maintained under continuous magnetic stirring at 50 °C for 1 h. The substrates were washed with a liquid detergent, rinsed with distilled water, and then immersed in 4 M nitric acid for 24 h. They were then ultrasonically cleaned and rinsed in ethanol and distilled water during 15 min at 60 °C and, finally, were dried at 100 °C for 2 h. The deposition was carried out using a KSV dip-coater with a withdrawal speed of 1.5 cm/min and the number of deposited layers on the glass substrates was set to eight. The deposited films were preheated at 200 °C for 10 min after each coating. The films were subsequently heated up to 500 °C for 4 h in order to obtain crystallized ZnO.

The prepared thin films were characterized by X-ray diffraction (XRD) using a PANalytical’s X-ray diffractometer operating at 40 kV and 30 mA using Cu Kα radiation (λ = 1.54 Å). The characterization by Scanning Electronic Microscopy (SEM) was performed with a Raith PIONEER System. The optical absorption spectra were obtained using a Safas UVmc2 UV–visible spectrophotometer and the PL measurements were carried out at room temperature using a He–Cd laser 325 nm.

3. Results and discussion

Fig. 1 shows XRD spectra of ZnO thin films prepared with different molar ratios of MEA to zinc acetate. All visible peaks are indexed as characteristic peaks of a polycrystalline ZnO hexagonal wurtzite structure. The broad peaks observed in the XRD patterns indicate small size particles. It is noticeable that increasing the amount of MEA, the intensity of (0 0 2) increases which demonstrates the enhancement in c-axis preferred orientation. This preferred orientation can be explained by the improvement of the formation of zinc oxy-acetate by the large amount of MEA in the sol. It is well known that in general the role of complexing agent (such as MEA) is to facilitate the Zn²⁺ condensation and promote the formation of ZnO due to the presence of amine which increases the pH of the solution. Since the (0 0 2) plane of ZnO has the minimum surface energy, higher ratios of MEA leads to higher condensation rate of Zn²⁺ ions along the (0 0 2) plane resulting in higher c-axis orientation. The enhancement of c-axis orientation with increasing MEA ratios has been also reported by Hosseini Vajargah et al. [34] and Sagar et al. [36]. Moreover, the increase in XRD peaks intensity is due to the increase in the film thickness with increasing MEA ratio as confirmed by the thickness investigations carried out by mechanical surface profiling. The measured thickness was of the order of 180, 220, 225 and 240 nm for the thin films deposited at ratio of 0.5, 1.0, 1.5 and 2.0, respectively. It has been also reported that the pH of the sol increases with increasing MEA ratio [38] which may lead to an increase in film thickness [39].

The crystallite size may be estimated from the full width at half-maximum of (0 0 2) diffraction peak using Scherer’s formula [40]:

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the full width at half-maximum of the XRD peak and \( \theta \) is the Bragg diffraction angle.

The XRD analysis revealed that the calculated crystallite size is between 17.6 and 12.4 nm. As shown in Fig. 2 the crystallite size decreases with increase in the stabilizer molar ratio.

The scanning electron micrographs of the ZnO films deposited at different molar ratios of MEA to zinc acetate are shown in Fig. 3. All the samples have a smooth and uniform morphology. The grains dispersion in the films is homogeneous. We can observe also the presence of some pores in the films deposited using sols containing MEA to Zn ratios lower than 2.0. In the case of the ZnO thin film deposited at MEA ratio of 2.0, there are no pores and the surface seems to be well compact. The micrographs reveal that the grains forming the ZnO films deposited at a stabilizer ratio of 0.5 are statistically bigger than those forming the other ZnO thin films. However, we can note some large grains in ZnO film deposited using a sol prepared with a MEA ratio of 2.0. The grains forming the films deposited at \( r = 1.0 \) and \( r = 1.5 \) are relatively small. We can explain this behavior by the fact that when a low amount of stabilizer is used, the number of stabilizer molecules remains insufficient to fully interact with the growth species; then some ZnO nuclei can grow further. It is well established that MEA prevents uncontrollable growth of particles and also avoids particles aggregation. Thus, once the ratio is less than the unity, the ZnO crystallites agglomerates to form large

Fig. 1. XRD patterns of ZnO thin films prepared with different stabilizer molar ratios.

Fig. 2. Crystallite size of ZnO thin films prepared with different stabilizer molar ratios.
grains. However, at moderate concentration of MEA in the sol ($r = 1.0$ and $r = 1.5$), stabilizer molecules can fully interact with all growth species and hence control growth rate and particle size. The result of these interactions leads to the formation of the small grains. In the case of higher ratio ($r = 2.0$), the MEA retarded the condensation process. However, it promotes the formation of ZnO since the presence of amine increases the pH of the solution [36]. We believe that the delayed condensation results in the development of few large crystallites because the nuclei’s are not formed at the same time. From XRD patterns and SEM micrographs, it is clearly seen that ZnO deposited thin films are fine grained and consisted of agglomeration of several crystallites. Therefore, the obtained samples contain very developed grain boundaries and free surfaces. These defects are sensitive to the stabilizer molar ratio which may affect ZnO thin films properties. It has been recently demonstrated that the physical properties of nanograined ZnO strongly depend on the presence of interphase and grain boundaries [41,42].

Fig. 4 displays the optical absorption spectra of ZnO thin films deposited at different stabilizer molar ratios. It is clearly seen that all ZnO thin films exhibit an excitonic absorption at about 375 nm. It is also noticeable that the films show a maximum absorption at 350 nm. However, the intensity of this maximum is dependent on the ratio: thin films deposited at $r = 0.5$ shows the lowest absorption values and the one deposited at MEA ratio of 1.0 demonstrates the highest ones at lower wavelengths. We can also observe that the absorption of the thin films deposited at $r = 1.5$ is greater than those prepared at $r = 2.0$. It has been recently demonstrated by Zawadzka et al. [43] that the assignments of the exciton peaks may be also verified by the temperature evolution of the PL spectra.

Fig. 5(a) displays PL spectra in wavelengths ranging from the ultraviolet (UV) to the near infrared for all the prepared thin films. In order to better see the effect of stabilizer ratio on the UV emission, the emission spectra in the UV region only is depicted in Fig. 5(b). All the PL spectra consist of sharp emission in the UV range and a broad emission bands in the visible region ranging from 1.45 to 2.75 eV (450 to 850 nm). It is clear that the widest visible emission is recorded for MEA ratio of 2.0. We can also note that the UV emission is maximum for $r = 1.0$ and is minimum for $r = 0.5$. A slight red-shift of the emission for $r = 0.5$ is also observed at 3.19 eV (388 nm). In addition, the UV emission of the sample deposited at $r = 2.0$ seems to be a superposition of two bands, the first band is centered at 3.26 eV (380 nm) while the second one is centered at 3.19 eV. Such a red-shift may be due to the increase of the particle size. The dependence of grain size on ratio is in agreement with XRD patterns and SEM micrographs.

Fig. 6(a) shows the dependence of the UV and visible emission intensity on MEA ratio. The increase of MEA ratio from 0.5 to 1.0, greatly enhance the UV emission peak. Its full width at half-maximum (FWHM) is increased, then the UV peak is weakened again and its FWHM is decreased. However, the latter remains higher than of the one corresponding to the ratio of 0.5. The visible
emission seems to have an opposite behavior. It is largely accepted that the UV emission belongs to the near band edge emission (NBE) and originate from the recombination of free excitons. While the visible emission arises from the recombination of holes with electrons trapped at defect levels. A method generally used for evaluating the concentration of defects in ZnO thin films is based on the ratio of the PL intensity of UV emission to the visible one. Fig. 6(b) depicts the intensity ratio of the UV to visible emission \(\frac{I_{uv}}{I_{visible}}\) of the ZnO thin films as a function of MEA ratio. This intensity ratio reaches a maximum at an MEA ratio of 1.0 after it decreased at MEA ratios of 1.5 and 2.0. The larger \(\frac{I_{uv}}{I_{visible}}\) ratio implied the higher quality of ZnO films [44], which means that the best ZnO stoichiometry is obtained for the ratio of MEA to Zn of 1:1.

In order to clarify the different visible emission bands and study their evolution behavior with the MEA ratio, we carry out a Gaussian curve fitting for these visible emission spectra as shown in Fig. 7. All the samples show two emission bands including green (2.3 eV) and red (1.9 eV). A small emission peak is observed in the red range centered on 1.6 eV. In the literature, it is well established that the visible emission due to the defect emission arises from the recombination of holes with electrons trapped at level defects in the gap. However, there is still no consensus on the origin and the energy levels within the ZnO gap. In addition, it is widely admitted that in n-type ZnO, the most favorable defects are oxygen vacancy \(V_o\) and zinc vacancy \(V_{zn}\) [45], yet; the majority of researchers consider that the green emission (centered on 2.3 eV) can be attributed to the transition related with \(V_o\) [18,46], while the red emission maybe related the transition between single and double ionized oxygen vacancies \(V_o^+\) and \(V_o^{++}\) and zinc vacancy \(V_{zn}\) acting as a deep acceptor [47]. Based on these works, we may consider that the emission at 1.6 eV results from transition between \(V_o^{++}\) and \(V_{zn}\) while the one at 1.9 eV originates from transition between \(V_o^+\) and \(V_{zn}\). The \(V_o^+\) state is unstable but can acts as a metastable state during optical illumination [45].

From Fig. 7(a), it can be seen that when the red emission intensity increases, the green one decreases indicating that \(V_o\) and \(V_{zn}\) are greatly affected by MEA ratio. The MEA ratio of 0.5 favors the formation of large density of \(V_{zn}\) because the number of MEA molecules is insufficient to fully interact with the growth species and consequently not stabilized. The result is the formation of large ZnO crystallites with a large density of zinc vacancies. For MEA ratio equal to 1.0, all growth species are stabilized and the resulting film is of higher quality (Fig. 6(b)). However, when a large amount of MEA is used, the organic molecules ones evaporated increases the oxygen vacancy density which may explain the enhancement of the green light emitted by the sample deposited at MEA ratio of 2.0.

4. Conclusion

In this work, effects of stabilizer molar ratios on the structural, morphological, optical and photoluminescence properties of sol–gel

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**Fig. 5.** ZnO thin films prepared with different stabilizer molar ratios: (a) room temperature photoluminescence spectra and (b) magnification of the UV emission region.

**Fig. 6.** Plots of (a) UV and visible emission intensities, and (b) intensity ratio of the UV to the visible emission versus stabilizer molar ratios.
nanostructured ZnO thin films prepared from zinc acetate solution were investigated. XRD measurements have revealed that all diffraction patterns are typical of the ZnO wurtzite hexagonal structure. The preferably c-axis orientation increases as a function of MEA to zinc acetate ratio. SEM micrographs have shown that ZnO thin films have a smooth and uniform morphology with particularly large grains for ratio of 0.5. Optical characterizations in the UV–visible range have indicated that the absorption of ZnO thin films is dependent on the stabilizer molar ratio. Room temperature PL results have demonstrated that thin film emissions are clearly influenced by MEA to Zn ratio. The red emission has shown an opposite behavior and the maximum green emission intensity has been obtained from the film deposited at MEA ratio of 2.0.

Fig. 7. Fitting curves of visible emission spectra of ZnO thin films prepared with different stabilizer molar ratios: (a) r = 0.5, (b) r = 1.0, (c) r = 1.5 and (d) r = 2.0.

References