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Deposition and characterization of ZnO:Mg thin films: the study of antibacterial properties

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Abstract
ZnO:Mg thin films with different amounts of Mg were deposited on a glass substrate using the spray pyrolysis technique. The structural, optical and antibacterial properties of the films were studied as a function of the dopant concentration. The ZnO:Mg films were characterized using methods such as x-ray diffractometry, scanning electron microscopy, scanning tunneling microscopy and UV–Vis spectroscopy. The samples display hexagonal wurtzite structure, with no secondary phase. Morphological studies indicated the deposition of a uniform film, and particle size decreases with Mg doping. Optical studies revealed that the optical band gap and optical transmittance increase with Mg concentration. The antibacterial activities of the samples against *Escherichia coli* (gram-negative) cultures were tested by the drop test method, which shows that Mg doping increases antibacterial activities of thin films.

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(Some figures in this article are in colour only in the electronic version.)

1. Introduction

In recent years, ZnO as an II–VI semiconductor has been the subject of extensive studies. It is a wide-band-gap (3.37 eV) compound semiconductor that is suitable for short-wavelength optoelectronic applications. The high exciton binding energy (60 mV) of ZnO crystals ensures efficient excitonic emission at room temperature [1]. The lack of a center of symmetry in its wurtzite structure, combined with large electromechanical coupling, leads to strong piezoelectric and pyroelectric properties of ZnO and the consequent use of ZnO in mechanical actuators and piezoelectric sensors [2]. Because of these remarkable physical properties, its availability and the low cost of manufacturing it, ZnO has found a great deal of application in transparent electronics, UV light emitters, piezoelectric devices, chemical sensors, high-frequency wireless communication and spintronics.

Increasing concern about microbial contamination has led to extensive use of antibacterial agents, especially antibacterial coatings, which would decrease the chances of bacterial propagation and reduce the sterilization cost. ZnO as an inorganic antibacterial agent has a key advantage owing to its biocompatibility, antibacterial activity in the neutral region (pH 7) even in darkness, being non-toxic to humans, ability to withstand harsh conditions and being more durable, in comparison with conventional organic materials [3], which makes it a good candidate for different antibacterial applications ranging from medical to industrial use. Although the exact mechanism of its antibacterial action is not yet known, several mechanisms have been proposed, including photocatalyst activities, electrostatic interactions [4], metal ion release, reactive oxygen species (ROS) generation, membrane damage [5] and cellular internalization of the nanoparticles [6]. ROS generation has been considered as the dominant mechanism of antibacterial behavior [5].

The results on the antibacterial activity of ZnO nanostructures show that its antibacterial activity increases with decreasing particles size [5], the crystallographic orientation has no effect [7] and an increase in the lattice constant leads to an increase in antibacterial activity [8]. Yamamoto *et al* [9] investigated the effect of CaO doping on antibacterial properties of ZnO.

Mg compounds have also been considered as good antibacterial agents [10]. Metal ion release is reported to be the dominant mechanism of antibacterial activity of Mg; Mg also inhibits the formation of biofilms [11]. It appears that doping Mg atoms into zinc oxide could enhance the antibacterial activity of zinc oxide.

In this work, thin films of ZnO with different amounts of Mg were successfully prepared via the spray pyrolysis method, and the structural and optical properties, in addition to the antibacterial activity, were studied.

2. Experimental details

2.1. Deposition of films

Spray pyrolysis is an excellent method for the deposition of thin films of metallic oxides, in which a starting solution containing metal precursors is sprayed by a nozzle via a carrier gas on the hot substrate. When the fine droplets reach the substrate, the solid compounds react on the surface and a new chemical compound forms [12]. ZnO thin films with various amounts of Mg were deposited onto glass substrates at $T_s = 450\,^{\circ}\mathrm{C}$ by spraying a 0.15 M solution of $Zn(CH_3COO)_2$ and $MgCl_2 \cdot 6H_2O$ dissolved in distilled water and 2-propanol (1:3). The Mg/Zn molar ratio was adjusted for each doping concentration.

2.2. Characterization of films

Typical x-ray diffractometry (XRD) spectra of the samples were obtained using an x-ray diffractometer (Cu K_α line; $\lambda = 0.154\,06$ nm). The intensity was determined in the range of $30^{\circ} < 2\theta < 70^{\circ}$ with 0.04° step size.

Scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) were used to observe the size and morphology of the samples.

For optical studies, the absorption spectra of the films were obtained by a UV–Vis spectrophotometer (UVD 2950).

The antibacterial activity of the films against the bacteria *Escherichia coli* was studied using the so-called antibacterial drop test [13]. *E. coli* HB 101 was cultured in an LB medium at 37 °C for 18–24 h. The bacteria cultured were diluted to reach approximately the concentration of bacteria corresponding to 1 of the MacFarland scale (10^8 colony-forming units ml^{-1}). Three groups of samples, each containing three coated thin films, were placed in sterilized Petri dishes and then 100 μl of bacterial suspension was added to the surface of each thin film. The samples were left at room temperature for 12 and 24 h. After each time period the bacteria-containing drops were washed from the glass surfaces using 1 ml of phosphate buffer solution (PBS). Then, 10 μl of a 3–5 times diluted solution were placed on an LB agar culture medium. The numbers of surviving bacteria in the Petri dishes were counted after incubation for 24 h at 37 °C.

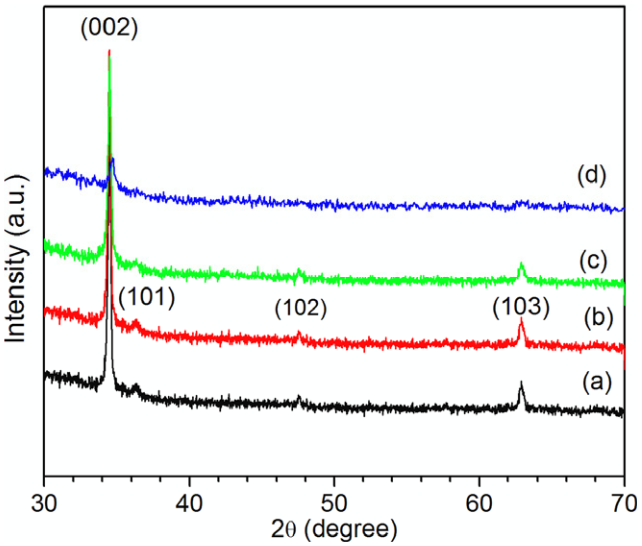

Figure 1. XRD pattern of ZnO:Mg thin films with (a) 0%, (b) 5%, (c) 10% and (d) 15% Mg content.

3. Results and discussions

3.1. Structural studies

XRD patterns of ZnO:Mg films with different Mg contents (as shown in figure 1) revealed a very intense and sharp peak corresponding to the (002) plane of the hexagonal wurtzite structure of ZnO. The high intensity of this peak indicates a very high *c*-axis growth-preferred orientation of the samples. But no peak corresponding to rocksalt MgO was detected, suggesting that Mg^{2+} can be incorporated into the ZnO lattice with no phase segregation taking place, which was not unexpected, because the Mg atom has rather similar ionic radii to the Zn atom (0.57 Å for Mg and 0.60 Å for Zn) [14]. The results also show that with increasing the amount of Mg doping, the (101), (102) and (103) peaks weaken, and with 15% Mg doping they disappear, leading to more crystalline order.

3.2. Morphological studies

The SEM micrographs of pure and 15% Mg content films are illustrated in figure 2. As can be seen from the images, the films present good thickness uniformity, a smooth dense surface and no visible defects. These images also indicate that particle size decreases with Mg incorporation.

For further morphological analyses, STM images of the samples were recorded (figure 3). Similar to SEM images, we observe a coating condense layer from spherical particles. The roughness profile indicates an increase in particle height with Mg incorporation and therefore the surface of films become rougher.

3.3. Optical studies

Figure 4 shows the optical absorption of the thin films when measured at room temperature. From this figure, all samples showed sharp absorption edges in the UV region. The observed shift in the absorption edge is from 363 to 352 nm with increasing dopant concentration from 0 to 15%, which clearly shows the incorporation of Mg into the ZnO lattice.

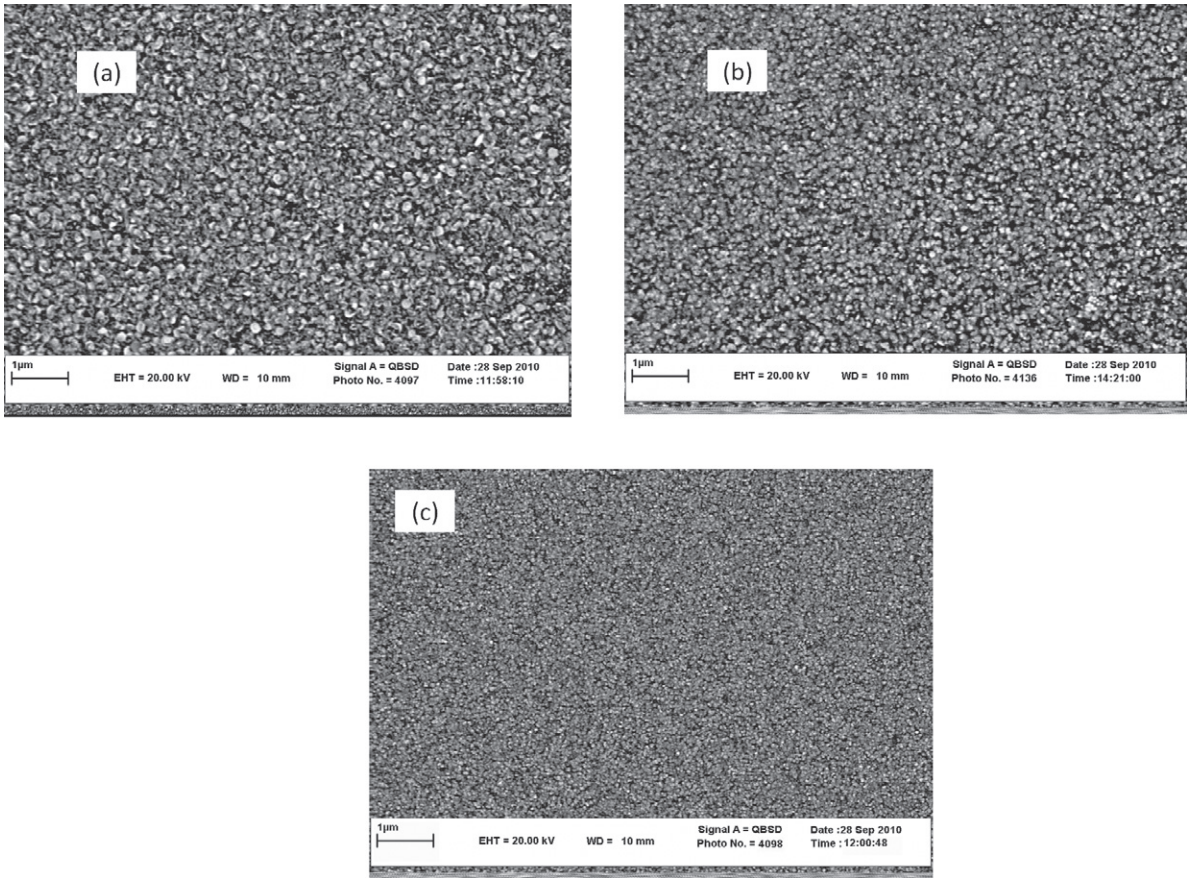

Figure 2. SEM images of ZnO thin films with (a) 0%, (b) 5% and (c) 15% Mg doping.

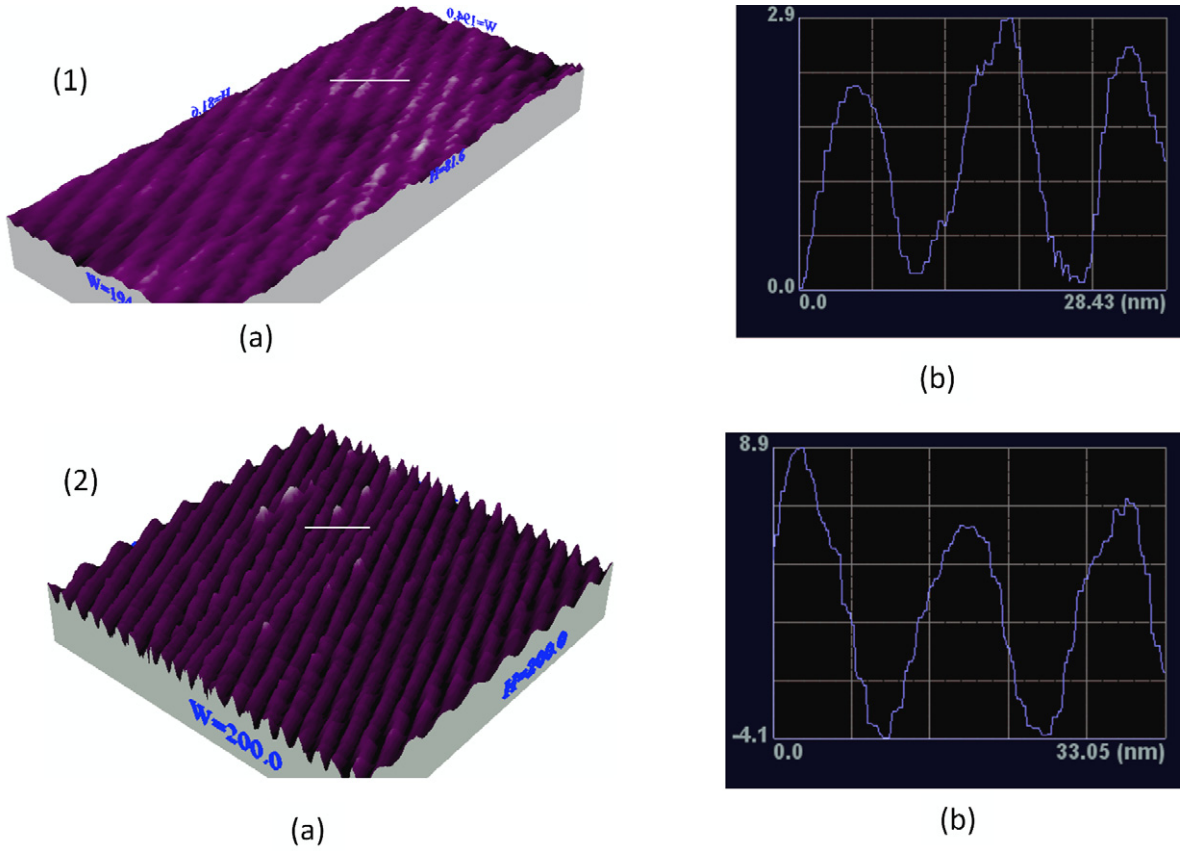

Figure 3. STM images of ZnO:Mg thin films of (1) 0% and (2) 5% Mg content: (a) height projection and (b) roughness graduation profile.

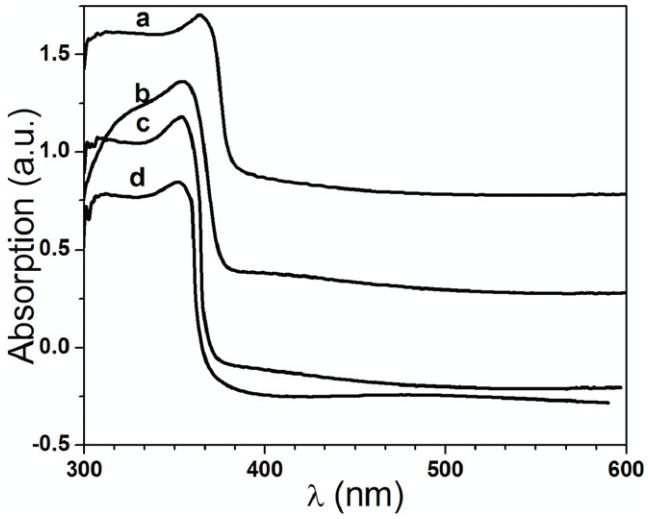

Figure 4. Optical absorption of ZnO:Mg thin films of (a) 0%, (b) 5%, (c) 10% and (d) 15% Mg content.

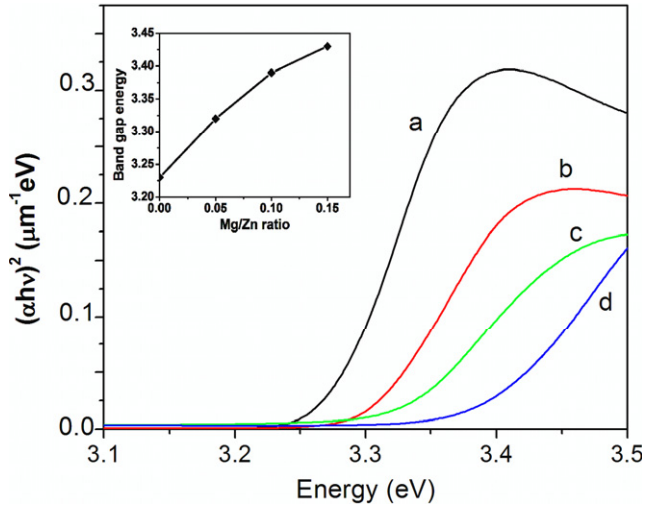

Figure 5. Plot of $(\alpha\hbar\nu)^2$ against energy for thin films of (a) pure ZnO and (b) 5%, (c) 10% and (d) 15% Mg content ZnO. The inset shows the variation in band gap energy with Mg incorporation.

The results show that an increase in Mg concentration leads to an increase in transmittance.

The direct band gap of the films was calculated using the Tauc relation,

$$\alpha\hbar\nu = A(\hbar\nu - E_g)^n,$$

where α is the absorption coefficient, A is a constant, $\hbar$ is Planck's constant, ν is the photon frequency, E_g is the energy band gap and n is equal to $1/2$ for the direct band gap semiconductor. Extrapolation of the linear region of a plot of $(\alpha\hbar\nu)^{1/n}$ on the y-axis against photon energy $(\hbar\nu)$ on the x-axis gave the value of the energy band gap E_g (inset of figure 5). Band gap studies show that with an increase of the Mg/Zn ratio, the optical band gap increases. This may be attributed to the fact that new defects are introduced after Mg atoms substitute Zn atoms and enter into the ZnO lattice due to the electronegativity and ionic radius difference between Zn and Mg [15]. As a result, the exciton bond increases with an increase in Mg content. Moreover, there are more electrons

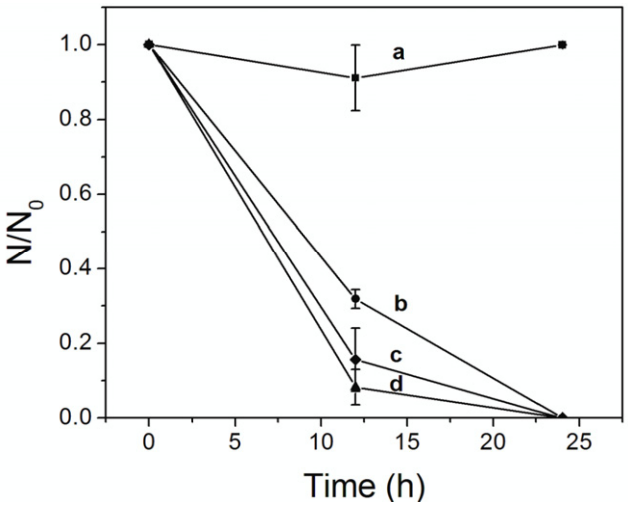

Figure 6. The relative number of bacteria that survived after an antibacterial drop test: (a) blank, (b) pure ZnO thin films, (c) ZnO:Mg thin films with 5% Mg content and (d) ZnO:Mg thin films with 15% Mg content.

contributed by the Mg dopant due to the lower electron affinity of Mg compared with Zn, which take up the energy levels located in the bottom of the conduction band. Since the Pauli principle prevents states with doubly occupied and optical transitions from being vertical, the valence electrons require extra energy to be excited to higher-energy states in the conduction band [15].

3.4. Antibacterial studies

The antibacterial properties of the thin films against *E. coli* were examined by the drop test; the results are shown in figure 6, where N/N_0 is the relative number of surviving bacteria. As is evident, after 12 h, all films show a reduced number of surviving bacterial colonies, and after 24 h, only a negligible number of bacterial colonies survived, indicating that all samples have significant antibacterial activity, which increases with Mg incorporation. This enhanced antibacterial behavior is as expected, because when we increase the Mg concentration, the particle size of the samples decreases. Therefore, the surface-to-volume ratio increases, giving rise to a more reactive surface to interact with bacteria. Moreover, due to less electron affinity, Mg atoms lose electrons more easily; as a result, surface Mg atoms, by the release of electrons, enhance the antibacterial activity.

4. Conclusions

ZnO:Mg thin films with different amounts of Mg were deposited on a glass substrate by using spray pyrolysis. The structural, optical and antibacterial properties of the films were studied as a function of the dopant concentration. All samples showed high c-axis orientation, and no phase segregation was observed. The doping process affected the morphology of thin films by increasing the particle height and decreasing their size. Optical analysis revealed that the band gap energy increases from 3.27 to 3.43 eV with dopant incorporation. The samples showed excellent antibacterial activity, which was enhanced on doping with Mg.

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