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Preparation of nanocrystalline thin films of ZnO by sol-gel dip coating

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Nanocrystalline ZnO thin films are deposited from sol-gel of zinc acetateand using dip coating onto two different substrates: glass and aluminium foil. (i) Films on glass substrates. Nanostructured ZnO thin films with different concentrations of Ni^{2+} doping (0, 1, 5, 10 and 15 wt%) are prepared for the first time by the sol gel method. The film surface is with a ganglia-like structure as observed by Scanning Electron Microscopy (SEM). The films comprise of ZnO nanocrystallites with hexagonal crystal structure, as revealed by means of X-ray diffraction (XRD). (ii) Films on aluminium foil substrates. The ZnO films are annealed at different temperatures (100 °C, 300 °C and 500 °C) and characterized by means of SEM and XRD. The film surface is with the characteristic ganglia-like patterns. The crystalline structure is hexagonal with the crystallite sizes increasing with the annealing temperature.

Key words: zinc oxide, thin films, crystallites, aluminium substrate, dip coating.

1. INTRODUCTION

In recent years, zinc oxide has become a particularly interesting metal oxide material because of its unique properties. ZnO is a semiconductor with a wide band gap (3.3 eV), large exciton binding energy, abundant in nature and environmentally friendly. These characteristics make this material attractive for many applications such as solar cells, optical coatings, photocatalysts, antibacterial activities, electrical devices, active medium in UV semiconductor lasers and in gas sensors [1].

Nanocrystalline ZnO is of special interest, because of the possibilities for modification and control of various ZnO-based nanostructures [2–4]. ZnO thin films are prepared by different techniques such as metal organic chemical vapor deposition [5], sol–gel [6–8], thermal evaporation, oxidation and anodizing [9–11]. The sol-gel process with utilization of dip coating is one of the versatile and low-cost techniques strategies to prepare thin films of particles. The recent research demonstrates the possibilities for utilization of homogeneous ZnO thin films, prepared by the sol-gel method [12, 13], which are attractive with desired thickness and nanostructure. The classical sol-gel method using complexing agent monoethanolamine (MEA) [14] is also applied for the deposition of ZnO films in order to compare them with the films obtained by polymeric formulations.

The aim of this paper is to compare the structural and crystallite features of ZnO thin films obtained onto two different substrates (glass and aluminium foil) in dependence on the doping with Ni^{2+} and on the annealing temperature.

2. EXPERIMENTAL

The compounds used to manufacture ZnO thin films were as follows: zinc acetate dihydrate (≥99.5%), 2-methoxyethanol (≥99.5%), monoethanolamine (≥99.0%) and nickel acetate tetrahydrate (≥99.0%); all of them from Fluka. Malachite green (MG) oxalate was from Croma-Gesellschaft mbH & Co. The microscope glass slides (ca. 76×26 mm) were from ISO-LAB (Germany). Aluminium foil (ca. 76×26 mm) was also used for the respective substrates of ZnO films. The aluminium plates were cleaned successively in hot ethanol and acetone.

Nanocrystalline ZnO thin films were deposited from sol-gel of zinc acetate, 2-methoxyethanol and monoethanolamine (Fig. 1) using dip coating apparatus onto two different substrates: glass and aluminium foil. The following samples systems were prepared:

(i) Zinc oxide thin films on glass substrates. Different concentrations of Ni^{2+} doping (0, 1, 5, 10 and

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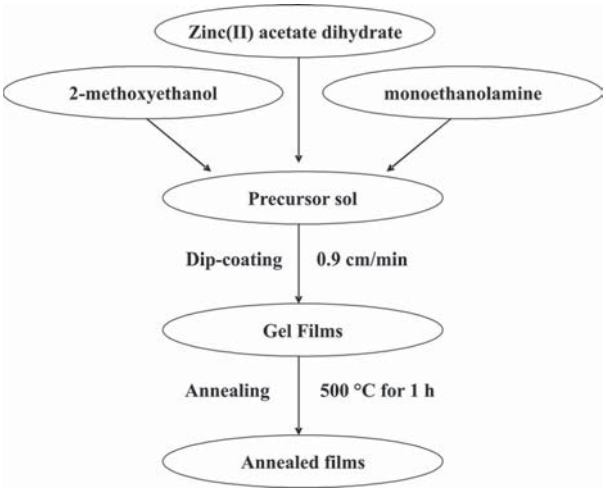

Fig. 1. Scheme of the experimental procedure for deposition of thin ZnO films by sol-gel dip coating

15 wt%) were achieved by nickel acetate tetrahydrate ($Ni(CH_3COO)_2.4H_2O$) dissolved in a mixture of zinc acetate ($Zn(CH_3COO)_2.2H_2O$), 2-methoxyethanol and then monoethanolamine (MEA) added finally as a stabilizer. The substances are mixed together in a round-bottomed flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60 °C upon magnetic stirring for 60 min and let overnight.

(ii) ZnO films on aluminium substrates. The sol was obtained using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), 2-methoxyethanol and monoethanolamine, mixed together in a round-bottomed flask and stirred at room temperature for 15 min. The obtained clear solution was heated up at 60 °C upon magnetic stirring for 60 min and let overnight.

The final sol was clear and homogenous, to serve as the coating substance for film preparation. No visible changes were observed upon standing of the precursor sol at room temperature for at least 2 months.

Dipping the glass or aluminium foil substrate in the sol and withdrawing it at a rate of 0.9 cm/min at room temperature prepared the gel films. It was found that a higher withdrawal rate results in films of lower quality. The films were deposited with 5 coatings and dried at 80 °C for 15 min after each successive coating. The final gel films onto glass substrate were annealed at 500 °C for 60 min in order to obtain the ZnO films. The films on aluminium foil were annealed for 60 min at different temperatures: 100, 300 and 500 °C

The as-obtained ZnO thin films on glass (undoped and doped with different per cent Ni^{2+}) and aluminium foil substrate were first imaged by a Scanning Electron Microscope (SEM) model JSM-5510 (JEOL), operated at 10 kV of acceleration voltage. The investigated samples were coated with gold by JFC-1200 fine coater (JEOL) before observation.

The X-Ray diffraction (XRD) spectra were recorded at room temperature on a powder diffractometer (Siemens D500 with CuKα radiation within 2θ range 30–70 deg at a step of 0.05 deg 2θ and counting time 2 s/step). The average crystallite size was estimated according to the Scherrer's equation [15]:

$$d_{hkl} = k\lambda / \beta \cos(2\theta)$$

where d_{hkl} is the average crystallite size (nm), λ is the wavelength of CuKα radiation applied (λ = 0.154056 nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak observed at 2θ = 25.20 (converted to radian) and k is a constant usually chosen ~0.9.

3. RESULTS AND DISCUSSION

3.1. Structure characterization of Ni-doped ZnO films on glass substrate

The dip coating is a simple and cheap technique for deposition of thin oxide films, but it requires soluble reagents. It is possible to control precisely the immersion and withdrawal speed, number of dipping cycles and solution viscosity for the purpose of deposition of a layer of oxide material. The plane view of SEM micrograph of annealed ZnO film shows smooth ganglia-like hills (Fig. 2a). The morphology is homogenous with the wrinkles of a width 0.5–1 μm, length ~5 μm and height about 1 μm. The Ni-doped ZnO films display also that peculiar pattern, as seen from the surface micrographs of samples with 1 to 15 wt.% Ni^{2+} (Fig. 2b-e). In the case of Ni-containing films, the ganglia are looking more distorted and branched at their ends. The ganglia-like hills are of typical width 0.1–0.5 μm, length from 1 μm to 5 μm and height about 2.5–3 μm. The increase of Ni^{2+} content decreases the volume and size of ganglia-like hills. The wrinkles are smaller and the morphology is not homogenous.

X-ray diffraction patterns of ZnO and Ni-doped ZnO films are presented in Fig. 3. These patterns correspond to the three main diffraction peaks of crystallized ZnO. This result shows that the as-prepared films, annealed at 500 °C for 1 h, have a polycrystalline hexagonal wurtzite structure. It seems that the doping with Ni^{2+} ions has no appreciable effect on the crystal structure of ZnO. These diffractograms show, however, that the intensities of diffraction peaks decline as the Ni^{2+} ion concentration

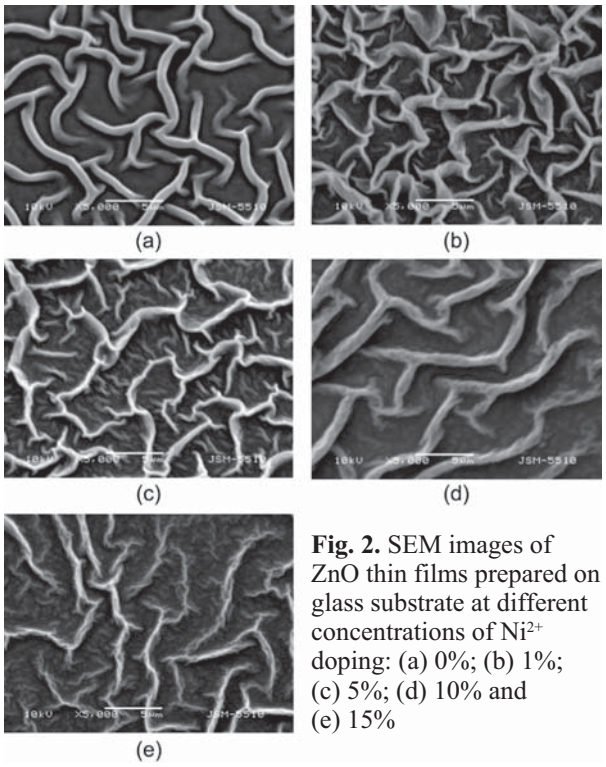

Fig. 2. SEM images of ZnO thin films prepared on glass substrate at different concentrations of Ni^{2+} doping: (a) 0%; (b) 1%; (c) 5%; (d) 10% and (e) 15%

increases, i.e. the nickel doping within ZnO films causes the crystallinity to degenerate. Since the intensity of diffraction peaks becomes weaker and the half-peak width becomes wider with the increase of Ni^{2+} doping concentration, the Ni^{2+} ions inhibit the aggregating growth of ZnO nanocrystals and affect the crystallization of ZnO. The average crystallite size of samples is estimated using the Scherrer's equation. When the Ni concentration increases, the average crystallite size decreases (Fig. 4), which implies on the role of Ni to destabilize the respective sol thus making smaller the zinc hydroxide making species.

3.2. Structure characterization of ZnO films on aluminium foil substrate

The of ZnO films, shown on the SEM images in Fig. 5, exhibit a different surface morphlogy depending on the annealing temperature. The ZnO films annealed at 100 °C (Fig. 5a) have different ganglia-like hills of width of 0.2–0.5 μm, length ~5 μm and height about 1–2 μm. Ganglia-like hills of typical width 0.5–1 μm, length from 5 μm to 10 μm and height about 2.5–3 μm are seen on the surface of films annealed at 300 °C (Fig. 5b). The thin films, obtained after heating at 500 °C (Fig. 5c), have different ganglia-like hills of width 1–2 μm, length ~15 μm and height about 3 μm. The ganglia-like structure seems reproducible irrespective on the conditions of film deposition and annealing.

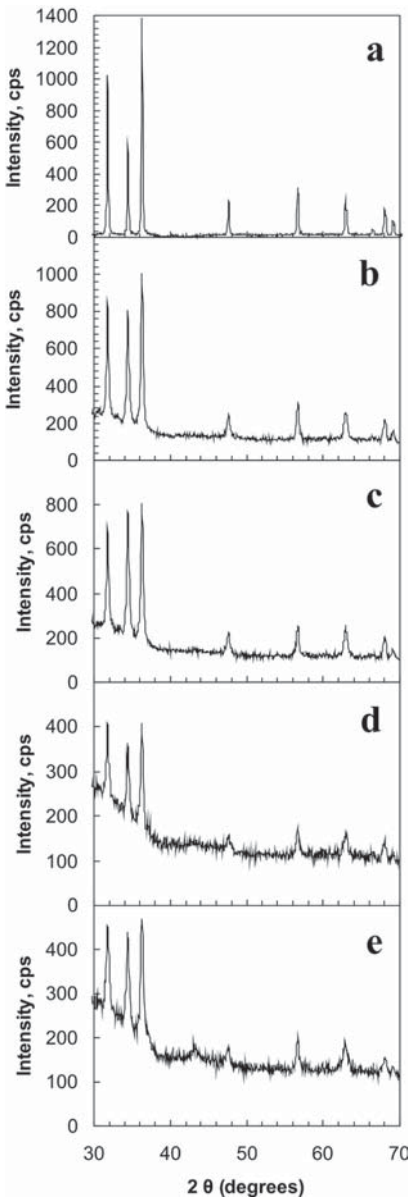

Fig. 3. XRD spectra of ZnO films prepared by sol-gel and doped with Ni^{2+} at (a) 0%; (b) 1%; (c) 5%; (d) 10% and (e) 15%. The respective shown in Fig. 4.

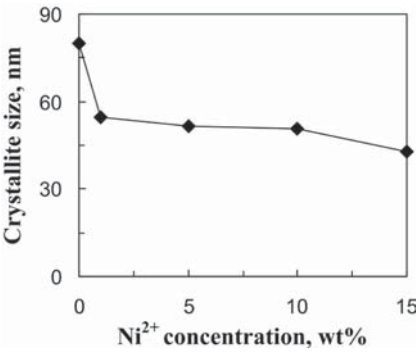

Fig. 4. Relationship between the crystallite size of ZnO and the percent of Ni^{2+} doping

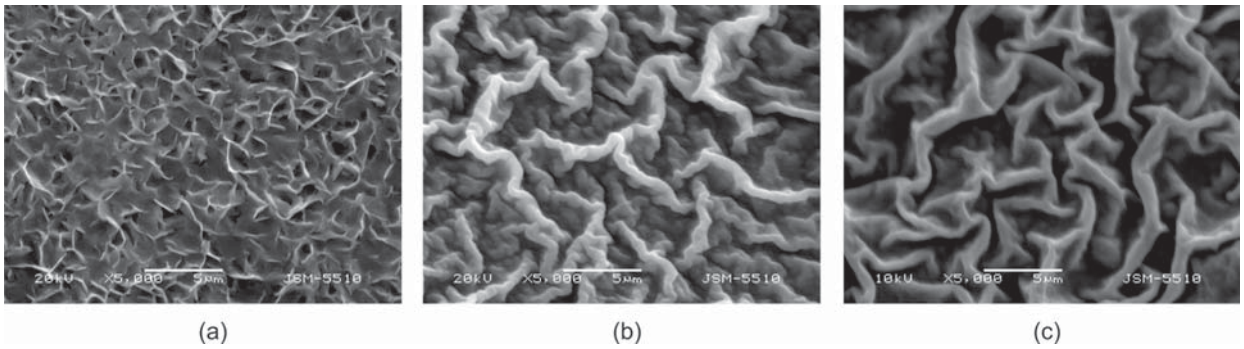

Fig. 5. SEM images of ZnO films prepared on aluminium foil at different annealing temperatures: (a) 100 °C; (b) 300 °C; (c) 500 °C. Increasing the temperature increases the scale of surface pattern of the film surface

Figure 6a shows the XRD data of ZnO films annealed at 100 °C. The lack of three characteristic peaks of ZnO (see below) shows that at this temperature the material is still in its hydroxide form

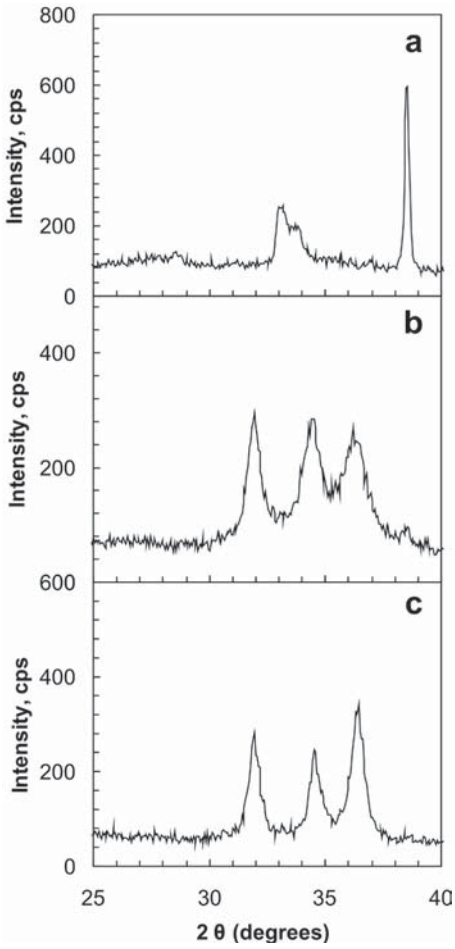

Fig. 6. XRD spectra of ZnO films prepared on aluminium foil by sol-gel and annealed at (a) 100 °C; (b) 300 °C; (c) 500 °C. The crystallite sizes are about 30.0 nm, 70.5 nm and 88.1 nm, respectively (see Fig. 7)

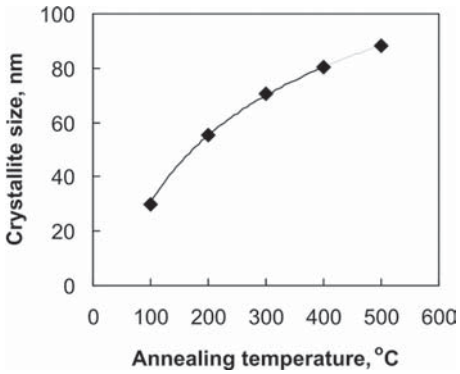

Fig. 7. Relationship between the crystallite size of ZnO and the annealing temperature for the thin films on aluminium foil

of rather amorphous state. Nevertheless, the mean crystallite sizes estimated by the Sherrer's formula are about 30.0 nm. The XRD data from Fig. 6a are compared with literature data, which prove the presence of one characteristic peak of $Zn(OH)_2$, which can be indexed as the orthogonal structure. Increasing the annealing temperature causes a transition from orthogonal in to hexagonal structure, respectively from $Zn(OH)_2$ toward ZnO. The (100), (002), (101) diffraction peaks of ZnO films appear clearly at a higher annealing temperature, which can be indexed as the hexagonal wurtzite structure of ZnO. The thin films consist in this case of polycrystalline grains with no preferential growth observed. The average sizes of crystallites are about 70.5 nm (for the films annealed at 300 °C) and 88.2 nm (at 500 °C) (Fig. 6b, c). Increasing the annealing temperature makes the diffraction peaks better pronounced and increases the size of crystallites. The relationship between annealing temperatures and the corresponding ZnO crystallite sizes are summarized and as illustrated in Fig. 7, respectively. The ZnO thin films prepared by us will find applications in the photocatalytic treatment of waters polluted by

organics due to their activity in UV and visible light (especially those doped with Ni ions).

4. CONCLUSIONS

Thin films of nanostructured ZnO are successfully prepared on glass and aluminium foil substrates using dip coating. The films are characterized by means of scanning electron microscopy and X-ray diffraction: The films (pure and nickel doped) comprise ZnO crystallites with a hexagonal wurtzite structure, which demonstrates that doping wit h Ni^{2+} ions has no appreciable effect on the crystal structure. When the Ni concentration increases, the average crystallite size decreases. The addition of 1 to 15 wt% of Ni^{2+} to the start solution modifies the morphology of films the ganglia-like hills and the wrinkles become smaller. Nanostructured ZnO films are prepared also, on aluminium foil at three different thermal treatment temperatures: 100, 300 or 500 °C. The deposited films have different ganglia-like hills with dimensions, which become much larger after treatment at elevated temperature. The crystallite size of as-prepared ZnO films increases with increasing of the film annealing temperature as well.

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ПОДГОТОВКА НА НАНОКРИСТАЛНИ ТЪНКИ СЛОЕВЕ ОТ ZnO СЪС ЗОЛ-ГЕЛНО ПОКРИВАНЕ

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(Резюме)

Нанокристалните тънки слоеве от ZnO са депозирани по зол-гелна методика с употреба на цинков ацетат. Методът е използван за покриване на два различни видове материали: стъкло и алуминиево фолио. (I) Слоеве върху стъклени повърхности. Нано-структурирани тънки слоеве на ZnO с различни концентрации на легиране с Ni^{2+} (0, 1, 5, 10 и 15 тегловни %) са получени за първи път по зол-гел методът. Повърхността на слоя е пипало-видно-омрежена (гагнгливево подобна) както е видно от сканиращата електрона микроскопия (СЕМ). Слоят се състои от нанокристали на ZnO с хексагонална кристална структура, по данни от рентгенова дифракция (XRD). (II) Филми с основа алуминиево фолио. Слоевете ZnO са отгрети при различни температури (100 °C, 300 °C и 500 °C) и са изследвани със СЕМ и XRD. Повърхността на слоя също е гагнгливево подобна. Кристалната структура на ZnO отново е хексагонална като размерите на кристалитите нарастват с температурата на отгряване.