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Zinc Oxide Nanostructures Doped with Transition Metals: Fabrication and Properties

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ZnO nanostructured films doped with Co and Ni deposited by hydrothermal method on silicon substrates covered with undoped ZnO sublayer were studied. SEM images of the films demonstrated them to consist of densely packed vertical nanopillars. Doping ZnO films with Ni or Co at concentrations up to $10^{19}\,cm^{-3}$ quenches their UV-excited photoluminescence. The doping also leads to the slight ferromagnetic behavior of ZnO.

Keywords: Zinc oxide; hydrothermal deposition; photoluminescence; Raman spectroscopy.

1. Introduction

Zinc oxide (ZnO) doped with transition metals such as Ni and Co attracts substantial interest of scientific community because of its potential application in the thermoelectrical devices, gas sensors, radiation detectors, solar and photocatalytic cells.[1–5] It can also exhibit ferromagnetic behavior at room temperature, acting as a diluted magnetic semiconductor. The origin of ZnO ferromagnetism is still not exactly known. Moreover, the samples fabricated in different laboratories across the world exhibit different magnetic behaviors.[5–10] However, there is a kind of consensus that properties of doped ZnO in most cases are determined by the interaction of ZnO intrinsic defects and impurity atoms. Since ZnO can be deposited by a number of methods[1,11] (electrochemical, chemical or thermal decomposition, CVD, etc.) it is important to evaluate the effects of the deposition parameters upon its properties.

This paper presents experimental results demonstrating the influence of the parameters of the hydrothermal deposition process, particularly the concentration of the transition metal in the precursor solution, on the properties of Ni- and Co-doped ZnO.

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2. Experimental

Highly-doped monocrystalline n^+-Si(111) wafers covered by 100 nm SiO_2 layer and 30 nm undoped ZnO sublayer deposited by atomic layer deposition (ALD) were used as substrates. Hydrothermal deposition of ZnO was carried out in the mixture of aqueous 0.1 M $Zn(NO_3)_2$ solution and hexamethylenetetramine (HMTA). Ni or Co nitrates in different concentrations were added to the solution as sources of these impurities. The pH of the solution was 5.2.

The substrates were placed front side down in the glass bath with the solution and annealed at 85 °C for 2 h. Then, the substrates were extracted from the hot solution, cleaned in DI water and dried in air.

Morphology of the fabricated films was studied with a Hitachi S-4800 scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy microanalysis (EDX) was carried out with a Bruker QUANTAX 200 analyzer. A DRON-3M X-ray diffractometer was used for XRD analysis. Photoluminescence (PL) spectra were recorded at room temperature using a spectroscopic complex based on a Solar TII MS 7504i monochromator-spectrograph equipped with a CCD camera. PL of the films was excited by the monochromatic light with the wavelength of 345 nm. Raman spectra were studied with an SOL Instruments 3D scanning laser confocal Raman microscope Confotec NR500.

3. Results and Discussion

The deposited films were found to consist of individual crystals closely packed in the compact continuous layer like it is illustrated by Fig. 1. The films' surface has hexagonally-shaped facets, typical for the crystalline ZnO.

According to the EDX analysis, the concentration of Ni in the film deposited from the solution with 0.025 M $Ni(NO_3)_2$ attains 0.04 at.% ($\sim 2 \times 10^{19}\,cm^{-3}$). The increase of Ni concentration in the solution corresponding to the use of 0.05 M and 0.1 M $Ni(NO_3)_2$ resulted in 0.1 at.% and 1.1 at.% ($\sim 5 \times 10^{19}\,cm^{-3}$ and $5.5 \times 10^{20}\,cm^{-3}$) of this metal in the films, respectively. The concentration of Co in the films was smaller than 0.01 at.%.

The Raman spectra shown in Fig. 2 reveal the peak at $437\,cm^{-1}$ typical for the high-frequency nonpolar [E_2 (high)] optical mode in ZnO and several peaks from the Si wafer ($\sim$ 300, 520, 950 and $980\,cm^{-1}$). The intensity of the E_2 peak decreases with an increase of Ni (or Co) concentration in the film. For the Ni-doped films deposited from the concentrated $Ni(NO_3)_2$ solutions, the additional peak at the $1\,045\,cm^{-1}$ is observed.

The XRD patterns have the peaks (100), (101), (002), (114) and (203) of ZnO evidencing its polycrystalline form. For the Ni-doped films the additional peak corresponding to metallic Ni(111) phase is identified.

The recorded PL spectra shown in Fig. 3 revealed that peaks' intensity in both near-UV and visible ranges decreases with an increase of the metal concentration. At the Ni concentration of 0.1 M in the solution PL of the sample disappeared. At the same concentration of Co and the Ni concentration of 0.05 M, there is a PL band with the maximum near 430 nm. At smaller concentrations of these metals no PL signal is presented on the spectra. The peak in the near-UV range is the exciton PL band equivalent to the energy of ZnO optical bandgap.[1,2] The band in the visible range corresponds to irradiative recombination via energy levels within the ZnO bandgap associated with oxygen vacancies and interstitial atoms.[1,10]

According to the results obtained, high concentration of transition metals can lead to degradation of structural properties of ZnO films. The intensities of the corresponding Raman and XRD peaks reduce

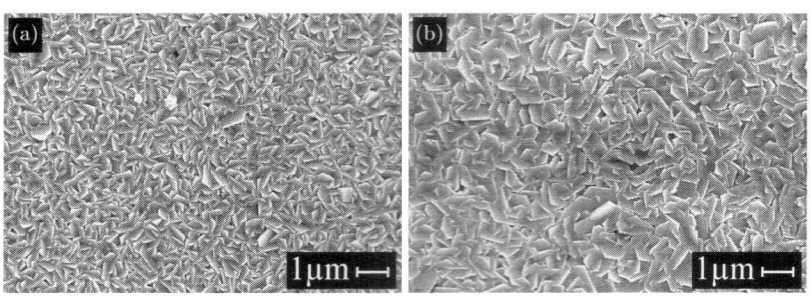

Fig. 1. Plain-view SEM images of ZnO films deposited on the surface of ALD ZnO sublayer from the solutions containing 25 mM of (a) $Ni(NO_3)_2$ and (b) $Co(NO_3)_2$.

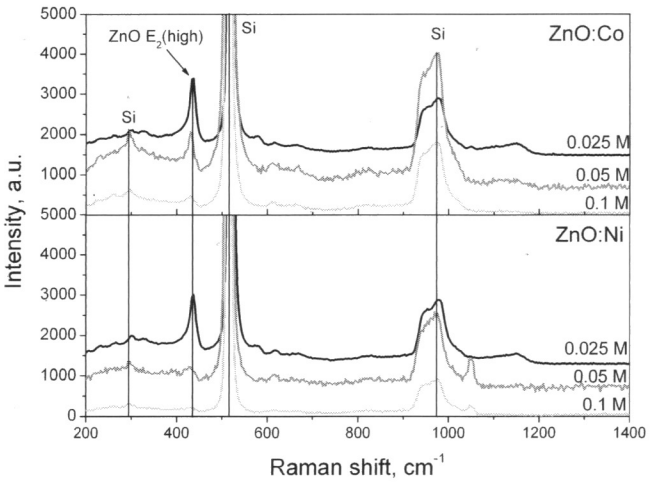

Fig. 2. Raman spectra of ZnO films deposited on the surface of ALD ZnO sublayer from the solutions with different concentrations of $Ni(NO_3)_2$ and $Co(NO_3)_2$ recorded with laser excitation at 473 nm.

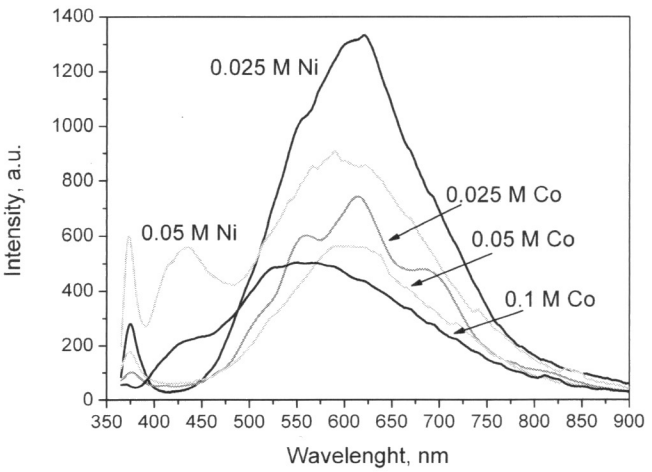

Fig. 3. Room-temperature PL spectra of ZnO films deposited on the surface of ALD ZnO sublayer from the solutions with different concentrations of Ni and Co.

with an increase of the metal content in the films. PL spectra revealed the same behavior. Thus, transition metal atoms at high concentrations are supposed to disturb the crystal lattice of the host ZnO nanocrystals leading to degradation of their optical properties.[9] The appearance of the PL peak at 430 nm can be associated with Zn interstitial atoms.[1]

The changes of properties of doped ZnO films with the growth of the transition metal concentration were first observed for ZnO:Ni films and then for ZnO:Co ones. According to the results of EDX analysis, the Ni concentration in the films obtained at equal deposition conditions is higher than the Co concentration. Thus, Ni atoms can be introduced into the ZnO crystal lattice more easily than Co atoms. This is also confirmed by the XRD data. Moreover, Raman spectra of the Ni-containing samples revealed the presence of the peak at 1 045 cm^{-1} corresponding to Ni oxide or hydroxide.

Measurements of specific magnetization of the above samples by the static panderomotoric method demonstrated slight ferromagnetism in the case of high concentrations of Ni or Co. Low level of this signal suggests that the transition metal concentration in the nonoxidized ZnO films is negligible.

4. Conclusion

The study of hydrothermal deposition of ZnO from aqueous $Zn(NO_3)_2$ solution containing $Ni(NO_3)_2$ or $Co(NO_3)_2$ revealed that the transition metals can act as impurities affecting the structural and optical properties of the host semiconductor. With the growth of Ni and Co concentrations the intensities of near-UV-range and visible-range PL gradually decrease. Raman spectra of the fabricated films indicated that their crystallinity is also decreased by the large content of these impurities. Weak ferromagnetic properties of the transition metal-doped ZnO films suggest that no magnetic metal clusters have been formed. We suppose that the fabricated doped ZnO films can find applications in photovoltaics, optoelectronics and spintronics.

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References

1. Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
2. A. Kołodziejczak-Radzimska and T. Jesionowski, *Materials* **7**, 2833 (2014).
3. K. Sato and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* **39**, L555 (2000).

4. S. J. Pearton, *IEEE Trans. Electron Devices* **54**, 1040 (2007).
5. S. Shi, Y. Yang, J. Xu, L. Li, X. Zhang, G.-H. Hue and Z.-M. Dang, *J. Alloys Compd.* **576**, 59 (2013).
6. J. M. D. Coey and S. A. Chambers, *MRS Bull.* **33**, 1053 (2008).
7. M. T. Doan, X. V. Ho, T. Nguyen and V. N. Nguyen, *Adv. Nat. Sci., Nanosci. Nanotechnol.* **5**, 025011 (2014).
8. A. Samanta, M. N. Goswami and P. K. Mahapatra, *J. Alloys Compd.* **730**, 399 (2018).
9. S. Fabbiyola, V. Sailaja, L. J. Kennedy, M. Bououdina and J. J. Vijaya, *J. Alloys Compd.* **694**, 522 (2017).
10. M. Balucani, P. Nenzi, E. Chubenko, A. Klyshko and V. Bondarenko, *J. Nanopart. Res.* **13**, 5985 (2011).
11. W. C. Zhang, X. L. Wu, H. T. Chen, J. Zhu and G. S. Huang, *J. Appl. Phys.* **103**, 093718 (2008).