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Synthesis and morphological characterization on PVP/ZnO nano hybrid films

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Metal/semiconductor (M/SC-nanoparticles) immobilized in polymer matrices have generated considerable interest in recent years due to their distinct individual and cooperative properties [1–4]. Specifically, such nanostructural composites have exhibited unique physicochemical, electrophysical, magnetic, and optical properties [1, 3, 4]. By varying the chemical and physical structure of the polymer matrix, it is possible to modify the size and coordination of the particles as well as the matrix-particle interaction. Although such nanocomposite films have been successfully synthesized and characterized, the fundamental mechanism governing their nanostructure and properties has not been fully understood. This paper studies the synthesis-structure relationship in sol-gel derived PVP/ZnO composite films.

Semiconductor nanoparticles immobilized in a polymer matrix have recently been investigated as biosensors for the detection of species in bio-fluids due to their high sensitivity and fast response [5]. The nanoparticle sensor has extensively high surface-to-volume ratio compared to bulk particles, and high sensitivity with high selectivity can be achieved in oxide sensors by reducing the crystallite size [6, 7]. This improvement is due to the availability of extensive sites that are attractive to the electrons present in the sensor film, and the low band gap that makes it easy for electron transfer from the valence orbit to the conduction orbit. The response time of the sensor can be reduced dramatically by using nanoparticles.

Zinc oxide has many applications including antireflection coatings, transparent electrodes in solar cells [8], gas sensors [9], varistors [10], surface acoustic wave devices, and electroluminescence and photoluminescence devices [11, 12]. ZnO-based sensors have been synthesized in various forms such as thin or thick films and pellets. The processing of ZnO semiconductor sensor based on thick film or pellets technology is practically excluded from the fabrication of intelligent microsystems, not only due to processing incompatibility but also the high power requirement. Thin film technology based on physical methods like vacuum evaporation or sputtering are very expensive and may suffer composition inhomogeneity and poor step coverage for topographies with high aspect ratios. The sol-gel technique on the other hand has several advantages such as easy control of film thickness, low-cost processing and coating of large complex shapes [13]. This technique is employed for the study reported here.

Although spherical and rod-like zinc oxide nanoparticles have been prepared using various methods [14–16], to our knowledge, there has been no report on the synthesis of ZnO-polymer nanocomposite thin films with the sol-gel technique. In the present work, we synthesize nano-sized ZnO semiconductor thin film modified by polyvinylpyrrolidone using the sol-gel dip-coating technique. Various analytical techniques are used to determine the surface morphology, the chemical composition, and the nanoparticle within the thin film. These techniques include the Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

Zinc acetate, acetic acid, ethanol, deionized water and poly-4-vinylpyrrolidone (PVP) were purchased from Aldrich chemicals (USA) and used as received. ZnO/PVP nanocomposite thin film coating on monocrystalline silicon wafer was conducted using sol-gel dip-coating technique. The substrates were cleaned by immersion in 1:1 concentrated H_2SO_4: 30 vol% H_2O_2 (piranha solution) for 5 min, followed by rinsing with de-ionized water, acetone and iso-propanol. The pre-cleaned substrates were dipped in a solution with zinc acetate and PVP in dimethyl formamide, corresponding to zinc acetate concentration of 0.6 M with a withdrawal speed of 150 mm/min. After each coating the sample was dried in the oven at 100 °C for 10 min. The coated thin films were then annealed at 200 °C for varying time duration, ranging from 1 h to 20 hrs, in open air at a heating rate of 2 °C/min.

The surface chemistry of ZnO/PVP nanocomposite thin film dip-coated on silicon substrate was studied using XPS technique utilizing PHI ESCA spectrometer (model 5400, Perkin-Elmer). The base pressure during analysis was 10^{-9} Torr and Mg-K_α X-radiation (1253.6 eV) with 350 watts power was used. Both the survey and the high-resolution narrow spectra were recorded with electron pass energy of 44.75 and 35.75 eV respectively, to achieve the maximum spectral resolution. Any charging shift produced by the samples was carefully removed by using a BE scale referred to C (1s) BE of the hydrocarbon part of the adventitious carbon line at 284.6 eV. Nonlinear least square curve fitting was performed using a Gaussian/Lorentzian peak shape after the background removal. The surface morphology of the thin film was studied using AFM (Digital Instrument, USA) in the tapping mode. The average nanocrystallite size within the film was estimated. The Fourier transform infrared spectra (FTIR) were

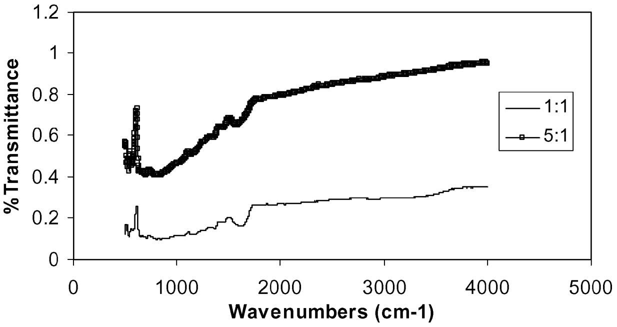
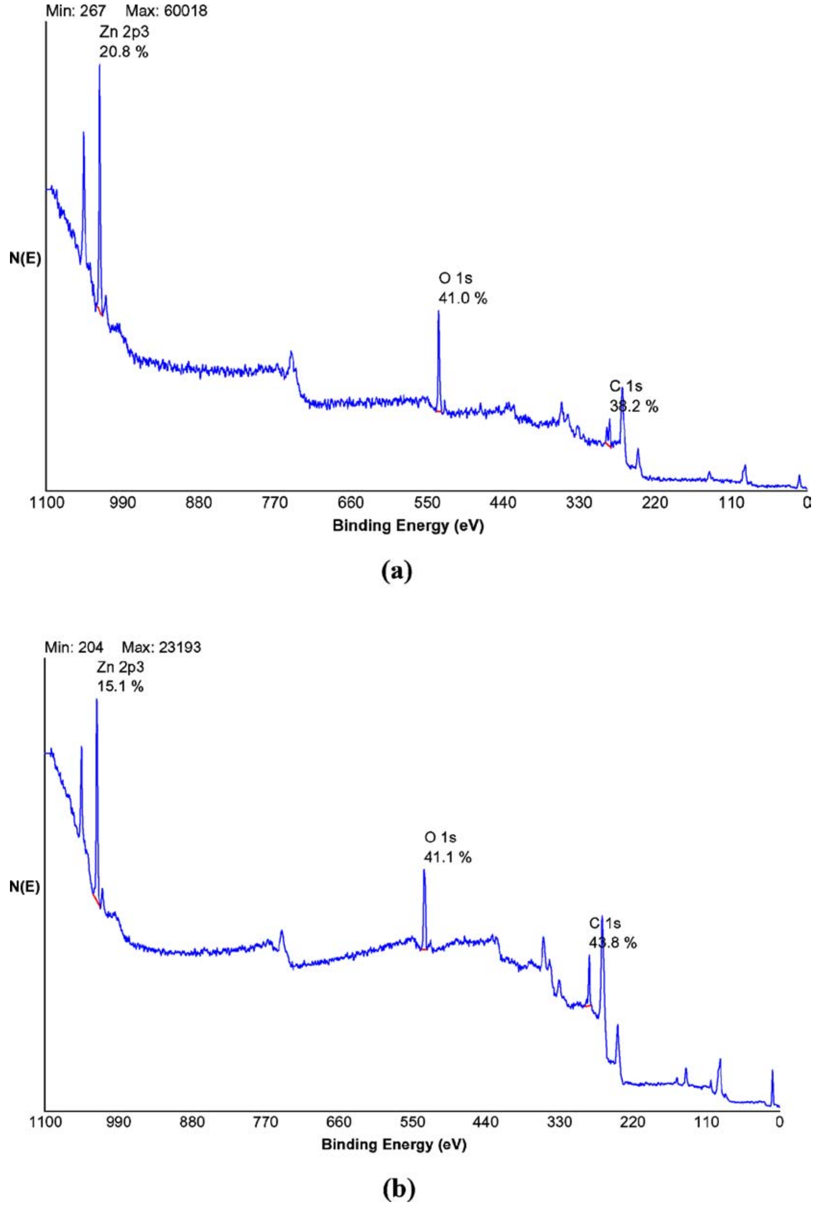


Figure 1 The infrared spectra of the ZnO/PVP nanocomposite thin film annealed at 200 °C for 20 hrs: (a) 1:1 and (b) 5:1.

recorded on a Nicolet Series II Magna-IR 550 FTIR Spectrometer in reflection mode. All measurements were made three times, at room temperature, to ensure repeatability.

Fig. 1 shows the infrared spectra of the ZnO/PVP nanocomposite thin films annealed at 200 °C for 20 hrs for the composition ratios 1:1 and 5:1. The observed peak at 1646 cm^{-1} is a distinct stretching mode of carbonyl on the poly-4-vinylpyrrolidone molecule. The peak at 1375 cm^{-1} is due to the bending mode of C—H, while that at 1200 cm^{-1} results from the stretching mode of C—N on the PVP molecule. The figure shows that the transmittance decreases as the PVP concentration increases, indicating enhanced adsorption with increase of PVP concentration. No peak is observed at 3300 cm^{-1}, indicating the complete decomposition of zinc acetate and the formation of ZnO after 20 hrs annealing at 200 °C.

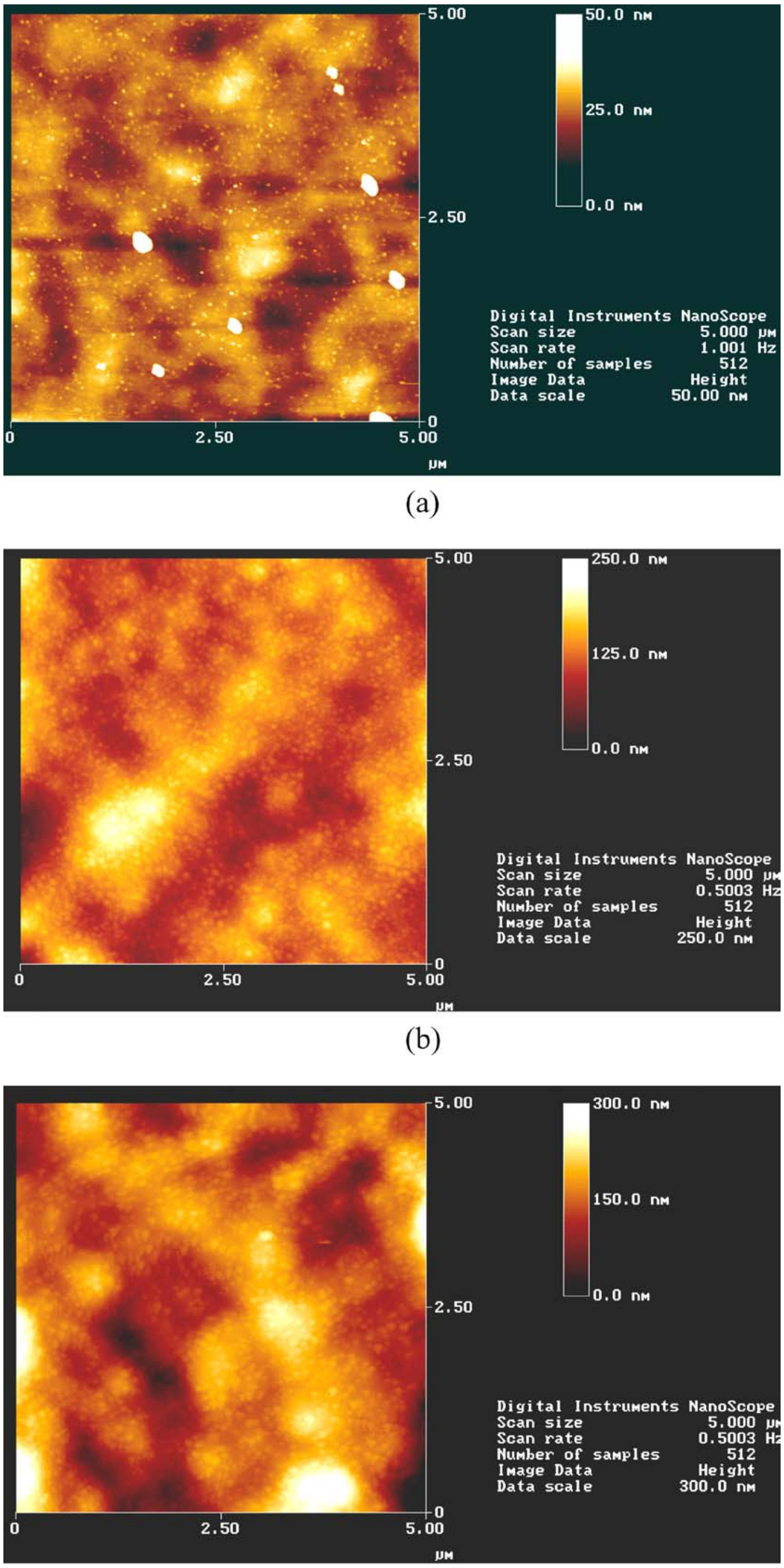
Fig. 2 shows the typical survey scans of XPS spectra of zinc acetate powder (a) and ZnO thin film dip-coated on the silicon substrate and annealed at 200 °C for 20 hrs (b). Fig. 2a shows that the C (1s) peak occurs at about 285 eV. Two separate peaks are evident, one appearing at the low binding energy of 285 eV due to the CH_3 functional group and the other at about 288.5 eV due to the carbonyl group. For the thin film annealed at 200 °C for 20 hrs, Fig. 2b shows that the intensity of the



(a)

(b)

Figure 2 Typical survey scans of XPS spectra of (a) zinc acetate powder and (b) ZnO thin film dip-coated on the silicon substrate annealed at 200 °C for 20 hrs.



(a)

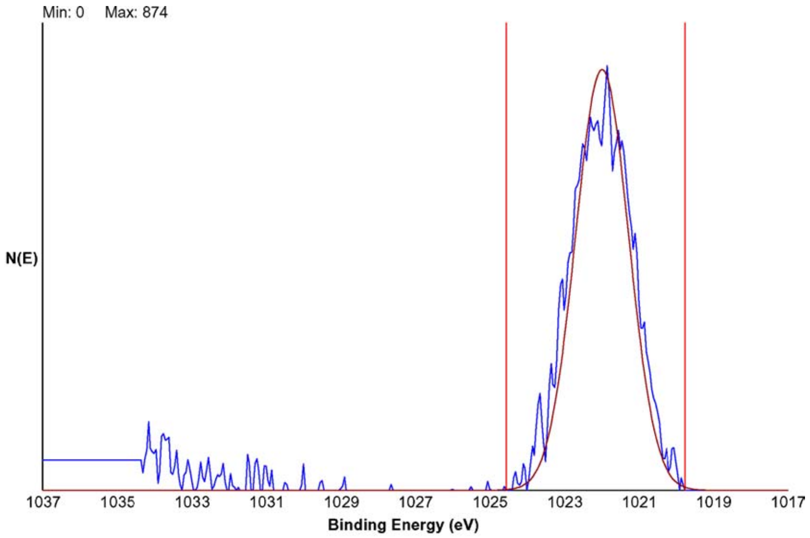
(b)

(c)

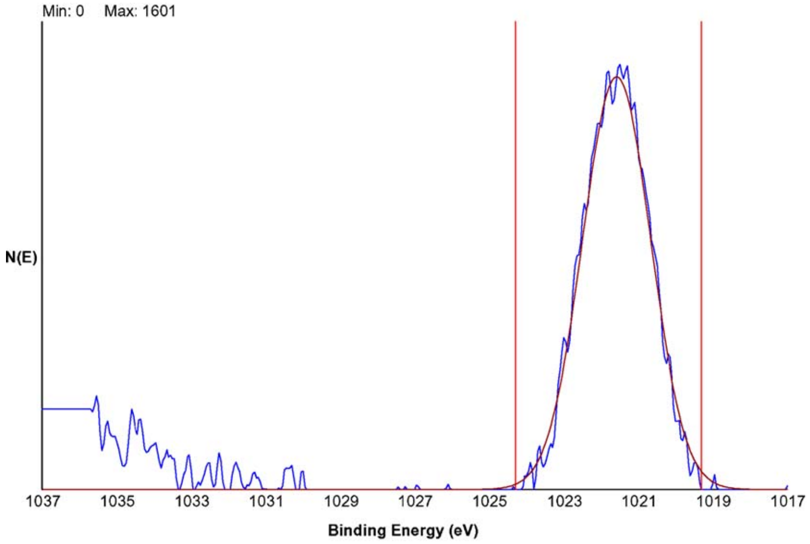
Figure 3 Typical AFM images of the ZnO/PVP nanocomposite thin films with varying ZnO/PVP ratios (a) 1:1, (b) 3:1 and (c) 5:1 on the silicon substrate annealed at 200 °C for 20 hrs.

carbonyl peak is significantly attenuated and is nearly nonexistent. This result indicates the decomposition of zinc acetate and the formation of ZnO thin film.

Fig. 3 shows the typical AFM images of the ZnO/PVP nanocomposite thin films with varying Zn^{2+}/PVP ratios (a) 1:1, (b) 3:1 and (c) 5:1 on the silicon substrate and annealed at 200 °C for 20 hrs. The ZnO nanoparticles are evident in the PVP polymer matrix. The size of ZnO particles in the PVP/ZnO nanocomposite ranges from 30 to 80 nm with the increase of ZnO content. This result indicates that the particle size increases with the increasing ZnO content. AFM



(a)



(b)

Figure 4 Detailed XPS scans of Zn(2p3/2) spectra for ZnO/PVP nancomposite thin films with varying ZnO/PVP ratios: (a) 1:1 and (b) 5:1.

reveals a uniform dispersion of spherical-shaped particles throughout the PVP/ZnO hybrid films. The spatial distribution of ZnO in the PVP/ZnO nancomposite film is denser with higher ZnO content. Therefore, the use of PVP polymer can be helpful in stabilizing the nanoparticles by decreasing their mobility, thereby preventing ZnO agglomeration into large particles.

Fig. 4 shows the detailed XPS scans of Zn(2p$_{3/2}$) spectra for ZnO/PVP nanocomposite thin films with varying Zn^{2+}/PVP ratios (a) 1:1 and (b) 5:1, dip-coated on the silicon substrates. The Zn (2p3/2) XPS peak that appears at 1021.8 eV coincides with the finding for ZnO. With the increase of ZnO content, the peak of Zn(2p3/2) is broadened. The full width at half-maximum (FWHM) increases from 1.84 to 2.15 eV. The broadening of the peak might be due to the increased size of ZnO in the PVP/ZnO nanocomposite.

Semiconductor nanoclusters embedded in polymer matrix can act as short circuited microelectrodes under band gap excitation and promote reduction and oxidation processes. Therefore, such a nanocomposite film can be used as biosensors for detection of some oxidative species such as superoxide anion radical in biological systems. However, the performance of these nanocomposite thin film biosensors is determined by the spatial distribution, size and shape of the dispersed nanoparticles. In addition, the fabrication of one-dimensional nanometer-sized materials is important for fundamental understanding of the mesoscopic phenomena and the development of nanodevices of the future.

The conclusions from this study are:

- The sol-gel technique is a viable method for producing M/SC-polymer nanocomposite films.
- ZnO nanoparticles are uniformly distributed in PVP polymer matrix after annealing the thin film at 200 °C for 20 hrs.
- ZnO nanoparticle concentration can be easily tailored by varying the ZnO/PVP ratio.
- ZnO nanoparticle size in PVP matrix increases with the increase of ZnO content.

References

1. D. WOEHRLE, in "Metal Complexes, Zero-Valent Metals and Metal Clusters Physically Connected with Macromolecular Compounds in: Macromolecule-Metal Complexes," edited by F. Ciardelli, E. Tsushida and D. Woehrle (Springer Verlag, Berlin, Heidelberg, 1996).
2. D. YU. GODOVSKI, *Adv. Polym. Sci.* **119** (1995) 81.
3. A. D. POMOGAILO, A. S. ROZENBERG and I. YE. UFLYAND, *M. Chemistry* **673** (1998) 2000.
4. L. I. TRAKHTENBERG, G. N. GERASIMOV and E. I. GRIGORIEV, *Russian J. Phys. Chem.* **73** (1999) 209.
5. B. H. SCHNEIDER, E. L. DICKINSON, M. D. VACH, J. V. HOIJER and L. V. HOWARD, *Biosensors & Bioelectronics* **15** (2000) 13.
6. K. V. GOBI and F. MIZUTANI, *J. Eletroanalytical Chem.* **484** (2002) 172.
7. T. DU, H. SONG and O. J. ILEGBUSI, in Ceramic Engineering and Science Proceeding, The 28th International Conference & Exposition on Advanced Ceramic & Composites, Cocoa Beach, Florida, Jan. 25–30, 2004.
8. K. L. CHOPRA and S. R. DAS (eds.), "Thin Film Solar Cells" (Plenum, New York, 1983).
9. J. MULLER and S. W. FRESENIUS, *J. Anal Chem.* **349** (1994) 380.
10. L. B. KONG, F. LI, L. Y. ZHANG and X. YAO, *J. Mater. Sci. Lett.* **17** (1998) 769.
11. W. C. SHIH and M. S. WU, *J. Cryst. Growth* **137** (1994) 319.
12. C. T. TROY, *Photonics Spectra* **31** (1997) 34.
13. L. KLEIN, "Sol-Gel Technology for Thin Films, Fibers, Performs, Electronics, and Specialty Shapes" (Part II, Park Ridges, NJ, 1998).
14. R. J. LAUF and W. D. BOND, *Ceram. Bull.* **63** (1984) 278.
15. X. H. WANG, J. SHI, S. DAI and Y. TANG, *Thin Solid Films* **429** (2003) 102.
16. Z. WANG, H. ZHANG, L. ZHANG, J. YUAN, S. YAN and C. WANG, *Nanotechnology* **14** (2003) 11.

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