Low-Temperature Synthesis and Magnetic Characterization of Doped-Zns Nanostructures

Perales-Pérez O.*, Dussan Devia S., Tomar M. S., Morales L. M., Mata O. and Jia W.

University of Puerto Rico, Mayagüez, PR 00681-9044, *oscar@ge.uprm.edu.

ABSTRACT

The composition- and size-dependence properties of nano-structured dilute magnetic semiconductors (DMSs) enable them to be considered as promising materials for spintronic and photoelectronic applications. Theoretical analyses suggest the possibility of room-temperature ferromagnetism in ZnS-based DMSs. The present work is focused on the synthesis and characterization of bare, V- and Cr-doped ZnS in order to get experimental evidence on the magnetic behavior of doped systems. Powders and thin films were produced by the chemical-bath deposition route at low temperature. The results evidenced the nanocrystalline nature and the homogeneous deposition of those materials onto glass and quartz substrates. Room-temperature SQUID characterization of nanocrystalline powders verified the actual incorporation of dopant species into ZnS host structure. Ferromagnetic or paramagnetic behavior was observed, depending on the type and concentration of the dopant.

Keywords: ZnS, chemical-bath-deposition, nanocrystalline thin films, diluted magnetic semiconductors, magnetic properties.

1 INTRODUCTION

In nanocrystalline semiconductors the decrease in crystal size leads to the change in their physical, chemical and optical properties. To cite a signature case, the observed increase in the band gap energy when the semiconductor crystal size is in the nanometer range can be attributed to the quantum confinement effect [1]. Doping these semiconductors with magnetic metal ions conduces to the formation of the so-called diluted magnetic semiconductors (DMSs). Zinc sulfide, ZnS, is an II-VI semiconductor that exhibits a band gap energy of ~ 3.66 eV in the bulk state [2]. This material finds applications in different devices such as, optical sensors, photovoltaic cells, photoconductors and other optoelectronic systems. Recently, it has been proposed that ZnS doped with transition metal ions, should exhibit ferromagnetic behavior at room temperature [3]. This expected ferromagnetic and luminescence behavior would enable the use of this DMS in bi-functional devices [4].

In this regard, Peng *et al.* [5] have reported the enhancement in luminescence with the increase of dopant concentration in ZnS doped with Mn ions. However, the material was still paramagnetic at room temperature. Despite of the expected room-temperature ferromagnetism in other ZnS-based systems, there is a lack of detailed research addressing the experimental verification of this possibility.

A variety of physical and chemical methods have been used to synthesize ZnS nanoparticles. Our earlier works verified the viability to produce nanocrystalline Mn- and Ni-doped ZnS powders and films by using the chemical bath deposition (CBD) route [6]. This method is based on the controlled release of sulfide and metal ions in aqueous solutions at 85^{o}C. Sulfide ions are generated by the thermal decomposition of thiourea whereas metal ions, strongly complexed by ammonia species, will be capable to participate in the sulfide-forming reaction only at a suitable solution temperature. The controlled availability of reactants at low temperatures favors heterogeneous nucleation and, hence, a film can be deposited onto practically any type of substrate. Depending on the concentration of reacting species, nanocrystalline powders can also be produced.

Based on the above considerations, the present work is focused on the synthesis and characterization of bare, Cr- and V-doped ZnS nanocrystals and thin films synthesized by the CBD route. Commercially available trivalent Cr and V ions were chosen because of their small ionic radii, which would favor their exchange with Zn species in host ZnS.

2 EXPERIMENTAL

2.1 Materials

Zinc sulfate hepta-hydrate ($ZnSO_4.7H_2O$), Chromium (III)-nitrate and Vanadium (III)-chloride salts were used as precursors. Thiourea (H_2NCSNH_2) was selected as source of sulfide ions. Ammonium sulfate, $(NH_4)_2SO_4$, and ammonium hydroxide, NH_4OH, provided not only suitable alkaline conditions but also acted as complexing species for metal ions. Hydrazine ($H_4N_2H_2O$) was used to improve film attachment to the substrate. Films were deposited onto glass and quartz substrates. Prior to their use, substrates were immersed in HCl, washed with detergent and rinsed in abundant deionized water.

2.2 Synthesis of Thin Films and Nanocrystals

Metal ions solutions were prepared for a specific fraction of dopant species in starting bath solutions, 'x'. Suitable weights of Zn and Cr or V salts, and ammonium sulfate were dissolved in deionized water at room temperature. Ammonium hydroxide, hydrazine and thiourea were added to this solution. Based on our preliminary work [6], the total concentration of metal ions was fixed at 0.03M. The substrate was immersed into the bath solution that was heated up to 85º C for 15 minutes. During this reaction time ammonium-metal complexes reacted with OH^- ions adsorbed onto the substrate surface to form a metal hydroxide intermediate compound. This intermediate will react with sulfide species released from the thiourea to form sulfide nanocrystals. The films will grow by incorporation of metal and sulfide species from the bath solution. Longer reaction times favored homogeneous nucleation that was conducive to the precipitation of powders in the same bath. Films and powders were removed out from solution, washed with deionized water and dried in air at 50°C.

2.3 Products Characterization

Structural analyses of the powders were carried out in a Siemens D5000 x-ray diffractometer (XRD) using the Cu-K α radiation (1.5405Å). The infrared spectra were obtained using a FT-IR Digilab FTS-1000 system. Atomic force microscope (AFM) di CP-II Veeco, was used in tapping-mode to study the surface morphology and homogeneity of the nanocystalline thin films. The magnetic properties of powders were measured at room-temperature in a Quantum Design superconducting quantum interference device (SQUID).

3 RESULTS AND DISCUSSION

3.1 XRD Analyses

Figure 1 and figure 2 show the x-ray diffraction patterns of bare, Cr- and V-doped ZnS powders synthesized at different atomic fractions of dopant species in bath solutions, 'x'. X-ray diffraction analyses revealed the coexistence of both cubic and hexagonal ZnS phases. Furthermore, the peaks broadening evidenced the nanocrystalline nature of the precipitates. The average crystallite size, estimated by using the Debye-Scherrer's equation for the (220) peak, was 5 nm. The excellent matching between the diffraction peaks of doped-ZnS with those for bare Zinc sulfide suggested that Cr^{3+} (ionic radii 0.062nm) and V^{3+} (0.064nm) can substitute Zn^{2+} ions (0.074 nm) in the host structure. Moreover, the absence of any shift in the peaks' angular positions indicated a negligible distortion of the ZnS-unit cell.

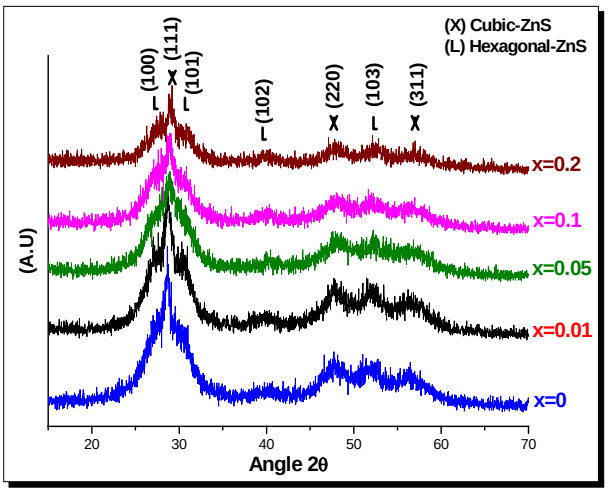

Figure 1: XRD patterns of bare, i.e. x = 0, and Cr-doped ZnS powders synthesized at different atomic fractions of dopant species, 'x'. The total concentration of metal ions was 0.03M. Diffraction peaks of both cubic and hexagonal ZnS phases were identified.

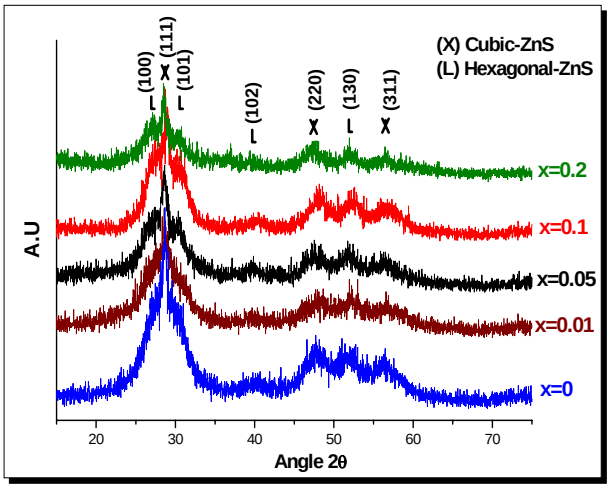

Figure 2: XRD patterns of bare, i.e. x = 0 and V-doped ZnS powders synthesized at different 'x' values. The total concentration of metal ions was 0.03M. The absence of peaks other than those corresponding to ZnS suggests the actual incorporation of V-ions into the host structure.

3.2 AFM Observations

2D-3D AFM images of Cr- and V-doped ZnS thin films, shown in Figure 3, evidenced the homogenous deposition of doped-sulfides (film thickness around 200 nm) onto glass substrates. Similar deposition quality was observed when the quartz was used as substrate. The topographic view in Figure 3-(c), clearly shows the decrease in the size of spherical aggregates when Cr ions co-existed in starting bath solutions. The size of the aggregates drops from 500

nm, for bare ZnS, down to 250 nm when Cr is incorporated in the film. Moreover, each aggregate consisted of nanosize individuals averaging 50-60 nm in diameter. The sizes of the V-doped ZnS aggregates were very similar to the ones in bare ZnS. The smoothness of Cr-doped ZnS films was evidenced by their low root mean square (RMS) surface roughness values. RMS surface roughness was 53 nm for bare ZnS, which is very high in comparison to 13 nm, 11 nm and 16 nm determined for ZnS doped with Cr at x= 0.05, 0.1 and 0.2, respectively. V-doped ZnS films were not as smooth as the Cr-doped ones. The corresponding surface roughness values ranged from 40nm to 89nm for 'x' between 0.05 and 0.2.

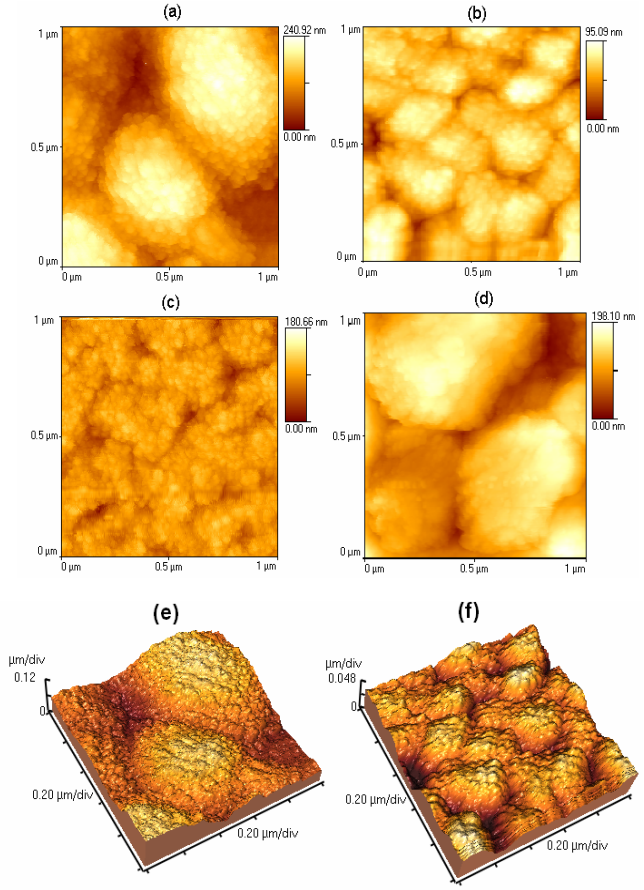

Figure 3: AFM images of (a, e) bare ZnS; (b, f) Cr-doped ZnS, x=0.05; (c) Cr-doped ZnS, x=0.2; and (d) V-doped ZnS, x=0.1, films deposited onto glass substrate.

3.2 FT-IR Analyses

FT-IR spectra corresponding to bare and doped ZnS nanocrystalline powders are shown in Figure 4. The band at 527 cm^{-1} can be assigned to the bending vibration mode in N-C-N. In turn, bands at 1061 cm^{-1} and 1611 cm^{-1} correspond to the C-N stretching and N-H bending vibration modes [7]. The band at 604 cm^{-1} can be assigned to the N-C-S bending vibration. This later functional group would have been generated by the thermal decomposition of thiourea. The presence of these four functional groups in FT-IR spectra can be explained by their strong adsorption onto the metal sulfide surfaces, even after intensive washing of the solids. Although the FT-IR spectra of Cr- and V-doped ZnS powders looked very similar, the band at 949 cm^{-1} was observed only in the V-doped case. This band can be assigned to C-C stretching vibration in the acyl-chloride (C-Cl-O) group. This functional group could have been formed by the reaction between thiourea groups and chloride ions in the V precursor salt. Finally, the band centered at 545 cm^{-1} should correspond to the stretching vibrations of the metal-oxygen bonds. This band, although weak, would suggest the presence of traces amounts of oxygen in the solids. The presence of oxygen could be attributed to residual amounts of metal-hydroxide, generated at the earlier stages of the sulfide forming-reaction. Also, some oxidation of the sulfide nanocrystals by atmospheric oxygen can not be ruled out.

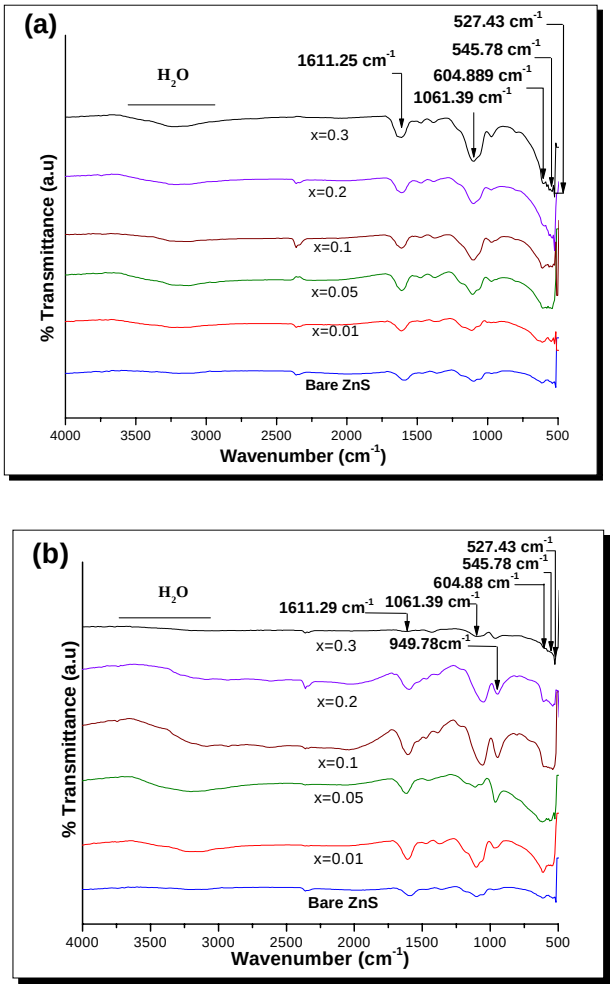

Figure 4: FT-IR spectra for bare, i.e. 'x' = 0, and doped ZnS nanocrystalline powders synthesized at different 'x' values. (a) Cr-doped ZnS. (b) V-doped ZnS.

3.3 SQUID Measurements

Room-temperature SQUID measurements suggested the actual incorporation of dopant species into host ZnS structure. Doped-ZnS powders exhibited paramagnetic or ferromagnetic behavior, depending on the type and concentration of dopant species. Otherwise, the M-H curves should have shown diamagnetism as in bare ZnS. The paramagnetic behavior was observed for 'x' values different from 0.2, (for Cr-doped ZnS) and 0.1 (for V-doped ZnS). In those cases, the magnetic susceptibility was directly proportional to the concentration of dopant species.

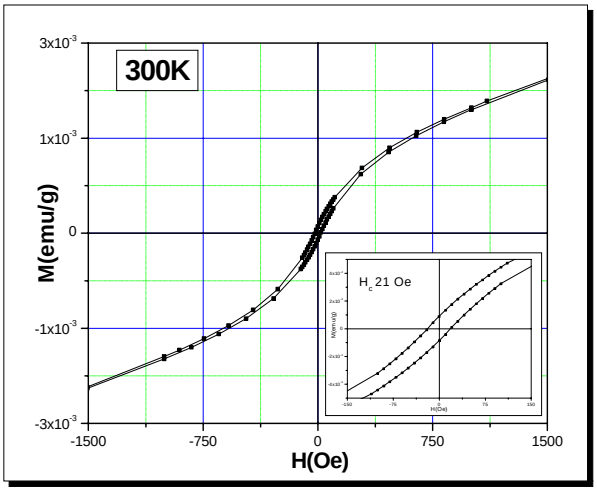

Figure 5: Room-temperature M-H curve for Cr-doped ZnS nanocrystalline powder, 'x' = 0.2. The inset shows the magnification of the same figure around the origin. A weak, but evident coercivity (21 Oe), was observed.

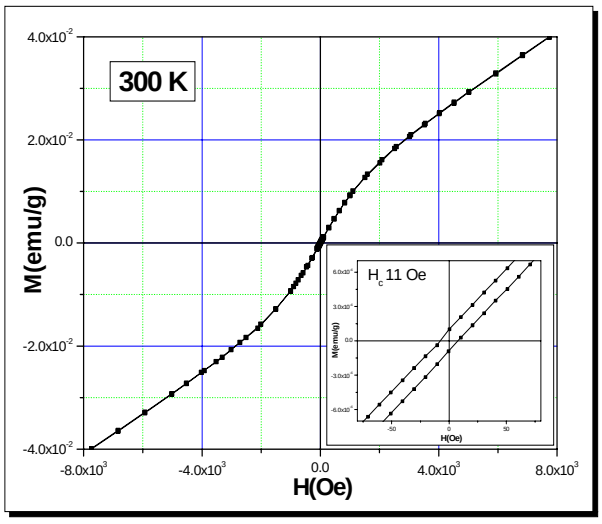

Figure 6: Room temperature M-H curve for V-doped ZnS nanocrystalline powder, 'x' = 0.1. The coercivity in this case was 11Oe.

Figure 5 shows the room-temperature M-H loop for the ZnS doped with Cr at 'x' = 0.2. Although a weak coercivity was observed (21 Oe), ferromagnetic behavior can be suggested for this particular composition. A similar behavior was observed for V-doped ZnS nanocrystals, 'x' = 0.1 (Figure 6). Also in this case, the M-H curve revealed a weak, but evident ferromagnetic behavior (coercivity ~ 11 Oe). Observed ferromagnetism could be attributed to double-exchange mechanism between *3d* electrons in the partially occupied *3d*-orbitals of the neighboring V^{3+} and Cr^{3+} ions. A similar reasoning was proposed by Sato *et al.* for divalent ions of V and Cr [3].

4 CONCLUDING REMARKS

Cr- and V-doped Zinc Sulfide nanocrystalline powders and thin films were synthesized successfully using chemical bath deposition (CBD) process at low temperatures. XRD analyses indicated a mixture of cubic and hexagonal phases in nanocrystalline bare and doped ZnS. AFM imaging revealed fairly uniform deposition of the smooth films. The size of the spherical aggregates in the films was decreased when Cr ions were incorporated into the host structure. Room-temperature magnetic characterization by SQUID evidenced the actual incorporation of Cr and V ions into the ZnS host structure, which exhibited paramagnetic or ferromagnetic behavior depending on the type and concentration of dopant species. A double exchange mechanism between *3d* electrons in the partially occupied *3d*-orbitals of the neighboring V^{3+} and Cr^{3+} ions can explain the observed magnetic behavior.

This material is based upon work supported by NSF-EPSCoR Start-Up and NSF-EPSCoR Nanotechnology Grants. Partial support from NSF-PREM Grant N°. 0351449 is also acknowledged.

REFERENCES

[1] L. Brus, J . Phys. Chem. 1986, 90, 2555-2560.
[2] K. Sooklal, B.S. Cullum, S.M.Angel, C.J.Murphy, J.Phys.Chem.100 (1996)4551.
[3] Sato. K., Yoshida. H. K., Semicond. Sci. Technol., 2002, 17, 367-376.
[4] J. K. Furdyna, J. Appl. Phys. 64, R29 (1988).
[5] W. Q. Peng, S. C. Qu, G. W. Cong, X. Q. hang, Z. G. Wang. J. Cryst. Grow. 282, pp 179-185 (2005)
[6] Perales-Perez O., Tomar M.S., Singh. S.P., Phys. Stat. Sol. (c), 2004, 1, 4, 803-806.
[7] P. A. Angely, S. Dhanuskody. Cryst. Res. Techno., 36, 2001, 11, 1231-1237.