Superlattices and Microstructures 86 (2015) 552–558

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Effect of nickel doping on structural and optical properties of ZnS nanoparticles

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ARTICLE INFO

Article history:
Received 18 July 2015
Accepted 18 August 2015
Available online 19 August 2015

Keywords:
Chemical precipitation method
ZnS
Ni-doped ZnS
XRD
HRTEM

ABSTRACT

In the present work, solution based simple chemical precipitation method has been used to prepare undoped and Ni-doped ZnS nanoparticles. Zinc acetate, sodium sulfide, and nickel nitrate have been used as precursors for the preparation of Ni-doped ZnS nanoparticles. The X-ray diffraction results revealed that the undoped and Ni-doped ZnS nanoparticles exhibit hexagonal Structure. The average grain size of the prepared nanoparticles was found to lie in the range of 2.6–4.2 nm. The SEM images show that the particles have smooth surface and the formation of agglomerated nanoparticles. The compositional analysis results confirm the presence of Ni, Zn and S in the prepared samples. The optical properties of undoped and Ni-doped ZnS quantum dots have been studied using absorption spectra. HRTEM results show that undoped and Ni-doped ZnS nanoparticles exhibit a uniform size distribution with average grain size lying in the range of 2.3–3.6 nm. The synthesized nanoparticles exhibited an emission peak centered at around 612 nm in the PL spectrum.

1. Introduction

Zinc sulfide, an important II–VI semiconducting material, has a wide optical band gap – 3.68 eV for the zinc blende phase, and 3.80 eV for the hexagonal wurtzite phase in the bulk form and high refractive index, its band gap energy has been found to increase as it goes from bulk to nanocrystalline form, which makes it a potentially good material for reflective coatings [1–3]. Zinc sulfide reflective coating also finds extensive applications in other optical devices [4], flat panel displays [5], photocatalysis [6], ultraviolet light-emitting diodes [7], etc. The semiconductor nanoparticles have optical and electrical properties, which are much different from those of bulk materials, and the properties of nanomaterials arise from the quantum confinement effect [8–11]. The nanocrystalline semiconductor particles with size smaller than 15 nm, the size range corresponds to the regime of quantum confinement, for which the spatial extent of the electronic wave function is comparable with the particle size [12,13]. Their optical property, due to quantum confinement effect, dramatically changes and in most cases better when compared to their bulk counterparts. The size dependence of the band gap is the most identified aspect of quantum confinement in semiconductors, the band gap increases as the size of the particles decreases [14].

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http://dx.doi.org/10.1016/j.spmi.2015.08.016
0749-6036/

Doped materials show different type of luminescent properties which strongly depend on the type of dopant ions. These dopant impurities play an important role in changing the electronic structure and transition probabilities of the host material. There are several reports on the photoluminescence properties of ZnS nanostructures doped with various types of impurities like Cu^{2+}, Mn^{2+}, Co^{2+}, Fe^{2+}, rare earth and transition elements etc. [15–18]. In doped ZnS nanocrystals, impurity ion occupies the Zn lattice site and behaves as a trap site for electron and holes. The electrons are excited from the ZnS valence band to conduction band by absorbing the energy equal to or greater than their band gap energy. Subsequent relaxation of these photo- excited electrons to some surface states or levels is followed by radiative decay enabling the luminescence in visible region. Various methods have been developed for the synthesis of Ni doped ZnS nanoparticles, including chemical precipitation [19], sol–gel [20], chemical method [21], chemical vapor deposition [22], molecular beam epitaxy [23] and spray pyrolysis [24].

In this work, a simple chemical precipitation method has been used for the synthesis and the structural and optical properties of the prepared samples have been studied.

2. Experimental

Synthesis of undoped and Ni-doped nanoparticles was carried out by simple chemical precipitation method. Aqueous solution of zinc acetate [$(CH_3COO)_2$ $Zn{\cdot}2H_2O$] and required amount of nickel nitrate [(Ni $(NO_3)_2{\cdot}6H_2O$] were stirred using magnetic stirrer up to 1 h at room temperature. Aqueous solution of sodium sulfide (Na_2S) was added drop wise to the solution (zinc acetate + nickel nitrate) and was stirred for 2 h. After the addition of sodium sulfide solution a precipitate with brown color was obtained. The nanoparticles were initially purified by precipitating the particles with excess double distilled water and the solution obtained was centrifuged at 2500 rpm for 15 min. The sample was obtained as precipitate and after that the samples were dried at 100° C for 6 h.

The structural properties of the prepared nanoparticles were studied using X-ray diffraction method using PANalytical X-ray diffractometer, the surface morphology of the samples has been studied using JEOL JEM-6390 scanning electron microscope (SEM), the composition of the prepared samples has been studied using energy dispersive X-ray analysis (EDAX, Thermo-Noran system Six) and the high resolution transmission electron microscope (HRTEM) images of the prepared ZnS and Ni doped ZnS samples have been recorded using a JEOL JEM 2100 microscope. The optical properties have been studied using the absorbance spectrum recorded using spectrophotometer (JASCO-V-570). The photoluminescence (PL) spectrum was recorded using Perkin–Elmer (LS45) fluorescence spectrometer.

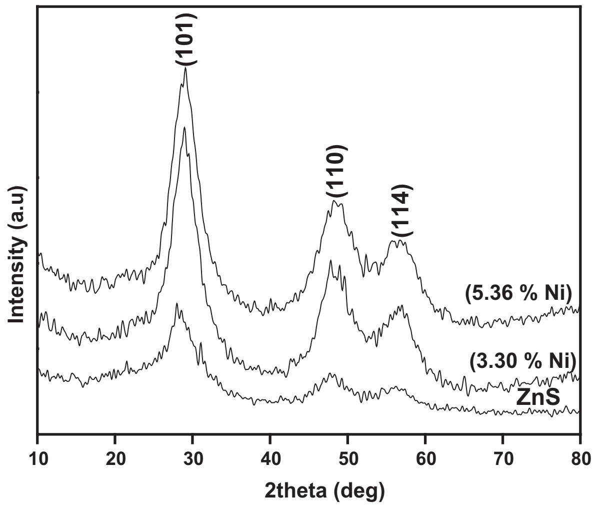

Fig. 1. X-ray diffraction pattern of ZnS and Ni doped ZnS nanoparticles.

Table 1
Structural parameters of undoped and Ni doped ZnS.

Sample	$2\theta(\text{deg})_{(101)}$	d spacing (Å)	Calculated lattice parameter values		Grain size (nm)
			a (Å)	*c* (Å)	
ZnS	27.99°	3.206	3.81	12.43	2.6
3.30% Ni	28.93°	3.102	3.78	12.40	3.4
5.36% Ni	29.17°	3.053	3.76	12.38	4.2