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Structural Characteristics and photoconductivity of Cerium doped Zinc Sulfide Nanoparticles synthesized via co-precipitation method

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ABSTRACT:ZnS:Ce^{3+} nanoparticles were prepared by a simple microwave irradiation method under mild condition. The starting materials for the synthesis of ZnS:Ce^{3+} quantum dots were zinc acetate (R & M Chemical) as zinc source, thioacetamide as a sulfur source, cerium chloride as cerium source and ethylene glycol as a solvent. All chemicals were analytical grade products and used without further purification. The quantum dots of ZnS:Ce^{3+} with cubic structure were characterized by X-ray powder diffraction (XRD), the morphology of the film is seen by scanning electron microscopy (SEM) also by field effect scanning electron microscopy (FESEM) and XRD. Upon exposure to 460 nm light at zero bias voltage, ZnS:Ce^{3+}/p-Si showed a high sensitivity of 4000% and fast response with 12 ms & 17 ms for rise and fall time respectively.

KEYWORDS:Zinc sulfide, nanoparticles, Photoconductivity, precipitation method, Microwave irradiation.

I. INTRODUCTION

The doped nanomaterials have been largely studied in recent years due to their widespread applications in various devices such as sensors, solar cells, lasers, photocatalysts, photodetectors, IR detectors, optical communication, colour television, flat panel display, phosphors, light emitting diodes, etc. [1–6]. ZnS is one of the important luminescent materials with the band gap of 3.7 eV. It is transparent in the visible spectral region having exciton binding energy of 40 meV. Induced sub-band gap transitions in ZnS occur at energies in the visible range that allows the optical detection of traps, radiative recombination centers and surface states. The emission properties of ZnS are frequently being used in solid-state photoluminescence (PL) and electroluminescence studies related with the mechanism of emission in semiconductors. In addition, the small size and high optical activity of ZnS nanoparticles (NPs) make them interesting for optoelectronic applications operating in the ultraviolet region [7].

This paper deals with the photoconductivity (PC) properties of Ce doped ZnS nanocrystals. Photoconductivity is considered to be an important tool for providing information regarding the nature of the photo-excitations. Since last decade the photoconductive properties of the inorganic nanoparticles have become subject of intensive study [8]. Not only because of fundamental interests in the nature of the electronic excitations but also due to their applications in

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wide range of optical and electronic devices. In semiconductors, PC generally arises due to generation of electron–hole pairs because of the interaction of photons with bound electrons of lattice atoms. The conductivity of material depends upon the carrier density and complex process of carrier generation, trapping, and recombination [9].

A good photoconductive device requires not only efficient charge separation but also efficient transport of charge carriers to electrode [10]. It is well known that the rise and decay curves of photocurrent are governed by the trapping states or recombination centers lying in the forbidden energy zone of a photoconductor. Therefore these curves can be used to understand the nature and distribution of traps and recombination centre [11].
There are a number of chemical methods for the synthesis of nanomaterials e.g. co-precipitation, sol gel, hydrothermal, solvo-thermal and auto-combustion etc [12] . Among these chemical techniques, co-precipitation is a popularly used method which provides simple, inexpensive, more productive, rapid preparation and easy control of particle size composition [13]. In this paper we report X-ray diffraction (XRD), SEM, FESEM and PC results of Ce^{3+} doped ZnS nanoparticles synthesized by co-precipitation method. Dark-conductivity and photoconductivity measurements are taken at low voltage. The sensitivity was taken under 460nm light exposure . The rise time and fall time have also been calculated under this visible illumination. There is perhaps no report on photoconductivity of Ce doped ZnS nanoparticles under visible illumination. The objective is to see if there is any change in behavior with the doping with Ce^{3+} ions in host ZnS NPs.

II. EXPERIMENTAL

A.Chemicals

The zinc acetate dehydrate (Zn $(CH_3COOH)_2.2H_2O$), Cerium chloride $CeCl_3$ and thioacitamide (C_2H_5NS) (R & M Chemical) were directly used without special treatment.

B. Sample preparation

The chemicals used for Ce doped ZnS were zinc acetate, cerium chloride and thioacitamide. In a typical experiment 5mM zinc acetate and 0.1mM cerium chloride were mixed in 20ml of ethylene glycol mixed with 60ml of distilled water. In the above solution 20ml of 6mM thioacitamide aqueous solution was added drop wise under vigorous stirring to form ZnS:Ce3+ nanoparticles. The beaker was placed in a high power microwave oven (1100 W) operated using a pulse regime with 20% power for 25 min irradiation time. The formed precipitates were centrifuged (4000 rpm, 10 min) and the residue was washed several times with distilled water and absolute ethanol and dried in vacuum oven at 60 0C for 5h and can be stored for extended period of time.

C. Instrumentation

The crystal structure of ZnS:Ce3+ nanoparticles were characterized by X-ray diffraction (XRD) using a (SHIMADZU-XRD 6000) with Cu Kα radiation (λ = 1.54178A°). For photoconductivity and dark conductivity measurements, a thin film was formed by spin coating method on a chip of p-Si(Sino Wafer Electronic material Co. Ltd.) then Pd electrodes grid using a shadow mask were done by using RF sputtering method (HHV AUTO 500 VACUUM COATER WITH TURBOMOLECULAR PUMPING SYSTEM). The direction of illumination is normal to field across the electrodes. The photo-response was measured using (Newport Orial Cornerstone 130 1/8m Monochromator) as a photo-excitation source. A stabilized dc voltage (0 – 5) V was applied across the sample to which a digital current source (KEITHLEY 2400) for the measurement of dark and photo current. Before measuring photoconductivity of the sample, the sample is first kept in dark till it attains equilibrium. A microwave oven with 1100 W power (LG) was used. Morphology was examined by scanning electron microscope(SEM) and Field Emission scanning electron microscope(FESEM).

III. RESULTS AND DISCUSSION

A.XRD ANALYSIS

The obtained peak positions (1 1 1), (2 2 0) and (3 1 1) indicate zinc blend structure of the samples corresponding to JCPDS file no. 80-0020. The average crystallite size is calculated from Scherer formula [14,15]:

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$D=0.9\lambda/(\beta \cos\theta)$ …….(1)

where D is the crystallite size, λ is the wavelength of radiation used, θ is the Bragg angle and β is the full-width at half-maximum (FWHM) measured in radian. The average crystallite size of the samples lie in the range of 1.97-2.19 nm. The peak broadening indicates nanocrystalline nature and distribution of local strain in the crystal structure arising from defects like dislocation, etc.(see figure 1)[16,17].

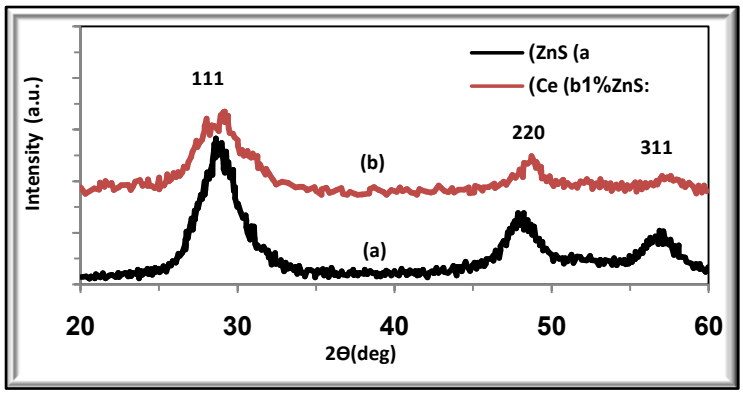

Fig. 1. Shows the XRD patterns of ZnS:Ce^{3+} NPs with concentration of Ce^{3+} (0% and 1%).

The strain and grain size of the samples were calculated by Williamson–Hall(W–H)method. According to this method, the FWHM may be expressed in terms of strain (**ε**) and particle size (D) by the equation [18]:

$$\frac{\beta \cos\theta}{\lambda} = \frac{K}{D} + \frac{\epsilon \sin\theta}{\lambda} \quad \text{……..(2)}$$

where K (0.9) is crystallite shape constant and other parameters have the same meaning as in Eq. (1).The strain **ε**is estimated from the slope of the line and the crystallite size from the intersection with the vertical axis (Fig. 2). The strain of as prepared ZnS:Ce^{3+} NPs are found to be −0.0453, −0.0526with 0% and 1% Ce^{3+} concentrations, respectively. Here negative sign indicates compressive strain in ZnS NPs. The particle sizes obtained at zero strain are 2.19 nm, 1.97 nm with 0%, 1% Ce^{3+}concentrations, respectively. The lattice parameters of cubic zinc blend are calculated by the formula:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad \text{……..…(3)}$$

where ‘a’ is lattice parameter, d_{hkl} is the interplaner separation corresponding to Miller indices h, k, and l. The calculated average value of lattice parameter for prepared ZnS:Ce (0% and 1%) NPs is 0.5321and 0.5324 nm.

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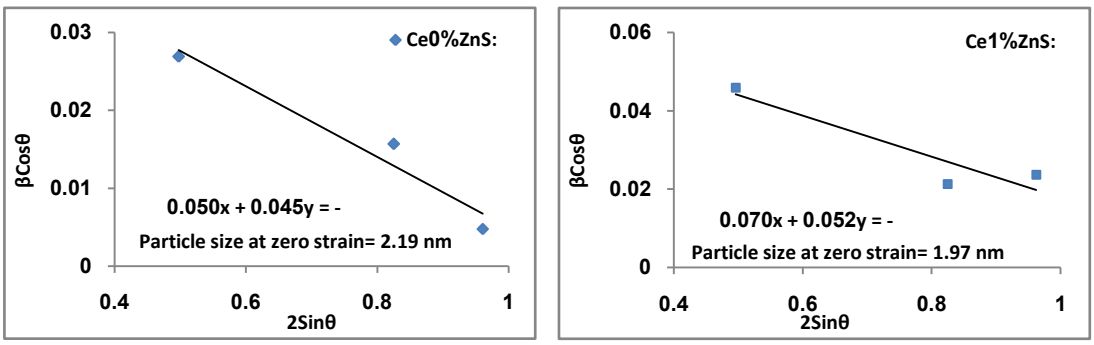
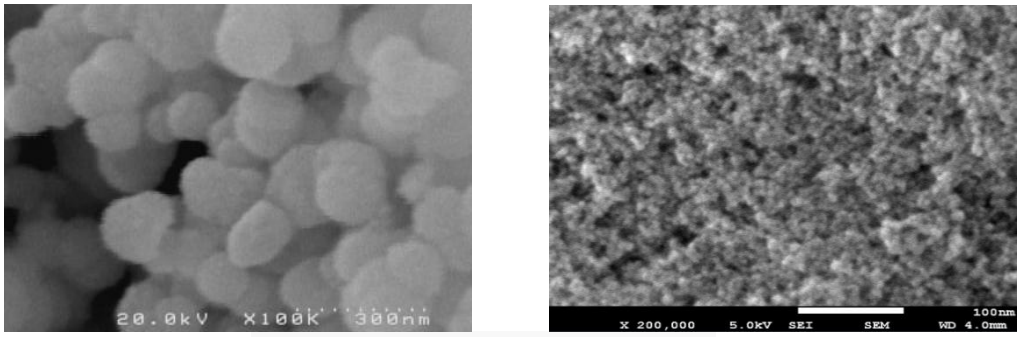


(a) (b)

Fig. 2 Williamson–Hall plot of ZnS:Ce^{3+} NPs; (a) 0% Ce, (b) 1%Ce.

1. Morphology study

The SEM and FESEM images of Ce-doped ZnS nanoparticles synthesized by co-precipitation method as seen in Figure 3a&b indicates that nano-sized particles seem to be homogenous with little agglomeration.



(a) (b)

Fig. 3. (a) SEM & (b) FESEM images of ZnS:Ce nanoparticles.

3. Photoconductivity study

a. Effect of field

The I-V characteristics results (photocurrent , dark current) are shown from the figure 4a, also the sensitivity of the detector upon exposure to 460nm light at zero bias voltage which is around 4000% is shown in the figure 4b&c. The Figure 4(b) shows the repeatability property(ON/OFF) of detector for 8 sec.

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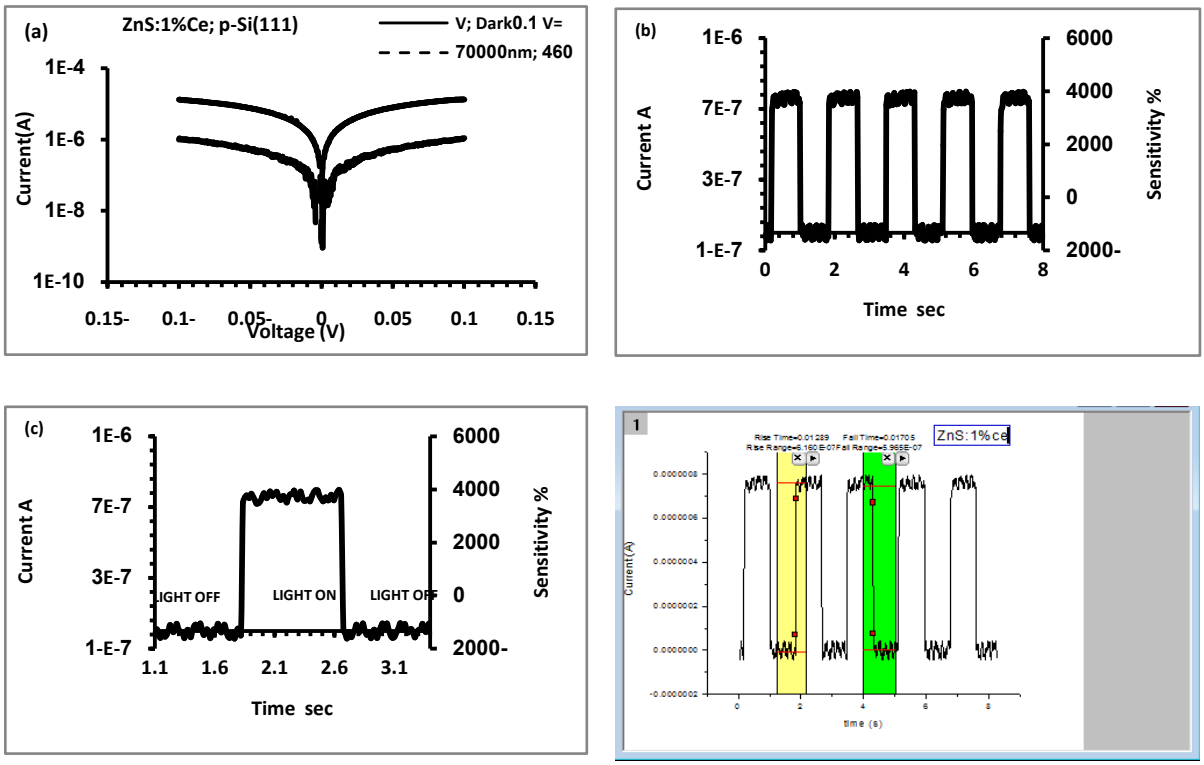

Fig. 4Electrical properties of fabricated ZnS:Ce^{3+}/p-Si photodectors; (a) I-V characteristics, (b) The repeatability property(ON/OFF) of detector for 8 sec, (c) The sensitivity of the detector. (d) values of rise time and fall time calculated by origin program. (b,c&d) at zero volt.

B.Spectral analysis

Fig. 5 shows wavelength dependence of photocurrent for ZnS:1% Ce nanoparticles. Measurements were made for different wavelengths of fixed bias voltage (0.5V) with the help of monochrometer. Photocurrent spectrum of ZnS:1%Ce nanoparticles shows apparently two peaks. The highest photocurrent is observed in UV region at approximately 340 nm and a broad peak centered around 420 nm. UV peak may be attributed to band to band transition [19]. The broad photocurrent peak may be attributed to electronic transitions between deep levels and conduction band. In this higher wavelength region, both excitation and quenching may take place and magnitude of the photocurrent would be the resultant value of the two mechanisms.

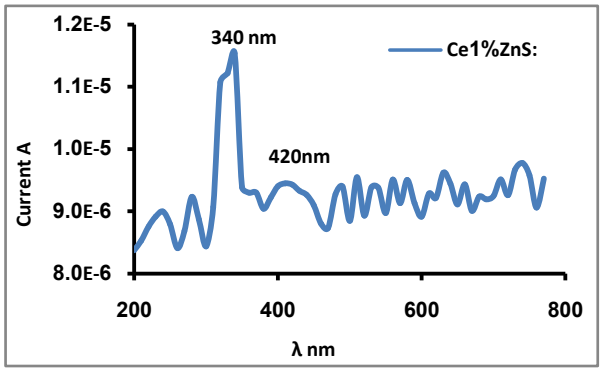

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Fig. 5. Variation of photocurrent as a function of wavelength for 0.5V.

IV. Conclusions

Ce doped ZnS nanoparticles were synthesized by co-precipitation method. The XRD pattern exhibits cubic (zinc blend) structure of ZnS. The size of nanoparticles is estimated to lie in the range of 1.97-2.19 nm. In this present investigation, nontoxic nanomaterials which can be prepared in a simple and cost effective manner have great promise as photoconductive device. Hence, the present study is useful towards authenticating the nanoparticles to be work without bias voltage with high sensitivity.

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