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Structural, optical and photoconductivity study of ZnS nanoparticles synthesized by a low temperature solid state reaction method

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ABSTRACT

In the present work, ZnS nanoparticles have been synthesized by a simple solid state reaction method at different temperatures. X-ray diffraction patterns show that the synthesized ZnS nanoparticles have a zinc blende structure of ZnS. SEM micrographs show formation of spherical nanoparticles of ZnS. UV–vis spectra show blue-shifting in an absorption edge corresponding to all the synthesized ZnS nanoparticles as compared to their bulk counterparts. FTIR study is performed to determine the absorbance and nature of bonds present in synthesized samples. Photoconductivity properties have been investigated by varying voltage and as a function of time. Photocurrent varies linearly for all the synthesized samples. Rise and decay exhibit negative photoconductivity in samples synthesized at lower temperatures.

1. Introduction

In recent years, nanostructured materials have been a subject of intensive research for their potential applications in the fabrication of nanodevices. Due to large surface to volume ratio and quantum confinement effects, the electronic, optical and magnetic properties of nanomaterials get significantly altered as compared to their bulk counterparts [1]. Nanomaterials belonging to II–VI semiconductors e.g. ZnO, ZnS, CdO and CdS have been successfully used in a number of applications such as transistor, light emitting diode (LED) and nanolasers [1]. Among these II–VI semiconductors, ZnS (zinc sulfide) is a technologically versatile and important semiconductor material for many photonic and optoelectronic applications, especially in nanocrystalline forms, due to its wide band gap (3.7 eV) and relatively large exciton binding energy (40 meV) [2]. The band gap of zinc sulfide nanostructures could be extended via quantum confinement effects that make zinc sulfide nanostructures very promising for applications such as photoconductors, nanophotodetectors, ultraviolet light sensors and photoconducting semiconductor switches [3–6]. Photoconductivity (PC) is a useful tool to study the properties of semiconductors. In semiconductors, photoconductivity generally arises due to generation of electron–hole pairs as a result of interaction of photons with bound electrons of lattice atoms [7]. Variation of photocurrent as a function of various parameters e.g. intensity of light, applied field, energy of illumination and temperature gives us useful information regarding the material [8]. Rise and decay curves are governed by the trapping states and recombination centers lying inside the material and can be used to understand the nature and distribution of traps and recombination centers [8]. Extensive study of photoconductivity properties has been performed in nanoparticles, thin films, nanorods, nanowires and mixed lattice of ZnO, ZnS and CdS [1,7–10,23–37]. Several authors have reported photoconductivity in ZnS nanoparticles and nanowires [7–10].

A number of synthesis methods have been used to prepare zinc sulfide nanoparticles including sputtering

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[11], co-evaporation [12], sol–gel method [13], gas phase condensation method [14], co-precipitation method [7], ion complex transformation [15], microwave irradiation [16], ultrasound irradiation [17], and solid state reaction method [18–21]. It has been found that the particle size and the properties of ZnS nanoparticles depend strongly on the specific preparation method and the applied experimental conditions. The solid state reaction method is a low cost, simple and mass scale production method and no solvent is needed in the reaction and hence no waste disposal issues associated with the solvent are needed to be considered [22].

In this work, zinc sulfide nanoparticles are synthesized by the solid state reaction method at low temperature using zinc acetate dehydrate and thioacetamide similar to the synthesis method used by Wang and Hong [19]. Wang and Hong have studied photoluminescence properties of the synthesized zinc sulfide nanoparticles. In the present work, we have studied photoconductivity properties of the synthesized zinc sulfide nanoparticles.

2. Experimental procedure

In the present work, zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and thioacetamide (TAA) (CH_3CSNH_2) of high purity were used to form ZnS nanoparticles procured from E Merk Ltd., Mumbai, India. These chemicals were directly used without special treatment. Zinc sulfide (ZnS) nanoparticles were prepared by the method adopted by Wang and Hong [19]. In a typical synthesis zinc acetate dehydrates and thioacetamide were ground separately by using agate mortar. Then, appropriate amount of zinc acetate dehydrate and thioacetamide powders was mixed together and ground thoroughly. Finally mixed powder was heated in a muffle furnace for 3 h at 150, 200, 300 and 400 °C designated as A, B, C and D samples respectively.

The crystal structure and morphology studies of ZnS nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. Optical absorption spectra of ZnS nanoparticles were recorded on a Varian Cary 5000 spectrometer. FTIR study is performed by a Thermo Nicolet Avatar 370 spectrometer. The photoconductivity and dark conductivity of ZnS nanoparticles were measured using a thick film of powder without any binder. For photoconductivity measurements, the cell was formed by putting a thick layer of powdered samples in between two Cu electrodes etched on a Cu plate (PCB), having a spacing of 1 mm. The powdered layer was pressed with a glass plate which has a slit for providing illumination-area of 0.25 cm^2. In this cell type device, the direction of illumination is normal to field across the electrodes. The cell was mounted in a dark chamber with a slit wherefrom the light is allowed to fall over the cell. The photo-response was measured with a 300 W mercury lamp as a UV–vis photo-excitation source. A stabilized dc field (50–500 V/cm) was applied across the cell, to which a digital dc nano-ammeter, NM-121 (Scientific Equipment, Roorkee), for the measurement of current and RISH Multi 18S with adapter RISH Multi SI 232 were connected in series. All the measurements in the present work are performed at room temperature in ambient air. Before photoconductivity characterization of the sample, the cell is first kept in dark till it attains equilibrium.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of samples A, B, C, and D synthesized by the solid state reaction method. The strongest peaks are identified to originate from (111), (220), and (311) planes in all samples belonging to a cubic (zinc blende) phase of ZnS (JCPDS Card no. 5-0566) [38]. The broadening of the peaks indicates the nanocrystallite nature of the sample. The crystallite size (or grain size) of ZnS nanoparticles was calculated from the Scherrer formula, $D = k\lambda/\beta \cos\theta$, where k denotes the Scherrer constant (the shape factor of the average crystallite and is assumed as $k = 0.9$), D is the particle size, λ is the wavelength of X-ray Cu Kα radiation (1.5406 Å), β is the full width half-maximum (FWHM) in radians of the respective peaks and θ is the Braggs diffraction angle in degrees. The 2θ values corresponding to peaks, d-spacing of the planes, miller indices and average crystallite size are shown in Table 1. From Table 1, we could find that the particle size increases as the temperature of synthesis increases. At high temperature, perhaps, the reaction gets more energy to grow with larger grain size [18]. This indicates that the size of the crystallites can be adjusted by controlling the temperature of the reaction [19].

Fig. 2(a) and (b) **s**hows SEM micrographs of ZnS nanoparticles of sample D. It is evident that particles are of spherical shape and are agglomerated. Due to agglomeration and limited resolution of the used SEM instrument, the actual size of the nanoparticles cannot be determined [39,54].

EDS spectra shown in Fig. 2(c), indicates the presence of Zn and S elements in the atomic ratio (Zn = 56.22% and S = 43.78%). No traces of other elements were noticed in the spectra indicating the purity of sample D.

Fig. 3 shows UV–visible spectra of samples A, B, C and D. The absorption edge is found to be 269, 277, 283 and 285 nm for A, B, C and D respectively. Blue-shift in the absorption edge for all the samples as compared to their bulk counterparts (326 nm) is due to the quantum confinement effect [41]. From Fig. 3, it is observed that the absorption edge gets shifted towards longer wavelength with an increase in temperature of synthesis. This is due to increased particle size with increase in temperature of synthesis as evidenced by Table 1. Increased particle size results in reduced band gap [53].

Fourier transform infrared (FTIR) spectroscopy shown in Fig. 4 for samples A, B, C and D in the range 400–4000 cm^{-1} was performed to study the absorbance properties and the nature of bonds present in the synthesized samples. Corresponding IR peaks and their assignments are listed in Table 2. In the given spectra the absorbance peaks from wave number 3332–3379 cm^{-1} are the peaks representing hydroxyl (–OH) group which shows vibrations of water molecules due to the presence of moisture in the samples [42]. The peaks at 1661–1662 cm^{-1} correspond to C=C group [43–44]. The broad peaks at 1556, 1559 and 1563 cm^{-1} may be attributed to S–S bond [44–45]. The peaks at 1407 and 1437 cm^{-1} are due to