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Photoluminescence properties of nanocrystalline ZnS on nanoporous silicon

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This paper embodies the report on the microwave solvothermal synthesizing of nanocrystalline ZnS particles for optoelectronic device. The effect of different parameters such as time, temperature, solvents, molar ratio of zinc and thiourea on the phase(s) formation of nanocrystalline Zinc Sulphide was investigated. The obtained nanosize ZnS materials were characterized by the X-ray diffraction, Optical absorption measurements, TEM and Photoluminescence studies. The crystallite size of the ZnS nanoparticles was estimated from the X-ray diffraction pattern by using Scherrer's formula. The as prepared material was obtained in the cubic phase, which showed a perfect match with the earlier reports. The Optical absorption edge of ZnS were blue shifted from the absorption edge of bulk ZnS. The estimated band gap value of ZnS was 4.01 eV. The ZnS nano materials were coated on nano porous silicon by screen-printing technique. Luminescence studies indicated room temperature emission in the wavelength ranges from 422.6 to 612 nm, which cover the blue emission to red emission. The emitted light that depending on the created pore size from porous silicon and the size of the ZnS nano particles.

1. Introduction

Low dimensional ZnS semi- conductor quantum materials; particularly quantum wire (1D) and dots (0D) have been predicted to exhibit many properties that can be used to realize novel optical devices. The potential advantage of these materials arises from the spatial confinement of photo-excited electrons and holes that modify their optical properties and other related properties [1,2]. Consequently, much effort has been expended in the preparation and analysis of group II-VI nano materials by various methods, due to their important opto-electronic application for LED and other optical devices based on

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electronic and optical properties [3]. ZnS is an important metal sulphide with various applications like the electroluminescent panels, light converting electrodes, quantum devices, multiplayer dielectric filters and solar cells etc [4–10]. Many research works have been carried out on these materials [11,12]. A variety of methods have been reported for the preparation of nano materials. These methods include soft solution synthesis, synthesized by high gravity environment, sol-gel synthesis, chemical vapor deposition, chemical bath deposition, electrodeposition, hydrothermal conditions, microwave irradiation etc [13–23].

The quantum confinement in semiconductor nanostructure has been investigated over few decades. A recent development concerns nano heterostructures containing layers of two different semiconductors, one nano semicondcuting material coated into the other semiconductor of tuned nano pores base material. In the recent research based on quantum mechanical approach, reports on nano crystalline semiconductor doped with luminescent ions have appeared [24]. It is very important to study which factor plays the dominant role in the luminescence quantum efficiency of these nano particles. A report discussed the quantum efficiency vs particle size; when the particle size decreases from 7 nm to 3.5 nm the quantum efficiency increases from 1% to 18% respectively [25]. Other researchers have found the efficiency of nano crystalline material is dependent on the doping ion concentration [26]. For bulk ZnS doped with Cu, it gave an emission of five regions from UV, blue, green, red and infra red [27], but the efficiency was quite low. In the present work, this nanostructured material emits a good quantum efficiency that covers the emission from blue to red region without doping of ions, depending upon the size of the particle itself.

Novel routes for the synthesis of opto electronic materials are an integral aspect of materials chemistry and physics. The microwave-assisted route is another novel method of synthesis and is a developing area in the field of research. The microwave plays the dominant role to reduce the preparation time and temperature; solvent plays an important role to control the morphology of nano materials ZnS. The higher molar ratio of Thiourea to ZnSO4 is favorable to produce the cubic ZnS phase with fine particles. The nano materials are later used to prepare thin films on nano porous silicon for opto electronic devices.

In the present context, the microwave solvothermal technique has been successfully employed for the preparation of ZnS nano materials and nano porous silicon by electrochemical route. The as prepared nano ZnS and nano porous silicon materials were characterized by XRD, surface morphology, TEM and electrical properties respectively. The device performances fabricated by depositing ZnS nano materials on nano porous silicon of different porosity were observed at the room temperature luminescence effect.

2. Experimental procedure

The ZnS nano materials were prepared via novel microwave solvothermal techniques by using zinc sulfate and thiourea as reactants in different solvents at low temperature (95-170°C) within short time (3 min to 5 min) by irradiation of microwaves. A microwave digestion system (MLS-1200) made by MLS Germany was completely adopted for material preparation. The system operated at an optimized frequency and activated at a maximum power of full range from 0-100%. The digestion teflon vessel contained a suitable ratio of reactants and solvent kept inside the microwave oven for irradiation. The pressure controlled the system and was operated at a maximum pressure of 10 bars; the compounds were treated under microwave irradiation. Programming the microwave system that controlled the rate of reaction. Using variables like temperature, time, solvent and molar ratio of Zinc ions to thiourea on the phase(s) formation, ZnS nano materials carried out the reaction. Optimized molar ratio (1:2) of analytical grades 0.1 M of $ZnSO_4$ and 0.2 M of thiourea were added to a Teflon container of 100ml capacity. The precursors were dissolved in ethanol as a solvent and poured upto 60% of the container [22]. The autoclave was maintained at optimized temperature for more than few minutes to 5 hours and then cooled it at room temperature. The white color synthesized material was filtered out, washed with distilled water for two or more times and finally with ethanol. The prepared white powder was kept dry for few hours in vacuum. Later, the prepared nano material was deposited on etched silicon wafer i.e created pores of nano meter in size. The different pore size was created from the pure silicon wafer by using galvanostatic electrochemical etching method [28] for different current densities. Varying the current densities 2mA/cm2 and 5mA/cm2 different porosity with a size of nano meter level was created.

The as prepared ZnS nano materials and nano porous silicon was characterized by X-ray diffraction. JOEL 8030 model XRD and CuK radiation was used. SEM have been widely used for characterization of surface topography, bulk chemical composition and structure of thin specimens. TEM is one of the versatile instruments available for surface study, fine grains and structural study through diffraction and imaging. In the present study, TEM of model Phillips Analytical EM 400T TEM has been used. The optical properties of ZnS nano materials were studied by UV-Visible spectrophotometer by U-3210, Hitachi Spectrophotometer.

The photoluminescence (PL) spectra were carried out at room temperature under the illumination of two different wavelengths: 270-nm line of ultraviolet light was used for excitation, to obtain PL emission spectra. After obtaining the PL peak wavelength from each PL emission spectra, the Ar+ lasers of different peak wavelength, in the range of 400-600 nm were used for illumination. The

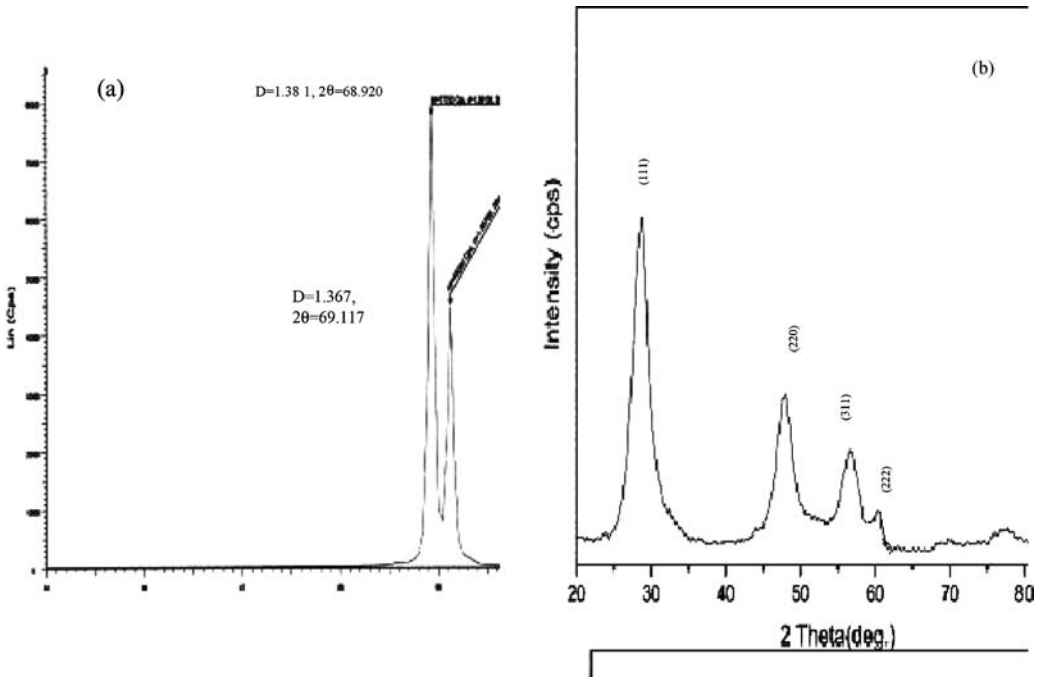

Figure 1 XRD pattern of the (a) etched silicon at a current density of 2mA/cm^2 (b) as prepared ZnS nanoparticles by microwave irradiation method.

PL signal was dispersed using the double monochromator, and the PL signal was analyzed using fluorescence spectrophotometer.

3. Result and discussion

3.1. X-ray diffraction studies

Structural analysis was made on the as prepared ZnS nano material by irradiating microwave under optimized condition and nano porous silicon also. X-ray diffractograms of the nano ZnS materials was obtained for the material dissolved in solvent like ethanol, water and ethylene glycol. The x-ray diffractograms (Fig. 1) indicated the polycrystalline nature of the materials. The prominent peaked corresponding to (111), (220), (311) and (222) reflections to ZnS were observed at 2β of 28.79, 47.63, 56.51 and 59.16o respectively. The as prepared materials exhibited cubic structure with preferential orientation in the direction of (111) direction. By using the same X-ray pattern, the full width at half maximum (FWHM) was obtained for all the materials. Phase identification was made and crystalline size of the materials was determined from FWHM by Scherrer's equation [29]. The average crystalline size was calculated to be 22 nm, which was in good agreement with TEM result. The lattice parameter was estimated and the values of 'a' was 5.40 respectively [30]. Fig-1a shows the diffraction pattern of nano porous silicon prepared by electrochemical etching with suitable ratios of the electrolyte under galvanostatic condition. The etching was carried out with same timings but with different current densities. After etching, the diffraction pattern showed that the silicon crystal was moving towards amorphous in nature as the current density was increased to above 5mA/cm2. The lattice parameters were agreed well with the earlier reports.

3.2. Electron microscope studies

The transmission electron imaging of nano ZnS is shown in Fig.2. The ZnS nano material was prepared under ZnSO4: Tu (1:2) as precursors dissolved in ethanol as solvent. It was observed that nano ZnS fringes were observed clearly and comparable with the XRD data's. The electron diffraction pattern of nano ZnS, diffraction rings assigned to (111) and (220) (Fig. 2a) of cubic nano ZnScrystallites were observed. In the TEM images, the shape of these nano particles was spherical shape and in some area agglomeration was also observed. The average size (Fig. 2b) of the particles was in the range of 10-20 nm, which was also a supportive data for this research and comparable with XRD result. Fig. 3a shows the plan view SEM image of p-type Si wafer surface before anodization. The smooth Si wafer surface was washed thoroughly with cleaning different processes before electrochemical etching. As a result, no contamination (particulates, dust, dirt and oils in fingerprints) was presented on the Si wafer surface. Fig. 3b and c show the plan view SEM image of the nano porous silicon (NPS) samples formed at current densities of 2 and 5 mA/cm2 for 10 minutes respectively. It was observed from the both micrographs, anodization of p-type Si resulted in a porous lattice. From Fig.3(c), the NPS sample etched at 5 mA/cm2 for 10 minutes had the common pore

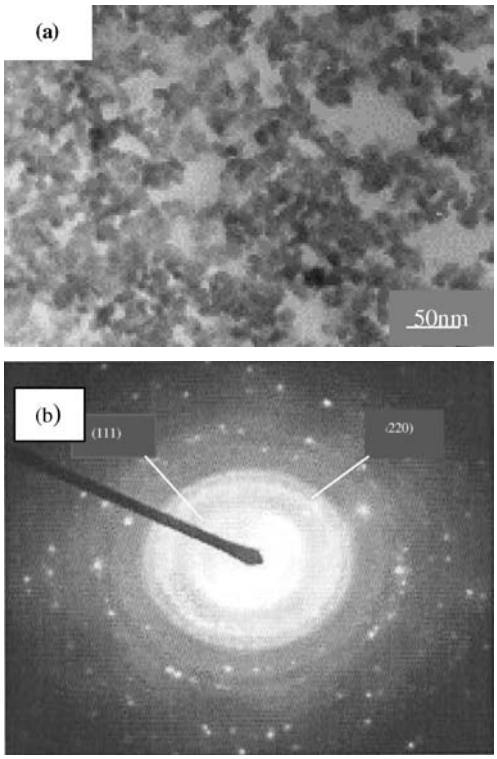

Figure 2 TEM of ZnS nanoparticles prepared under microwave irradiation method.

size of 40-120 nm, while from Fig.3 (b), the pore networks with 15-50 nm in common size were distributed over the NPS sample etched at 2 mA/cm2 for 10 minutes. As the anodization current density decreased for the same etching time, the opening structures became smaller in sizes, and the pore network became more homogeneous and more interconnected. The increase in the anodization time also resulted in the mass of chemically dissolved, which became higher, because of longer residence of Si substrate in HF aqueous solution. By adjusting the current density of anodization with fixed etching time, the other relation could make in term of the pore size and the topological distribution.

3.3. Optical absorption studies

Optical absorption studies were carried out on the ZnS nano materials coated on nano porous silicon. The ZnS nano material is a direct band gap semiconductor and the absorption coefficient at various wavelengths has been calculated with [29] optimum thickness. The band gap of the ZnS nano materials was determined by plotting a graph between h vs (h)2. The extrapolation of the linear region to the x-axis estimated the band gap of the material. Fig 4 indicates the direct band gap of 4.01 eV for the as prepared ZnS nano material with absorption coefficient of 104 cm^{-1} was obtained. The spectra of the corresponding ZnS nano materials were superimposed with a periodic

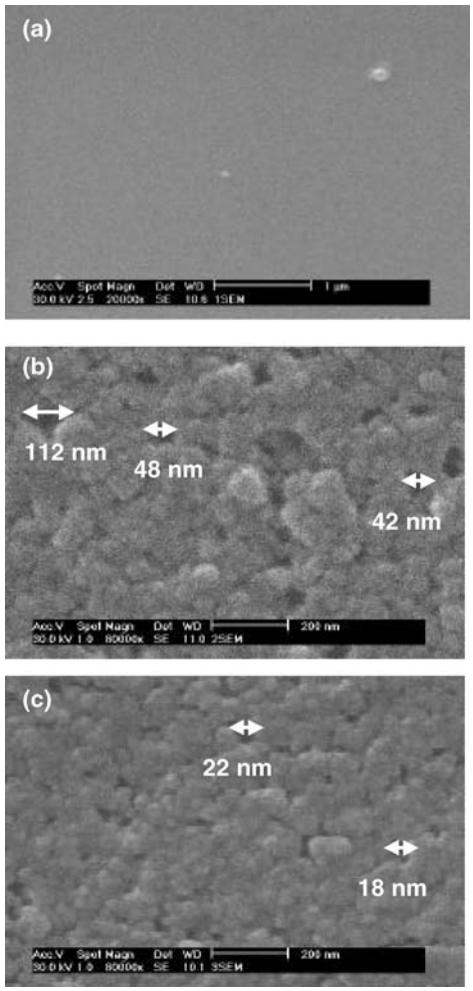

Figure 3 SEM micrographs of the nanoporous silicon samples etched at the current density of 0.9 mA/cm^2 for (a) un -etched Si wafer (b) 15 min, and (b) 10 min, respectively.

oscillation, which increased in frequency with, decrease wavelength [31]. As the particle size decreases the optical absorption was maximum at 310 nm.

3.4. Luminescence measurements

3.4.1. PL studies for NPS and nano ZnS

The excitation peaks for NPS corresponding to higher energy at 382nm, which lead to emission spectrum with 612nm. The room temperature photoluminescence data of the nano porous silicon surface formed at current densities 2 and $5mA/cm^2$ were prepared. It was observed that the emission peak (Fig. 5a, b) shifted from 612nm to 720nm as the current density and size of the pore increases. The luminescence effect for the as prepared ZnS nano material without doping showed a very less intense in the visible region. The main probe to enhance the luminescence intensity was achieved by doping of metal ions like Mn2+, Cu2+ etc into the ZnS nano materials [32]; But in this work, the intensity have been enhanced by material itself

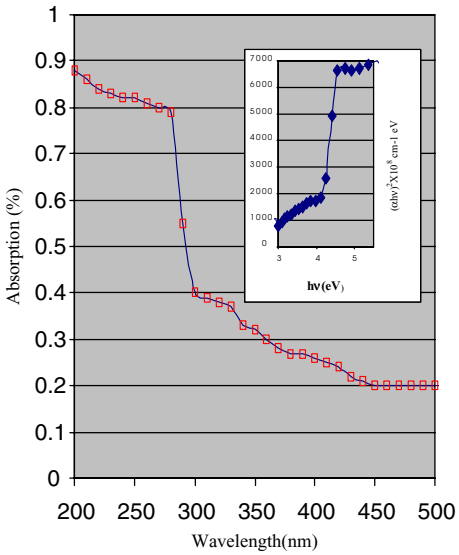

Figure 4 Optical absorption studies of nanocrystalline ZnS thin film.

without doping of any ions. The excitation source was the UV lamp with a wavelength of 270nm, which was greater than the band gap of the ZnS nano material. The emission spectrum of ZnS nano materials in the UV region two peaks was identified. The earlier report stated that only one UV peak was observed at 430nm for the ZnS colloid [33] and that peak was assigned to sulfur defects. After irradiation the peak was shifted towards deep UV region, which was attributed to transitions involving either interstitial Zinc or Sulfur atoms. In the present work, the emission spectra were observed at 422.2nm and 435.6nm respectively [34]. This transition involved a type of defect like interstitial state or vacancy respectively. Fig-5c indicates the two wavelengths that were compared with

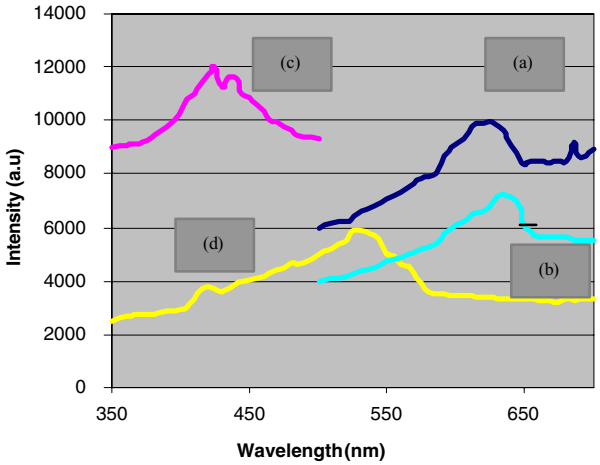

Figure 5 Photoluminescence emission spectra of (a) nanoporous silicon etched at 2mA/cm^2 (b) nanoporous silicon etched at 5 mA/cm^2 (c) ZnS nanoparticles prepared under microwave irradiation coated on ITO glass (d) ZnS nanoparticles coated on nanoporous silicon (2mA/cm^2).

the earlier reports and resulted that the emission at 422nm belongs to interstitial sulfur or Zinc and 435.6nm corresponding to the Zinc or Sulfur vacancies.

3.4.2. PL studies for NPS/nano ZnS

The emission spectrum was measured for the nano materials deposited on the nano porous silicon. At an optimum nano size of nano porous Si / nano ZnS, the luminescence spectra showed the radiative recombination at the lower wavelength for the nano ZnS material and higher wavelength for nano porous silicon. Under optimized condition, the as prepared nano ZnS material with NPS radiated its light emission very close to white region [Fig. 5d]. The maximum emission was obtained by tuning the size of the pores from the silicon material with the same size of nano ZnS material that was introduced into that pore. The emitted light was red emission from NPS, blue from nano ZnS and green emission from nano ZnS/NPS. The three materials altogether emitted white light emission. The maximum emission was observed at 530nm with an excitation of 420 nm for nano ZnS material coated on nano porous material (average pore size of 10-50nm)[30]. The emission results were compared with the previous reports, the emission wavelength was slightly towards blue side region that showed the uniformity of the material coverage, which was very good.

4. Conclusion

Nano ZnS material of size 10-20nm was prepared from microwave irradiation. The prepared materials were characterized and confirmed that the size was in nano meter range. For the device purpose, a thin layer of nano ZnS was successfully deposited on nano porous silicon. From the emission spectrum, it was observed that wavelength identified for the nano porous silicon at red region and towards blue side for the ZnS nano materials which covered the whole visible spectrum. Under optimized condition, the result showed that the optical properties for the nano ZnS/nano porous silicon emitted white light at a wavelength of 530nm. This emission in white color light would be very much useful for electronic industry. The obtained result was compared with the earlier reports and agreed well with each other. Further work is in progress to improve the intensity and brightness of the white light emission.

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