



SYNTHESIS, STRUCTURAL AND MORPHOLOGICAL ANALYSIS OF ZNO/CDS CORE-SHELL HETEROSTRUCTURE

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Abstract- In the present work synthesis, structural and morphological analysis of ZnO nanowires with CdS layer core-shell heterostructure is reported. The sol-gel and hydrothermal method was used to synthesize the core shell heterostructure. X-ray diffraction spectrum, field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), UV-Visible spectroscopy were used to identify and analyze the structural properties, samples morphology and energy band gap of as prepared heterostructure. The crystallite size of ZnO has been obtained approximately 24 nm and that for CdS is approximately 20 nm. HR-TEM and FESEM images show that the CdS shell was deposited on ZnO nanowires and the thickness of core-shell structures was found to be in the range of 30 to 80 nm. UV-visible spectroscopy was used to examine the energy band gap revealing the fact that energy band gap reduces to 2.30eV for present structure from 3.37eV for pure ZnO.
Keywords: Core-shell, XRD, UV-Vis, FESEM, TEM, Hetrostructure.

1. INTRODUCTION

From last few centuries major proportion of our energy requirement has come from non-renewable sources such as fossil fuel, oil and coal. Burning these fuels generates harmful gases and is a major source of environmental pollution. Their supply is limited and will finally run out at some point of time in the future. Hence the need of the time is to find more renewable and clean ways of generating energy. The natural renewable energy resources are sun, wind, wave, biomass and geothermal energies. Nanomaterials are widely studied and promising materials for energy conservation from these renewable energy sources [1]. In particular II-VI group of semiconductors are of significant interest for solar energy conversion due to their optical, optoelectronic and photovoltaic properties [2-4]. ZnO and TiO₂ are two materials widely being studied for applications in a variety of optoelectronic applications. Though the efficiency of TiO₂ based devices is higher and ZnO with larger bandgap and rapid internal recombination of photogenerated electron hole pairs result in lower optical efficiency. This factor reduces the application of ZnO in optoelectronic field and is the area of research these days because ZnO based devices are still significant due to higher electron mobility and non toxic nature of ZnO. ZnO is a direct band gap material with band gap of 3.37 eV and absorb very small proportion of solar spectrum (3-5%) [5]. Different studies such as doping and combining with other semiconductors have been carried out to extend the spectral response and improve the photoresponse of ZnO. One approach is semiconductor heterojunction/heterostructure formation which can potentially improve the optical absorption capacity [6]. To extend photoconversion to the visible range various semiconductors have been coupled to ZnO nanostructures. CdS is one of such material which has similar lattice structure as ZnO and a band gap of 2.4 eV. Various one-dimensional (1D) ZnO nanostructures such as nanowires, nanorods, nanotubes, nanoribbons etc. have been studied widely for their applications in optics, electronics, piezoelectronics, sensing etc. Being a non toxic material and due to better charge transport 1D ZnO nanostructures are potential candidates for exploration of optoelectronic properties and are widely used for clean and sustainable solar energy conversion devices [7]. There are different techniques for synthesis of one dimensional nanostructures such as nanowires, nanobelts, nanotubes etc. The different techniques for fabrication of one dimensional nanostructures are MOCVD, chemical vapor deposition, solution based methods, template assisted methods [8-15] etc. In the present work sol gel method and hydrothermal techniques are used. For shell layer deposition different methods like successive ionic layer deposition, pulsed layer deposition, spray pyrolysis etc are used [16-18]. In the present work chemical bath deposition method is used which is low temperature, simple and cost effective technique.

2. MATERIAL AND METHODS

The chemicals used were zinc acetate dihydrate (C₄ H₆ O₄ Zn₂H₂ O), monoethanolamine (NH₂CH₂CH₂OH), zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O), hexamethylenetetramine (C₆H₁₂N₄) ammonium hydroxide (NH₄OH), cadmium sulfate (CdSO₄) thiourea (NH₂CSNH₂) All chemicals were purchased from Sigma Aldrich and of analytical grade and used without further purification. ZnO nanowires with CdS layer core-shell heterostructure was synthesized by chemical solution method. ZnO seed layer is deposited on ITO substrate by spin coating method. The precursor used is solution of zinc acetate dihydrate and monoethanolamine. The prepared sample is annealed at a temperature of 400°C for 3 hrs. Then nanowires array was

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grown on annealed seeded layer by hydrothermal method using aqueous solution of zinc nitrate hexahydrate and hexamethylenetetramine with equal concentration of 50mM. Chemical bath deposition method was further used to make the shell structure on the ITO substrates with nanowires array at a temperature of 600C for 80 min. After this the substrate was taken out and rinsed with de-ionized (DI) water and dried. The precursor for CdS shell is prepared by ammonium hydroxide with 1M concentration, cadmium sulphate with 1mM and thiourea with 15mM concentration as sulphur source in DI water.

3. RESULTS AND DISCUSSION

Different characterization techniques such as X-ray diffraction (XRD), FESEM, TEM and UV-Visible spectroscopy have been utilized to characterize the samples structural properties, morphology, and band gap of as prepared sample.

3.1 XRD Analysis

Figure 1 shows X-ray diffraction pattern of ZnO-CdS core shell nanowires array. The as prepared sample was analysed by using PANalytical X'Pert Pro diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation at 45kV and 40 mA over the 2θ range of 10-80. The diffraction peaks corresponding to (100), (002), (101), (103) crystal planes suggests the formation of hexagonal ZnO nanowires structures that is also confirmed by the values in JCPDS file(800075). The peaks corresponding to hexagonal CdS are corresponding to crystal planes (103), (203), (210). The obtained core-shell nanostructures share the peaks of both the ZnO and CdS and no other peaks were detected. An average crystallite size of CdS and ZnO has been obtained using the Scherrer formula for crystallite size:

$$D = 0.94\lambda / \beta \cos \theta \quad (1)$$

Where λ is the wavelength of the X-ray radiation (0.154056 nm), θ is diffraction angle and β is the full width at half maximum (FWHM). The average crystallite size value for ZnO comes out to be approximately 24 nm and that for CdS is approximately 20 nm.

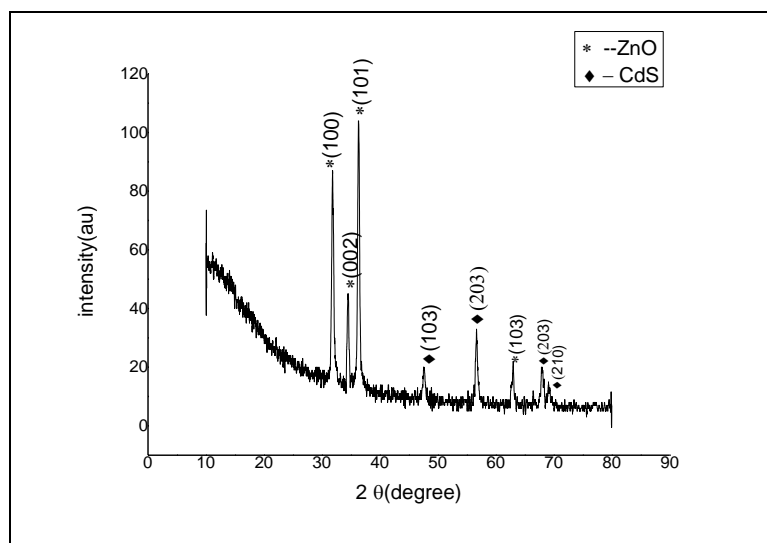


Fig. 1-XRD spectrum of ZnO-CdS core shell structure

3.2 FE-SEM Analysis

Morphology of grown core-shell nanostructures was imaged by FE-SEM (SU8010-HITACHI). Fig. 2 shows the FE-SEM image of as prepared core-shell structure. The image clearly shows the formation of ZnO-CdS coaxial core shell nanowire structure. The wire like structure can be seen with the hexagonal face structure which is also confirmed by the XRD peaks corresponding to hexagonal ZnO as shown in Fig. 1.

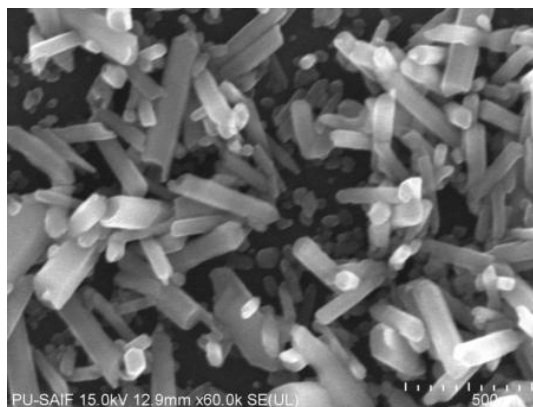


Fig. 2 FE-SEM images of ZnO-CdS core shell structure

3.3 TEM Analysis

Transmission Electron Microscopy (TEM) was used to analyze the structure in detail as it is not possible to analyze the inner core structure with FE-SEM. The images in Fig. 3 and Fig. 4 clearly show the formation of core shell structure. In Fig. 3 the diameter of core shell structure is 62.6 nm and that for core is measured as 55.1 nm. It is clearly revealed from the images that the diameter of core shell structure is below 100 nm. Though it is not constant throughout the nanowire array because no templates are used but the thickness of core-shell structures comes out to be in the range of 30 to 80 nm.

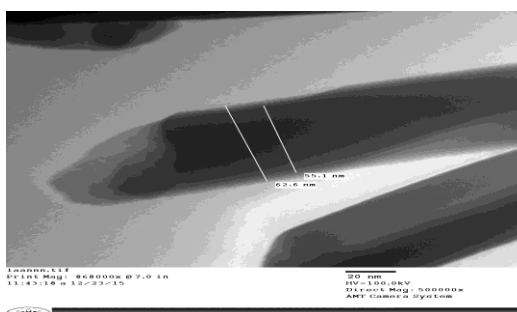


Fig. 3- TEM image of ZnO-CdS core-shell structure

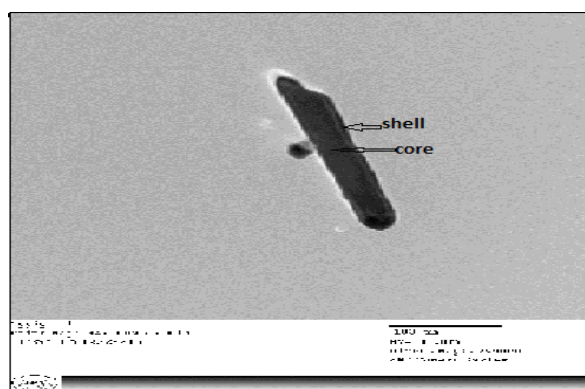


Fig. 4 -TEM image of ZnO-CdS core-shell structure

3.4 UV-visible spectroscopy

The UV-visible spectroscopy was used to study the absorption spectrum of as prepared sample and to find the band gap of ZnO-CdS core shell nanostructures. Figure 5 shows the absorption spectra of nanostructures recorded at the room temperature in the wavelength range of 300–800 nm. UV-visible spectroscopy was used to analyze the energy band gap (as shown in inset

of fig 5) that comes out to be 2.30 eV which is less than that of bare ZnO nanowires i.e. 3.37 eV. So band gap reduction was achieved by core shell hetrostructure.

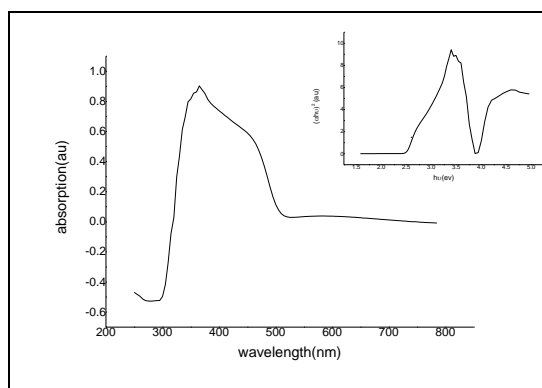


Fig. 5- UV-Visible and Tauc plot of ZnO-CdS core-shell Structure

4. CONCLUSION

The ZnO-CdS core shell nanostructure has been synthesized using sol-gel and hydrothermal method. The XRD pattern shows the crystal structure of ZnO and CdS. On the basis of observation of FESEM and TEM results it can be concluded that the core shell structure has been formed with the width below 100 nm. Further the UV-Vis absorption spectra shows the reduced band gap of the ZnO-CdS core shell structure than the ZnO nanowires. Now this structure can be used as a photoanode in dye sensitized solar cell as this hetrostructure also reduces the recombination rate of free electrons generated by sun light falling on dye in DSSC and fasten the charge transport through the photoanode.

5. ACKNOWLEDGEMENT

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