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Particle Size Analysis for Different Substrate of ZnS/ZnO Thin Film in CBD Technique

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Abstract: The studies of the semiconductor core shell nanoparticles have advanced at a rapid pace because of the fact that their optical properties can be systematically tuned by varying their sizes. ZnS/ZnO thin films were deposited on FTO and glass substrate by using chemical bath deposition (CBD) technique. The chemical baths contain the solutions to zinc acetate, thiourea, ammonia and deionized water. The deposition of the samples was prepared by 300min. The deposition parameters such as pH of the bath; deposition time, temperature etc. be optimized. The morphological analysis of thin films is studied by using Scanning Electron Microscope instruments. The SEM pictures to revealing that it is in flower like structure of micrometer size of FTO and cluster formation of glass substrate. The estimated average grain size of FTO is 50-60nm it is whitish well substrate covered and for glass is 30-40nm. Elemental analysis of ZnS/ZnO thin film is determined by using EDAX. The proportion of the constituent elements measured was Zn = 34.39% for FTO substrate is higher than the glass substrate Zn=16.06%. The proportion of the constituent elements measured was S=1.35%, O=54.95% for FTO substrate is lower than the glass substrate S= 3.00% O=62.31%. The optical absorbance of thin films samples was measured by UV spectroscopy within wavelength range of 200-800 nm. The optical band gap between ZnS/ZnO thin film for FTO and glass substrate is 2.56 and 3.55eV. The quantum yield of ZnS/ZnO thin films is determined by using PL excitation and emission studies. A comparison between the value of bulk ZnS/ZnO of both FTO and Glass substrate shows that the band edge is red-shifted. PL intensity is increased to FTO substrate and decreased from glass substrate. The Physical properties of core shell ZnS/ZnO thin film materials are raised in the optoelectronic devices.

Keywords: ZnS/ZnO thin film, CBD, UV, PL, SEM, and EDAX studies.

1 Introduction:

The semiconducting materials are expected to be the novel materials for the Optoelectronic devices. ZnS/ZnO is a Wide energy band gap between II–VI group elements. ZnS/ZnO has been used extensively as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathode luminescence (CL) devices. It's due to an enhancement the chemical stability are compared to other chalcogenides materials. ZnS/ZnO is having a wide optical band gap (3.67eV, 3.3eV), rendering it a very attractive material for ZnS/ZnO optical application especially in nanocrystalline structures are zinc blende and wurtzite [1, 2]. ZnO is a white powder that is insoluble in water, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. It occurs naturally as the mineral zincates.

This semiconductor has several favorable properties, including good transparency, high electron density,

wide band gap, and strong room-temperature with luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes. The optical transition is direct band structure [3]. It is widely used in infrared optical materials transmitting from visible wavelengths is just over from 12 micrometers. ZnS/ZnO thin films were deposited by chemical methods of FTO and glass substrate. Characterizations are carried out an optical properties, luminescence, surface Morphology and elemental analysis studies [4].

2 Experimental:

A typical process was followed to deposit ZnS/ZnO thin film. The deposition bathed to consist of aqueous solution to 50ml(0.2M) Zinc acetate, 50 ml(.2M) Thiourea, 10ml(25%) ammonia(NH₃) and deionized water to make a total volume of 50ml[5,6]. In this study, Ammonia solution was added for the CBD process. The solution was placed in a glass beaker and controlled at 65°C for 5hrs. The pH value of the prepared solution was adjusted to the deposition by using

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NH_3 and kept at a value of 10. Film deposition starts with the NH_3 is added. During the deposition the bath solution was stirred. The growth time was 300 mins. At the end of the deposition process the substrate was removed from the glass beaked and clean by acetone and dried .The film grown on the backside of the substrates was removed by using 1:10 HCL solution [6,7].

3 Results and Discussion:

3.1 UV analysis

Table 3.1: Optical Parameters of ZnS/ZnO thin film

| Sample | Absorption coefficient (k), cm^{-1} | Thickness of the film (t) Nm | Refractive index (n) | Energy Gab (Eg) (eV) | Reference |
|--------|--|------------------------------|----------------------|----------------------|-----------|
| FTO | 58.76 | 256.5405 | 6.81 | 2.56 | [8,9] |
| Glass | 67.88 | 106.5397 | 3.06 | 3.55 | [5,10] |

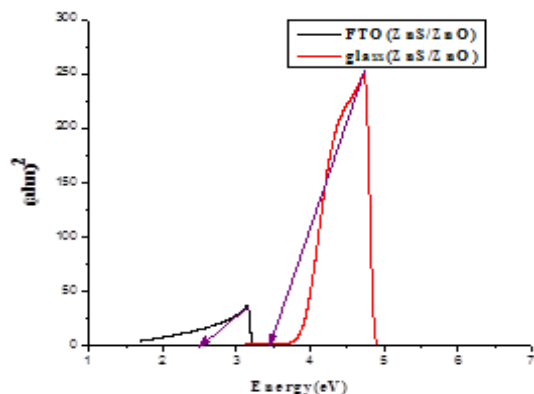


Fig 3.1(a) optical band gap of ZnS/ZnO nanoparticles.

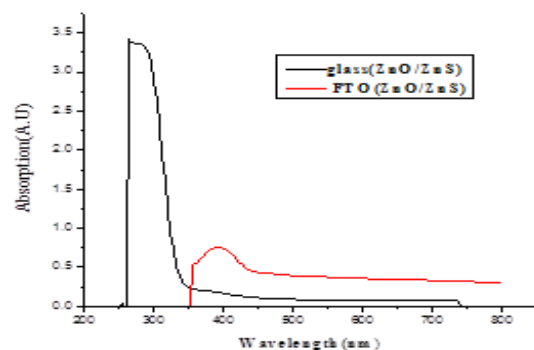


Fig 3.1(b) typical absorption spectrum of ZnS/ZnO nanoparticles.

The optical properties of ZnS/ZnO are coated into glass and ZnS/ZnO is coated on FTO substrates are determined from UV-Spectral measurements in the range of 200-800nm. Fig 3.1(a) UV-visible absorption spectra, Fig 3.1 (b) UV-visible energy spectra as shown. The materials are studied for the optical parameter of an Absorption coefficient (k),

Thickness of the film (t), Refractive index (n) and Optical energy band gab (E.g.).The ZnS/ZnO was prepared by the chemical bath deposition technique. The pH 10 and bath temperature is 65°C it's maintained and coated into glass and FTO substrate. In the absorption coefficient of unlike substrate is significantly changed because glass (ZnS/ZnO) is 33.8% and FTO (ZnS/ZnO) is 7.8% [6].Fig 3.1 (b) shows the absorption vs. wavelength spectra of ZnS/ZnO thin films of thickness 256 nm and 106 nm respectively. The optical energy band gaps between FTO and Glass is 2.56 and 3.55, Absorption coefficient (k), are 58.76 and 67.88, refractive index (n) are 6.81 and 3.06 respectively [5,8,9]. The plot of absorption coefficient ($\alpha h\nu$)² vs. photon energy (hν) of thin films is shown in the Fig 3.1 (a). These results are seen in the Table 3.1.1.

3.2 PL analysis

ZnS/ZnO nanoparticles are to be investigated the luminescence properties. Fig 2 (a) and 2(b) show the photoluminescence excitation and emission spectrum of ZnS/ZnO. Owing to these two levels in the energy gap, two optical transitions to the observed UV range can occur. For the pure sample of FTO and Glass substrate emission peaks are observed at about 503nm and 496nm excitation peaks are observed at about 501nm and 494nm when excited by UV light [11,12]. The value of the optical band gap energy is found to be 2.56eV and 3.55eV. A comparison of the value of bulk ZnS/ZnO of both FTO and Glass substrate shows that the band edge is red-shifted. The quantum yield of ZnS/ZnO thin film has been determined by using PL excitation and emission of FTO and Glass substrate is 1.00 and 0.96. PL intensity is increased from FTO substrate and decreased to glass substrate. PL Emission and Excitation wavelength of ZnS/ZnO thin film in Table.3.1.2.

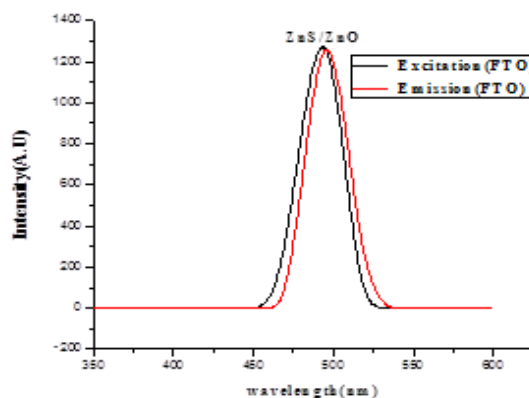


Fig3.2 (a): Room temperature photoluminescence Excitation and Emission spectrum of ZnS/ZnO Nanoparticles (FTO).

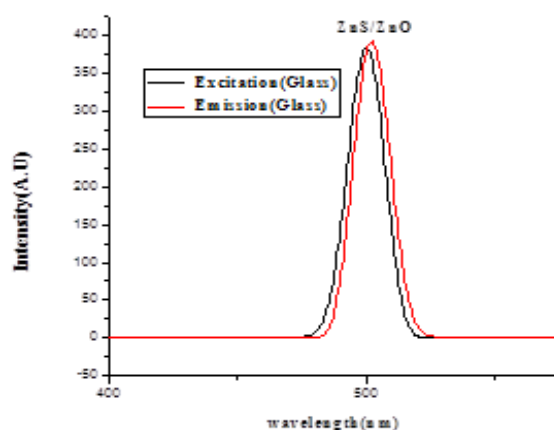


Fig3.2 (b): Room temperature photoluminescence Excitation and Emission spectrum of ZnS/ZnO Nanoparticles (glass).

Table 3.2 PL Emission and Excitation wavelength of ZnS/ZnO thin film.

| Substrate | Excitation Wavelength (nm) | Emission Wavelength (nm) | Energy gap (E_g) (eV) | Quantum yield |
|-----------|----------------------------|--------------------------|---------------------------|---------------|
| FTO | 501 | 502 | 2.56 | 1.00 |
| Glass | 494 | 495 | 3.55 | 0.96 |

3.3 Morphology analysis

Scanning electron microscopes is a versatile technique for studying microstructure of thin film. The surface morphology of ZnS/ZnO thin film coated into FTO and Glass substrate characterized by scanning electron microscope (SEM) with an accelerating voltage 20kv. ZnS/ZnO thin film, we employed with an FTO and Glass substrate at instance duration 60 min as shown in Figs. 3.3(a) to (d). Fig 3.3(a-d) shows that ZnS/ZnO films at x 30000 and 50000 magnification of scale bar length is 200nm and 1 μ m for FTO and glass substrate. The SEM pictures to reveal that it is in flower like structure of micrometer size for FTO and cluster formation for glass substrate. The estimated average grain size of FTO is 60nm and it is whitish and well substrate covered and of glass is plain. The SEM micrographs of the films deposited with FTO and Glass substrate shows the distribution of grains, which covers the surface of the substrate completely [13].

Table3.3: Analysis for SEM pictures

| Sample | Magnification(x) | particle size(nm) |
|--------|------------------|-------------------|
| FTO | 30000 | 50 |
| | 50000 | 60 |
| Glass | 30000 | 30 |
| | 50000 | 40 |

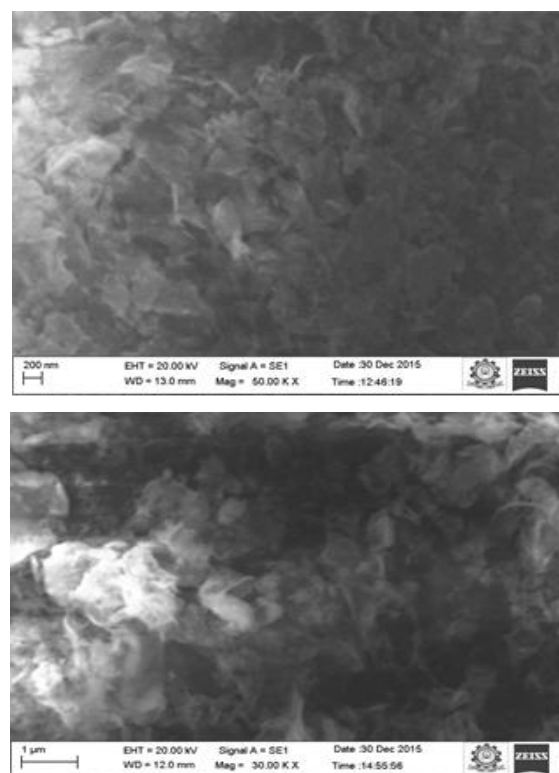


Fig3.3 (a) and (b): SEM images for ZnS/ZnO nanoparticles (Glass).

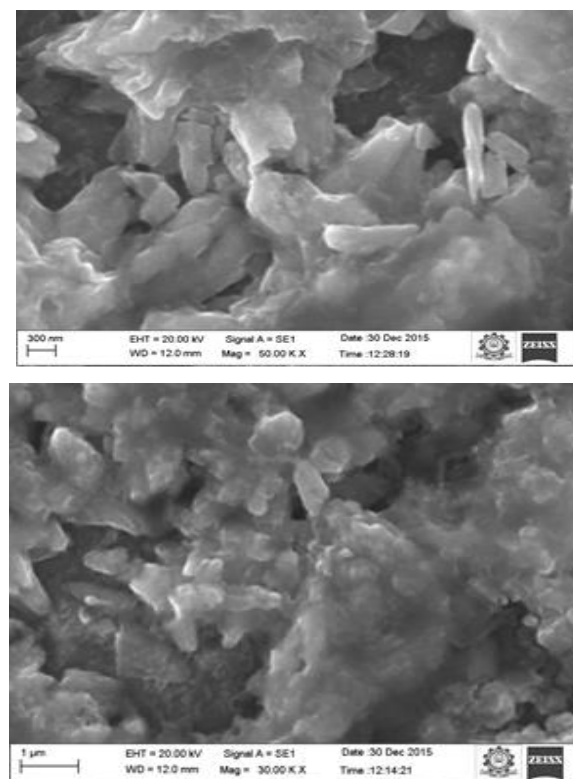


Fig3.3 (c) and (d): SEM images for ZnS/ZnO nanoparticles (FTO).

3.4 Elemental analysis

Table 3.4 Elemental analysis of ZnS/ZnO thin film

| Element | FTO-Substrate | | Glass-Substrate | |
|---------|---------------|-----------|-----------------|-----------|
| | Mass% (g) | Atom% (g) | Mass% (g) | Atom% (g) |
| O | 25.42 | 54.95 | 37.39 | 62.31 |
| S | 1.25 | 1.35 | 3.61 | 3.00 |
| Si | 5.85 | 7.20 | 19.61 | 18.62 |
| Zn | 65.04 | 34.39 | 39.38 | 16.06 |
| ca | 2.44 | 2.11 | - | - |
| Total | 100 | 100 | 100 | 100 |

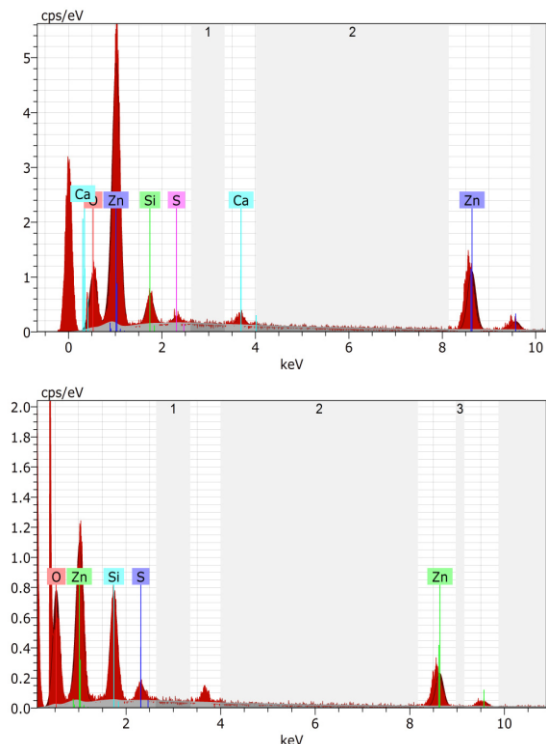
substrate is lower than the glass substrate S= 3.00% O=62.31%. These results are seen in the Table 3.4.

4 Conclusion:

ZnS/ZnO thin films have been successfully deposited by chemical bath deposition technique. The films are in good quality, adherent and uniform. There is a good agreement on optical results, luminescence, and microstructures and elemental analysis. UV spectra revealed that the absorption band was red shifted from the bulk. The calculated band gap values are in the range of 2.56 and 3.55eV. The PL spectrum consists of 503nm and 496nm emission bands. Morphology studies of the ZnS/ZnO films were characterized using SEM. The estimated average grain size of FTO is 50- 60nm and it is whitish and well substrate covered and for glass is 30-40nm. The chemical constituents and their compositions of the films have been estimated by the energy dispersive X-ray analysis. The deposited films are identified as Zn, S and O. The proportion of the constituent elements measured was Zn = 34.39% for FTO substrate is higher than the glass substrate Zn=16.06%. The proportion of the constituent elements measured was S=1.35% and O=54.95% for FTO substrate is lower than the glass substrate S= 3.00% O=62.31%. The particle size of FTO is greater than the glass substrate. Composites also provide design flexibility because many of them can be molded into complex shapes. Structural, electronic and thermal are the applications.

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**Fig. 3.4**

Dispersive X-ray spectroscopy (EDAX) is an analytical technique used for the study elemental analysis of the sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on an investigation between samples of interaction between electromagnetic radiation and matter in response hit with charged particles. In order to clarify the element composition of the prepared thin film and evaluation of approximate atomic ratios, the energy dispersive analysis of X-ray (EDAX) was conducted. It shows the analysis of ZnS/ZnO thin film. The EDAX analysis revealed the presence of Zn, S and O elements in thin film. The presence of silicon (Si) is due to FTO and glass substrates. The presence of calcium (ca) in FTO is due to impurities [5].

The proportion of the constituent elements measured was Zn = 34.39% for FTO substrate is higher than the glass substrate Zn=16.06%. The proportion of the constituent elements measured was S=1.35% and O=54.95% for FTO

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