

STRUCTURAL AND SURFACE MORPHOLOGY STUDIES OF ZINC SULPHIDE NANOPOWDERS

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ABSTRACT - Zinc sulphide (ZnS) is one of the first semiconductors discovered. Zinc sulphide (ZnS) nanostructures have attracted increasing attention due to their potential application in both conditional optical devices and new generation of nano-electronics and nano-optoelectronics because of their special structure-related chemical and physical properties. Nano powders of ZnS were prepared by control precipitation method due to its simple, inexpensive and reproducible quality. Nano powders of ZnS were prepared by utilizing zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] and sodium hydroxide in deionised water. Complementary investigation such as X-Ray Diffraction, SEM are used to study structural and morphology of ZnS nano powders Microstructural studies indicate that powders were crystalline in nature. It is found that grain size for the preferential orientation is about 20nm. It has traditionally shown remarkable versatility and promise for novel fundamental properties and diverse applications.

Keywords: Nano electronics, Morphology, XRD, Nano powder

1. INTRODUCTION

Cluster of atom / molecules having dimensions in the order of nanometer (less than 100 nm) is known as nanopowders or nanomaterials. It shows atom-like behaviors which result from higher surface energy due to their large surface area and wider band gap between valence and conduction band when they are divided to near atomic size. Nanostructured materials have gained special interest in recent years due to their novel properties providing new ideas in physics to explain it. The properties of nanosized materials have generated a great deal of interest because of the science involved in these studies and technological applications of these materials. Semiconductor nanoparticles have attracted much attention because of their novel electric and optical properties originating from surface and quantum confinement effects.

1.1 Aim of the work

The aim of the present work is to prepare the ZnS Nanopowder by control precipitation method and to study its structural properties

1.2. SIZE DEPENDENCE OF PROPERTIES

Many properties of solids depend on the size range over which they are measured. Microscopic details become averaged when investigating bulk materials. At the macro-or large-scale range ordinarily studied in traditional fields of physics such as mechanic, electricity and magnetism, and optics, the size of the objects under study range from millimeters to kilometers. The properties that we associate with these materials are averaged properties, such as the density and elastic moduli in mechanics, the resistivity and magnetization in electricity and magnetism, and the dielectric constant in optics. When measurements are made in the micrometer or nanometer range, many properties of materials such as mechanical, ferroelectric, and ferromagnetic changes.

1.3 Application Of Nano powders

Nano powder has many applications in different fields and some are given below:

- ❑ Ceramics used in nano sized powders are more ductile at elevated temperatures compared to coarse grained ceramics and can be sintered at low temperatures
- ❑ Nano sized powders of iron and copper have hardness about 4-6 times higher than the bulk materials because bulk materials have dislocations.
- ❑ The detection of viruses and bacteria at earliest as possible is a primary goal in the medical community to cure various different diseases. This goal is satisfactorily done by the Nano particles. Gold coated Nano particles are used to detect HIV viruses. Metal nano Powders are used to detect dendrimers.
- ❑ Ultra small super paramagnetic iron oxide (USPIO) Particles in the blood recognize target which is

important in detecting cancer cells shown in Figure 1.1.

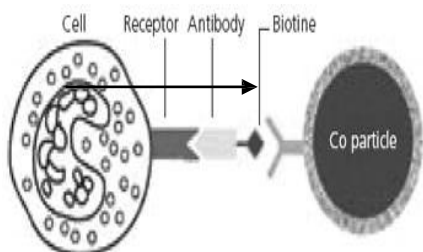


Fig.1.1: Technique for MRI to detect cancer cell

2. PREPARATION TECHNIQUES

Variety of nanomaterials such as metals, semiconductors, insulators or dielectric etc, are prepared either as nanopowders or thin film form and for this purpose various preparative techniques have been developed. Newer methods are also being evolved to reduce size with maximum reproducible properties. Any preparation methods involve the three main steps shown in fig 2.1

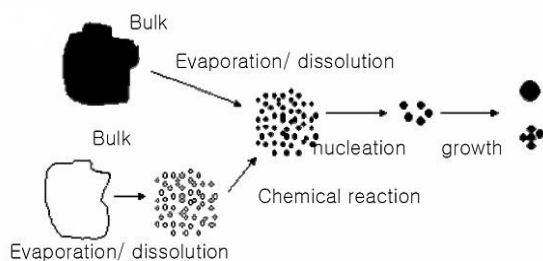


Fig.2.1 Formation of Nanoparticle

2.1. CONTROLLED PRECIPITATION METHODS

The technique of controlled homogeneous precipitation is applicable to prepare nanoparticle of water insoluble compounds. In particular II-VI and IV-VI compound semiconductors are of great importance. A number of compounds such as CdS, PbS, CdSe, PbSe, ZnS, and ZnSe have been prepared.

For forming compound of M_mX_n , a solution of M^{+n} ions with a complexing agent (or ligand) L added to it is prepared. Formation of complex ions $[M(L)_i]^{+n}$ is essential to control the reaction and avoid immediate precipitation of the compound in the solution when the precipitating anions are added to it. The precipitating agent is generally a compound which, upon hydrolysis,

slowly generates the anions in the solution. For example, thiourea generate S^{2-} ions. The cations are generated by decomposition of the complex ions according to the equation



For example, when the solution is heated. Compound formation starts when the ionic product ($[M^{+n}]^m [X^{-m}]^n$) exceeds the solubility product (ie., the ionic product at saturation) and progresses slowly to form nanopowders.

2.2. PREPARATION OF ZINC SULPHIDE NANOPOWDERS

Nanopowders can be prepared by many methods, and each method has its own characteristic merits and defects in producing homogeneous and uniform size nanopowders. Among many methods available, controlled precipitation method is chosen for this study due to its simple, inexpensive and reproducible quality.

Zinc Sulphide nano powders were prepared from the precursor solution by dissolving the salt of Zinc acetate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ of 1 gm in 50ml deionised water. The solution is stirred at 60°C. To which sodium hydroxide solution of 2 gm (50ml) is added drop by drop using burette. The experimental setup is shown in figure 2.2. After about 2 hours zinc sulphide powders were filtered and heated in a furnace at different temperature for 2 hours to get crystalline Zinc Sulphide nano powders. The pH of the solution at the end of reaction is about 9.8.

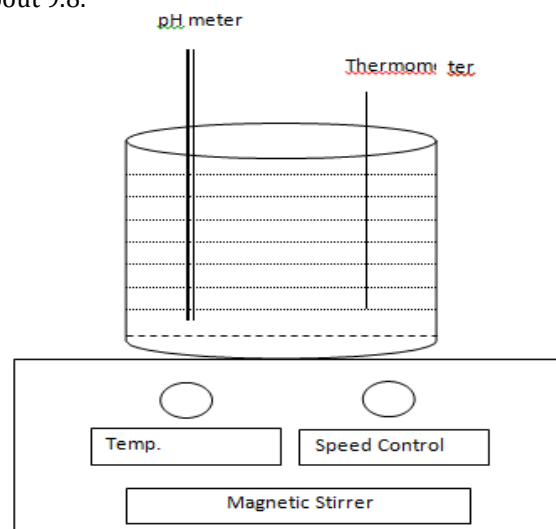


Fig.2.2. Experimental setup for preparing Zinc sulphide nanopowders

2.3 ANALYSIS TECHNIQUE

2.3.1. Scanning electron microscope (SEM)

This is one of the most useful and versatile instruments for the investigation of surface topography, micro structural feature, etc. It provides a pictorial display of the surface layer with a high depth of focus greater than that possible in an electron microscope thus providing better details than that by the conventional replica technique. Thus a surface with a comparatively rough topography can be examined with resolution of about 30 to 150 Å.

The principle involved in imaging is to make use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the specimen. These generally have very low energy say <50 eV compared to $\approx 30\text{keV}$ of the primary electrons and hence only those secondaries which are generated at the surface layers can leave the surface. These secondaries are formed by the interaction of the primary electron beam with the loosely bound electrons of the surface atoms and their emission is very much sensitive to the incident beam direction and the topography of the surface atoms and the contrast is primarily due to these factors rather than the compositional variation of the surface layer. The more oblique is the surface the greater will be the surface area from which secondary electrons can emit. The secondary electron yield is not much affected by the compositional variation of the material, but may be so in the case of contaminations.

2.3.2. X-RAY DIFFRACTION STUDIES

The Phenomenon of x-ray diffraction is employed to determine the structure of solids as well as for the study of x-ray spectroscopy. Considering only the first order reflections from all the possible atomic planes, real or fictitious, the Bragg's law may be written as

$$2d \sin \theta = \lambda.$$

The reflections take place for those values of d , θ and λ which satisfy the above equation. For structural analysis, x-rays of known wavelength are employed and the angles for which reflections take place are determined experimentally. The d values corresponding to these reflections are then obtained. Using this information, one can proceed to determine the size of the unit cell and the distribution of atoms within the unit cell.

It may be noted that the x-rays used for diffraction purposes should have wavelength which is the most appropriate for producing diffraction effects. Since $\sin \theta$ should be less than unity that is, $\lambda < 2d$. Normally, $d \sim 3\text{Å}$ and hence $\lambda < 6\text{Å}$

Longer wavelength x-rays are unable to resolve the details of the structure on the atomic scale whereas shorter wavelength x-rays are diffracted through angles which are too small to be measured experimentally.

In x-ray diffraction studies, the probability that the atomic planes with right orientations are exposed to x-rays is increased by adopting one of the following methods:

1. A single crystal is held stationary and a beam of white radiations is inclined on it at a fixed glancing angle θ i.e., θ is fixed while λ varies. Different wavelengths present in the white radiations select the appropriate reflecting planes out of the numerous present in the crystal such that the Bragg's conditions is satisfied. This technique is called the *Laue's technique*.
2. A single crystal is held in the path of monochromatic radiations and is rotated about an axis, i.e. λ is fixed while θ varies. Different sets of parallel atomic planes are exposed to incident radiations for different values of θ and reflections take place from those atomic planes for which d and θ satisfy the Bragg's law. This method is known as the *rotating crystal method*.
3. The sample in the powdered form is placed in the path of monochromatic x-rays, i.e. λ is fixed while both θ and d vary. Thus a number of small crystallites with different orientations are exposed to x-rays. The reflections take place for those values of d , θ and λ which satisfy the Bragg's law. This method is called the *powder method*.

2.3.3. X-RAY LINE BROADENING

Phenomenological line-broadening theory of plastically deformed metals and alloys was developed almost 50 years ago (Warren and Averbach 1950; Warren 1959). It identifies two main types of broadening:

- (i) size and, (ii) strain components

Size Components

Depends on the size of coherent domains (or incoherently diffracting domains in a sense that they diffract incoherently to one another), which is not limited to the grains but may include effects of stacking and twin faults and sub grain structures (small-angle boundaries, for instance)

Strain Components

It is caused by any lattice imperfection (dislocations and different point defects). The theory is general and was successfully applied to other materials, including oxides and polymers.

3. EXPERIMENTAL METHOD, RESULTS AND DISCUSSION

3.1. Structural and morphology studies

Where the XRD pattern of as prepared ZnS nanopowders. The pattern does not have prominent peaks indicating amorphous in nature. Figures 3.2 shows the XRD pattern of ZnS films annealed at 350. Powders annealed at 350°C do not shows significant peaks whereas powders annealed at 500°C shows different peaks indicating crystalline nature. The obtained XRD patterns aggress with standard JCPDS card [05-0556] indicating polycrystalline nature with cubic crystal structure. The random growth or polycrystalline of film is due to amorphous nature of the substrate. The planes are indexed as (1 1 1), (2 2 0), (3 1 1) and (2 2 2) with respect to standard card and the d-spacing and 2theta values are given in table. It is seen that the powders annealed at 350 and 500°C has preferential growth along (1 1 1) plane.

XRD lines shows broadened in their shape when compared with standard JCPDS line. These effects can be classified into instrument and specimen broadening. Instrument broadening originates from the non-ideal optical effects of the diffractometer and from the wavelength distribution of the radiation. In the present work instrumental broadening is corrected by using a standard defect free silicon sample.

Specimen broadening arises due to small crystallite (grain) size and strain (lattice distortion). Grain size causes the radiation to be diffracted individually. The prepared ZnS powder shows polycrystalline in nature, and hence large number of grains with various relative positions and orientations cause variations in the phase difference between the

wave scattered by one grain and the others. A uniform compressive or tensile strain (macrostrain) results in peak shift of X-ray diffraction lines, whereas a non-uniform of both tensile and compressive strain results in broadening of diffraction lines (microstrain). Thus grain size and microstrain effects are interconnected in the line broadening of peaks which makes it difficult to separate.

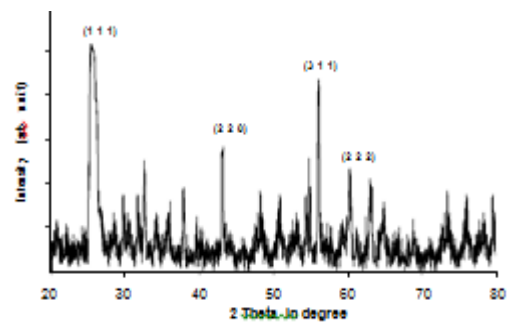


Fig 3.2: XRD pattern of ZnS annealed at 350°C

Pos. [°2Th.]	Plane	d-spacing [Å]	Rel. Int. [%]
27.9962	1 1 1	3.21360	100.00
47.0012	2 2 0	1.89128	47.65
56.1467	3 1 1	1.61201	52.28
59.2167	2 2 2	1.55617	27.74

Figure 4.3: XRD pattern of ZnS annealed at 350°C (Table indicates its 2θ and d-spacing value)

Strains originate mainly due to a mismatch between crystallite in polycrystalline powders and or difference in coefficients of thermal expansion of the crystallite. The following well known Scherrer's formula is utilized to determine grain size and microstrain

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{ and } \epsilon_{hkl} = \frac{\beta}{4 \tan\theta} \quad (1)$$

Where D is the size of the grain in the direction perpendicular to the reflecting planes, θ is the diffraction angle, K is the shape factor and is equal to 0.9, λ is the wavelength of x-ray and β the full width at half maximum of prominent peaks in radian ε_{hkl} is microstrain. It is

observed that as annealing temperature increases crystallite size of preferential orientation peaks increases from 30 to 45nm due to coalescence of grains Also microstrain found to decreases from 0.00034 to 0.00021 as deposition temperature increases. Crystalline Figure 3.3 shows the scanning electron micrograph of ZnS powders. It shows well defined grains and the size is found to be 200 to 400 nm.

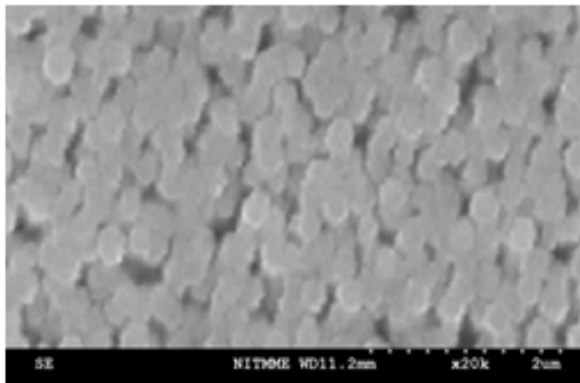


Fig 3.3 -SEM Of ZnS nanopowder

3.2. CONCLUSION

Nanopowders of ZnS were prepared by chemical method utilizing zinc acetate and sodium hydroxide as precursor salt in deionised water. Microstructural studies indicate that prepared powders were crystalline in nature with highly oriented along (1 1 1) plane. X-ray line broadening technique is adopted by referring with Silicon sample to correct instrumental broadening effect. It is found that grain size for the preferential orientation is about 20nm. Also X-ray pattern indicate a small shift in 2theta value as compared with standard value. This is because at temperature 500°C the nucleation or growth processes are excited to higher energy state resulting in strain between particles. This leads to microdefect like microstrain, lattice mismatch etc., Further work has to done to still minimize the grain size either by chemical or physical route.

References:

1. Williamson G K, Hall W H 1953 Acta Metall. 122.
2. Sciti D, Celotti G, Pezzotti G, Guicciardi S 2007 Appl. Phys. A. 86 243.
3. A. L. Patterson, Phy. Rev. 56, 978 (1939).
4. Agrafiotis C, Tsetsekou A, Stournaras C J, Julbe A, Dalmazio L and Guizard C 2000 Solid State Ionics 136 1301
5. Anderson Kris, Fernández Silvia Cortiñas, Hardacre Christopher and Marr Patricia C 2004 Inorg. Chem. Commun. 7 73
6. Nanomaterials: Synthesis, properties and application (WashingtonDC: Naval Research Laboratory)
7. Esaki Leo 1999 Nanostructured Mater. 121.