

STRUCTURAL, OPTICAL, MECHANICAL AND SEMICONDUCTOR PROPERTIES OF ZNS THIN FILMS USED IN SOLAR CELL

Rohit Srivastava¹,

Electrochemistry Research Lab, Department of Chemistry,
St. Andrew's College, Gorakhpur. 273001(U.P), India
Email: srivastav.rohit24@gmail.com

Md. Rashid Tanveer²,

Associate Professor, Electrochemistry Research Lab, Department of Chemistry,
St. Andrew's College, Gorakhpur. 273001(U.P), India
Email: rashidtanveer1@gmail.com

Abstract:

Zinc sulphide is a chemical compound having the formula ZnS. This is the most common form of zinc found in nature, which is found mostly in the mineral sphalerite. The pure substance is white, & it is commonly used as a pigment, despite the fact that it is generally black due to numerous impurities. Zinc sulphide may be transparent in its thick synthetic form, & it is utilised as a window for visual & infrared optics. With broad band gap energy of 3.66eV, ZnS is an important semiconductor compound of the II-VI group. Zinc sulphide (ZnS) is found in nature as the mineral sphalerite; however, the ore form usually contains a lot of iron, manganese, or cadmium impurities. It is a unique compound that forms two types of crystalline structures. These two polymorphs are wurtzite and zinc blende. Wurtzite has a hexagonal structure, while zinc blende is cubic. The most common use of zinc sulphide is as a pigment for paints, plastics and rubber. It is a good phosphorescent and is frequently used in electronic industry. ZnS thin films can be synthesized by many methods such as CBD, CVD, spray pyrolysis, electro deposition, etc. However, the most common is the spray pyrolysis method in which aqueous solution of ZnCl₂ and thioacetamide (TAA) are mixed at 300°C to form crystalline ZnS thin films. These films with different concentration of Zn have varied applications in semiconductor devices, communications, integrated circuits, solar cells, light emitting diodes, crystal displays, lithography, etc.

Keywords: ZnS, crystalline forms, synthesis, electro deposition, optical properties, applications

Introduction

1.1 Structure of Zinc Sulphide

There are two primary crystalline forms of ZnS, & this dualism is a good illustration of polymorphism. The coordination geometry at Zn & S is tetrahedral in each form. Zinc blende or sphalerite is another name for the more stable cubic form. Wurtzite is the mineral name for

the hexagonal form, which may also be made synthetically. At roughly 1020 °C, the shift from sphalerite to wurtzite takes place. A tetragonal form is also known as polhemessite, a highly uncommon mineral having the formula (Zn, Hg) S.

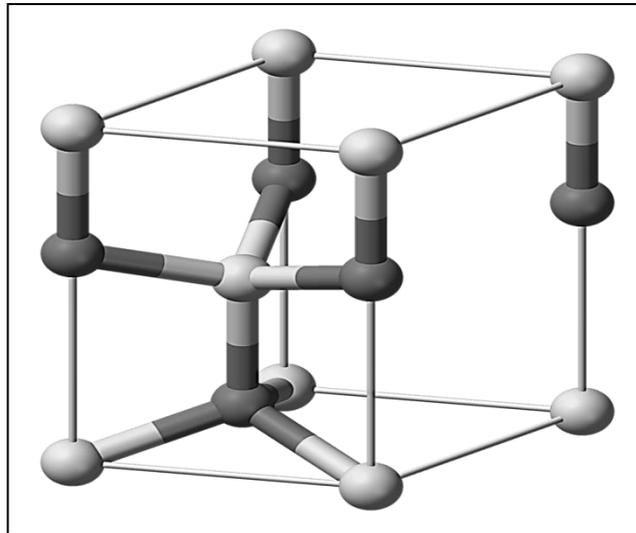
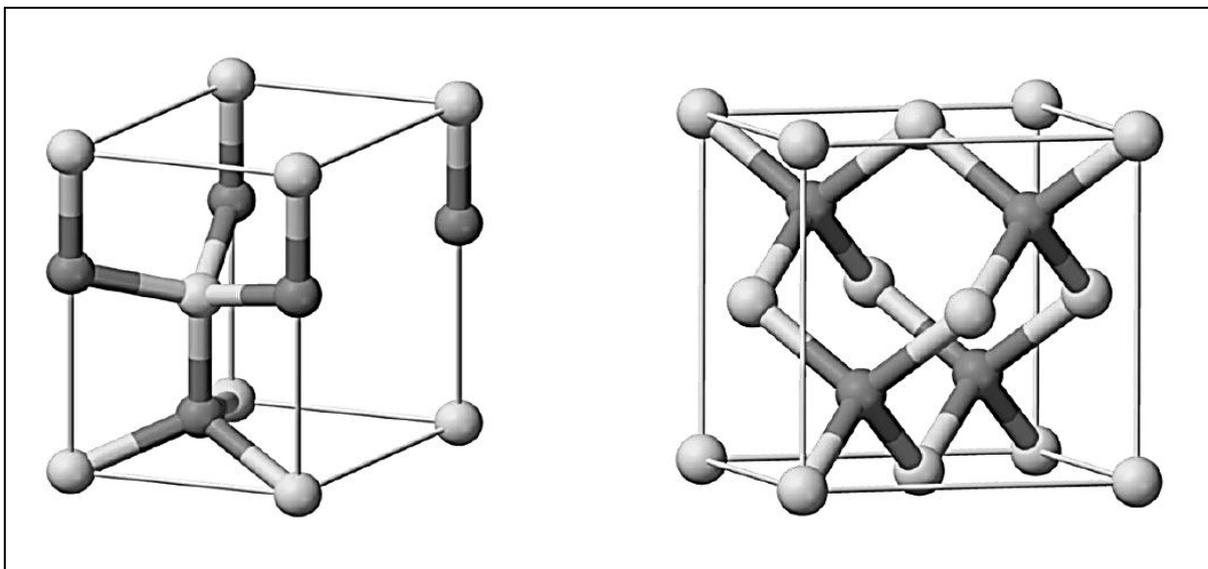


Figure 1: Structure of ZnS

1.2 Crystal Structure of Zinc Sulphide

Zinc sulphide crystallises in two polymorphic forms. The first is sphalerite having the structure 3C or b face-centered cubic phase, also known as zinc blende, which is the most essential structure for optical materials & is the 30 isotropic cubic structures. The anisotropic hexagonal structure & high-temperature form of wurtzite having the structure 2H or a hexagonal close-packed phase) is the second. Single crystals of Wurtzite may be created by quenching it at temperatures exceeding 1020 °C, albeit they often feature a high-volume proportion of stacking defects. Only at extreme pressure do two more versions of the zinc sulphide structure exist. At pressures of 12–65 GPa, sphalerite or wurtzite produces the rock



salt structure, which is distorted orthorhombic at higher pressures.

Figure 2: Structure of ZnS (i) Sphalerite, (ii) Wurtzite

1.3 Properties of Zinc Sulphide

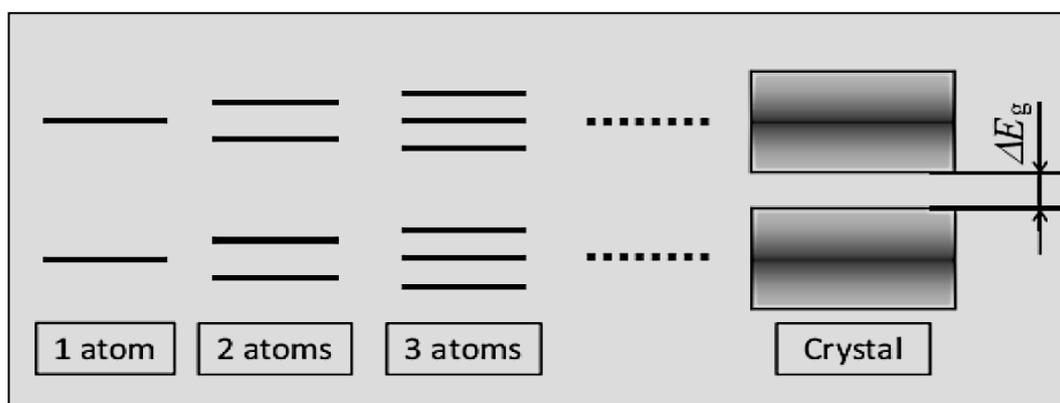
In nature, zinc sulphide is found in two forms: zinc blende as cubic structure & wurtzite as hexagonal structure. The fundamental difference between the two modifications is the lattice's atomic planes' relative positions. Natural crystals of zinc sulphide are inappropriate for systematic research because they include several contaminants, the concentration of which is difficult to quantify. As a result, most studies are conducted on single ZnS crystals generated in the laboratory.

Zinc sulphide has a relatively poor electrical conductivity. Donor levels are deep inside the prohibited range, which causes this. In, Ga, Cl, Br, I, & numerous other elements are common impurities found in zinc sulphide. "There hasn't been any study done on single crystals of zinc sulphide that exhibit p-type conduction. The increased depth of acceptor levels compared to donors, as well as the charge compensation process in which impurities give rise to acceptor levels that need the existence of defects that function as donors, provide challenges in the fabrication of p-type crystals. Be a result, ZnS is commonly referred to as a highly compensated n-type semiconductor. The nature of the electron transitions associated with light absorption may be determined via photoconductivity spectra. Piper was the first to test the photoconductivity of pure ZnS crystals, claiming that the photoconductivity spectrum of pure crystals had one maximum at 3.68eV photon energy. The spectrum is complicated by the existence of impurity or defect levels in the prohibited band. Electrons from the impurity levels can then be stimulated to the conduction band, resulting in additional maxima indicating the optical activation energies of these levels. The most common elements employed in the doping of zinc sulphide are silver, copper, & manganese. Television equipment, luminescent panels, light amplifiers, optrons, & other electroluminescent devices all employ zinc sulphide phosphors as screen coatings." Optical filters & selective mirrors are made from thin ZnS sheets. Nuclear radiation counters also employ zinc sulphide. Optical sensors, phosphors, photoconductors, catalysts, & solid-state solar window layers are just a few of the uses.

1.3.1 Optical properties

Nanocrystalline systems have sparked a lot of attention because of their unique optical features that set them apart from bulk crystals. Nanoparticle confinement of electrical carriers, effective energy & charge transfer over nanoscale distances, &, in many systems, a significantly increased surface function are all major contributing aspects to the success. "The optical properties of these materials can be fine-tuned by controlling the crystal size & the chemistry of their surfaces. Applications based on the optical properties of nanomaterials include optical detectors, lasers, photocatalysts, photoelectrochemical, sensors, imaging, phosphor displays, solar cells, & biomedicine. A variety of parameters, including feature size, shape, surface characteristics, & doping & interaction with the environment or nanostructures, impact the optical properties of nanomaterials. The most basic example is the

blue shift in the absorption & photoluminescence spectra of semiconductor nanoparticles as particle size decreases.” Semiconductors' electronic structure dictates their optical absorption, which is widely used to study the materials' optical & electrical properties. Optical absorption occurs when light interacts with a material. When the frequency of light is in resonance with the energy difference between the electronic states, a photon is absorbed by the material & the transition is permitted or partially permitted by selection rules. This is indicated by a decrease in transmission or an increase in absorbance in the light passing through the sample. As the frequency of light is varied, a sample's absorption spectrum is created. There are no two substances exactly same when it comes to their spectrum. As the particle size reduces, the excitonic peak in a direct band gap semiconductor becomes more clearly defined. When compared to bulk semiconductors, nanoparticles have a notable blue shift in the absorption spectrum because to quantum size confinement.



1.3.2 Size-Dependent Optical Properties – Quantum Confinement

Many fundamental optical characteristics of particles are dependent on their size. To begin investigating these phenomena; it is necessary to first comprehend the impact of particle size on the electrical structure of a solid. When looking at the energy levels of a single atom, one can discern distinct energy levels, each of which is filled by one electron according to Pauli's principle. However, it's important to remember that each of these electrons has a spin associated with it. Spin up & spin-down are the two options available. As a result, two electrons with different spins may be found at the same level. The energy levels are divided when a second atom is added. Adding more atoms causes the energy levels to divide even more, with the number of splitting being precisely equal to the number of atoms in the system. Finally, there are so many sublevels at one energy level in a bulk material that a quasi-continuous system of "energy bands" is seen. Nanomaterials' optical capabilities are among the most utilised & beneficial for technical applications spanning from sensing & detection to optical imaging, from light energy conversion to optoelectronics, food safety, security, biomedicine, environmental protection, & many chemical & biological sensors & detecting systems.

Figure 3: Energy levels of a system consisting of one, two, or more atoms, upto a bulk crystalline solid.

According to Pauli's principle, the energy levels are split for each added atom, the number of splitting is equal to the number of atoms. In the case of a bulk solid, each energy level is subdivided in many sublevels, one has a quasi-continuous "energy band". Consequently, the energy of the gap in-between two levels decrease with increasing number of atoms in the system.

1.3.3 Mechanical properties:

The mechanical properties of nanoparticles differ from those of microparticles & bulk materials. Thus, nano-manufacturing & nanofabrication become more successful as a result of the mechanical strength of the materials used in the process. Mechanical impacts from nanoparticles can affect the tribological properties of nanoparticle-containing lubricants, as well as strengthen composite coatings.

Understanding the fundamental mechanical properties of nanoparticles, such as hardness & elastic modulus, would be extremely helpful in designing nanoparticles for specific purposes & assessing their roles & actions. As far as the literature goes, microparticles have been investigated for decades. Based on the research, there are three types of possible outcomes & underlying causes. In the case of spherical polymer nanoparticles, there are yet no consistent size-dependent mechanical features. It was revealed that the compressive modulus of polystyrene nanoparticles (diameter: 200 nm) was lower than that of identical bulk materials due to the presence of ionic functional groups. Polypropylene (PP) nanoparticles, on the other hand, have a higher elastic modulus than the bulk material. There is a correlation between T_g & elastic modulus because the deformation of the polymer chain inside a particle is influenced by T_g , crystalline phase, & crystallinity.

According to conventional wisdom, crystalline metal nanoparticles do not include dislocations. However, dislocations have been proven to be one of the processes that contribute to the mechanical change in nanoparticles. For six-fold symmetry gold nanoparticles, Ramos et al. observed that the hardness & elastic modulus were larger than the bulk phase because of stacking faults & dislocations. They integrated theoretical modelling with nanoindentation & compression testing to reveal the deformation behaviours of single-crystal gold nanoparticles on sapphire substrates, as reported by Mordehai & Nix et al. As particle size rose, so did the indentation strength, as dislocations formed in competition for space beneath the indenter. Gerberich & colleagues reported comparable behaviour with silicon nanoparticles, noting that their hardness (particle diameter: 40 nm) was quadrupled above that of bulk silicon. They proposed that the particle's ability to tolerate high pressure is due mostly to internal dislocations or line faults. They also found that dislocations were responsible for the production of the super hard silicon nanoparticles by Zhang et al. using atomistic modelling. Additional to dislocations or defects, compressive stress-induced changes in nanoparticle lattice strain & bond energies have been hypothesised as an explanation for the strengthening & weakening of mechanical properties. The bulk module of different semiconductor nanoclusters was shown to be size dependent in Cherian et al first-

principles' electronic-structure calculations, which they linked to the strong contact with the passive.

1.3.4 Semiconductor Properties

They are both inherent, wide-band gap semiconductors. Sphalerite & wurtzite are II-VI semiconductors, such as gallium arsenide, may be found in many other semiconductors, including gallium nitride. Cubic ZnS forms have 3.54 electron volt band gaps at 300 Kelvin, while hexagonal ZnS forms have 3.91 electron voltage band gaps. Both an n-type & p-type doping may be applied to ZnS in the same process.

1.4 Applications of Zinc Sulphide

1.4.1 Luminescent material: With a few ppm of sufficient activator, zinc sulphide shows intense phosphorescence (as observed by Nikola Tesla in 1893), & is now employed in a variety of applications, ranging from cathode ray tubes to X-ray screens to glow in the dark items. The colour produced when silver is employed as an activator is vivid blue, with a maximum wavelength of 450 nanometres. Manganese produces an orange-red hue with a wavelength of roughly 590 nanometres. Copper has a long-lasting glow & a characteristic greenish glow-in-the-dark appearance. Electroluminescent panels also employ copper-doped zinc sulphide ("ZnS + Cu"). When illuminated with blue or ultraviolet light, it also shows phosphorescence owing to impurities.

1.4.2 Optical material

Zinc sulphide is also employed as an infrared optical material since it transmits wavelengths from visible to little over 12 micrometres. It may be moulded into a lens or utilised planar as an optical window. "It's manufactured as microcrystalline sheets from hydrogen sulphide gas & zinc vapour, & it's marketed as FLIR-grade (Forward Looking Infrared) since the zinc sulphide is milky-yellow & opaque. When this substance is hot isostatically pressed (HIPed), it may be transformed to Cleartran, a water-clear form." Irtran-2 was the name given to the first commercial versions; however, that name is no longer used.

1.4.3 Pigment

Zinc sulphide, often known as sachtolith, is a common pigment. Zinc sulphide creates lithopone when mixed with barium sulphate. It has the highest influence next to Titanium white. The pigments are mostly used in primers, plastics, fillers, putties and emulsion paints.

1.4.4 Catalyst

When illuminated, fine ZnS powder acts as a photocatalyst, producing hydrogen gas from water. During the production of ZnS, sulphur vacancies can be added, which progressively changes the white-yellowish ZnS into a brown powder & increases photocatalytic activity by increasing light absorption.

Conclusion:

The ZnS thin films were synthesized on electrodes by using the electrodeposition method. In this paper we have investigated the structural, morphological, optical and semi conduction

properties of these films. On characterisation it has been found that these films have a direct band gap of nearly 3.50eV.

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