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IMPENDING APPLICATIONS OF ZINC SULPHIDE SEMICONDUCTOR NANOMATERIALS AND THIN FILMS

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ABSTRACT

Nano-sized semiconducting materials have found to be of considerable interest because of their structural, chemical and physical properties. They are different from those of the corresponding bulk materials because of their three dimensional confinement of electrons and appropriate band gaps. Zinc sulphide, a metal chalcogenide has unique properties and number of different applications in various sectors. In recent times lot of efforts has been done to improve the characteristics of zinc sulphide nanomaterials with the intention of discovering new possible applications. Numerous zinc sulphide nanostructures have ample of innovative applications some of which includes as a field emitters, field effect transistors (FET), catalysts, fuel cells, electrical devices, electroluminescence, solar cells, ultraviolet light and sensors. Gas sensors, biosensors, nano generators and nano sensors are going to the potent tools in future for the study and analysis of different physical and chemical systems.

KEYWORDS: Zinc sulphide, applications, nanostructure, sensor, analytical devices.

1. INTRODUCTION

Zinc sulphide semiconductor and the nano form have conventionally revealed noteworthy adaptability and hope for the splendid elementary properties and assorted applications. ZnS can exist both as cubical or hexagonal lattice structures and sizeable amount of impurity can be added to natural crystal to enhance the physical, optical and chemical properties.[1-4] Because of their three-dimensional confinement of electrons and holes in a compact volume, nano-sized semiconducting materials have garnered a lot of attention recently due to their structural, chemical, and physical characteristics that differ from those of the comparable bulk materials. The band gap energy of zinc sulfide can be adjusted in the ultraviolet spectrum, and it has a broad 3.6 eV band gap. With a decrease in particle size, radiative or non-radiative recombination of an exciton at the surface states becomes prominent in its optical characteristics, and the band gap may grow as a result of quantum confinement of excitons in semiconductor nanomaterials. Because of these features ZnS is a good photoluminescence, electroluminescence and cathodoluminescence device and therefore it is more chemically stable in comparison to other chalcogenides.

2. Potential applications of ZnS nano films

Some of the potential applications of ZnS nano films are discussed below.

(a). Field Emissions (FE)

The fabrication of external electromagnetic fields results in a process known as field emission, which is the release of electrons (EF). Free electrons may be formed in a number of different ways, including when electrons move from the valence band to the conduction band in semiconductors, when electrons move off the surface of solids or liquids, or when electrons move from individual entity in a vacuum or in free air. Figure.1 (a) presents a diagrammatic illustration of the FE phenomena. The process of tunneling below the surface potential barrier is the one that must be utilized to retrieve electrons from a solid. As can be seen in Figure.1 (b), emitters can have many different tip geometries. Some examples of these are i) a round tip, ii) a blunt tip and iii) a tapered tip. Studies of FE phenomena generally take place at 25^0C since variations in temperature have only a very little impact on the phenomena. A variety of different factors, including the work function of the emitter materials, the local electric field the distance between a sample and the anode and the form of the tip, all have the potential to influence the emission current. In Table 1, we have compiled a summary of applications of noteworthy inorganic metals and semiconductors.

As a precursor, a amalgamation of commercial zinc sulphide powder, carbon nanopowder and sulphur powders was utilized.[5-7] When compared to the results of earlier experiments, the evaporation and agglomeration rates that occurred in this situation were much lower. ZnS powder and carbon nanoparticles come into contact with one another, to initiate the first step in the fabrication of ultrafine ZnS nanoribbons. When 2 ZnS is combined with carbon; the result is 2 Zn and CS_2. Nanoribbons are produced whenever zinc vapor and sulphur vapor react with one another at about 1000^0C. Figure.2 displays scanning electron micrographs of nanoribbons at a range of phases during their formation.[8]

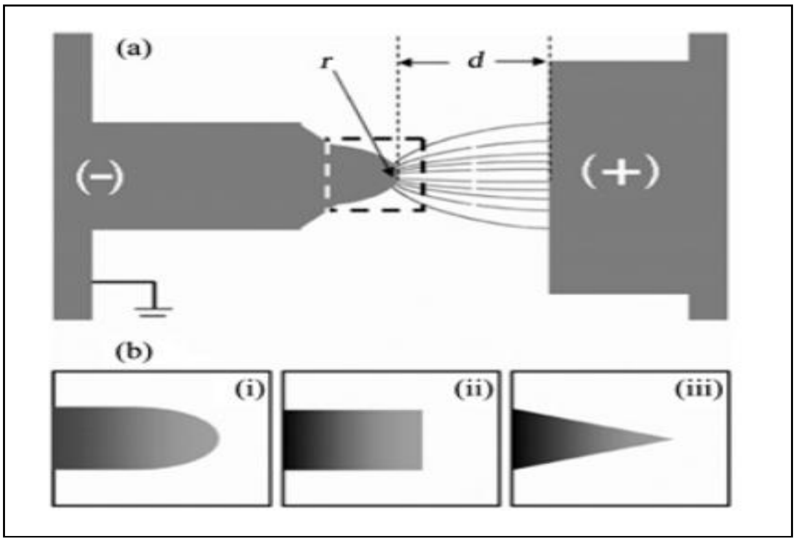

Figure 1: (a) A graphical diagram of the release process, screening the emission coming from the emitters tip ; (b) tip geometries like (i) circular tip, (ii) blunt tip and (iii) tapered tip etc.

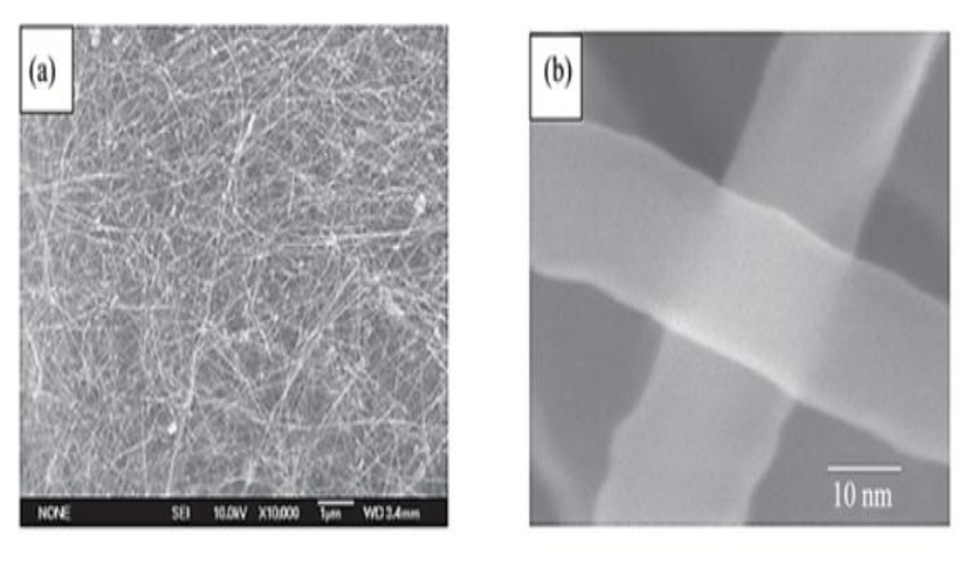

Figure 2: (a) and (b) represents the low and high magnification of SEM images showing uniform thickness and width of the structures along their entire length.

Table 1: The work function Φ of some inorganic semiconductors, C nanotubes, and important metals.

Semiconductors and C nanotubes	ZnO	C nanotubes	AlN	WO_3	SiC	Si	GaN	GaAs	CdS	ZnS
Work function (eV)	5.3	5	3.7	5.7	4.0	3.6	4.1	4.77	4.2	7.0
Metals	Au	Ag	Al	W	Sn	Cu	Fe	Mo	Cd	Zn
Work function (eV)	5.1	4.26	4.28	4.5	4.42	4.65	4.5	4.37	4.07	4.3

As said before, pure zinc sulphide is not the greatest material for field emitters, whereas ultrafine zinc sulphide, which is a mixture of commercial zinc sulphide particles, carbon powders and sulphur, performs exceptionally well as a field emitter. These strategies may be utilized not only to improve the FE features of chalcogenide nanostructures, but also to transform other inorganic semiconductor nanostructures into field emitters.

(b). Field Effect Transistors (FETs)

To construct core/shell ZnS/SiO_2 nanowires, the vapor-liquid-solid growth method is utilized. These nanowires are then utilized in the making of FET nanodevices. This device, when submerged in liquid, can be utilized for sensing the biological and chemical activity by measuring the change in electrical conductivity that takes place in response to the addition of proteins or chemicals. Figure.3 depicts the schematic representation of the sensor circuit. Because proteins like bovine serum albumin (BSA) have a particularly great affinity for the plane of silica, hence charged BSA can be used to perform the gate function. The electrical conductivity of the nanowire-based transistor dropped when it was added to PB solution containing bovine serum albumin at a concentration of 0.0005 g/L. This happened after the transistor was submerged in the mixture which indicates the adsorption of BSA to the facade of the nanowire which is accountable for the experimental decline in conductivity. This reduction in conductivity has been utilized for the recognition of BSA proteins. This result clearly shows that adsorption of BSA to the nanowire surface is responsible for the observed drop in conductivity.

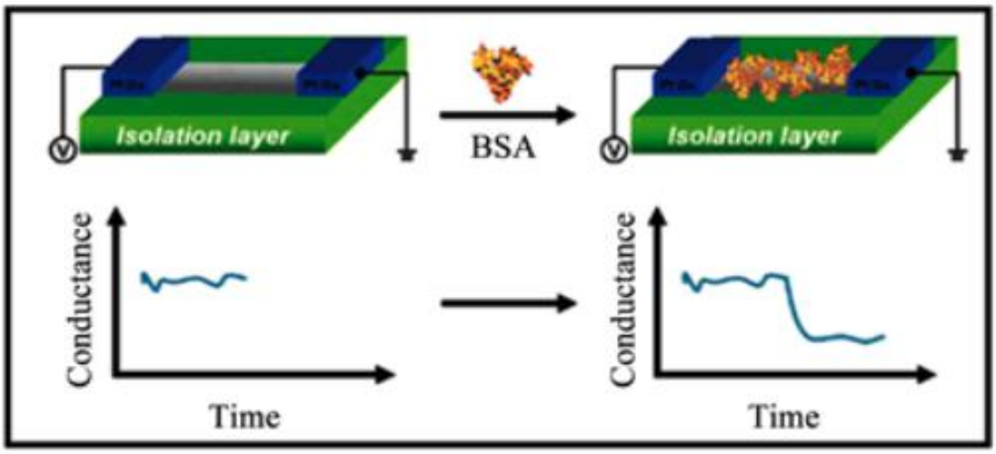

Figure 3: Block diagram of a FET device acting as a sensor; connecting BSA to a net negative charge should decrease conductivity.

The conductivity of the device falls when BSA is fused into the device, because the nanowire in the device is of the n-type. However when a positively charged protein is added to the device, it gets improved. This is because positively charged proteins are electrically conductive.

(c). Catalytic actions

ZnS is a straight wide gap semiconductor that possesses high stability towards redox reactions and hydrolysis. This property makes ZnS an attractive material for use in semiconductor devices. These features are preserved even when the size of the entity is decreased to a few nanometers, which suggests that ZnS may keep some of its original characteristics even after the reduction. Due to this, ZnS nanoparticles have an intriguing possibility of being utilized as catalysts for the purpose of protecting the environment by eliminating organic and harmful pollutants from water. In wastewater treatment, they are utilized as photo catalyzes for the breakdown of organic pollutant, p-nitro phenol and polynuclear hydrocarbons. Sodium sulphide, enhances the process of photo reduction of carbon dioxide to formic acid in the most effective and efficient manner. The beginning of catalytic activity is triggered in ZnS by the rise in the electron reduction potential following photo excitation (1.75 V compared to a normal hydrogen electrode). An oxidizing potential exists for the holes at a voltage of around 1.85 volts. It was discovered that the decline took place in ZnS suspension.[9-12] The quick production of electron-hole pairs via photo excitation and the highly low reduction potentials of electrons, ZnS nanostructures showed to be effective photo catalysts in these experiments.

(d). Fuel cell

It has been demonstrated that ZnS nanoparticles exhibit catalytic activity that is used for the breakdown of ethanol. As alcohol can be fermented from different organic compounds it has the potential to be a very good fuel for the production of power. The electro catalytic conversion of ethanol into H_2O and CO_2 in oxygen includes the transport of 12 electrons for each ethanol molecule and progresses through two intermediates, an carbonyl compound and an carboxylic acid. The following is a table containing the enthalpies of spontaneous combustion for each species:

$$C_2H_5OH + 0.5O_2 \rightarrow CH_3CHO + H_2O \quad 190.5kJ \cdot mol^{-1}$$
$$CH_3CHO + 0.5O_2 \rightarrow CH_3COOH \quad 268.3kJ \cdot mol^{-1}$$
$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \quad 849.8kJ \cdot mol^{-1}$$
$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad 1308.6kJ \cdot mol^{-1}$$

After making the comparison between these values and those of ZnS, it is obvious that ZnS must always be stable to oxidation or reduction when ethanol is present. This leads one to believe that it has the potential to be a reliable compound for the oxidation of ethanol. To regulate electron transport across the plane of the matter, it is essential that ZnS nanostructures be shielded by ligands of a sufficiently tiny size. The occurrence of ZnS particles are permissible for the oxidation of ethanol to take place in the apparatus depicted in Figure.4. Electrodes that did not contain ZnS particles did not produce a current at any point in time. A progressive rise in the volume of the circulating stream was brought about due to the ethanol that was added in sequence. The effects generated by a pure ITO electrode were considerably more equivalent to those created by a unadulterated graphite electrode, although the pure ITO electrode's effects were substantially lower. The pure carbon electrode was responsible for a noteworthy rise in current but there was no evidence of ongoing degradation.[13-15] This study reveals that ZnS nanoparticles may be employed as electro catalysts in the process of converting ethanol directly in a fuel cell by using a fuel cell as the reaction vessel. Ethanol may be produced from a large number of organic compounds through the fermentation process; thus, there is huge demand for the catalysts that are required for this process.

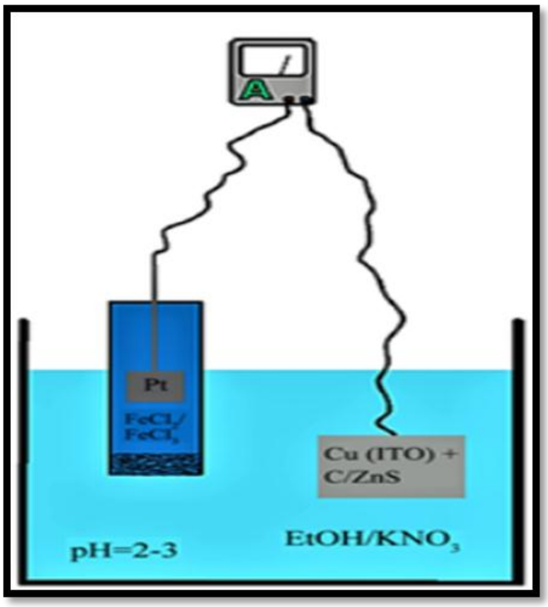

Figure 4: Representation of an ethanol fuel cell with ZnS nanoparticles as catalyst and a $FeCl_3$ /$FeCl_2$ counter electrode.

(e). Nano Generator

Using the piezoelectric capabilities of various materials, nanogenerators are able to transform nanoscale energy into the current. A technique of thermal evaporation that included residual oxygen was used in the manufacture of ZnO-ZnS heterojunction nanowire arrays. Figure.5 (a) is a three-dimensional strain output image that was discovered by performing an AFM scan on a heterostructure composed of ZnO-ZnS nanowire arrays having locale of 30*30 μm^2. This image was discovered by the AFM scan performed on the heterostructure. Nanowire networks with a heterostructure nearly develop in a upright direction on the substrate with a composition that is constant. An AFM that was set to operate in contact mode and had a Pt-coated Si conductive tip was utilized for the reason of researching the piezoelectric responses of ZnO-ZnS[16-19], heterostructure nanowire arrays. The deflection of the nanowire results in the creation of an electrical voltage and current at each entity tip. The output voltages typically float around 6 milli volts on average. The interface among W-ZnO and the Pt tip is the primary contributor to the output voltages of the ZnO-ZnS heterostructure nanowire arrays.[20-23] This is because ZnO is located above this heterostructure nanowire arrays.

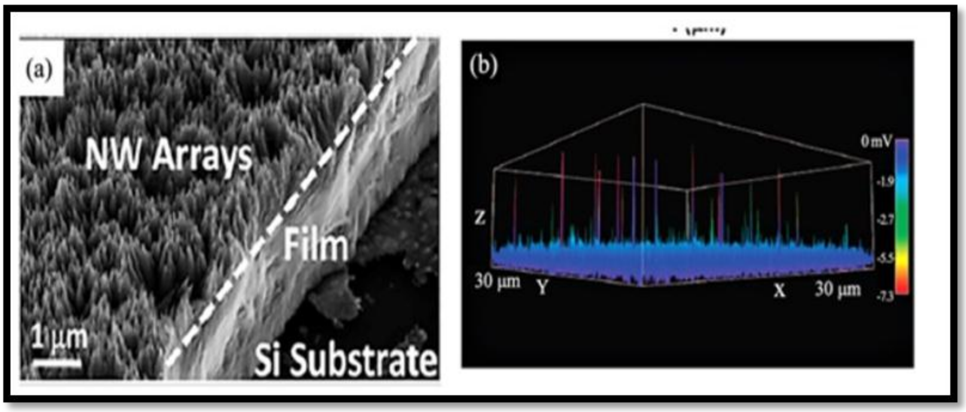

Figure 5: (a) Vertical growth of ZnO-ZnS nanowire assortment in the buffer coating and (b) their three-dimensional strain output image obtained after AFM scanning area of 30 × 30 µm^2.

3. CONCLUSION

This research has uncovered several key facts concerning defect-induced changes in nanomaterials' physical characteristics. Additional work is needed to actualize defect-based property tuning. This challenge has a huge scope, and if it is solved, it will offer an alternative technique for adjusting and acquiring application-specific features. This paper highlights the findings of the current research and looks ahead to the future of these materials, which might be used in different applications such as photocatalytic devices, electronics, optoelectronics, sensors and energy converters. Large band gap II-VI compounds are considered as the most important materials for high-performance optoelectronics devices like light-emitting diodes (LEDs) and laser diodes in the ultraviolet spectral region.

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