
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction:

The productions of semiconductors were basically produced by a type of materials in the periodic table. These materials were called II-VI compound materials. They were known as "crystal phosphors" and were used as cathode ray tube screen materials in the third decade of this century. In the last fifties, II-VI compound materials had a boom in colored television tubes and their present production output is nearly comparable with Si. Of course their outstanding merits are not in their semi-conducting properties which have to compete with Si but nevertheless they are semiconductors-adequately understandable and describable by the concepts of semiconductor physics [3].

Compounds which are formed by metals, such as, Zn, Cd and Hg of column II of the periodic table and the chalcogens O, S, Se and Te of column VI have wide energy gaps between the valence and conduction bands which give them a great advantage. This wide energy gap gives those materials higher optical transmission probabilities for absorption and luminescence so it was used in the early days for luminescence in the visible region. These compounds have high ionicity which makes them good candidates for having high electro-optical coupling and electromechanical coupling constants. In the last 50 years, physicists are interested in studying the physical properties of the II-VI

compounds which has stimulated considerable research into methods for growing signal crystals as well as thin films of these materials [3, 5].

ZnS, which is among II-VI compounds, is a good material to study and use in the preparation and characterization for both academic research and industrial purposes because ZnS is a very promising candidate for such technological application, especially for light emitting diodes and hetero junction devices [3].

2.2 description of Zinc Sulfide crystal structures

ZnS has two forms zinc blende and wurtzite which are found in the natural. Wurtzite form of ZnS is stable at high temperature and it has been found that the inversion temperature of 1020°C and 1150°C are suitable to change the hexagonal to cubic [5]. In addition it is reported that there is some variation in the lattice constants of both cubic and hexagonal modifications. This variation could happen because of impurities and imperfections in the crystal structure. The replacement of S by O is common impurity. ZnS has a wide band gap of 3.72 eV (333.6 nm) for the cubic phase and 3.77 eV (329.2 nm) for the hexagonal-wurtzite phase. [2].

2.2.1 Zincblende structure

All of the II-VI compounds form crystals with the zincblende (fig. 2.1). In the unit cell, there are four ZnS and all atoms are in special positions with 4S and 4Zn. If both kinds of atoms were the same, the arrangement would be the same as in diamond. That means that four atoms from one kind are surrounding one atom from another kind. For example, each (Zn) is surrounding with four nearest neighbors of (S), and vice versa, at a distance of $\frac{1}{4}\sqrt{3}a$ at the corners of a regular tetrahedron, where (a) is the cubic lattice parameter. There are twelve next-nearest neighbors of atoms of the same kind at the distance $2\sqrt{2}a$. Six of these are distributed at the corners of a hexagon in the same

plane as the original atom; the remaining six forms a trigonal antiprism with the three above and three below the plane of the hexagon. [5].

2.2.2 Wurtzite structure

The II-VI compounds can crystallize to form wurtzite (fig. 2.2). There are two molecules in the hexagonal unit cell with two Zn and two S. At the corners of tetrahedron there are approximately four S atoms surrounding Zn atoms. There are twelve next-nearest neighbors; six at the corners of a hexagon in the same plan as the original atom. The remaining six are at the corners of a trigonal prism. [5].

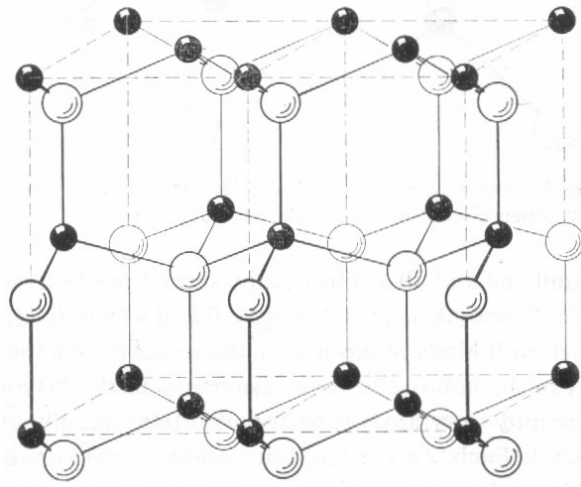


Figure. 2.1. Zincblende. The arrangement of metal atoms (small filled circles) and non-metal atoms (large-open circles) in Zincblende, the cubic form of ZnS. [3].

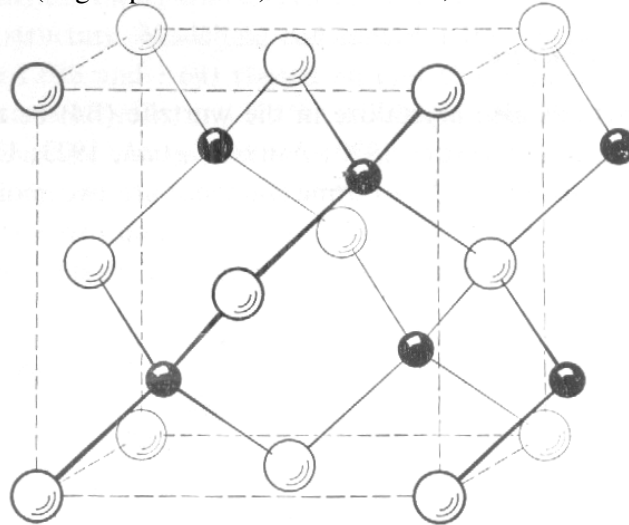


Figure. 2.2. Wurtzite. The arrangement of metal atoms (small filled circles) and non-metal atoms (large-open circles) in wurtzite, the hexagonal form of ZnS. [3].

2.3 Bonding in II-VI compounds

The electromagnetic interaction between the positively charged nuclei and negatively charged electrons of the constituent atoms create the forces that bind a solid. Actually, it has been found that the electronic structure of the different atomic states plays an important role in the interactions but still it is not yet possible to make or formulate a theory for the binding in all solids.

In general, the binding forces depend on the positions of the atoms in the periodic table, the semiempirical theory of chemical bonding and the structure. Actually, Chemical bonds are classified into three general types: ionic bonds, covalent bonds and metallic bonds. The bonds in the most II-VI compounds are adequately described by any of these extreme types, but have characteristics intermediate to those usually associated with the terms ionic and covalent.

The following chart will illustrate the three types of the chemical bonds.

Table 2.1 the types of bonds and there position in the periodic table

| TYPES OF THE BONDS | POSITION IN THE PERIODIC TABLE |
|---------------------------|--|
| Ionic Bonds | Between atoms that are located in the extreme left-and right hand portions of the periodic table. |
| Covalent Bonds | Between atoms that are located near the centre of the periodic table. |
| Metallic Bonds | Between the elements displaying characteristic high thermal and electrical conductivity that are located principally in the lower left region of the periodic table. |

When an electron from metallic element transfers to nonmetallic element, ions are formed. Ionic bond is produced as a result of an attraction due to Columbic force between the excess positive and negative charges. In ZnS, for example, transfer of

$4s^2$ electrons from Zn to the 3p orbital of S forms ions with stable closed shell configurations: $Zn^{+2}(3s^2 3p^6 3d^{10})$ and $S^{-2}(3s^2 3p^6)$. Although the II-VI compounds were originally classified as ionic solids, but according to calculations of the crystal energies of the sulfides and selenides. It was concluded that the binding is not necessarily completely ionic. The interatomic separations that are found in II-VI crystals with the zincblende or wurtzite structure can not be explained only by pure ionic model. The study shows that the calculated distances between the II and VI atoms is larger than those observed. This is due to covalence effects, the covalent shortening increases with increasing atomic number. The distribution of electrons can be obtained from the X-ray diffraction; studies of this kind have been made on ZnS and obtained projections of the electron density in ZnS planes which concluded that the bonding was a mixture of ionic and covalent. [5].

2.4 Sulfur

There are many elements which are found in the free state in the nature. Sulfur is one of them which is known and used by our earlier ancestors. Sulfur is a very important element. Students and chemists recognize the importance of sulfur and their compounds in chemical industry and environment. More than 100 million tons are produced per annum. This element is very important not only for heterogeneous catalysis and for application of solid state electrochemistry with respect to technological aspects but also for the evolution of our geosphere.

2.4.1 Physical and Chemical Properties of Sulfur

Sulfur is a much known element which has many characteristics that make it a special and an important element which is used in many fields in physics and chemistry. Sulfur is a bright yellow nonmetal. Pure sulfur has no taste or smell and it is not harmful to people while its compounds smell very strongly and some of them are harmful to people (poisonous). Sulfur is used a lot in the inorganic industry.

Oxygen O, sulphur S, selenium Se and tellurium Te, that occupy column VIA of the periodic table. All are nonmetals, and their oxides form acidic solutions in water. The atomic number of sulphur is 16, its atomic weight 32.07 amu, and its electron configuration is $(1s^2 2s^2 2p^6 3s^2 3p^4)$, with six valence electrons outside a neon core. The first ionization potential of the atom is 10.357 V, the second is 23.405 V, so the atom holds its electrons quite strongly. Further more, it is available in the nature to the amount of 0.052%. It has been mentioned that the structure of S affects on its existence. If a neutral atom gains two electrons, it completes the stable argonic structure. The sulphur ion S^{2-} is stable in aqueous solution, where the polar water reduces the energy penalty of the charge. Two sulphur atoms can make a "coordinate covalent" single bond, and this S_2 molecule is found in the vapor at high temperatures. Sulphur does not form S_2 with a double bond, as oxygen does. If two electrons are added to this molecule, the result is the disulphide ion, S_2^{2-} , which is also stable in aqueous solution. [8].

2.4.2 Forms of sulfur

Sulfur has different solid forms in the nature. These forms are called autotropes. These forms differ from each other in the physical properties. There are eight sulfur atoms bonded together as a ring-shaped molecular in the two most important allotropes. .The crystal structure of orthorhombic sulfur (fig. 2.3), the cell parameters are a: 1043.7 pm, b: 1284.5 pm, c: 2436.9 pm, $\alpha: 90^\circ$, $\beta: 90^\circ$, $\gamma: 90^\circ$

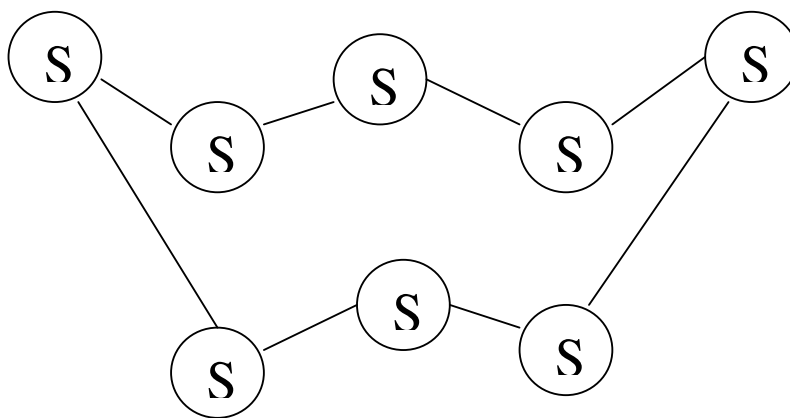


Figure. 2.3. Covalent Sulphur molecular solid at room temperature with the formula S_8

As it is mentioned about that there are many solid forms of sulfur. For example, Alpha, Beta, Plastic, Roll, flowers and Molten. Each one has different physical properties. For example, Alpha sulfur forms a bar crystals in an arrangement called orthorhombic system. It is stable below $96^\circ C$. On one hand, Beta sulfur forms bright yellow chisel-like crystals in an arrangement called the monoclinic system. This type of sulfur is stable in $96^\circ C$ to the melting point $118.9^\circ C$. The third form of sulfur is called plastic sulfur. Pouring molten sulfur into cold water will produce plastic sulfur which is soft and rubbery. It is made of long chains of sulfur atoms. Other forms such as roll and flowers sulfur has a mixture of different sulfur allotropes.

The temperature of the sulfur may determine the physical characteristics of some sulfur form such as Molter sulfur. For example sulfur becomes a runny amber liquid when it is above its melting point. When more heat is applied the molar sulfur becomes thicken and darker. This is because the ring-shaped molecules break a pant and form long jumbled chains. When the temperature is near the boiling point, the sulfur becomes a black liquid because the chains begin to fall a part. In conclusion, temperature has a main hand in producing different sulfur forms because it plays in its structure which determines different physical properties. [9].

2.5 Zinc

Zinc was known thousands of years ago. Egyptians used zinc in the form of bronze as long as 2200Bc while Romans used brass-another form of zinc- around 200Bc.

Brass most probably came into usage when Smith Sonita was unknowingly smelted with copper to yield a new alloy, more yellow and more attractive than bronze. In that time, zinc was not considered as metal. It was discovered as metal in 1520 AD. During the Medieval period ,zinc mining was developed in Spain, Cornwall, Sweden, Saxony, and some areas of eastern Europe but mining was still unorganized. It was first organized in U.S.A in 1720 than in Europe in 1790. Because of the importance of zinc, zinc production raises to 704 million tones in 1992. [8].

2.5.1 Physical and chemical Properties of Zinc

Zinc is available in the nature. It is an abundant as rubidium, at the same time, it is more abundant than copper. Zinc is located in the 12th column of the periodic table. As other metal, zinc has its physical and chemical properties. It is a bluish-grey metal. In air zinc is just like a sheet of aluminum but it is heavier than aluminum and it does not bend easily. Its atomic number is 30, atomic weight 65.38. Its natural occurring isotopes are 64 (49%), 66 (28%), 67 (4%), 68 (19%) and 70 (0.6%). Its density is 7.14 g/cc, electrical resistivity 6.16 $\mu\Omega$ -cm, heat capacity 0.0925 cal/g-K, and heat conductivity 0.268 cal/cm-s-K. Zinc melts at 419.5°C and boils at 907°C. Its crystal form is hexagonal close packed, with $a = 0.266$ nm, $c = 0.494$ nm. The ionic radius of Zn^{++} is 0.074 nm. The ionization potentials of zinc are 9.36V and 17.89V. The electron configuration of zinc is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$. The atom shows a valence +2 in their compounds. Zinc is covered by a protective transparent layer of hydrogen gas or (polarization), as a result of this hydrogen layer pure sulfur does not react with water or dilute acids.

Arsenical zinc is used for making hydrogen in the chemical laboratory. The reduction potential of zinc is -0.76V , and of cadmium, -0.40V , so both are relatively reactive. [8].

The crystal structure of zinc is hexagonal close-packed (fig. 2.4), the cell parameters are a: 226.49 pm , b: 266.49 pm , c: 494.68 pm , $\alpha: 90^\circ$, $\beta: 90^\circ$, $\gamma: 120^\circ$

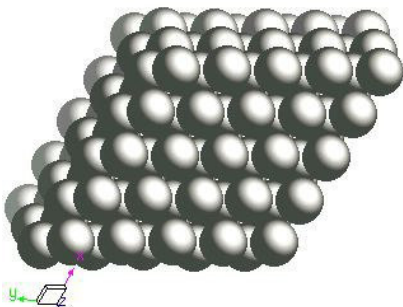


Figure. 2.4. Structure of Zinc crystal.

2.6 Nanostructures Syntheses and fabrication techniques

Two categories of syntheses and fabrication techniques are generally used. One is called "bottom-up" techniques and the other one called "top-down" techniques. The "bottom-up" can be approached by using the chemical properties of single atoms to automatically arrange themselves into some useful conformation such as dots or wires. [2]. It all begins from atoms and molecules that get rearranged and assembled to larger nanostructures. Thermal decomposition, laser assisted vapor-liquid-solid and thermal evaporation are some examples of "bottom-up" synthesis methods.

"top-down" techniques which are fabricate nanoscale objects out of bulk materials by cutting, milling, and shaping those materials into the desired shape, order and dimension by using micro fabrication method such as wet etching, dry etching and reactive ion etching. It begins from a bulk piece of material, which is then gradually or step-by-step

removed to form objects in the nanometer-size regime. Nanowires can be synthesis by two methods gas-phase synthesis and solution-based synthesis.

A lot of techniques have been used in the synthesis of one – dimensional nanostructure materials. This technique can be summarized in fig. 2.5.

Techniques of Synthesis and formation one-dimensional nanowires

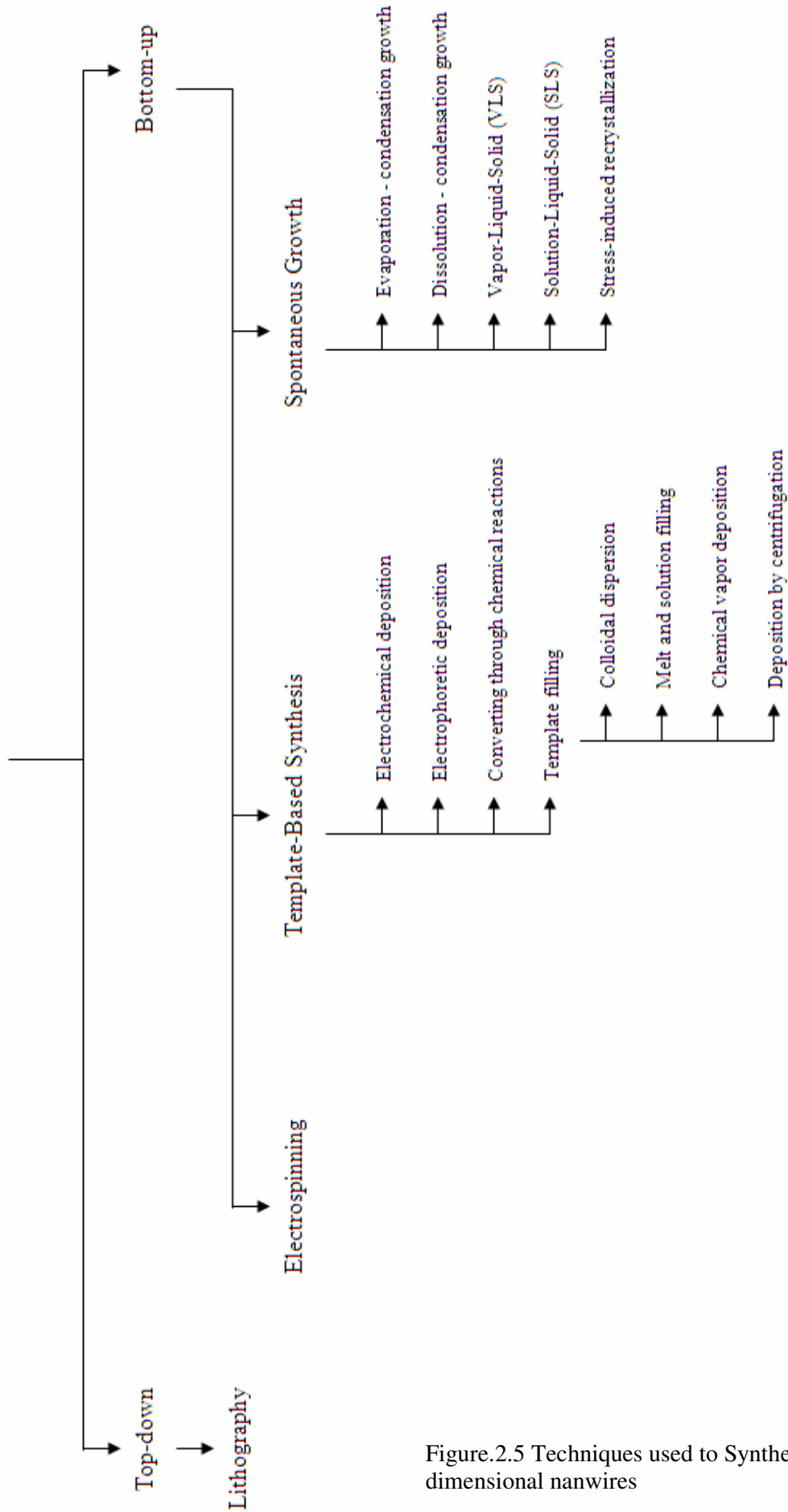


Figure.2.5 Techniques used to Synthesis one-dimensional nanowires

2.7 Gas-Phase Synthesis

2.7.1 Vapor-liquid-solid (VLS)

VLS was found in the early 1960s. This mechanism is very important so it has success in the growth of semiconductor nanowire. Actually VLS is the mechanism which is mostly used in producing and creating nanowire. This method has been used to fabricating nanowire with assistance to some facilities. To use this method some equipments are needed. A horizontal ceramic tube furnace is required which is attached to constant gas flow (such as Ar gas or N_2 gas). Au particles are used as a catalyst and it is deposited on Si wafer and they are exposed to heat which reach a temperature of (about $363^\circ C$). The substrate is annealed. As a result of that Au react with Si to form Au-Si alloy droplets which is the base of nanowire growth. (Fig 2.6).and (Fig 2.7).

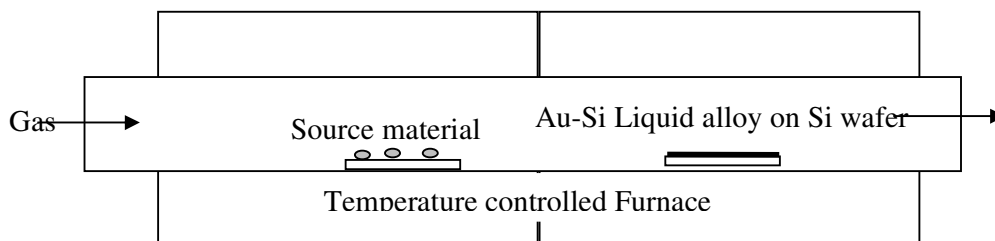


Figure. 2.6 Schematic of tube furnace for vapor– liquid-solid growth.

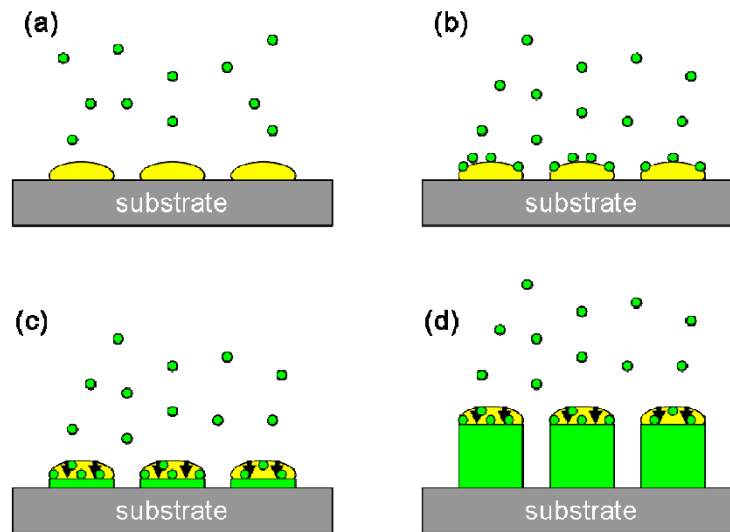


Figure. 2.7 The schematic diagram of traditional adsorption-induced VLS model : (a) mass transport of vapor species, (b) intermediate reaction at the vapor–liquid interface, (c) penetration of the product to the melt and subsequent diffusion to the liquid–solid interface, and (d) incorporation into the solid at the liquid–solid interface and growth [11].

2.7.1.1 Physical vapor deposition (PVD)

It is the short form of physical vapor deposition. The thermal evaporation of sources that is a bulk version of the desired nanomaterial, produces the vapor species. Most of these materials are commercially formed in powder form. This material could react with a gas to be cooled and redeposit on a substrate. The small molecules can be released from its bulk materials by many methods. Those methods will stimulate and remove the molecules by thermal processes or by kinetic energy deposition. The thermal excitation can be obtained from thermal evaporation (electron beam heating or flame synthesis), or by laser ablation (when a short nanosecond pulse from a laser is focused onto the surface of a bulk target), sputtering is a method which use kinetic energy to release molecules from its bulk by bombardment with atoms or ions. [14]. The main benefit of PVD is that it can provide for easy control over the chemistry of the synthesized material, with relatively little control of the system parameters. [13].

2.7.1.2 Chemical vapor deposition (CVD)

CVD is the second type of VLS. It is the short form of chemical vapor deposition. A chemist believes that chemical reaction plays very important role in creating something new. According to CVD, a chemical reaction creates the vapor species. For examples, when chemical reaction happens between Zn and H_2S flow gas / ZnS vapor species will be produced. Chemists have found that it is important in CVD to control the atmosphere as it is difficult to achieve the correct setup.

2.7.1.3 Laser-assisted catalytic growth

In this method a heated flow tube is used, the target is placed in the tube with constant flow of carrier gas such as (Ar) or (H_2). The target consists of mixture of catalyst metal and nanowire materials. The laser beam is focused in the target so, the evaporation is obtained by laser beam. Then this vapor is carried by gas and solidifies into substrate (fig. 2.8). Laser ablation has advantage compared to other synthesis techniques because laser can be used to generate nanometer-size for many material.[12]. In some cases the laser beam provides an enough kinetic energy; which is deposited to nanomaterial molecules. The molecules can move and solidifies by themselves. So, in this method it is some times no need to use carrier gas.

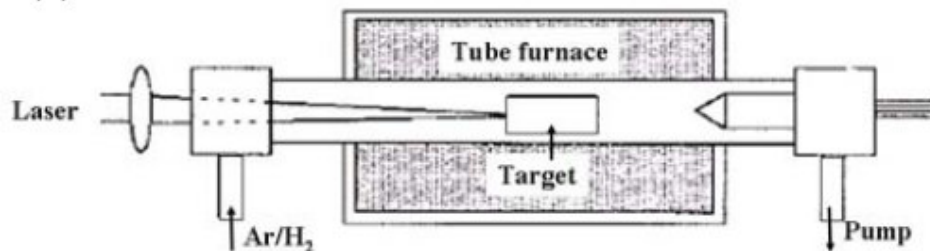


Figure. 2.8 Schematics for a laser ablation nanowire growth apparatus.[12]

2.7.2 Vapor-solid (VS) process

This method can be used to synthesize nanowires without using a metal catalyst as a liquid droplets. It is an evaporation-condensation growth, the source material is heated near its melting point then carrier gas will transport the vapor particles and condensed onto a substrate the deposition happens at cooler temperature. Vapor-solid mechanism and the Vapor-liquid-solid are nearly the same. The difference is that in (VS) the one component of the gaseous atoms might play the role of the catalyst itself. (fig. 2.9). Dissolution – condensation process differs from evaporation – condensation in growth media. In the Dissolution – condensation process, the desired nanowire materials are first dissolved into a solvent or solution, and then diffuse through the solvent or solution and deposit onto the surface resulting in the growth of nanowires.

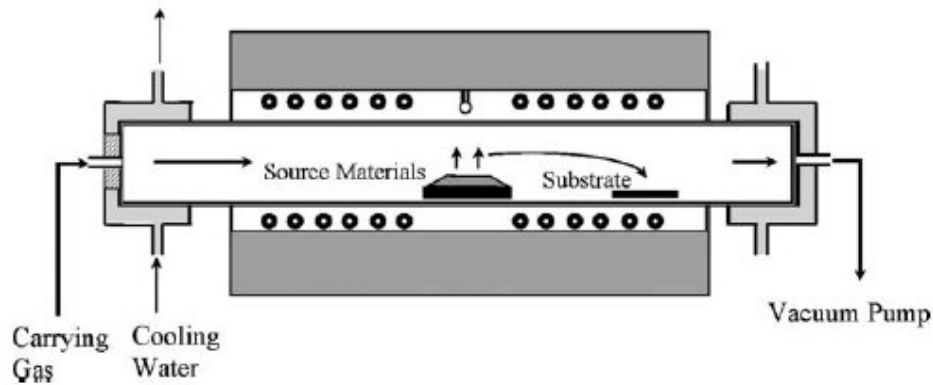
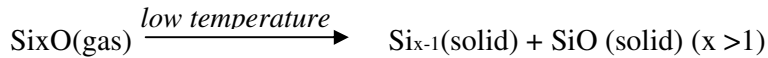
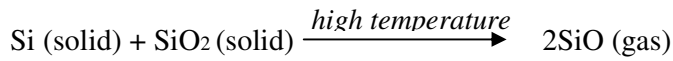


Figure. 2.9 Schematic of tube furnace for vapor-solid growth.

2.7.3 Oxide-Assisted Growth (OAG)

Some materials can be developed into nanowires from their oxide decomposition. For example, it was found that no need to use metal catalyst for producing Si nanowires, SiO_2 has been found to be an effective catalyst which makes Si nanowires to grow. In this method the target is a mixture of Si and SiO_2 powders and no metal catalyst is needed. Wang et al used this method to produce Si nanowire by laser ablation of the target [15]. By this method a very uniform Si nanowires were formed with

diameter of 20nm and 100 μ m in length. The mechanism of the Oxide-Assisted Growth can be described by the following reactions.



By laser ablation, Si reacts with SiO₂ to form SiO or Si_xO (x>1) vapor phase. This vapor phase is the key factor for the nucleation and growth of Si nanowires because it deposits on the substrate and decomposes into nanoparticles at a relatively low temperature of 900-1000 °C.[12]. The nanowires have a thin oxide layer covering a crystalline Si core. (fig. 2.10).

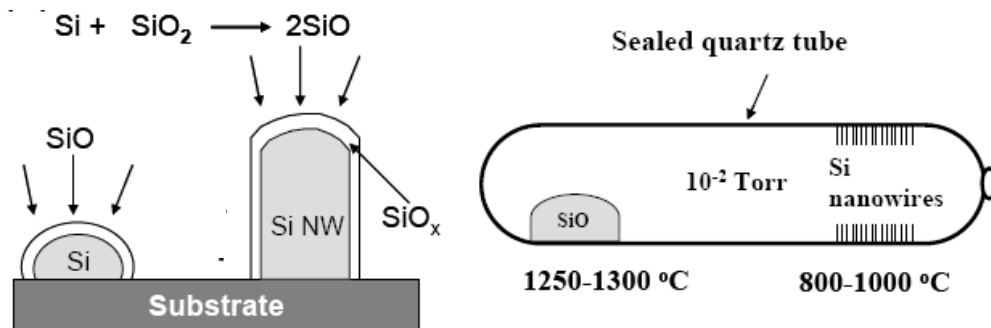


Figure. 2.10 Schematics description of the oxide assisted Si nanowire growth process and Experimental set-up for oxide assisted method.[12]

2.8 Solution-Based Synthesis

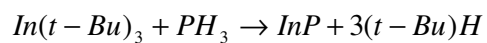
2.8.1 Electrochemical deposition method

Electrochemical deposition is one method which is used in Template-Based synthesis technique. There are many kinds of template but the most commonly used is anodized alumina membrane, Alumina membranes with uniform and parallel pores structure are made by anodic oxidation of aluminum sheet in solution of sulfuric, oxalic

or phosphoric acids [16]. These pores are arranged in a regular hexagonal array with a density of 10^{11} pores/cm². The template with pores of diameters ranging from 10 to 200 nm is placed in a deposition solution and is connected to the cathode. Pores can be filled with desired nanowire material by deposition of solid material on an electrode. That can be done when anode is placed in the deposition solution parallel to the cathode. When the electrical current is applied to the circuit, the cations reduce at the cathode so, the growth of nanowires occurs inside the pores of the template.

2.8.2 Solution-Liquid-Solid (SLS) Method

A low temperature solution-liquid-solid (SLS) method for the synthesis of highly crystal nanowires was first introduced by Buhro and coworkers [15]. This method is the same as VLS growth method but it can operate at low temperature and use solution phase reactions. SLS method is used to produce crystalline nanowires of III-V semiconductors. A metal with low melting point such as (In,Sn,Bi) was used as a catalyst and the desired material was generated through the decomposition of organometallic precursors. Growth of (InP) can be used as example, The precursor used is typically an organometallic compounds as $\text{In}(t\text{-Bu})_3$ and PH_3 which are dissolved into a hydrocarbon solvent. In the solution the precursors react to form (In) and (P) compounds for the growth with the following reaction:



Indium metal functions as the catalyst for the growth of (InP) nanowires. In melts and forms liquid droplets. Both (P) and (In) dissolve into the droplets and precipitate to form the (InP) nanowires. (fig. 2.11).

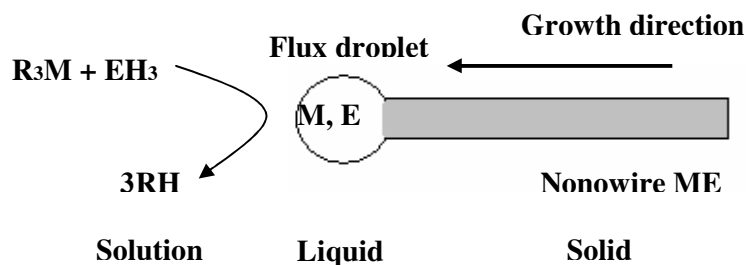


Figure. 2.11 Schematics showing the growth of nanowire through the solution-liquid-solid mechanism.

2.9 Prior approaches used to fabricate ZnS nanowires

In 2003 X.M Meng reported the synthesis of ZnS nanowires by using the VLS mechanism[17]. High-purity ZnS powder were put in an alumina boat which was located at the center of the quartz tube. A silicon wafer substrate covered with 3nm Au film was placed in the tube at a distance of about 30cm from the center of the alumina boat. The tube was evacuated to 2×10^{-2} Torr and then a mixture of Argon gas and 5% of hydrogen gas was kept flowing through the tube. The pressure inside the tube was kept to be 300 Torr and the flow rate was 50 sccm, the furnace was then heated at a rate of $25^\circ \text{C}/\text{min}$ to 800°C and held at that temperature for 30 min. the furnace temperature was then raised to 1100°C for 3 h and then the furnace was kept to cool to room temperature. The deposited products were characterized with scanning electron microscopy(SEM), X-ray diffraction(XRD) and transmission electron microscopy (TEM). The SEM image of the deposition showed that the substrate was covered uniformly with a high density of ZnS nanowires with diameters in the range of 10-20 nm and lengths of several micrometers.

Heesung Moon in 2006 [18], presented a synthetic method of fabricating zinc sulfide nanowire by chemical vapor transport and condensation. That was done by the reaction of zinc oxide and iron sulfide powders on a silicon substrate coated with $50\mu\text{m}$

gold film . ZnS is formed when ZnO reacts with FeS under a temperature of (1200°C to 1380°C) according to the reaction formula $ZnO(powder) + FeS(powder) \rightarrow ZnS + Fe_3O_{4-x}$. Equal amounts of pure ZnO and FeS powders were mixed in an alumina boat, which was inserted to a quartz tube into a horizontal tube furnace. The furnace temperature was increased to 900 °C to 950 °C in constant Ar flow. ZnS nanowires were grown on gold coated silicon substrates through a simple chemical vapor transport-condensation based on the vapor-liquid-solid(VLS) mechanism. In the previous reaction FeS has an advantage in prevent oxidation of the produced ZnS nanowires because at high temperatures the iron atoms decomposed form FeS and react with oxygen atoms. As a result of that Fe_3O_{4-x} were produced in the alumina boat. The sample was cooled down to room temperature, it was found that the substrate surface was covered by white ZnS nanowires. The produced ZnS nanowires was characterized using scanning electron microscopy, transmission electron microscopy and dispersive X-ray spectroscopy (EDXS). The image from (SEM) showed that the ZnS nanowires had a diameters ranging from 10 to 30 nm and lengths up to several hundred micrometers.

ZnS nanowires were successfully synthesised by Z. Xianghui in 2005 [19] in large quantities via simple thermal physical evaporation without using any metallic catalyst. A bout 1 gram of ZnS powder was loaded in a quartz boat which was then placed in the center of tube furnace and silicon wafer was located at about 10cm from the boat. Argon gas was used as a carrier with constant flow of 95sccm also hydrogen gas was used with flow rate of 7sccm, the furnace temperature was raised to 100 °C for 30 minute with 0.05 Mpa furnace pressure. After colling down a white layer was deposited on Si wafer.

A synthesis of ZnS nanowires on an Anodic Aluminum Oxide (AAO) template coated with Au was reported by H. Xintang and T. Ming in 2006.[20]. Pure ZnS powder was placed in the middle of a quartz tube and the substrate was placed next to the senter along the down stream of flow of Ar mixed with 5% of H_2 at rate 50 and 16 sccm. The furnace was heated to $800^\circ C$ and after 30 min the temperature was raised to $1100^\circ C$ and fixed at that degree for 150 min. After that the quartz tube was removed from the furnace and it was cooled down to $400^\circ C$ under the flow of Ar gas. White product was found on the template and single crystal ZnS nanowires were obtained on the whole area of the AAO template. The products were charcterized and analyzed by (SEM), (EDS) and (TEM). The produced nanowires had a diameter of 80nm with length of several tens micrometers.

Thiourea which is an organic compound of carbon, nitrogen, sulfur and hydrogen, with the formula CSN_2H_4 or $(NH_2)_2CS$ can be used as a sulfur source for producing ZnS nanowires when the thiourea is mixed with zinc acetate . The mixture is dissolved in a pure water and ethylenediamine to produce an aqueous solution of EN, or pure a solvent of ethylenediamine. This method was reported in 2006 by G.H. YUE [21] to synthesis ZnS nanowire. The solution was placed in a Teflon cup then the temperature was raised to $180^\circ C$ for several hours. After cooling down, a white product was obtained through filtering and washing with alcohol and distilled water to remove impurities. In this experiment the concentration of zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was 0.40 M and thiourea 0.80 M. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM).

2.10 Thermoluminescence

The emission of light from a material following the initial absorption of energy from an external source for example ultra-violet or high energy radiation is called Luminescence. The emission can be fluorescence or phosphorescence. That is according to the characteristic lifetime τ between absorption of the excitation energy and emission of the luminescence. If $\tau \leq 10^{-8} s$, the process will be fluorescence. On the other hand if $\tau \leq$ few seconds, the process will be phosphorescence. The delay of time between the two processes can be explained by using a ground state energy level (g) and an excited state level (e), as shown in (figure 2.12). Fluorescence is the emission of light which follows the excitation of an electron from (g) to (e) and its subsequent return to level (g). lifetime in the excited state may be very short because the excited electron is transmitted immediately to ground state. On the other hand in phosphorescence, the residence of excited electrons in the metastable level (m) delay the return of electron to ground state so, the lifetime is longer in this case. As the temperature increases the probability for the thermal excitation from the trap is increase exponentially. [5]

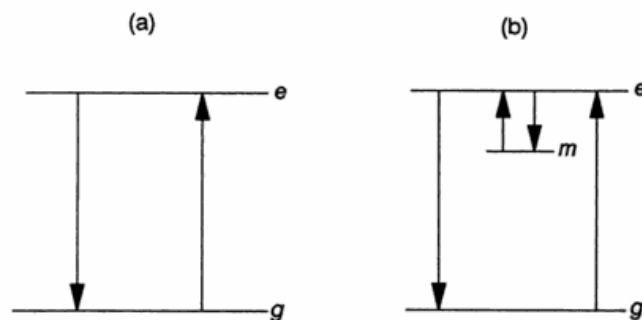


Figure (2.12). (a) Excited e and ground stat (g) energy levels showing absorption and emission for the process of fluorescence. (b) metastable level (m) giving rise to a delay between excitation and emission during the process of phosphorescence.

The thermoluminescence phenomenon had been noted as early as 1663 when it was reported that a diamond was observed to emit light when warmed in the dark. Thermoluminescence is the phenomenon by which certain crystals are able to store

energy transmitted to them by radiation and then emit this energy in the form of visible light when heated. In 1953, it was proposed that thermoluminescence can be used as a radiation detector. To be useful for dosimeter, a TL material must have a relatively strong light output and be able to retain trapped electrons for reasonable periods of time at temperatures encountered in the environment. Thermoluminescence detectors often use crystals that are purposely flawed by adding a small concentration of impurity as an activator. Some thermoluminescence detectors do not require an activator but rely instead upon inherent impurities and defects in the natural crystal.

2.10.1 General model of thermoluminescence

As shown in (figure 2.13), thermoluminescence process can be explain by a simple model. The outer atomic electronic energy levels in an inorganic perfect crystal lattice are broadened into a series of continuous allowed energy bands separated by forbidden energy regions. The valence band is the highest filled band which is separated by several electron volts from lowest unfilled band which is called the conduction band. Electrons are excited out of the valence band into the conduction band when a crystal is exposed to radiation. That will leave a vacancy in the valence band called a hole. The electron and hole are free to wander independently throughout their respective bands. Within the forbidden region between the valence and conduction bands there are discrete local energy levels as a result of the presence of lattice defects or impurities. These discrete energy levels trap electrons which on subsequent heating and recombination causes thermoluminescence. The temperature required to release the electron and produce the thermoluminescence are determined by the energy gap between the valence and conduction bands. If the temperature of the crystal is increased, the probability of releasing an electron from trap is increased, so the emitted light will be weak at low temperatures, pass through one or more maxima at higher temperatures, and decrease again to zero as no more electron filled traps remain.

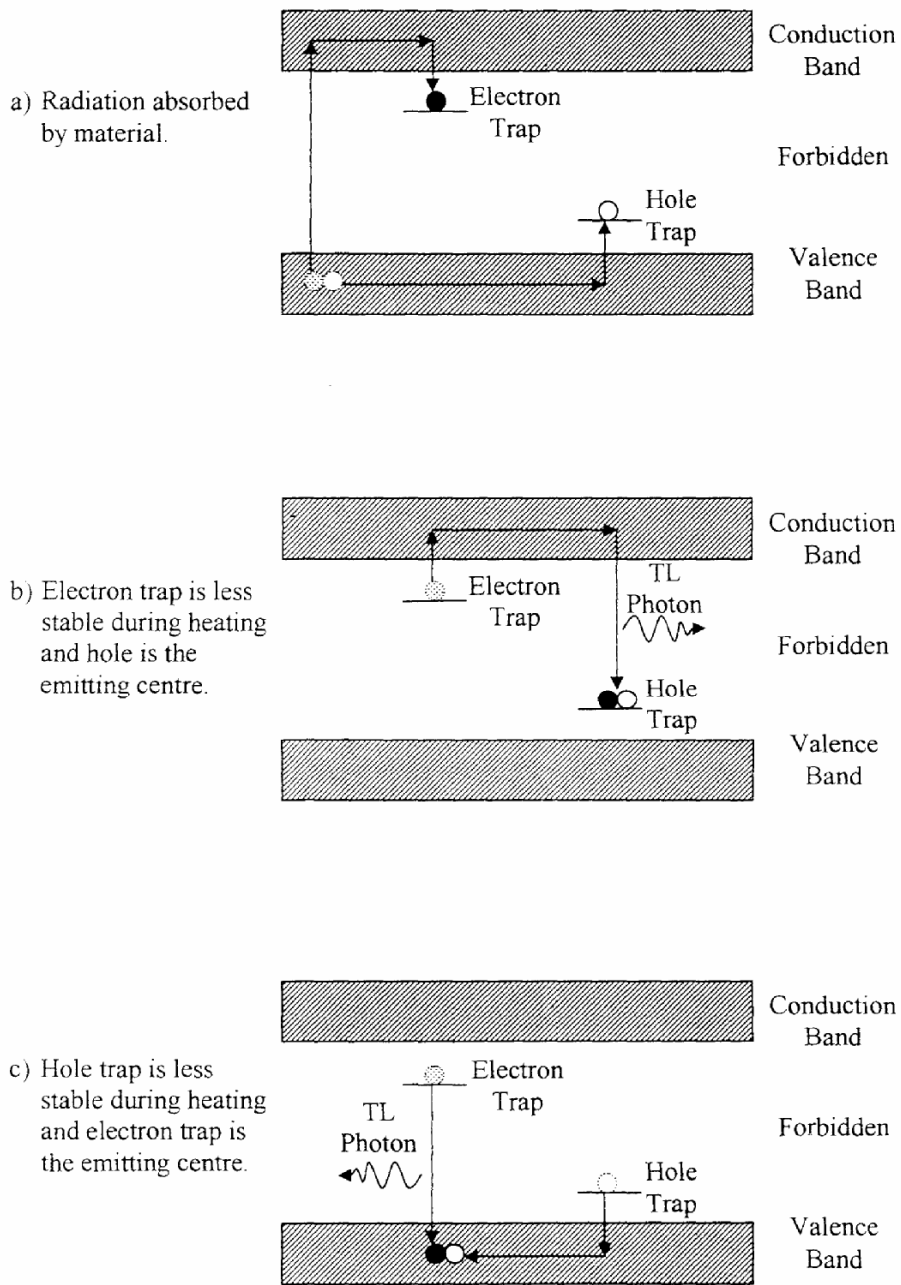


Figure 2.13 Schematic band model for thermoluminescence.

There are two ways that the TL photon can be emitted, depending on the relative stability of the electron trap or hole trap. First, the electron trap may be less stable than the hole trap, resulting in it being raised to conduction band, and become a photon emitting center for the TL photon. Secondly, the hole traps may be less stable than the

electron trap, it will then wander through the valence band until it eventually recombines with an electron trap, thus emitting a TL photon. TL can be used as a dosimeter and can be used to estimate the age of rocks and pottery. Lithium Fluoride (LiF:Mg) is the most used as a dosimeter for recording the external dose.

Lithium Fluoride and Calcium Fluoride are the most popular dosimeters used. Lithium Fluoride (LiF) has activators such as magnesium (Mg) or titanium (Ti) these impurities make the dosimetry more active. LiF chip has dimensions of $3.2\text{mm} \times 3.2\text{mm} \times 0.9\text{mm}$. The trading name of Lithium Fluoride dosimeter is TLD100, TLD600 and TLD700 these differences came from the percentage ^6Li and ^7Li inside the phosphors.

2.10.2 Annealing

The original TLD sensitivity has to be recovered after irradiation and readout so, it is necessary to anneal the TLDs. Unfortunately, the TLD sensitivity is dependent on the details of the anneal cycle, so good control of the anneal cycle is important. Various annealing cycles have been proposed over the years, for different types of dosimeters.

Before the dosimeter is used again, its memory has to be erased so, annealing can be assumed the most important step in TL because this step erases the dosimeter memory and makes it ready to be used to measure a new absorbed dose. The annealing process is carried out inside a furnace and selection of suitable temperature and time for the dosimeter to be held inside the furnace is the critical point in annealing. If new material is used as a dosimeter for a first time, it is necessary to perform at the first an annealing study which can be done as following:

- irradiate 10 TLDs samples to a test dose in the range of the field application.
- Anneal the irradiated samples at a given temperature (eg., 300°C) for a given period of time (e.g., 30 minutes).
- Read the samples.

- Repeat the three steps above increasing the annealing temperature of $50^{\circ}C$ each time up to the maximum value at which the residual TL (background) will remain constant as the temperature increase.
- Plot the data as shown in (Fig.2.14). as it can be observed , after a threshold temperature value T_c , the residual TL signal remains constant.
- Repeat now the procedure , keeping constant the temperature at the value T_c and varying the annealing time by steps of 30 minutes and plot the results. The plot should be similar to the previous one.
- Choose now the best combination of temperature and time.[9]

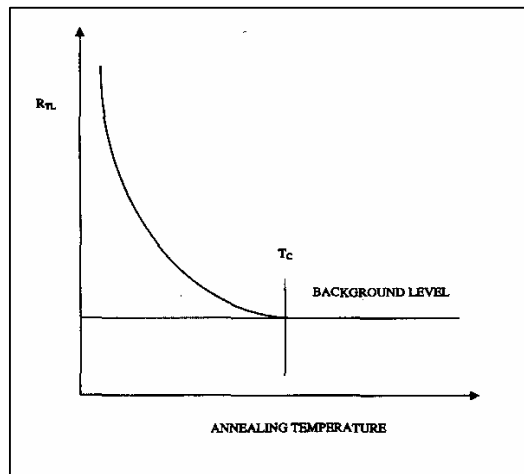


Figure 2.14. TL intensity Vs annealing temperature.

For the dosimeter LiF:Mg,Ti (TLD100,600,700) there are many annealing cycles. The first one is a long cycle 1 hour at $400^{\circ}C$ + 20 hour at $80^{\circ}C$. The second annealing cycle is 1 hour at $400^{\circ}C$ + 2 hour at $100^{\circ}C$. The third one is a fast anneal 15 min at $400^{\circ}C$ + 10 min at $100^{\circ}C$.

2.11 Instruments for characterization of nano particles

It is not possible for the researchers and scientists to use normal equipments such as optical microscope for characterizing and exploring the structures, composition and properties of nanoscale wires. To understand the materials behavior, it is important to know the composition and microstructure for those materials in the highest level of

resolution. That high resolution can not be maintained by the traditional optical microscope because theoretically the maximum resolution that can be obtained with a light microscope is limited by the wavelength of the light which is used to probe the sample. In early twentieth century that problem was solved by using electrons. The electrons can be used like a beam of electromagnetic wave because electrons have both wave and particle properties. As a result of that many kinds of electron microscope were invented. Many analytical techniques such as transmission electron microscopy, scanning electron microscopy, energy dispersive x-ray spectroscopy and x-ray diffraction have successfully used to characterize the structure of nano particles.

2.11.1 Transmission electron microscopy (TEM)

The first Transmission electron microscope was built by Ernst Ruska in the 1930s. (TEM) can be defined as a technique in which a beam of electrons is transmitted through a thin specimen. That electron beam interacts with the specimen as it passes through it and an image of specimen is created. The image can be magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen, monitor, or a layer of photographic film, or sensor such as CCD camera. (fig. 2.15). show a diagram of Transmission electron microscopy.

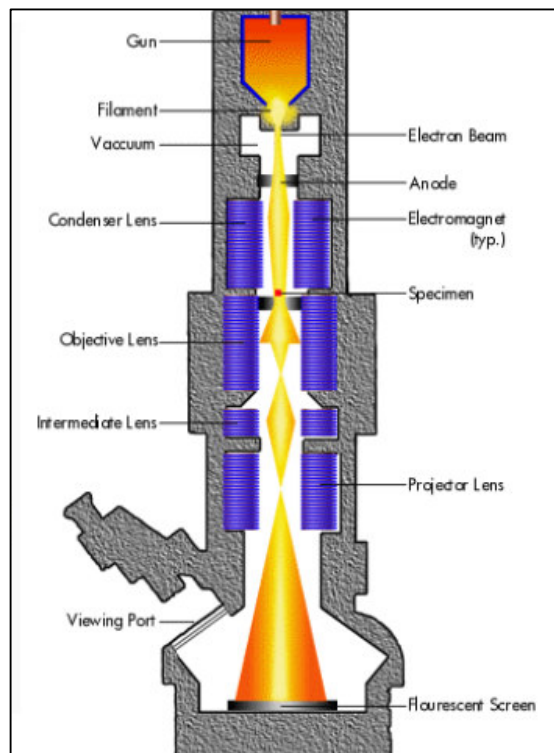


Figure. 2.15 Schematics diagram of Transmission electron microscopy

The working principle of TEM can be explained as following, an electron beam is produced through a filament which is made from a material that can produce a lot of electrons when it is heated an example for this material is tungsten. Electrical current is used to heat the filament and then the produced electron beam is accelerated due to the very high voltage between the cathode (filament) an the anode. The accelerated electron beam can be focused by using leans. The leans function as the optical leans in the normal light microscope which collect the light and focus it in one point, the same thing will happen for the electron beam by using the lens. Those lenses consist of electric or magnetic field. When the electron pass through the magnetic field it is effected by the force which make it deflect and by this method the electron beam can be focused in one point. The electrons beam has enough energy to be transmitted through the sample and some of electrons will scatter at different angles. The transmitted electron signal is greatly magnified by a series of electromagnetic lenses. The magnified transmitted

signal may be observed into two ways. The first way by direct electron imaging, this gives information about the microstructure of the material. The second way by electron diffraction imaging, this method is used to determine the crystallographic structure of the sample. That means TEM provide two methods in which the observation of specimen can be used. Those methods are diffraction mode and image mode. In diffraction mode, an electron diffraction pattern is obtained on the fluorescent screen, originating by the electron beam. The diffraction from the sample area is illuminated by the electron beam. The diffraction pattern is entirely equivalent to an X-ray diffraction pattern. The image mode produces an image of the illuminated sample area with different brightness. The image can contain contrast brought about by several mechanisms. Switch TEM between diffraction mode and image mode can be done as follows. The diffraction pattern and image are formed at the back focus plane and image plane of the objective lens. If the back focus plane is taken as the objective plane of the intermediate lens and projector lens, we will obtain the diffraction pattern on the screen. It is said that the TEM works in diffraction mode. If the image plane of the objective lens is taken as the objective plane of the intermediate lens and projector lens, we will form image on the screen and this is the image mode (fig. 2.16).

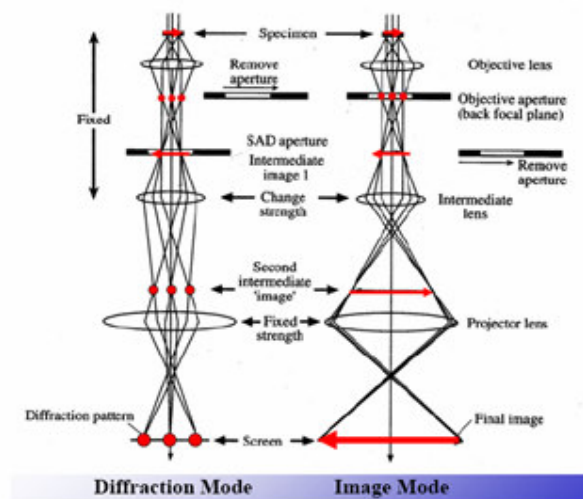


Figure. 2.16 Schematics diagram for Switching TEM between diffraction mode and image mode.

2.11.2 Scanning Electron Microscopy

In the scanning electron microscopy a focused high energy beam of electrons are used to get information about the sample including external morphology, chemical composition and crystalline structure of materials making up the sample. This kind of required electron beam can be maintained by the electron gun which emits electrons from the filament. Electron beam is accelerated and then be focused by electromagnetic leans. Before interacted with the sample, the electrons can be raster the sample surface by using a set of scanning coils. The electrons interact with few nanometers to several microns of the sample as a result of that different signals are produced such as secondary electrons, backscattered electrons, diffracted backscattered electrons and x-ray which carry information about the sample. Secondary electrons and backscattered electrons are detected by a special detector which produces light according to received electrons. A series of treatments are done for this light which finally produce an image for the sample which is displayed in a cathode ray tube. Diffracted backscattered electrons are used to determine crystal structures and characteristic x-ray is used for elemental analysis. (fig2.17)

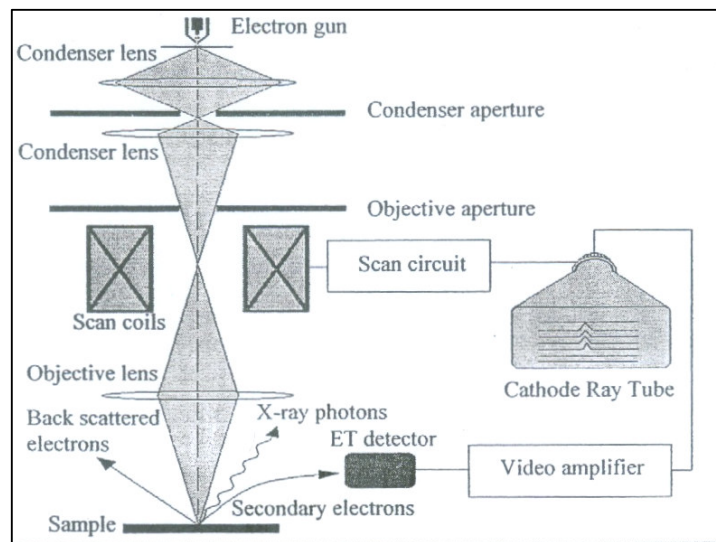


Figure. 2.17 Schematics diagram of a scanning electron microscope. [22].

2.11.3 Energy Dispersive x-ray Spectroscopy (EDS)

This instrument is attached with SEM but in this time the analysis is done by using x-ray emitted from the sample instead of using secondary electron. EDS analyzes chemical compositions of a sample so, the compounds of sample can be known by this analytical technique. The working principle of EDS is similar to that of SEM technique except that x-rays are produced from the sample and received by a special detector which consists of a thin silicon crystal doped with lithium with thin gold electrodes. (fig. 2.18). When an X-ray photon hits the detector, it produces a large number of electrons and holes in the Si(Li) region. Electrons are then accelerated to the positive side, and holes to the negative side. Thus, a pulse of current is generated. The pulse current is proportional to the X-ray energy. Characterized x-ray energy is unique for each element so, the compounds which the sample contains can be known from EDS pattern as it is shown in. (fig. 2.19).

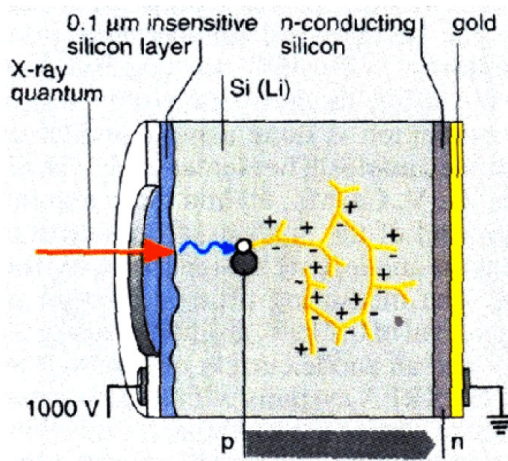


Figure 2.18 Electron dispersive x-ray spectrometer detector.

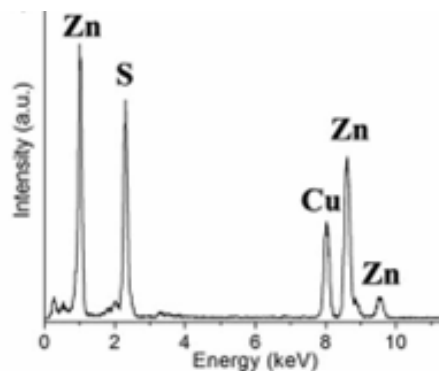


Figure 2.19 EDS pattern obtained from ZnS nano particles sample.

2.11.4 X- Ray Diffraction

X-ray has a wave length of order Angstroms which is equivalent to magnitude of atomic dimensions so; x-ray is suitable to make some investigation for the sample by using x-ray diffraction. Information about crystalline size, interlayer distance and chemical composition can be provided by using this technique. The principle of this technique is based in Bragg's law, when a beam of x-ray is focused to a crystalline compound this beam is scattered and by taking the resultant constructive Interference pattern and take in the account the direction and intensity of the diffracted beams, the unknown sample can be easily achieved by comparing its x-ray diffractogram with an internationally recognized database.

According to Bragg's law the intensity of scattered waves is at maxima if the path difference is equal to integral of wavelength that mean ($2d \sin \theta = n\lambda$) where (d) is the spacing between the deferent planes in the crystal. (θ) is the angle between the incident x-ray and the surface. The diffraction happens if the crystals are parallel to the surface so, it is necessary to rotate the sample so that the Bragg's law is satisfied and record more than one maxima at deferent angles (θ) . When the sample is rotated and the Bragg's law is satisfied for some θ 's the constructive scattered x-ray has to be sure that is collected by the detector. That can be done by rotating the sample by a constant angular velocity ω so the angle of incidence of the primary beam changes and at the same time rotating the detector by angular velocity equal to 2ω hence, the scattering angle is always twice of the temporary incidence angle so, the scattering angle equals 2θ . (fig. 2.20).

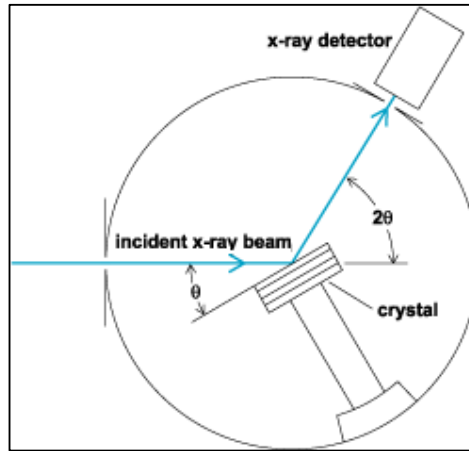


Figure 2.20 Schematic of Bragg spectrometer.

XRD pattern of synthesized ZnS nano particles on a Si substrate is illustrated in (fig2.21) . By using miller indices the distance between planes (d) can be calculated from the equation

$$d(h,k,l) = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For the miller indices $h = 1, k = 0, l = 0$ the atomic distance is equal to distance between plans so, the (d) for this plane can be calculated from the Bragg's equation

$$2d \sin \theta = n\lambda \quad \text{which is also equal to (a).} \quad a = d = \frac{n\lambda}{2 \sin \theta}$$

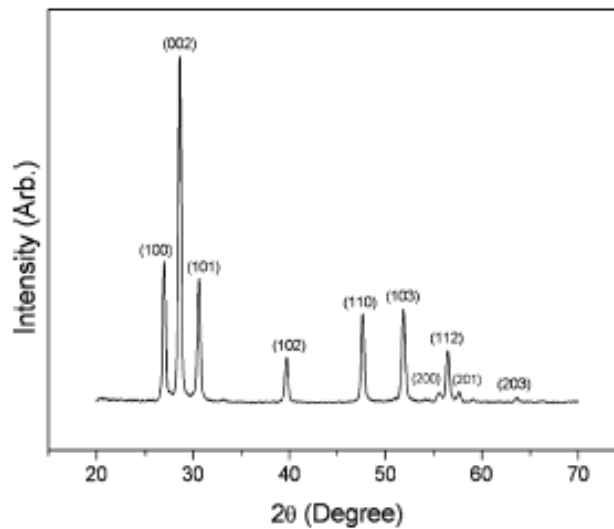


Figure 2.21 XRD pattern of synthesized ZnS nano particles on a Si substrate

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