Chapter one

1.1 Introduction:

Zinc oxide (ZnO) is a (II-VI) material and possesses a variety of excellent properties. These properties are of interest for technological as well as medical applications (devices). Beside of interest for photonic applications, it is a bio-safe and biocompatible and has the strongest electromechanical coupling. The relatively large electro-mechanical coupling makes ZnO an excellent piezoelectric material . Moreover, ZnO possesses self-organized growth property. His makes it possible to grow good crystal ZnO material on any surface being amorphous or crystalline. This property combined with the excellent other properties makes ZnO interesting for many applications, among it, light emitting didoes, laser diodes, energy harvesting components. Since the waste ambient mechanical energy is the most abundant source of energy, ZnO is of potential for developing such energy provding material. On the other hand, low temperature chemical growth can be used to grow ZnO nanostructures of good quality. The temperature can be as low as room temperature (but longer duration of growth is needed). This enables the use of soft and foldable material, like e.g. plastic as a substrate, and hence develops plastic electronics. This will lead to reduce the cost of electronic components considerably. The chemical growth can be combined with first apply a seed layer to lead to nucleation cites and hence achieve a uniform growth.

1.2 Aim of this work:

The aim and justification of this research is as follows :

* To investigate different methods of nano materials synthesis : bottom up and top - down approaches .

* The synthesis of nano materials is better categorized by growth temperatures i.e high temperature or low temperature methods.

* When we say synthesis we mean most probably bottom up approaches with low temperatures which is a suitable approach to research in Sudan. More over Znic Oxied is one of the most researched materials ,now a days. And there are thousands of papers published annually, about 15 publications per day

1.3 Research problem

-Improvement of staichiomerty and the structure of ZnO crystallites .

-Grain growth and decreasing number of point effect.

1.4 Layout:

This thesis consist of four chapters, chapter one is intended to the introduction, research problem, significance, method of the research, and the layout ,then chapter two is for the theoretical background and literature review ,chapter three stated for the method and results , finally chapter four is for the discussion and conclusion.

1.5 Literature review

1- Kamran ul Hasan,a) etal,(2012).

Many applications require a low-cost and large-scale mode of flexible electronics with reasonably high photoresponse that can be detected without high precision measurement systems. We demonstrate a very easy to fabricate ZnO UV sensor, made on common pencil drawn circuit over a paper. ZnO nano-crystals were extracted in a high throughput via a simple and green route. This sensor is well capable of detecting UV light and demonstrates features comparable to those of made with complex and expensive techniques.

2- A. Asthana · K. Momeni ,etal (2011)·

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We report here investigations of crystal and electronic structure of as-synthesized and annealed ZnO nano-belts by an in-situ high-resolution transmission electron microscope equipped with a scanning tunneling microscopy probe. The in-situ band gap measurements of individual ZnO nano-belts were carried out in scanning tunnel in spectroscopy mode using the differential conductance $dI/dV - V$ data. The band gap value of the as-synthesized ZnO nano-belts was calculated to be ~2.98 eV, while this property for the annealed nano-belts (~3.21 eV) was close to the band gap value for bulk ZnO materials (~3.37 eV).

The difference in the band gap value of the as-synthesized ZnO nano-belts and annealed ones was attributed to the planar defects (e.g. stacking faults and twins). These defects can alter the electronic structure by producing localized resonant states that result in band gap reduction.

Chapter Two

Physical properties

2.1 ZnO nano-Structures:

Zinc oxide crystallizes in two main forms, hexagonal quartzite[1] and cubic zincblende. The quartzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn(II). ZnO converts to the rocksalt motif at relatively high pressures about 10 GP[2]. a Hexagonal and zincblende polymorphs have no inversion symmetry (reflection of a crystal relative to any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and pyroelectricity of hexagonal ZnO.The hexagonal structure has a point group 6 mm (Hermann-Mauguin notation) or C6v (Schoenflies notation), and the space group is P63mc or C6v4. The lattice constants are a = 3.25 Å and c = 5.2 Å; their ratio c/a ~ 1.60 is close to the ideal value for hexagonal cell c/a = 1.633.[3] As in most group II-VI materials, the bonding in ZnO is largely ionic (Zn^{2+}–O^{2-}) with the corresponding radii of 0.074 nm for Zn^{2+} and 0.140 nm for O^{2-}. This property accounts for the preferential formation of quartzite rather than zinc blende structure,[4] as well as the strong piezoelectricity of ZnO. Because of the polar Zn-O bonds, zinc and oxygen planes are electrically charged. To maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in ZnO – its surfaces are atomAAically flat, stable and exhibit no reconstruction. This anomaly of ZnO is not fully explained yet[5].

2.2 Nano structures Synthesis:

There are several methods for creating nano-particles, including attrition, pyrolysis and hydrothermal synthesis.

In attrition, macro- or micro-scale particles are ground in a ball mill, a planetary ball mill, or other size-reducing mechanism. The resulting particles are air classified to recover nano-particles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air classified to recover oxide particles from by-product gases. Traditional pyrolysis often results in aggregates and agglomerates rather than single primary particles. Ultrasonic nozzle spray pyrolysis (USP) on the other hand aids in preventing agglomerates from forming.A thermal plasma can also deliver the energy necessary to cause vaporization of small micrometer-size particles. The thermal plasma temperatures are in the order of 10,000 K, so that solid powder easily evaporates. Nano-particles are formed upon cooling while exiting the plasma region. The main types of the thermal plasma torches used to produce nano-particles are dc plasma jet, dc arc plasma, and radio frequency (RF) induction plasmas. In the arc plasma reactors, the energy necessary for evaporation and reaction is provided by an electric arc formed between the anode and the cathode. For example, silica sand can be vaporized with an arc plasma at atmospheric pressure, or thin aluminum wires can be vaporized by exploding wire method. The resulting mixture of plasma gas and silica vapour can be rapidly cooled by quenching with oxygen, thus ensuring the quality of the fumed silica produced[6].

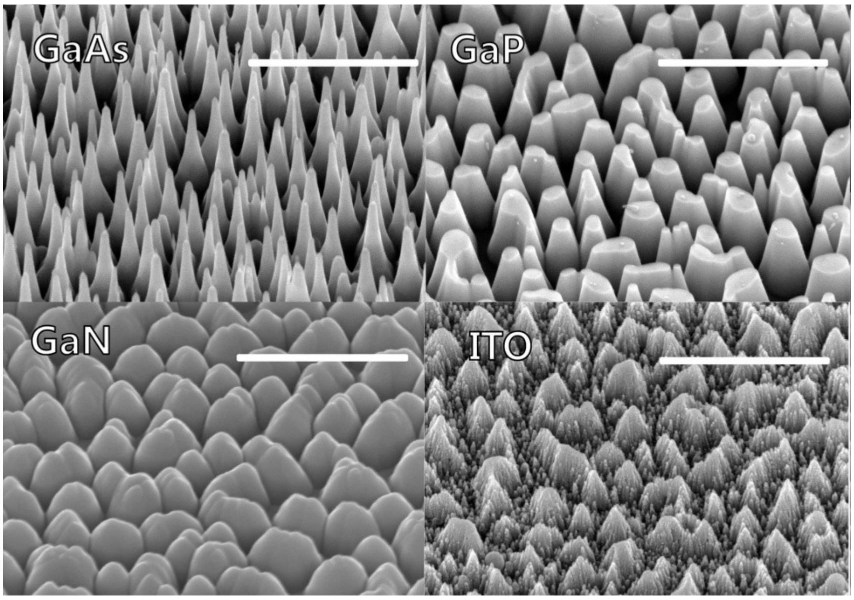
In RF induction plasma torches, energy coupling to the plasma is accomplished through the electromagnetic field generated by the induction coil. The plasma gas does not come in contact with electrodes, thus eliminating possible sources of contamination and allowing the operation of such plasma torches with a wide range of gases including inert, reducing, oxidizing, and other corrosive atmospheres. The working frequency is typically between 200 kHz and 40 MHz Laboratory units run at power levels in the order of 30–50 kW, whereas the large-scale industrial units have been tested at power levels up to 1 MW. As the residence time of the injected feed droplets in the plasma is very short, it is important that the droplet sizes are small enough in order to obtain complete evaporation. The RF plasma method has been used to synthesize different nano-particle materials, for example synthesis of various ceramic nano-particles such as oxides, carbours/carbides, and nitrides of Ti and Si (see Induction plasma technology)[6].

Inert-gas condensation is frequently used to make nano-particles from metals with low melting points. The metal is vaporized in a vacuum chamber and then supercooled with an inert gas stream. The supercooled metal vapor condenses into nanometer-size particles, which can be entrained in the inert gas stream and deposited on a substrate or studied in situ[6].

Nano-particles can also be formed using radiation chemistry. Radiolysis from gamma rays can create strongly active free radicals in solution. This relatively simple technique uses a minimum number of chemicals. These including water, a soluble metallic salt, a radical scavenger (often a secondary alcohol), and a surfactant (organic capping agent). High gamma doses on the order of 104 Gray are required. In this process, reducing radicals will drop metallic ions down to the zero-valence state. A scavenger chemical will preferentially interact with oxidizing radicals to prevent the re-oxidation of the metal. Once in the zero-valence state, metal atoms begin to coalesce into particles. A chemical surfactant surrounds the particle during formation and regulates its growth. In sufficient concentrations, the surfactant molecules stay attached to the particle. This prevents it from dissociating or forming clusters with other particles. Formation of nano-particles using the radiolysis method allows for tailoring of particle size and shape by adjusting precursor concentrations and gamma dose[6].

2.3 Different approaches to Nanotechnology:

To utilize what ’Nanotechnology’ offers is acheived by first have control over the material that enables the technology. This means to have control nano-material[8].

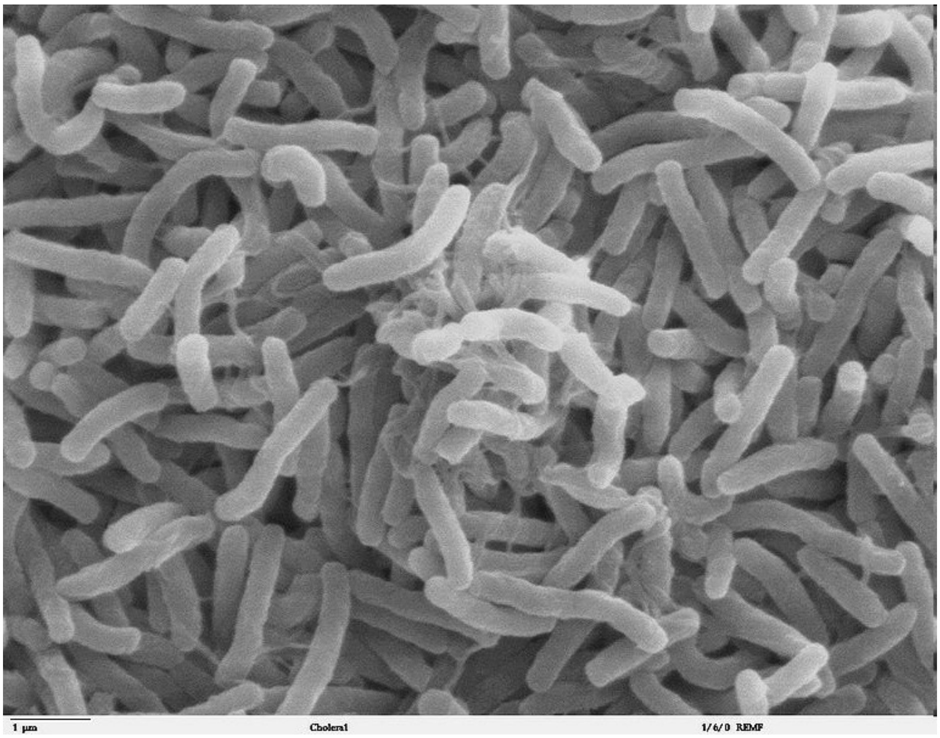


Figur2.1 Bottom-up approach.(usually <u>molecular</u>)

To obtain nano-materials there are two main approaches:

Top-down approach.. Different approaches to Nanotechnology

Bottom-up approach[8].



Figur 2.2 Bottom-up approach.(Cholera bacteria)

Top–down and bottom–up are two, approaches for the manufacture of products,Different approaches to Nanotechnolg , To utilize what 'Nanotechnology' offers is acheived by first have control over the material that enables the technology. This means to have control nano-[8]

2.3.1 material. To obtain nano-materials there are two main approaches:

Top-down approach.

Bottom-up approach.

Top–down and bottom–up are two approaches for the manufacture of products.

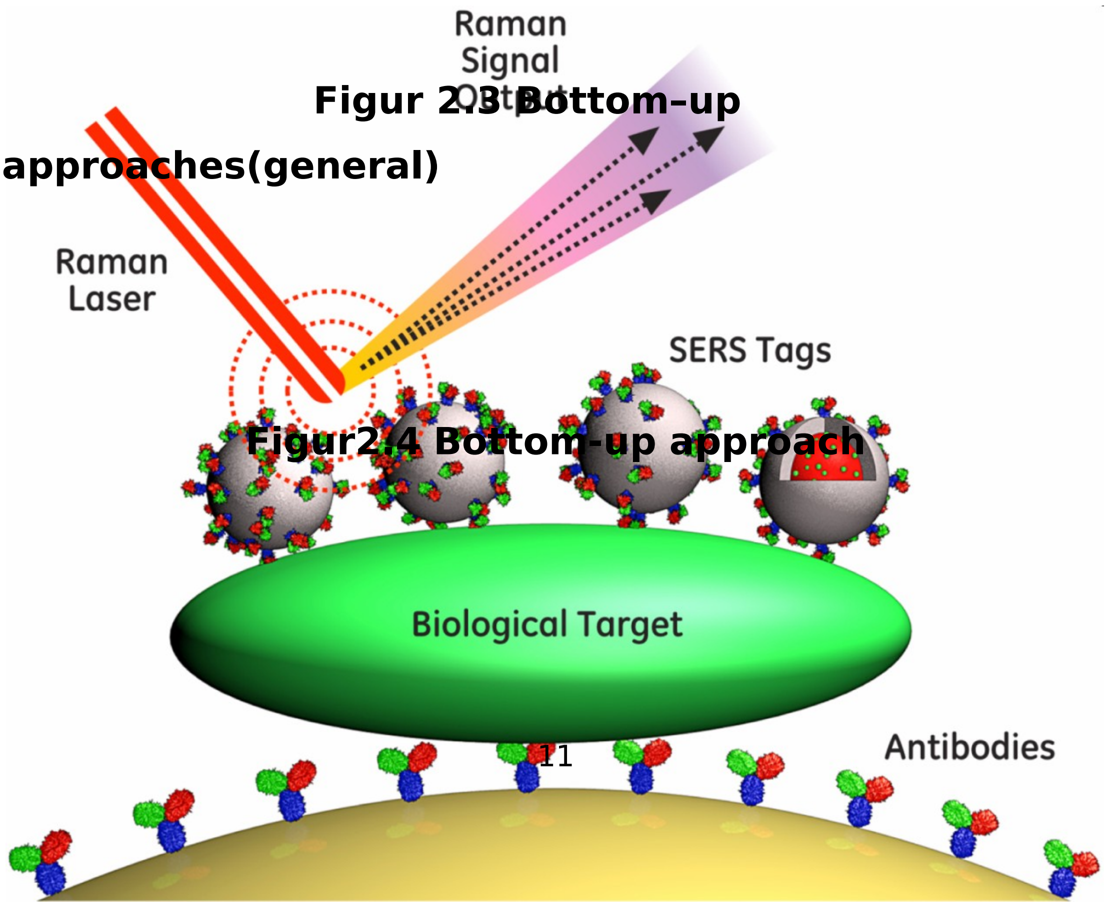
2.3.2Top-down approach:

Top-down approaches seek to create nano-scale devices by using larger,m externally-controlled ones to direct their assembly. This means we take a big thing and break it down to small things. Obviously this requires complex instrumentation in most of the cases. In the top-down approach, smaller structures are created from larger ones with lithographic techniques. However, this way has to include a miniaturization procedure adjusted with new lithographic methods and materials systems in order to reach the nm-range**.[Max-PlanckInstitut Für Metallforschung Stuttgart] [8].**

2.3.3 Bottom-up approach:

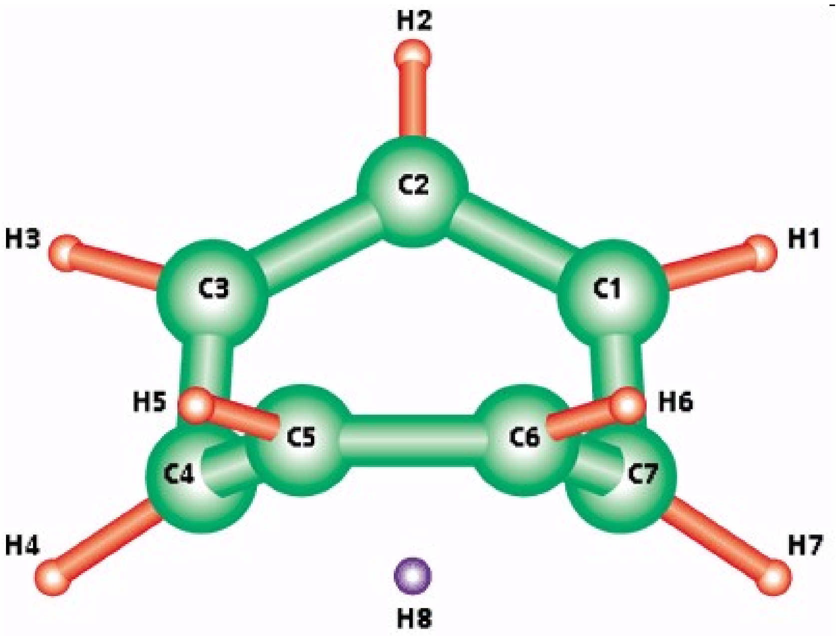
Bottom–up approaches seek to have smaller (usually molecular) components built up into more complex assemblies. In general, the bottom-up approach is realized as follows: small structural blocks are built from atoms, molecules, or from single device level upward. The method (9).

Figur 2.3 Bottom–up approaches(general)



Figur2.4 Bottom-up approach

Different approaches to Nanotechnology



Figur 2.5 Bottom-up approach Biologists and chemists have ever been working with Nano-technology.

2.4 Characterization:

Nano-particle characterization is necessary to establish understanding and control of nano-particle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), x-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF), ultraviolet-visible spectroscopy, Rutherford backscattering spectrometry (RBS), dual polarisation interferometry and nuclear magnetic resonance (NMR).While the theory has been known for over a century (see Robert Brown), the technology for nano-particle tracking analysis (NTA) allows direct tracking of the Brownian motion; this method. therefore, allows the sizing of individual nano-particles in solution.The majority of these nano-particle characterization techniques are light-based, but a non-optical nano-particle characterization technique called Tunable Resistive Pulse Sensing (TRPS) has been developed that enables the simultaneous measurement of size, concentration and surface charge for a wide variety of nano-particles. This technique, which applies the Coulter Principle, allows for particle-by-particle quantification of these three nano-particle characteristics with high resolution[7].

Chapter three

Experimental

3.1 Introduction

In order to prepare a seed solution containing ZnO nanoparticles~5-10 nm procedures can be adapted the following :

3.2 Materials and Equipments

- Potassium hydroxide supplied by CENTRAL DRUG HOUSE(P). Sodium hydroxide supplied by CENTRAL DRUG HOUSE(P).
- Zinc acetate dehydrate $ZnC_4H_6O_4$ (molecular weight =219.51, Density=1.735 g/cm³, purity=99%).
- Distilled water ,de-ionized water supplied by medical laboratories labs - Sudan university of science and technology).
- Magnetic stirrer.
- Beaker and conical flask.
- Thermometer (0-100) ℃.

3.3 Methodology :

Zinc acetate dihydrate was mixed in absolute methanol (99%)

Then 0.01 M concentration of zinc acetate (274mg) add in 125ml of methanol and stirred ,heated to 60 ℃ under continous stirring.

Figur 3.1 heat the solution to 60℃ under continuous stirring

109mg of potassium hydroxide(0.03M) concentration , shacked the solution until it become transparent, added drop-wise from potassium hydroxide solution (to heated zinc acetate) under continous stirried ,then heated to $60^{\circ}C$ for 2hours some drops of solution was taken on substrate leave to dry then the sample clean by ethanol.

3.4.1 The aqueous chemical growth solution :

100ml of de-ionized water was added to zinc acetate (400Mm).then some drops of sodium hydroxiede was added to the zinc solution .

Figur 3.2 The solution transparent.

Then the seeded substrate loaded having its face down in the aqueous solution and then load the solution inside an oven heated at temperature $90^{\circ}C$ for 3 hours and clean carefully the unloaded substrate in de-ionized water then dried .

The samples ready for characterization.

Figur 3.3 solution inside an oven heated at temperature 90◦c for3hours solution .

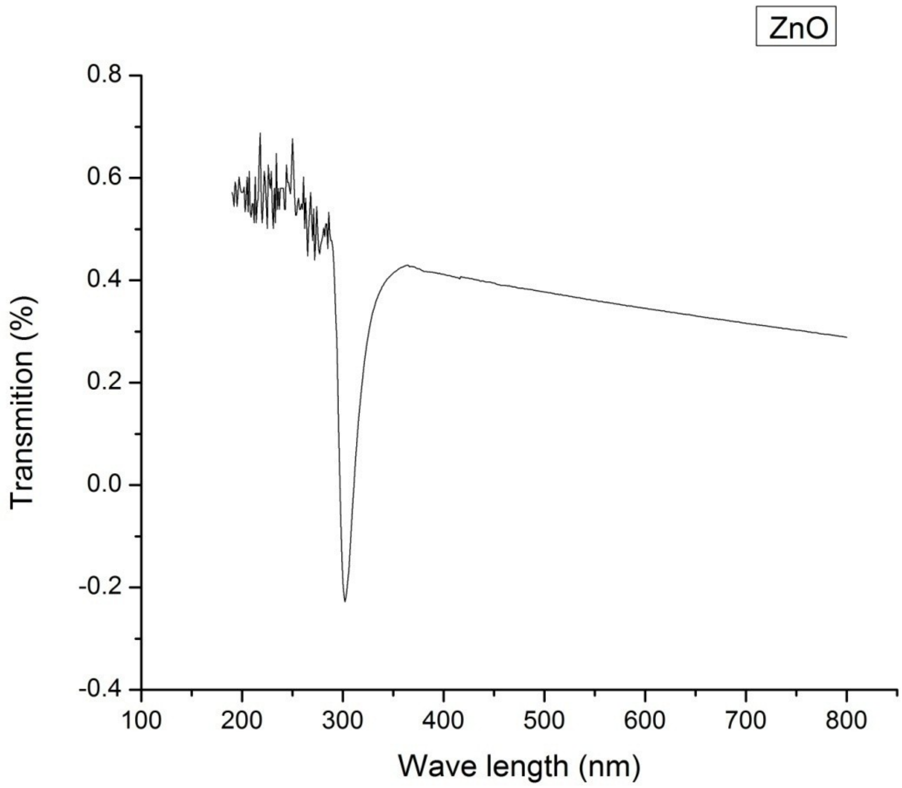
Chapter four

Results and discussions

4.1 UltraViolet spectroscopy

Using the UV-1800 UV-Visible Spectrophotometer supplied by Shimadzu, at Al-Neelain university see Figure 4.0 the synthesized ZnO nano structure was characterized. The UV spectrum of ZnO nano structre synthesized by law temperature chemical growth procedure shown in Figure(4.1).

Figure 4.0 UV-Visible Spectrophotometer

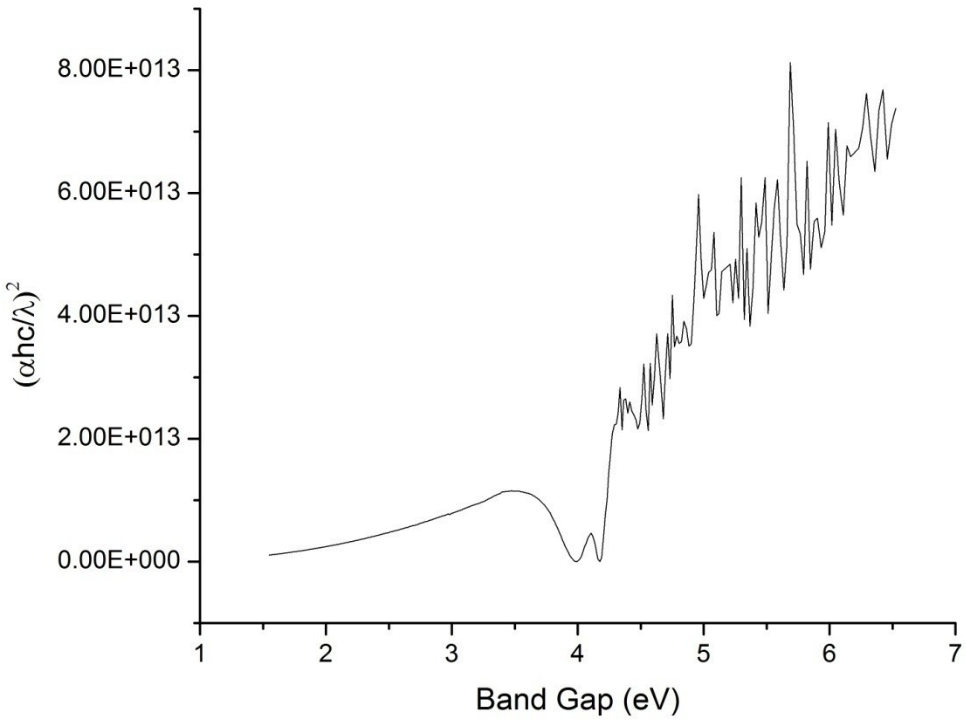


Figur 4.1 Relation btween wave length(nm) and transmition%.

As shown in Figur(4.1) the synthesized nano particles had a very effective UV blocking effect. The transmission in the range 280-320(nm) is approximately zero, indicating that the ZnO nano particles have a high shielding effect .

Band gap energy estimation

Figur(3-5) shows the band gap estimated value of the synthesized ZnO nano structre the obtained result (4.1eV) is higher than expected result from the literature 3.8 eV and that may be related to the effect of impurities and unclean environment .and this effect the result .



Figur 4.2 Relation between band gap(eV) vs (αhc/λ)²

Table (1.4) show the band gap values of present work compared with previous experimental and theoretical results.

4.2 Band gap of ZnO nano particale:

This work	experimental	Theoretical
4.1	3.3[a]	3.37[b]

(a),(b) c,kligshim , phys .status solid I B71,547(1975)

4.3 Conclusions

ZnO offers tremendous potential in future applications. Encouraging accomplished as reviewed in this work. There are still important issues waiting to be further investigated.

ZnO possesses self-organized growth property. This makes it possible to grow good crystal ZnO material on any surface. This property combined with the excellent other properties makes ZnO interesting for many applications . Last but not the least, ZnO is easy prepration , the material available, and can be characterization, and uses.

4.4 Remarks

.Nano-materials infiltrate into human immune system and may cause problem .

.Increasing or decreasing of the temperature is a mean reason of ZnO formation defect.

.The impurity of nano-ZnO refer to the impuritized materials.

.Obtaining a maximum quantity of nano-ZnO from disposition process depend on substrate.

4.5 References

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