Study of Structural and Optical properties of Tungsten trioxide (WO_3) thin films modified with Copper Oxide (CuO) Nano particles

By

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Starting with the name of Allah, the Most Gracious and the Most Merciful.

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A thesis submitted to

Department of Physics

For the award of the degree of

MS Physics

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FACULTY OF BASIC AND APPLIED SCIENCES

DEPARTMENT OF PHYSICS

Dated: 29/5/2017

FINAL APPROVAL

It is certified that the work presented in this thesis entitled "**Study of Structural and Optical properties of Tungsten tri oxide (WO_3) thin films modified with Copper Oxide (CuO) Nano particles**" by **Asma Latif** bearing **Registration No. 342-FBAS/MSPHY/S15** is of sufficient standard in scope and quality for the award of degree of MS Physics from International Islamic University, Islamabad (IIUI).

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Declaration

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Dedicated to my dearest parents and brothers for their love and support. Am here because of my parent prayers.

Bundle of Thanks

Acknowledgement

All praises to ALLMIGHTY ALLAH, the most merciful and beneficent, who gave me the chance in my life to gain knowledge, improve my skills and the power to plan my research work with full devotion. Blessing be on MUHAMMAD (peace be upon him), who is forever a model of guidance and knowledge for humanity.

I stand dedicated to convey my heartiest thanks to all my teachers, associates, colleagues and well-wishers. I could not has manage successfully to complete my thesis without the help of my devoted supervisor **Dr. Tariq Mehmood** from National Centre for Physics (NCP).

I pay my special thanks to my CO-supervisor **Dr. Shamaila Sajjad** showing his interest to accomplish this task. She taught me, by example, how to bear life's hardships, to be strong, brave, and persistent, never give up and stay optimistic, courageous and passionate. She trained me how to stay mature and enjoy who I am. Her faith inspired me to persevere through difficult situations. I avail the opportunity to express my deepest love, respect, and admiration to my entire family members, for their support, understanding and helping touch throughout these years. Without them, I couldn't accomplish the things I have done today. I pay to special thanks to my senior fellow **Ms. Sania Shaheen** who encourage me and taught me in my work.

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Abstract

Nano bricks Tungsten oxide thin films have been synthesized by hydrothermal strategy using Na2WO4_2H2O as tungsten source, distilled water and hydrochloric acid HCL used to form. Copper oxide Nano particles have been synthesized by precipitation method. Modified WO_3 with CuO Nano particles by the method of Spin coating (3000 rpm for 30 sec). X-ray diffraction (XRD), Scanning electron microscopy (SEM), and Energy dispersive X-ray spectroscopy (EDS), UV-visible spectroscopy (UV-vis) have been used to characterize the structure, morphology and composition of the Nano bricks like morphology. UV-vis spectroscopy shows that maximum absorption of WO_3 is found at the wavelength of 530 nm with band gap 2.3 eV that value exactly match with the literature while for modified with CuO Shows 2 peaks at wavelengths of 380 nm and 483 nm respectively represents the bang gap of 2.5 and 3.1eV. The modification shows the dual band gap of WO_3/CuO. The band gap of CuO lies from 1.2 to 2.1eV. The value of band gap energy of CuO can exceed to 3.1eV in the field of various application. EDS Analysis shows the composition and elements presents on the films. The value of band gap of WO_3 increases after spin coating of CuO.

Aim and Objectives:

To deposited thin films of Tungsten trioxide on FTOs by using hydrotherm

Modification of Tungsten trioxide with Copper Oxide Nano particles by using spin coating

To increase the Band gap energy of Tungsten trioxide WO_3 after modification of CuO by the method of spin coating.

CHAPTER 1:

1 Introduction:

1.1 Thin films:

A thin film is basically two dimensions structures of thin layer.it has large value of surface to volume ratio and it can be made by the process of atoms condensations, molecules or ions. Its thickness found from nanometers to few micrometers.by this thickness structural, physical and optical applications can be formed. Recently thin film science has gained much more importance in the field of research.

1.2 Thin film technology:

Thin film can also be define as: It is a low dimensional materials which can be created by atomic, ions and molecular condensation of matter. The devices which based on thin films play main role in the formation of modern sciences and technology. Thin films are basically those materials which are created by random nucleation and growth of atoms, ions or molecules on a substrate.

Structures of thin films totally depends upon the deposition parameters and its thickness. Thickness can be vary or change from several nanometers to tens of micrometers. Interference phenomena of light depends upon the optical properties of the thin films. When light passes through the some material layer properties like transmission, absorption, reflection, scattering and polarization are changed. Electromagnetic wave theory can be used for interpreted its results. The properties of thin films are affected by the size of thin films.

For about half a century, thin film technology has been used for the production of electrical devices, optical coating and decorative parts are also form from the thin film technology for the daily basis, and thin film technology is being used. Thin film technology can also be contributed for development of semiconductor devices .thin films have a lot of applications in different field's i.e.

- Space science to aircrafts.
- Microelectronics to optics.
- Superconductivity to photo-voltaic.

Thin films have a great importance in the development of high speed and small sized devices.

1.3 Factors affecting the Growth, Properties and Structures of the film:

There are many factors which totally affected the growth, properties and structures of thin films. Some are given below:

- Temperature of substrate.
- Temperature of source.
- Gas presence in the chamber.
- Substrate nature.
- Annealing.
- Presence of substrate surface defects.
- Contamination by impurities.

Poortmans and Arkhipov. [1] gives the definition of thin films as, thin films are basically deposited by the nucleation and growth of atoms, ions or molecules on the available substrate. Its properties depends upon the thickness of films and thickness ranges are nanometers to several micrometers. The thin films having one dimension is to be very small and high surface to volume ratio. He found that thin films can be differentiate from thick films if surface to surface properties changes from the bulk materials [2].

Baran explained the development of new materials and devices [3].

Harsha [4].stated that thin films has been used for the production of optical coating and electronic devices.

1.4 Applications of thin films:

Sharma et.al [5] described the different applications of thin films which were used for the fabrication of solid state electronics devices and integrated circuits in microelectronic studies. The transparent and conductive materials of the thin films were being used for electronic display. Like liquid crystal display, light emitting diodes, electro chromic devices, plasma and florescent displays.

Thin films were also used for the optical coating, used as interference filters for solar panels and solar reflectors. Diamond like carbon films were also used in the formation of hard coating of surface.

Thin films (2 Dimensions) behaves different from the Bulk materials having high surface to volume ratios. Two layers of atoms or surfaces are so close to each other which cannot present in the bulk counterpart [6].

- Piezoelectric devices.
- Rectifications and amplifications.
- Sensor elements.
- Storage of solar energy and conversion into another form of energy.
- Magnetic memories.
- Superconducting films.
- Interference filters.
- Reflecting and anti-reflecting coatings.
- Field effect transistor(FET)

The present development by using thin films technology tending to:

- Metal oxide semiconductor transistors(MOST)
- For sensors
- For switching system
- High density memory for the computers.

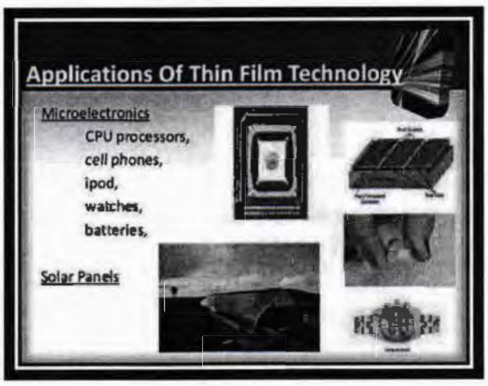


Figure 1.1 Various applications in the field of thin film technology

A thin film solar cell is known as the second generation solar cell which can be made by deposition of two or more than layers of photovoltaic materials on the substrate.

1.5 CuO/WO_3 thin films:

Many researchers presents the CuO/WO_3 obtained by different methods of synthesis.WO_3 and cupric oxide CuO both are most important semiconductors materials with their band gap of 2.6 eV and 1.2-1.5 eV respectively[7].These materials can be used for the thin film technology such as solar cell formation. CuO is mostly used in the production of solar cell which gives favorable efficiency of the solar cell.

1.6 Why solar is best energy solution:

Sun is the amount of energy that sends towards our planet earth is about 35,000 times more than what we currently produce and consume. Some amount of this energy commonly called solar radiations goes back to the space but most of the energy is absorbed by our atmosphere and other elements founded in the inner atmosphere. This radiations energy can be easily harnessed for our daily purpose like heating our houses, lightning bulbs, running automobiles, and even airplanes. We are lucky that we never going to run out of this massive radiation energy resource, even for thousands and thousands of years.

1.7 Efficiency of solar cell:

Efficiency of solar cell can be defined as

$$\eta = \frac{V_{OC} I_{SC} FF}{P_{in}}$$

1.8 Tungsten trioxide WO_3:

One of the transition metal oxide is tungsten oxide (WO_3) .after some time the discovery of electro chromic (EC) effect in WO_3 was discovered by Deb in 1969[8]. Then found that discovery was not just for the electro chromic devices but also many other related applications. [9-13].

Electro chromic devices are mostly used for the technological developments and energy saving devices [14-15]. Among inorganic material, the most detailed studied material is tungsten tri oxide, amorphous WO_3 films have exhibited highest coloration efficiency in the visible region of spectrum.

Tungsten trioxide is basically n type semiconductor, having indirect band gap of values lies from 2.2 to 2.8 eV. Tungsten trioxide is also called tungsten oxide or tungstic anhydride WO_3, it is the chemical compound which contains oxygen and the transition metal tungsten.

- Binding energy(BE) 35.8 eV
- Molar mass 231.84 g/mol
- Melting point(MP) 1,473 C
- Formula WO_3
- Density 7.16 g/cm^3
- Color yellowish green

1.8.1 Structure:

Structure of tungsten oxide is discuss as three dimensional network of corner sharing wo_6 octahedra. This network connection is same as cubic Reo_3 and AMO_3 structure in the absence of A-cation [16].

The phase transition of monoclinic II (-43C) but at room temperature, monoclinic shows most stable phase. Triclinic also observed. Gerand et.al was also reported that there is another most stable form at room temperature is hexagonal (h-wo_3) in 1979 [17].

Tungsten trioxide displays a cubic perovskite like structure that built upon the corner sharing of regular octahedral with oxygen atoms and tungsten atoms at the center of each octahedron. The alternating disposition of O and WO_2 planes provide a crystal network. The crystal structure of WO_3 is temperature dependent.

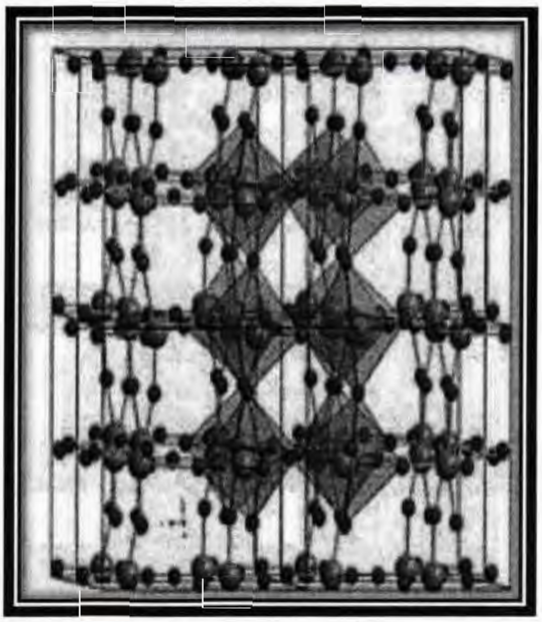


Figure 1.2 Crystal structure of tungsten trioxide WO_3

1.8.2 Properties of WO_3:

WO_3 is n type, wide energy gap and indirect semiconductor. Its value of energy gap exist between 2.2 and 2.8 eV. From few years, it has been observed the favorable properties such as electro chromic, photochromic, photo catalysis, photoluminescence [18-29].

In few years later, by the scientific community got a great interest about Nano sciences and nanotechnology due to new physical and chemical characteristics that obtain when the size of material becomes nonmetric [30-31].there are many oxidation states of tungsten for example 2, 3 4, 5 and 6 there are many forms in which tungsten compound found.

- Tungsten (VI) oxide gives lemon yellow color (WO_3).
- Tungsten (IV) oxide gives brown and blue color (WO_2). [32].

Due to their properties, it has many applications such as electro chromic [33],photochromic[34], photo catalyst [35],and gas by different routes such as pyrolysis [39-40],thermal decomposition [41],sol-gel [42] colloidal process [34],and ion-exchange method [35,36].

The physical properties of the material are greatly affected by its structural direction and morphology. For altered applications different methods of preparations having their main benefits in view point of film worth and fabrication cost of material has been studied. The amorphous and polycrystalline having two extreme structural order of thin films of WO_3 though the tungsten oxide was known as favorable candidate for electro chromic devices, these films are used in the sun glasses, automotive rear view-mirrors, building windows and sun roofs. [43]

1.8.3 Phase transformation depends upon the temperature:

WO_3 have different crystal structures as a function of temperature. Low temperature monoclinic structure from -140 to -50^0 C, triclinic structure from -50 to 170° C, the monoclinic structure of tungsten trioxide at room temperature shows from 17 to 330° C, at the temperature of 330 to 740° C shows orthorhombic structure and tetragonal at above 740° C. the room temperature monoclinic structure of WO_3 is most stable form.

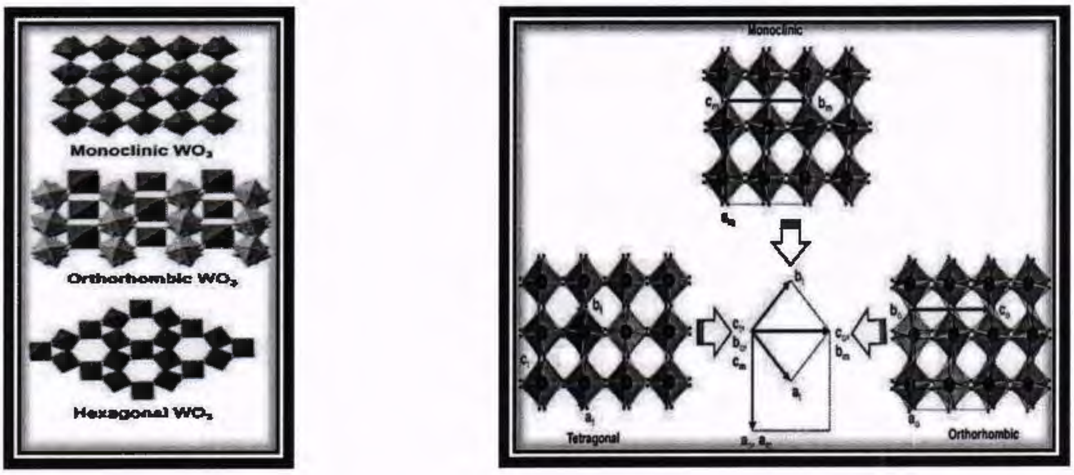


Figure 1.3 phase transformation of WO_3 Structure

Crystal class	Axis system
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$

Figure 1.4 Crystal structures with their respective Axis

1.9 Copper Oxide (CuO):

Copper (II) oxide is also known as Cupric oxide is an inorganic compound its formula is CuO.it is one of two stable oxides of copper, other being is Cu_2O. Consists of copper and oxygen elements. There are basically three forms of copper oxide:

1. Paramelaconite (Cu_4O_3).
2. Cuprous oxide (Cu_2O)
3. Cupric oxide (CuO)

1.9.1 Paramelaconite (Cu_4O_3):

Cu_4O_3 is a black in color and very uncommon material which lies formula Cu^{1+} Cu^{2+} O_3. Cu_4O_3 has tetragonal system of crystal. In 1870, it was first time discovered in copper queen mine located in Bisbee, United States (US) back [44].Cu_4O_3 is not easy to make in both forms of bulk or particles. Because maintenance of both Cu (I) and Cu (II) atoms. But by the CuO reduction, Cu_4O_3 can be produce by sputtering process and CVD. The optical band gap of films of Cu_4O_3 is to be 2.47 eV [45]

1.9.2 Cuprous Oxide (Cu_2O):

Cuprous oxide is first known p-type semi-conductor which is different from CuO due to its color or crystal structure and physical features. It is the cubic crystal both ionic and covalent nature having different levels of exactions. [46]. Literature shows that copper oxide (CuO) is more stable than Cu_2O. Because Cu^{2+} ions are most stable in the atmosphere. [47]

1.9.3 Cupric oxide (CuO):

CuO Nano materials increase much significance because of its potential size effects, big surface area, interesting properties at Nano scale differs from their bulk counter parts. It has black to brown color with monoclinic crystal structure have space group C_2/C. Copper oxide has an open 3d shell, it accomplished to absorb light in near infrared region [48]. Cuprous oxide is also p-type semi-conductor but not effective as CuO.

1.9.4 Properties of CuO:

Band gap		1.2-1.55 eV, direct
Refractive Index		1.4
Dielectric constant		18.1
Crystal structure:		Monoclinic
Formula	:	CuO
Molar mass	:	79.545 g/mol
Density	:	6.31 g/cm^3
M.P	:	1,326 °C
B.P	:	2,000 °C
Color	:	Black

1.9.5 Optical properties of CuO:

The band gap of Nano material is defined as the absorption region is controlled by absorption threshold. The band gap of CuO is blue shifted with ranging from 1.2 eV to 2.1 eV associated with bulk [49]. But some other researchers also testified the band gap value of CuO Nano particles to be 4.13 eV [50].

CuO mostly absorb light in visible region and slightly in UV region due to large band gap of material. Its optical properties totally depends on its size, type of dopant and synthesis technique. [51-52]

1.9.6 Optical properties of WO_3:

The widely used material to make carbides, hard metals, solar cell applications, power batteries etc. is WO_3. Infrared spectroscopic ellipsometry is a very common and useful technique for the characterization of Nano structure tungsten trioxide thin films, because film thickness and dielectric function can be determined simultaneously. Transmittance can be determine at different ranges of wave length. Transmission depends on the thickness of film. Thin films scattered less light due to small size of film. If scattering will be large then infrared region will see. While optical absorption of thin films wavelength ranges from 300-900 nm.

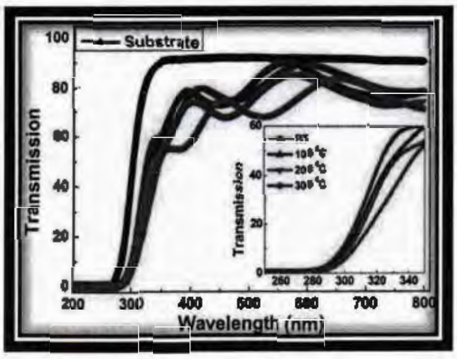


Figure 1.5 Optical properties of thin films

1.9.7 Structure of CuO:

The Crystal structure of CuO is stable monoclinic. The length of their latter parameters are not equals to each other. Its structure shows a rectangular prism which is formed having parallelogram in its base. CuO structure having two sides are parallel with each other but the third one makes an angle of 90°.Copper oxide is one of the most common and earlier semiconductor material for many applications especially for solar cell fabrication. It's interesting that it is the environmentally friendly, most abundant and nontoxic.

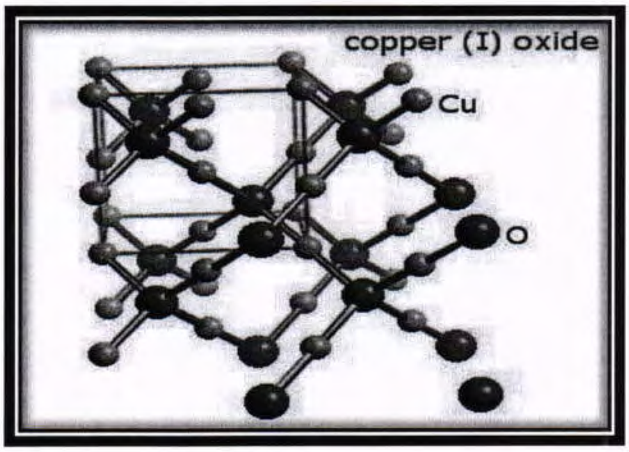


Figure 1.6 Structure of CuO

1.10 Why thin film:

- It has small thickness required, because of its high absorption, small diffusion length and higher velocity of recombination of e-hole.
- Various simple, sophisticated deposition techniques to form thin film solar cells.
- Various varieties of structures like poly crystalline, epitaxial and amorphous are available.
- Multi Junction, Tandem cells are possible.
- Various types of junctions, PEC, Schottky, hetero and homo are possible.
- Compatibility with solar thermal devices.

1.10.1 WO_3/CuO thin films are useful:

Tungsten trioxide is semiconductor of n-type. Tungsten oxide considered as an interesting Nano material, due to its attracting magnetic properties, piezoelectric and electro-optical

Wu.et al. has been reported, if WO_2 Nano rod fix in mesoporus carbon (MC) as counter electrode (CE) in DSSCs (Dye sensitized solar cells) gives efficiency of about 7.76% [53].

There is another metal oxide is cupric oxide (CuO). It is basically P-type semiconductor (SC),which has narrow band gap of value 1.35 eV, using for the great potential of field emitters.it shows non toxicity, abundance oxide on earth and shows low cost of copper.it has long term stability. Considered best and environmentally friendly [54].

CuO/WO_3 p-n junctions, are applied for enhanced photo catalytic performance and an efficient photovoltaic cells by their controllable electronic structures at electrolyte interface, good energy band alignment. [55-66].

1.10.2 Properties of CuO/WO_3 :

High efficiency to lead high photocurrent.

Higher rate of photon capture.

Higher efficiency to recombination of e-hole.

Loss of electron hole rate is low.

Cheap source material.

A lot of supply.

Resistance to higher temperature.

High current flow by electrode structure.

Electrolyte that uses are nontoxic, commonly found, ideally and non-corrosive respectively

2 Literature Review:

There were many semiconductor material like methylene blue etc. found as semi conducting properties [67]. After some years, that type of dye was considered as one of the organic type semiconductor phenomena [68].Organic semiconductors materials are considered as low-cost as compared with an inorganic materials of semiconductor.

An organic solar cells having sandwich structure, in this structure an active layer is interject between cathode and the anode.one electrode (anode) should be clear, such as (ITO or FTO)while other electrode (cathode)is took from metal class. Metals like Ag, Au, Cu, Ca, etc. are used in these devices.

CuO thin films are most necessary material for the fabrication of solar cell due to its properties of photoconductive and photochemical. For many sensors, CuO is also most important material which can be used for discovering the presence of dangerous gases. CuO play an excellent role in the lithium ion batteries because of negative electrode [69].

Extremely efficient solar cell system provides optically active layers to absorbed about whole light thus increasing the value of e- hole pair generation [70].

CuO has direct band gap and p type semiconductor, due to these properties of CuO, can be mostly used for the fabrication of photovoltaic devices. Which includes hetero junction solar cells as well as dye sensitized solar cells. [71, 72]. CuO having high power conversion efficiency of about 20% under air mass 1(AM 1) solar illumination.

Omayio et al. reported about the power conversion efficiency η=0.232% on CuO based solar cell with the alignment of P-CuO/n-ZnO: Sn[73]. Panah studied the p-CuO hetero junction solar cell with photo current and open circuit voltage[74].the conversion efficiency in the CuO based solar cell totally depending upon the roughness and surface morphology that's plays an important role for absorber efficiency improvement.[75]

Bhaumik et al. reported a favorable change in the optical properties, with the changing of phase percentage, size of stable copper oxide at room temperature and morphology.it approached the 2.88% of efficiency on glass/ZnO/ITO/FTO/CuO nanostructures thin films [76].

Few years ago, Wanninyanke et al.adjusting of CuO Nano paticles in solar cells. They played important role to improve the power conversion efficiency rate of 40.7% at hopeful concentration of CuO [77].

Barshilia et al; 2008[78], reported that the optimized absorber coatings can be made by accommodating the thickness of coating. Hamid et al; in 2008[79]; Richharia in 1990,1996[80], Wackelgard in 1998[81] and Shashikala et al; in 2007[82] reported that some materials like black copper, black nickel, black brass, black cobalt, etc. have been observed for the usage of solar cell absorber coating.

Similarly, Maruyama in 1998[83] and Singh et al; in 2009[84] reported that the black copper which is also called copper oxide (CuO) has been considered as one of the viable solar selective absorber coating, because of its properties having low thermal emittance and high solar absorptance, shows an important role as a semiconductor material in the formation of the solar cell.

The conduction property of copper oxide basically p type is usually attributed to the negative charge copper vacancies [85].

For few years ago, it has been reported that the single layer of black copper film based upon the black copper oxides for solar coating applications [86].

H. Kidowaki et al; [87] also studied about the fabrication of ITO/CuO/WO3/Al. p-n type hetero junction solar cells has been fabricated with the power conversion efficiency (PCE) of 0.36% [88].

The transition metal oxide which include WO_3, due to the properties of high work function and non-toxicity have been considered as an excellent hole transport layer in the organic photovoltaic (OPV) devices for the improvement of efficiency of solar cell [89].

Wu et al. studied that the use of WO_2 Nano rods pushes in mesoporus carbon (MC) role as the counter electrode in dye sensitized solar cells (DScs) gave conversion efficiency as high as 7.76%, that value is much higher than that of a pt. DSSCs value about 7.75%

WO_3 can be synthesized by different routes such as physical vapor deposition [90], including thermal evaporation [91], chemical vapor deposition [92], liquid phase method like sol-gel method and hydrothermal method [93].

There are many other methods to prepare in both form of thin film or power form of WO_3.some other routes included spray pyrolysis[94],magnetron sputtering[95],spray pyrolysis[96],e-beam lithography[97], Nano lithography, spin coating, and temple growth techniques[98].

Sun et al;[99]worked on the tungsten trioxide dehydrate($WO_3.2H_2O$) gel by applying drop wise mixing of concentrated acid (HCl) in the solution of sodium tungstate dehydrate about (10-30nm) sized tungsten oxide particles were attained.

Balazsi and Pfeier[100] reported an amorphous gel of $WO_3.2H_2O$ by adding sodium tungstate solution with HCl solution at low temperature of about 5^0 C.

Choi et al; [101] synthesized the $WO_3.2H_2O$ solutions (30nm) by flowing Na_2WO_4 (sodium tungstate) solution through a columned packed, with protonated Cation exchange resin. large numbers thin films of metal oxides have been fabricated by using vayssieres et al method of aqueous chemical growth ,the films that synthesized are 1-D,3-D,2-D nanostructures of WO_3(tungsten tri oxide),Cr_2O_3 [102], ZnO [103],Fe_2O_3[104] respectively.

Solarska et al. and Amano et al. accomplished improvement in enhancing the incident photon to current efficiency by impurity doping and modification of morphology [105,106].

Yagia et al, concluded that thin films of WO_3 were sintered at the higher temperature of about 550^0 C gave photo anodic current having value of 3.7mA/cm^2.at 1.2v voltage [107].

Huo and his Co-workers reported the ultra violet photo response properties of WO_3 films containing devices and attained hexagonal tungsten trioxide structures having excellent UV characteristics [108].

Cheng et al. reported and improved the energy conversion efficiency of dry sensitized cells of tungsten trioxide (WO_3) thin films [109].

Gu et al. reported WO_3 square platelets having smooth surfaces by using hydrothermal process [110] and similarly $WO_3.H_2O$ square plate let's have been achieved by low temperature hydro thermal method [111].

Zhou et al. concluded the synthesis of WO_{3-x} networks, like 3-D tungsten oxide Nano wires on a favorable substrate [112].

Chiet et al; and Li et al; [113,114] reported WO_3 Nano wires network by using the routes of hydro thermal evaporation and vapor deposition respectively.

Zhao et al;[115] reported two dimensional tungsten trioxide Nano wires networks.

In our present study we assay to design Nano structures WO_3 thin films by simple hydrothermal approach .WO_3 thin films were explored to study about the optical attenuation and electro chromic characteristics.

The first report of hydro thermal growth of crystals was by the German geologist Kari Emilvon Schafhautl in 1845, he promoted microscopic quartz crystals of strontium carbonate and barium at 200^0 C and pressure of about 15 atm, in1851, French crystallographer Henri Hureau generate crystal of different minerals by hydrothermal synthesis.

We found that the activity of CuO/WO_3 photo catalyst was similar to that of $CuBi_2O_4/WO_3$, because the former is easy to make. We also reported the effect of CuO loading on the degradation of different other organic compound, in present study we discuss about the difference between the reaction mechanisms with CuO/WO_3 and $CuBi_2O_4/WO_3$.

Coating and optical materials plays an essential role in finding the efficiency of solar conversion process. These films are called anti-reflective coating or treatment. The use of such materials and films improves the efficiency of solar cells and stimulates innovation in active and passive solar energy conversion, photovoltaic, solar energy is converted into the heat, light and electrical power respectively.

Among these WO_3 and CuO plays an important role as cheap alternatives. Wo_3 is an in direct band gap of 2.4-2.8 eV at room temperature.

The chip of CuO semiconductors (SC) are relatively higher optical absorption, low cost of raw materials and non-toxicities.

CuO and Cu_2O are basically p-type semiconductors with the value of band gap of energy 1.5 eV and 2.0 eV, respectively. That is closest to ideal energy gap of 1.4 eV for the fabrication of solar cells and allows for the good solar spectral absorption (Li, B., Wang et al in 2008).

Cu_2O/WO_3 thin films solar cells have been studied and concluded.

As CuO is a solar material because of low cost, nontoxic nature, great availability for use in the solar cell fabrication, a theoretical efficiency of solar is about 9-11%.semiconductors with band gap of 1ev and 2ev are favorable material for photo voltage cells (Werfel. P et al in 2009) and (V. D. Mihaletehi et al in 2010).

In comparison, the hydrothermal approach is promising for fabricating WO_3 film because of its merits of low reaction temperature, flexible substrate selection and easiness in scaling up. Lately, there have been reports on the synthesis of various one-dimensional (1D) WO_3 nanostructures such as Nano rods [116] and Nano ribbons [117].

Simply controlling the precipitation reaction temperature between the copper nitrate trihydrate [Cu(NO3)2_3H2O] and NaOH under a hydrothermal process. The results showed as-prepared samples with sizes of _3–7 nm, regular flake-like morphology, and uniform size distribution. A series of controlled experiments confirmed that the temperature and the partial pressure inside the autoclave changed the morphology and phase of CuO nanoparticles during the hydrothermal process. To study the effect of temperature on the morphology and phase control Chakraborty et al. [118] synthesized CuO nanoparticles by the hydrothermal route using two different organometallic and inorganic precursors of copper acetylacetonate [Cu(C5H7)2:Cu(AA)2] and Cu(NO3)2_3H2O. The resulting flower-like CuO nanoparticles has been found.

The tungsten trioxide (WO3) and cupric oxide (CuO) are an essential semiconductor materials with energy gap of 2.6 eV and 1.2 - 1.5 eV, respectively [119]. Later many years they have been applied as an attractive materials for many industrial tenders. The WO3 has fascinated significant attention due to its applications as electro chromic [120], photo catalytic [121] photovoltaic [122]. The CuO is extensively used in solar cells fabrication [123], batteries [124], and for photo catalytic decomposition of water [125]. However, both oxides are favorable materials for gas sensor applications [126]. The WO3 displays typical *n*-type conducting behavior both in oxidation and reduction reaction on their surface. In comparison, CuO shows *p*-type semiconducting property.

Chapter 3

3 Characterization techniques and synthesize:

3.1 Characterization techniques:

There are so many different methods which are used to fabricate thin films generally consists of certain amount of impurities, defects, unwanted phases and in homogeneities. The properties of thin films are importance to measure for the study of devices and the materials. The chemical compositions, crystalline structures, optical, electrical and mechanical properties are considered essential in evaluating thin films.

The characterization of thin films have been used by different techniques.

1. X-ray diffraction (XRD)
2. Scanning electron microscopy (SEM)
3. Energy Dispersive Spectroscopy (EDX)
4. Ultraviolet visible spectroscopy (UV- visible)

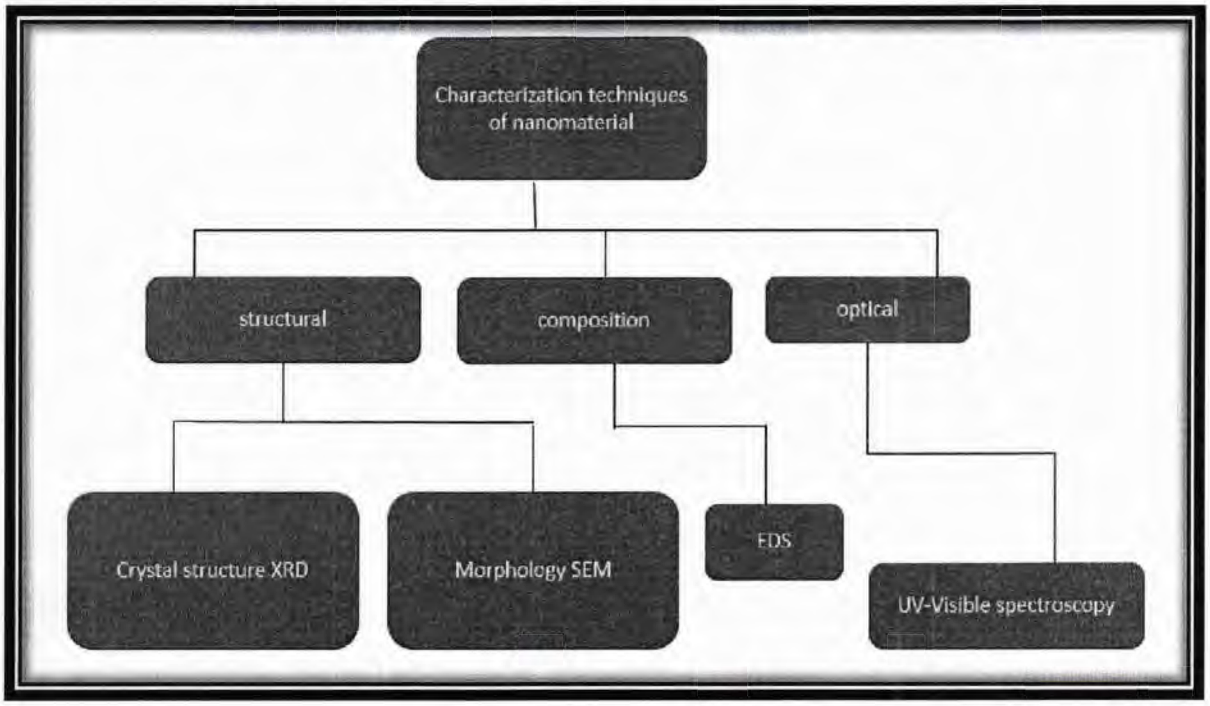


Figure 3.1 Characterization techniques

3.1.1 X-ray diffraction (XRD)

XRD is an essential characterization technique which is used to measure the properties of structure like identification of unknown materials, lattice parameters, orientation of single crystal and preferred orientation in poly crystalline thin films as well as the bulk materials. We can calculate the dislocation energy grain size, micro strain and stresses of thin films as well as bulk materials. X-ray diffraction is nondestructive and having no requirement for sample preparation or the removal of thin film from the substrate. Also used to measure the scattering of x rays from the materials after interaction between electrons of atoms and X- rays. When in coming X- rays and electrons interact with each other shows elastic and in elastic scattering. The x rays scatters from electrons of sample convey information about the material. When x-rays are allowed to interact with crystalline material or phases, these X- rays diffracted from planes of atoms that exist in the crystal lattice and interfere with each other to form diffraction pattern. The periodic design of atoms can form diffraction pattern with sharp peaks but amorphous materials can not show any sharp peak in the diffraction pattern. Every crystalline object gives the identical pattern at every time and in the mixture of materials, each material substance shows its own pattern that independent of others. Different methods can be used for measuring of diffraction like double crystal diffraction method, Laue method, powder diffraction method, small angle X- rays scattering method.

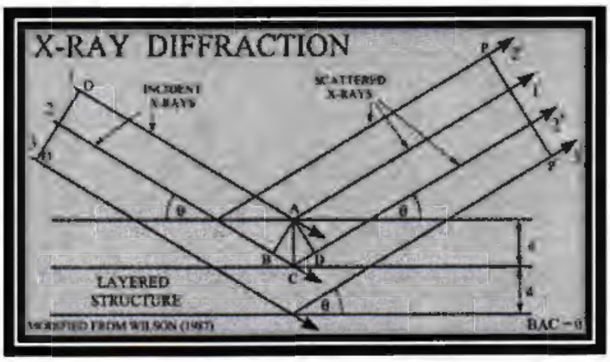


Figure 3.2 X-Ray Diffraction principle

Bragg's law can be written in the form

Mathematically:

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

Here;

d=spcing between planes of the sample

n=order of diffraction

λ=wave length of x rays

θ =Angle of scattering

3.1.2 Scanning Electron Microscopy (SEM):

The surface morphology of thin films optical coating is very risky from application point of view, by using SEM, surface smoothness and grain morphology can be studied. Usage of electron microscope was accepted due to the limiting magnification and resolving power of the optical microscope. If we contrast the optical microscope with electron microscope having very large value of magnification as well as the resolving power. The necessary parts of are an electron microscope are electron gun, detectors and beam controller. It is basically imaging machine with the high value of resolution. Electron gun is found at the top which exits numbers of electrons beam at the sample that is taken under observation. These number of electrons do not naturally go to the target material, then gets to the next part of SEMs. There are two types of electron gun, 1 gun is called thermionic gun, and it gives thermal energy to filament and to run away electrons towards the specimen from the gun. 2 gun is called field emission gun which make an electrical field of great strength to pull electrons from the atom associated with it.

Working of lenses in the SEM is to form detail and clear images. Instead of glass, theses lenses are made up of magnets, so that these lenses are able to change or bend the way of electrons. The other function of lenses in the SEM is to control and focus the beam. SEMs are very sensitive equipment. Sample chambers also work the specimen site with respect to dissimilar angles orientations, so frequently remount the sample during the working stage.

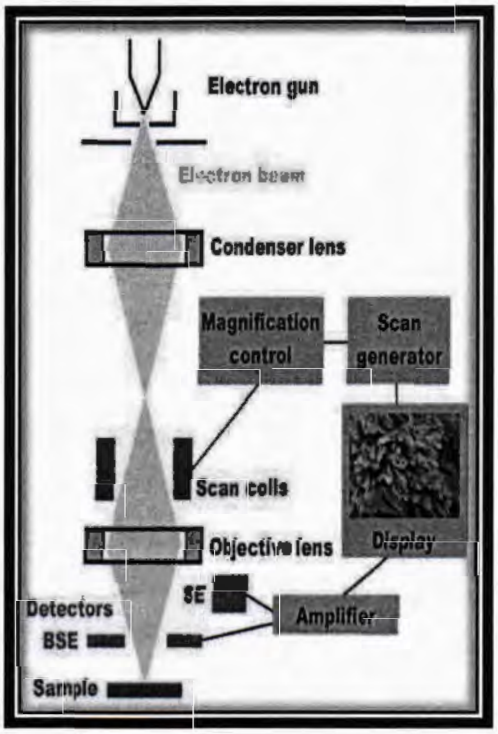


Figure 3.3 Scanning electron microscopy principle

3.1.3 Ultraviolet –visible Spectroscopy:

Ultraviolet and visible absorption spectroscopy is an important technique that is used for the absorption measurement of the material in visible and ultraviolet range. The light source is an important part of UV spectrophotometer. Monochromatic or sample holder prism for diffraction grating and used for the separation of wavelength and detector.

The information of wavelength and the intensity of the sample during absorption in UV and visible light regime provided by UV is spectroscopy. When the beam of light strike on the sample then the material consists of π-electrons or nonbonding electrons in molecules which absorb much amount of energy that excited these electrons to the higher state.

By using Beer-Lambert, transmission and absorption of light can be explained, that provides information of the fraction of light before and after when it falls and pass through the sample material respectively. For the fixed length of the path, absorption concentration is directly proportional to the absorbing species. To comparing the band width with the width of absorption features, monochromatic source of radiation is mostly used. Mostly apparatus band width is set to keep below the width of spectral lines for reference measurements, will reduced the energy pass to detector by decreasing the spectral band width.

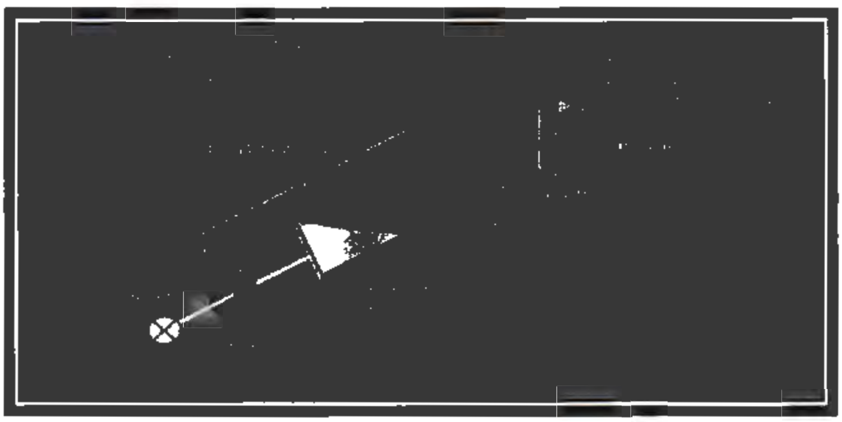


Figure 3.4 UV-visible spectroscopy principle

3.1.4 Energy Dispersive Spectroscopy (EDS):

A characterization technique of the chemical compound depend up on the knowledge that each and every atom has its own features structure and can create X-rays of its own nature and spectrum.

Working of EDS:

EDS is furnished with the SEM, incident beam can eliminate some of electrons from inside shell due to in elastic collisions. Holes are created which are occupied by electrons from outer shells. These electrons jump down the shell and discharge some energy in the form of x-rays of its own wavelength and frequency. A main benefit of EDS is that it can be carried out in area of several size along a line, across surface of the product.

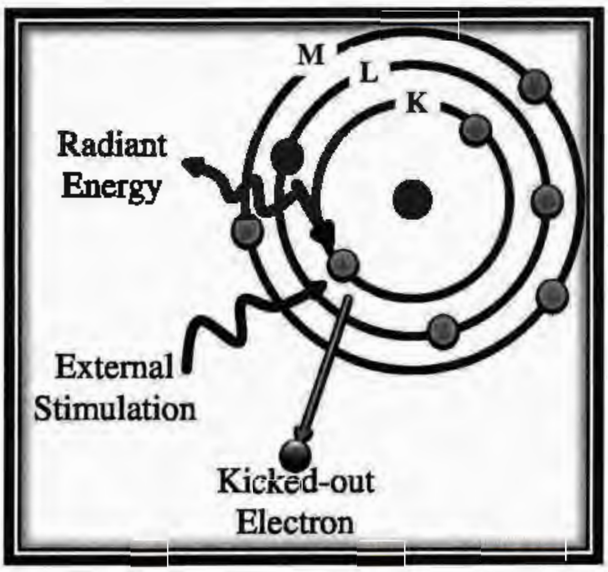


Figure 3.5 Energy Dispersive X-Ray spectroscopy principle

3.2 Experimental work:

3.2.1 Synthesis techniques of Tungsten trioxide thin films:

There are different types of Synthesis techniques for the formation of WO_3 thin films. WO_3 thin film can be synthesized by different methods like, hydrothermal deposition, sputtering method, pulse laser deposition, electro deposition method and chemical vapor deposition. There are some Synthesis techniques having problematic, need high temperature, taking long reaction time, costly apparatus, use of some toxic compounds etc. but here hydrothermal deposition method is commonly used.

3.2.2 Hydrothermal Synthesis for the Growth of WO_3 thin films:

For the deposition of Tungsten trioxide thin films hydrothermal method is mostly used. Hydrothermal method is low temperature method on the fluorine doped tin oxide (FTO).

3.2.3 Cleaning FTO substrate:

The first step is to clean the FTO substrate. We mostly choose F-doped tin oxide substrate for the growth of thin films instead of indium tin oxide ITO, because ITO is two times higher conductive than FTO. But ITO having poor resistivity and thermal stability. It makes good choice for the conducting substrate. As FTO to form an ohmic contact with special p-type materials like Cu_2o here. ITO films reduces above 350° C quickly. But FTO or ITO coating usually stable up to 600-700° C.

First of all keep FTO in the acetone for 1 hour for the sonication in the ultrasonic bath then transfer FTOs in the ethanol for 30 minutes and at the end in the distilled water for 30 minutes. FTO annealed for 20 minutes at 100^0 C after the step of sonication.

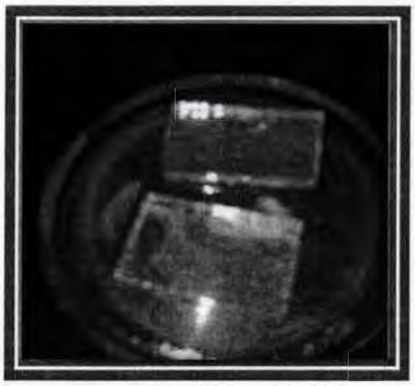


Figure 3.6 Washing FTO's by Sonication

3.2.4 Deposition of thin films on FTO:

Adding 1.46 g sodium tungstate in 50 ml of distilled water and stirring for 30 minutes. Adding HCl to form tungstic acid by drop wise until the PH of solution reaches 1(acidic solution). After that solution transferred into the 100 ml autoclave with FTO substrate in such a way that the WO_3 seed layer facing down (conducting side) for 4 hours at 160° C respectively. At the end, samples were removed from the solution, substrate washed with the distilled water for 3-4 times, then annealing FTOs for 30 minutes at 100° C.

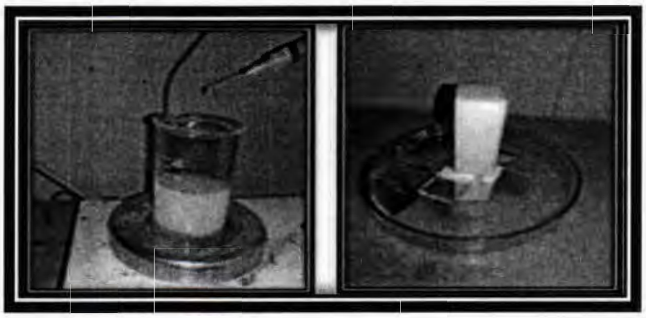


Figure 3.7 (a) Formation of tungstic acid

Figure 3.8 FTO's adjust in Teflon stand

Figure 3.9 Formation of Tungsten trioxide Nano particles in hydrotherm

3.2.5 Flow chart of deposition of WO_3:

Na_2WO_4 and distilled water

↓

Stirring for 30 minutes

↓

Adding HCl drop wise till PH reaches 1

↓

Solution goes to autoclave at 160°C

↓

Autoclave cool at room temperature

↓

Deposited thin films wash with deionized water

↓

Annealed film at 100°C for 30 minutes.

Figure 3.10 Flow Chart of WO_3 thin film

3.2.6 Chemical mechanism by hydrothermally

$$Na_2WO_4 + 2HCl + nH_2O \rightarrow H_2WO_4 \cdot nH_2O + 2NaCl$$

$$H_2WO_4 \cdot nH_2O \xrightarrow{\text{Hydrothermal treatment}} WO_3 + (n+1)H_2O$$

Figure 3.11 Hydrothermal chemical mechanism

3.2.7 Synthesis of CuO nanoparticles:

Materials and equipment used:

Copper nitrate Cu $(NO_3)_2$

Distilled water

Sodium hydroxide pallets NaOH

Magnetic stirrer, hot plate and beakers.

Method:

Adding 4 g of Cu $(No_3)_2$ in the 100 ml of distilled water. Stirring it for almost 15 to 20 minutes by using magnetic stirrer. Copper nitrate dissolve in it and gets light blue color of solution.

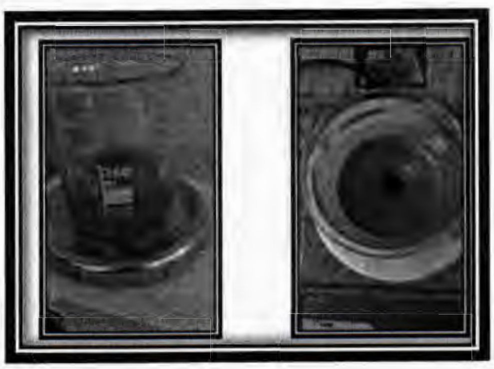


Figure 3.12 Adding copper nitrate into distilled water

Figure 3.13 Stirring and heating at 60° C

Then prepare another solution of NaOH in the distilled water of about 50 ml. adding sodium hydroxide pallets in the distilled water until the PH of solution reaches 9-10. After it adding NaOH solution drop by drop in the Cu $(No_3)_2$ solution. The color changes after some intervals of time. After that centrifuge the particles and wash it with distilled water for 3-4 times. Dry the particles at hot plate for 5 hours at the temperature of 60 C^0. At the end, calcination process occur for 2 hours at 500^0 C.

Figure 3.14 Change color on heating at 60^0 C

Figure 3.15 Centrifuge the CuO

Figure 3.16 washing CuO particles with distilled water

Figure 3.17 calcination at 500^0 C

Flow chart of CuO Nano particles:

Cu $(No_3)_2$ + distilled water

↓

Stirring above solution almost 15-20minutes

↓

Gives light blue color solution

↓

Add NaOH solution drop wise in above solution

↓

Centrifuge above solution

↓

Wash and dry the particles

↓

CuO Nano particles

Figure 3.18 Flow chart of CuO Nano particles

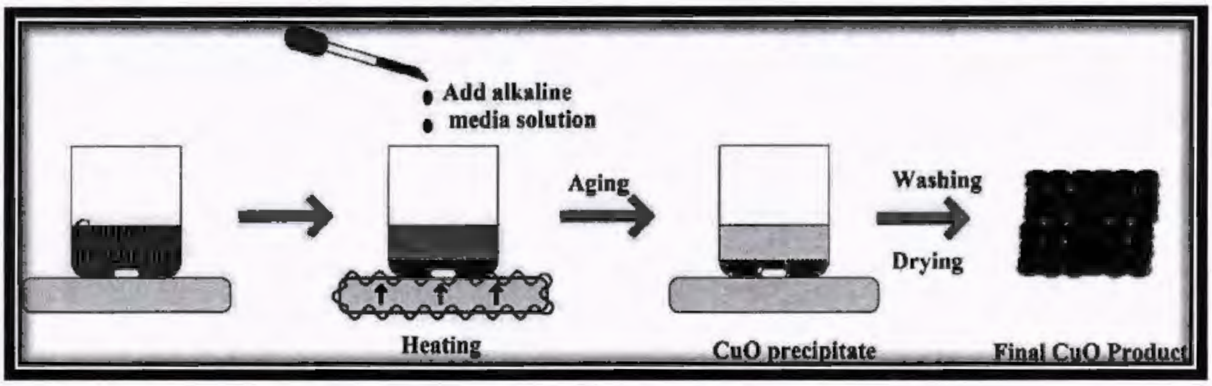


Figure 3.19 precipitation Synthetic process for CuO Nano particles

3.2.8 Coating of copper oxide Nano particles on FTOs by spin coating:

Adding 0.01 g of copper oxide Nano particles in 10 ml of ethanol and stirring it for almost 4 hours. After that spin coat the above solution at the rate of 3000 rpm for about 30 sec. Calcination of coated film at 500^0 C.

Figure 3.20 spin coating solution stirring

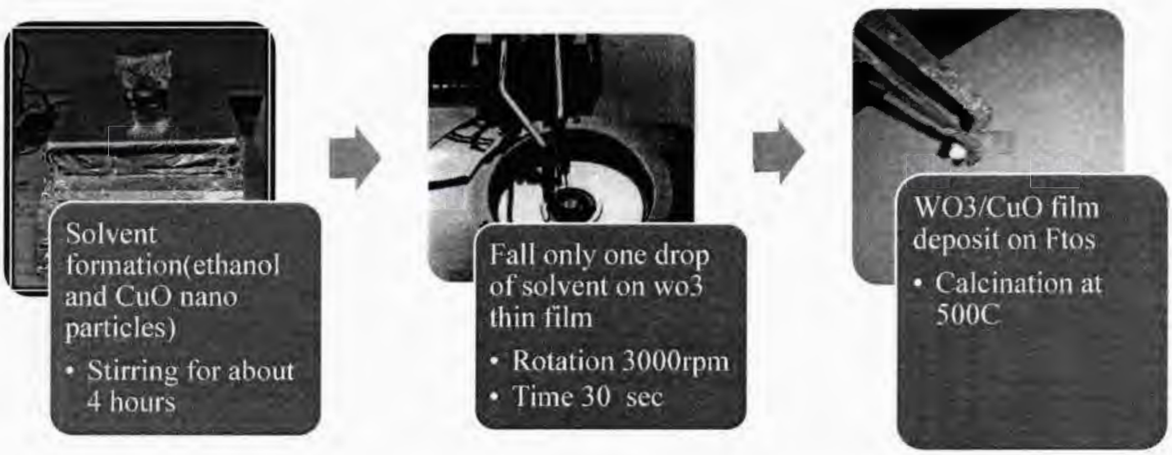


Figure 3.21 Modification of WO_3 films with CuO by spin coating

4 RESULTS AND DISCUSSION:

4.1 Scanning Electron Microscopy (SEM):

4.1.1 SEM Analysis of WO_3 thin films synthesized by hydrothermally:

Nano grains of Tungsten trioxide shown by SEM images like Nano bricks. WO_3 Nano grains shows random distribution over the surface of the substrate. These Nano bricks like morphology exactly match with the previous work **S.S Mali** and **P.S. Patil**. Figure 4.1 shows the SEM images of WO_3 thin films at different magnifications (500 nm, 1μm, 2 μm, 5 μm).

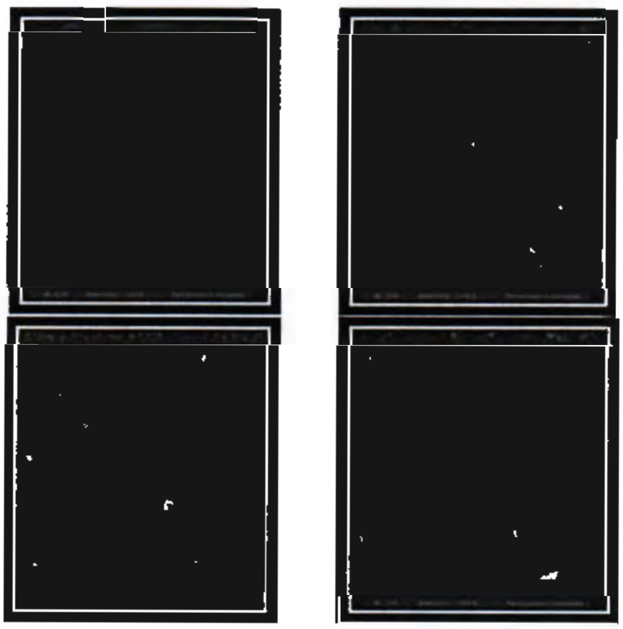


Figure 4.1 SEM images shows morphology of WO_3 thin films at 140 C for 4 hours

4.1.2 SEM Images of WO_3/CuO thin films synthesis by spin coater:

Figure 4.2 represents the SEM morphology after coating of CuO Nano particles on the thin film of WO_3 which shows that WO_3 Nano bricks became sharp and clear edges. Shows a uniform layer on thin film coating of CuO also tells about the shape and size of Nano grains changes. Nano grains of CuO are spread up to the end of the FTOs substrate. Figure 4.2 represents the SEM images of WO_3/CuO thin films at different magnifications (2 µm, 10 µm, 5 µm and 50 µm).

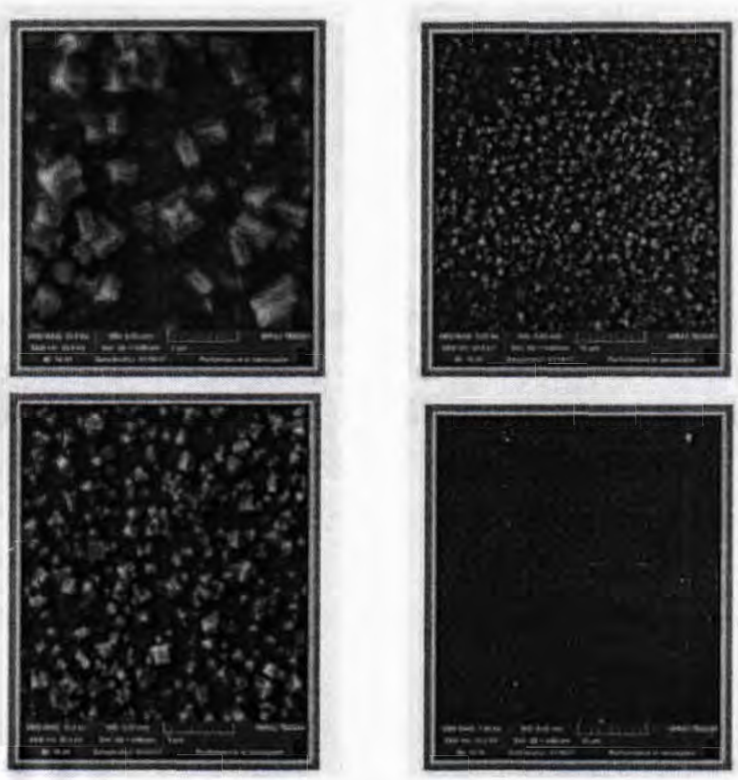
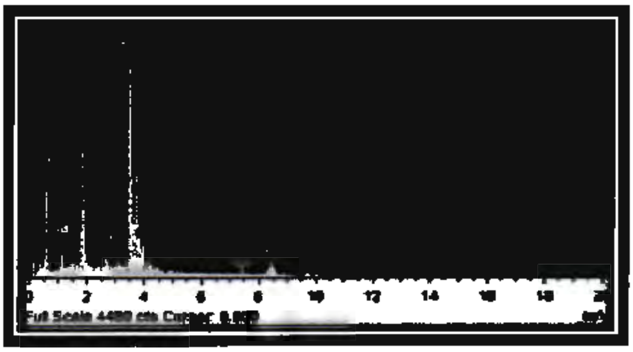


Figure 4.2 SEM images of WO_3/CuO thin films morphology with spin coating

4.1.3 EDX Analysis of WO_3 thin films on FTOs:

EDX Analysis is carried out for the analysis of WO_3 thin films. It gives out the material data and observed peaks of W, O, Sn respectively. FTO shown by Sn. That represents films prepared very thin. Figure 4.3 shows the atomic percentage and elemental composition in thin films.

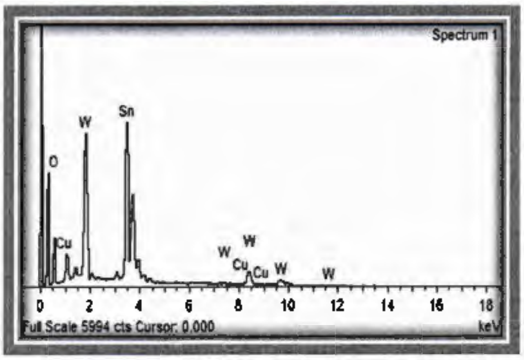


Element	Weight%	Atomic%
C K	3.68	10.79
O K	31.79	69.95
Na K	1.17	1.80
Sn L	44.71	13.26
W M	17.87	3.42
Totals	100.00	

Figure 4.3 EDX Analysis of pure WO_3 thin film

4.1.4 EDX Analysis of WO_3/CuO thin films:

EDX Analysis is carried out for the analysis of WO_3/CuO thin films. It gives out the material data and observed peaks of W, O, Sn, Cu respectively. FTO shown by Sn. That represents films prepared very thin. Figure 4.4 shows the atomic percentage and element in thin films.



Element	Weight%	Atomic%
O K	24.65	73.68
Cu K	0.07	0.05
Sn L	46.84	18.87
W M	28.44	7.40
Totals	100.00	

Figure 4.4 EDX of WO_3/CuO

4.2 X-RAY DIFFRACTION

4.2.1 X-Ray Diffraction pattern of Tungsten trioxide Thin Films on FTOs:

Figure 4.5 shows XRD pattern of Tungsten trioxide thin film synthesized by hydrothermal route The diffraction peaks of product WO_3 can be indexed to mixed phases of monoclinic and tetragonal phases match with the Jcpds no's (83-0950) and (85-0808). The prominent peaks observed at (101), (022), (200), (112). The prominent peak observed at 26^0 having miller indices (101). The sharp and intense diffraction peaks shows a high degree of crystallinity of the product. No additional peaks are found. These results perfectly match with literature **Zhihui Jiao, Xiao Wei Sun, S. S. Mali** and **P. S. Patil**. The grain size can be calculated by Schereer formula

$$D=K\lambda/FWHM(Cos\theta)$$

Where; D is grain size in Nanometer

K is dimensionless constant (0.94)

λ is wave length (0.154 A^0)

θ is diffraction angle in radians

The calculated grain size of WO_3 by above mention formula is 40 nm. The peaks denoted by stars are of fluorine doped tin oxides (FTOs).

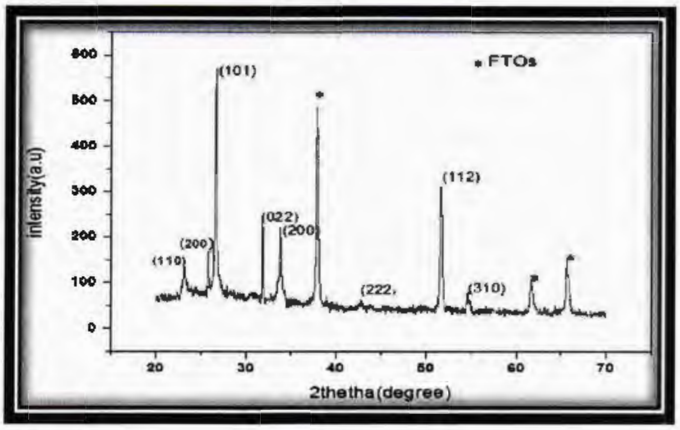


Figure 4.5 XRD pattern of WO_3 thin films

4.2.2 X-RAY Diffraction (CuO Nanoparticles):

Figure 4.6 represents the XRD results of CuO Nano particles by co-precipitation route. The diffraction peaks of product can be indexed to monoclinic structure phase match with the Jcpds no (04-0836). The prominent peaks observed at (11-1), (111), (110), (200), (220), (311). The prominent peaks observed at 35^0 having miller indices (11-1). The sharp and intense diffraction peaks shows a high degree of crystallinity of the product CuO. No additional peaks are found. the pattern of monoclinic CuO Nano particles exactly match with the earlier work followed by **Jana et al, in 2010** and **Figueireda et al. in 2009.** Due to high PH value of reaction medium peaks became sharper and stronger the intensity. The crystalline size can be calculated by Scherer formula:

$$D=K\lambda/FWHM(Cos\theta)$$

Where; D is crystalline size in Nanometer

K is dimensionless constant (0.94)

λ is wave length (0.154 A^0)

θ is diffraction angle in radians

The calculated crystalline size of CuO Nano particles by above mention formula is 15 nm.

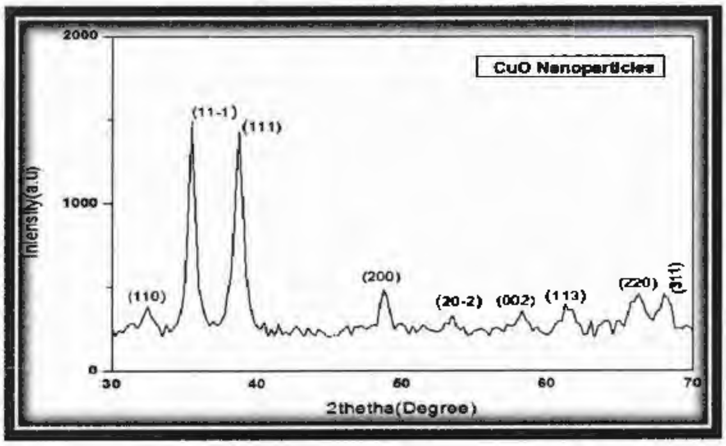


Figure 4.6 XRD pattern of CuO Nano particles

4.2.3 X-RAY Diffraction (WO_3/CuO thin film):

Figure 4.7 represents the CuO/WO_3 thin films XRD pattern with spin coating method. The diffraction peaks of product can be indexed to mixed phases of monoclinic and tetragonal phases match with the Jcpds no's (83-0950), (85-0808) and (04-0836). The prominent peaks observed at (001), (11-1), (222), (211), (200), (111). The prominent peak observed at 13^0 having miller indices (001). The sharp and intense diffraction peaks shows a high degree of crystallinity of the product. No additional peaks are found. Coating of CuO on tungsten oxide films represents the decrease in particle size. The reason is that the ionic radii of Cu is smaller than ionic radii of W. The grain size can be calculated by Scherer formula:

$$D=K\lambda/FWHM\ (Cos\theta)$$

Where; D is grain size in Nanometer

K is dimensionless constant (0.94)

λ is wave length ($0.154A^0$)

θ is diffraction angle in radians

The Calculated grain size of WO_3/CuO by above mention formula is 23 nm. The peaks represented by stars are FTOs, plus signs are WO_3 and # sign shows CuO Nano grains.

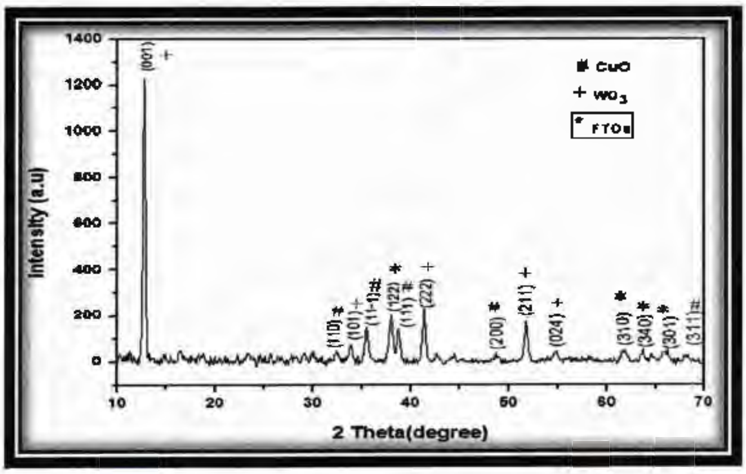


Figure 4.7 XRD Pattern of WO_3/CuO thin film

4.3 UV-visible Spectroscopy:

4.3.1 UV-vis spectroscopy of pure tungsten trioxide WO_3 thin film on FTO:

Figure 4.8 shows the UV-vis Analysis of WO_3, the maximum peak shows absorbance at 40 (au) and at wavelength of 530 nm, which is in the Visible range of electromagnetic radiations. Band gap calculated by following formula

$$E=hc/\lambda$$

h=Planck's constant (J-s)

C=speed of light (constant) (m/s)

E=energy band gap of photons (eV)

λ =wavelength of light (nm)

The calculated band gap of WO_3 at 530 nm is 2.3 eV. Light is absorbed from 530-800 nm, which Covers Visible range.

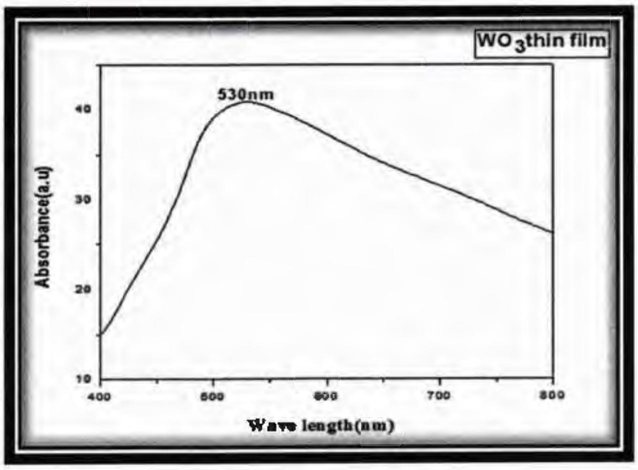


Figure 4.8 UV-vis spectroscopy of WO_3

4.3.2 UV-vis spectroscopy of WO_3/CuO:

Figure 4.9 shows the UV-vis spectroscopy of WO_3/CuO thin films.2 peaks are observed at absorbance values of 49 (a.u) and 44 (a.u) with wavelengths of 380 nm and 483 nm, the absorbance for wavelength of 380 nm observed for CuO and 483 nm is for WO_3 respectively. Band gap calculated by given formula

$$E=hc/\lambda$$

h=Planck's constant (J-s)

C=speed of light (constant) (m-s)

E=energy band gap of photons (eV)

λ =wavelength of light (nm)

WO_3/CuO shows a good absorption in UV and Visible ranges.

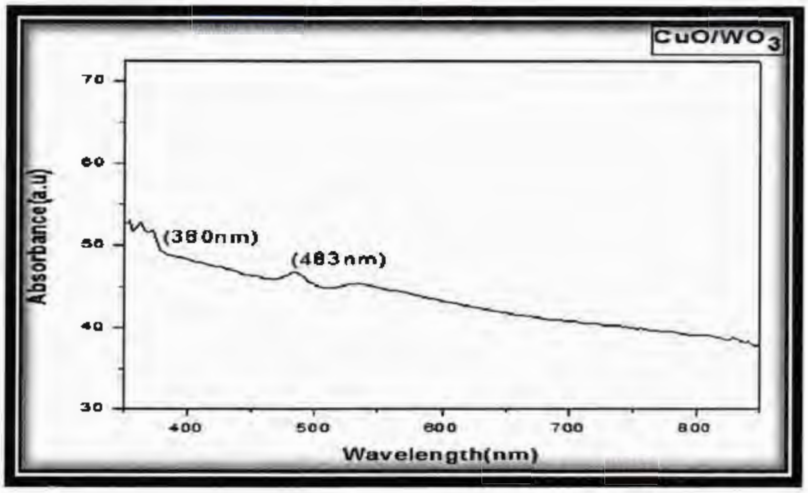


Figure 4.9 UV-vis Spectroscopy of WO_3/CuO thin films

Conclusions

Tungsten trioxide WO_3 thin films are synthesized by the route of hydrothermal. Tungsten trioxide thin filmsWO_3 are modified with the CuO Nano particles by using the method of spin coating. SEM Analysis represents that prepared WO_3 thin films having brick like morphology but in the modified case WO_3 Nano bricks are coated with CuO Nano particles and it is possible to distinguish the edges of individual Nano bricks. CuO Nano particles synthesized by precipitation method. EDS Analysis represents the composition and elemental percentage of material that exhibit on the substrate. XRD pattern shows the successful preparation of pure WO_3 thin films with grain size 40 nm as well as the modification of WO_3 thin films with CuO, the particle size decreases up to 23 nm. UV-vis spectroscopy shows that maximum absorption of WO_3 is found at the wavelength of 530 nm with band gap energy of 2.3 eV while for modified with CuO Shows 2 peaks at two different wavelengths represents increase in band gap energy (2.5 eV) of WO_3 after coating of CuO Nano particles.

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r molecules on the available substrate. Its properties depends upon the thickness of films and thickness anges are nanometers to several micrometers. The thin films having one dimension is to be very small nd high surface to volume ratio.He found that thin films can be differentiate from thick films if surface to urface properties changes from the bulk materials[2]. Baran explained the development of new materials nd devices[3]. Harsha[4].stated that thin films has been used for the production of optical coating and lectronic devices. 1.4 Applications of thin films: Sharma et.al[5] described the different applications of thin lms which were used for the fabrication of solid state electronics devices and integrated circuits in nicroelectronic studies. The transparent and conductive materials of the thin films were being used for lectronic display. Like liquid crystal display,light emitting diodes,electro chromic devices,plasma and orescent displays. Thin films were also used for the optical coating,used as interference filters for solar anels and solar reflectors.Diamond like carbon films were also used in the formation of hard coating of urface. Thin films (2 Dimensions) behaves different from the Bulk materials having high surface to olume ratios. Two layers of atoms or surfaces are so close to each other which cannot present in the ulk counterpart [6]. ?

6**Piezoelectric devices.** ? Rectifications **and** amplifications. ? **Sensor elements. ? Storage of solar energy and conversion** into another **form of energy. ? Magnetic memories. ? Superconducting films. ? Interference** filters. ? **Reflecting and anti-reflecting coatings.**

Field effect transistor(FET) The present development by using thin films technology tending to: ?

6**Metal oxide semiconductor** transistors **(MOST)** ? For **sensors ? For switching system ? High density memory for**

e computers. Figure 1.1various applications in the field of thin film technology A thin film solar cell is nown as the second generation solar cell which can be made by deposition of two or more than layers of hotovoltaic materials on the substrate. 1.5 CuO/WO3 thin films: Many researchers presents the uO/WO3 obtained by different methods of synthesis.WO3 and cupric oxide CuO both are most important emiconductors materials with their band gap of 2.6ev and 1.2-1.5ev respectively[7].these materials can e used for the thin film technology such as solar cell formation.CuO is mostly used in the production of olar cell which gives favorable efficiency of the solar cell. 1.6 Why solar is best energy solution: Sun is the mount of energy that sends towards our planet earth is about

535,000 times more than what we **currently produce** and **consume.Some** amount **of this energy** commonly called **solar** radiations **goes back to the space but** most of the energy **is** absorbe by our **atmosphere** and other elements founded in **the inner atmosphere.** This radiations **energy can be easily harnessed for**

ur daily purpose like heating our houses,lightning bulbs,running automobiles,and even airplanes. We are cky