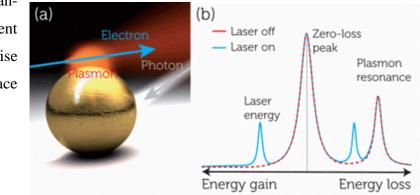
CHAPTER I

Plasmonics Study on Semi-conductor materials

INTRODUCTION

Plasmonics is a rising field that makes utilization of the Nanoscale properties of metals. Though plasmonics is a wide zone of study, its application for solar based cells has seen are cent surge of enthusiasm as is clear from the expanding number of productions ever the last couple of years. Metals nanoparticles surface Plasmons that are the aggregate swaying of energized free electrons and described by a full frequency. They can be either limited with respect to metal nanoparticles or spreading as on account of planar metal surfaces. By controlling the geometry of the metallic structures, the surface Plasmon reverberation or Plasmon engendering properties can be tuned relying upon the applications. The resonances of honorable metals are generally in the unmistakable or infrared district of the electromagnetic spectrum, which is the scope of enthusiasm for photovoltaic applications. The surface Plasmon reverberation is influenced by the size, shape and the dielectric Properties of the encompassing medium. Silver and gold have overwhelmed trial inquire about

in this are analbeit different metals likewise bolster surface Plasmon.



1.1 Photovoltaic applications:

Three distinctive instruments that could be used for photovoltaic applications are: (a)The dissipating from the metal particles that likewise go about as dipoles (far-field impact),

(b) The close field improvement and

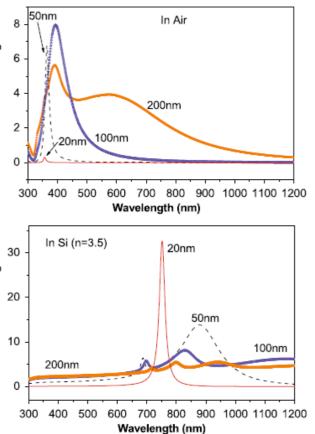
(c) Direct age of charge bearers in the semiconductor substrate. Most announced photocurrent improvement comes about for inorganic gadgets are clarified by the main component of dispersing and for natural gadgets by close field upgrade.

1.2 Foundation Study

Thin-film solar powered cells are directly viewed as the course to ease photovoltaics. This is accomplished by diminishing the photoactive layer, which is generally silicon. However ease is accomplished by trading off the efficiency of these cells. This is on the grounds that as the dynamic layer is weakened the charge transport properties disintegrate accordingly influencing cell execution. For a similar reason light catching turns into an essential factor. Customary techniques for

light catching use surfaces that a have highlights that are similar or 8 substantially bigger than the 🗄 thickness of the real thin-film solar powered cells. This would not be possible for thin-film cells. Finished surface can likewise bring about extensive surface h recombination.

Misfortunes because of expanded 30 surface zone, in this manner debasing the cell execution. Thus standout amongst the most s a pivotal components deciding the efficiency of thin-film cells is the catching impact or light the measure of light scattered into the Fig. 1. The normalised scattering cross-section of different diameter spherical



particles vs. wavelength in two different media: (a) air and (b) silicon. substrate. When energized, surface

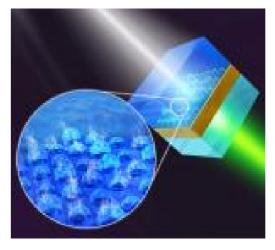
Plasmon excitation can bring about scrambling and mammoth improvement of the electric field. Metal particles in the request of wavelength of light go about as little dipoles dissipating the incident radiation, which is coupled to the methods of the hidden semiconductor

Metals demonstrate this conduct in light of the nearness of free charge transporters. Profoundly doped semiconductors and metal oxides can likewise indicate Plasmon impacts but since of the lower number of free charge bearers, their reverberation is for the most part in the infrared. The relative significance of retention and dispersing is measure Dependent. In this manner for photovoltaic applications the measure of the particles should be enhanced to guarantee most extreme dissipating. Assimilation commands for little particles o50 nm

What's more, utilized for applications like solar oriented coating and helpful applications [4, 5]. Dispersing for particles around 100 nm is more significant to solar based cell applications. However the molecule sizes can't be too vast as this prompts multi post motions which tend to diminish the disseminating efficiency of the nanoparticles. Fig. 1 demonstrates the impact of size on the dispersing cross-area and furthermore the impact of

having the particles in a high refractive list medium like silicon utilizing Mie scrambling hypothesis [6]. Fig. 1(a) demonstrates the standardized dissipating Crossarea (standardized to the geometric cross- segment) of various estimated circular particles in air and the resulting red move for similar particles in Si is unmistakably

clear in Fig. 1(b). This is on account of the reverberation crests move to longer wavelengths with increment in measure and additionally under the influence of a substrate with high refractive file. The move is alluring for Si gadgets as expanded disseminating at longer wavelengths



would empower great light catching near the bandgap of Si, where Si typically retains pitifully. In any case, as molecule measure expands disseminating diminishes and furthermore multipole motions are started as is unmistakably found in Fig. 1(b)

which can't couple efficiently to the substrate modes and the vitality is lost. Bigger particles alongside bigger surface scope prompt expanded parasitic retention and reflection decreasing the coveted optical assimilation in the semiconductor layer [7]. The expansion in dispersing cross-area for 20 nm measured particles in Si when contrasted with air is unmistakably clear. However particles in this range have a tendency to assimilate all the more emphatically (not appeared in the figure), thus the general dissipating is traded off. Utilizations of Plasmon impact.

CHAPTER II

Literature Reviewed

2.1 Phenomanal effect of Plasmons resonance

As whenever incoming photon interacts with the high charge density electronic cloud of metallic surface at the scale of nanometers, it brings about oscillations and multiple excitations. This causes the reemmision of photon of specific wavelength at the frequency called plasmonic frequency and hence it can either amplify the incoming photons or light efficiency, reduces the wavelength or scattering or either selective wavelength subtraction or multiplication of particular photon.

This ancient antique cup shown below is examined under white backlight light and its color changes from emarld green to glowing red. This cup is later examined as made of red river mud and glass from alluvian river sand which has tiny constituents of gold in it. The small particles of gold suspended and spread in this antique cup had undergone plasmonic resonance at particular angle and reflection, so as it selectively produces the plasmon effect at wavelength of red light,



The stunning Lycurgus cup reveals a brilliant red when light passes through its sections of glass containing gold-silver alloyed nanoparticles. Photograph: British Museum Images

2.2 Plasmons for third generation solar cells

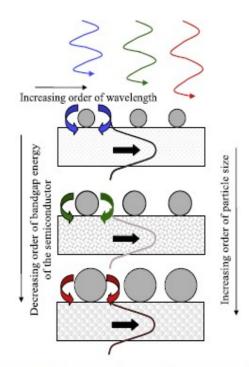
The third era solar based cells are frequently alluded to as the 'future' of solar based cells since they guarantee minimal effort high efficiency solar based cells intending to accomplish efficiencies nearer to the thermodynamic furthest reaches of 93% [6]. This requires circumvention of the Shockley– Queasier point of confinement of single bandgap gadgets. One such approach is utilizing various vitality edge gadgets like pair cells, where a progression of changing bandgap materials are stacked in arrangement

in the diminishing request of bandgap. This builds the ghostly affectability of the gadget in this way expanding the transformation efficiency.

The bandgap of the structures can be built utilizing quantum speck (QD) structures and a 'hot

bearer' cell approach taken to catch the electrons previously they thermalize. Improving photocurrent in low dimensional structures like quantum spot or quantum-well structures can be very testing a direct result of the low conductance of these structures, which is the impact of poor optical and properties electrical of these gadgets. The close field could be misused for expanding the efficiency from quantum

dabs which have a short transporter



transport separate. Consequently surface plasmons can give level quantum dot structure using size tunable metal nanoparticles. wavelength dependent light catching to pair cell applications where shorter wavelengths are coupled in the best layer utilizing littler metal nanoparticles and the more extended wavelengths assimilated in the consequent layers utilizing bigger measured metal nanoparticles as appeared in Fig. 2. Photoluminescence (PL) or electroluminescence (EL) vitality is related with the span of QDs, however an expansion in the force of PL or EL utilizing surface plasmons would demonstrate expanded outflow. Here again in view of the correspondence standard an expansion in discharge would associate to an expanded assimilation in the QD structures. Surface plasmons have exhibited

expanded photoluminescence and electroluminescence from silicon nanostructures by electromagnetic coupling of the silicon quantum dab emanation dipoles with dipolar plasmon methods of Ag nanoparticles [5, 8]. Comparative emanation has additionally been accounted for were lit up utilizing a 10 mW, 532 nm Nd:YAG laser and the outflow was caught on a thermoelectrically cooled Si-CCD camera. The pinnacle emanation is at 823 nm which relates to a bandgap of 1.5 eV and is expanded by just about half at this wavelength utilizing silver nanoparticles.

It is normal that the upgrade crest at 950 nm as appeared in Fig. 3(b) could be effortlessly tuned to the coveted wavelength by fluctuating the molecule estimate, e.g., for this situation going for littler particles which will move the reverberation to the blue side. These outcomes are promising evidence of-idea comes about and fusing them into solarlight based cell structures can conceivably help the execution of the cell making a third era cell more feasible. The improved electric field around the surface plasmons can possibly help nondirect forms like up- change, one of the vital viewpoints being investigated for the third-age solar oriented cells [1,2]. In the up- transformation process at least two underneath bandgap photons are typically retained into a luminescent material behind a solar based cell and radiating photon with higher vitality which would then be able to be retained. In the event that the luminescent material is arranged in the region of the improved electric field, the procedure is prone to be upgraded numerous overlay. Upgrade of up-transformation radiance of erbium-doped Al2O3 has been accounted for by putting it close silver island films of shifting sizes. A most extreme upgrade of 220 times was seen at 520 nm [14]. The expansion in control from the up-transformation procedure to date has been exceptionally unassuming yet surface plasmons can conceivably increment this incentive by numerous overlap adding to an expanded general cell efficiency.

The upside of this process is that the luminescent material is electrically disengaged from the solar based cell in this manner furnishing more optical tunability alongside the Plasmons.

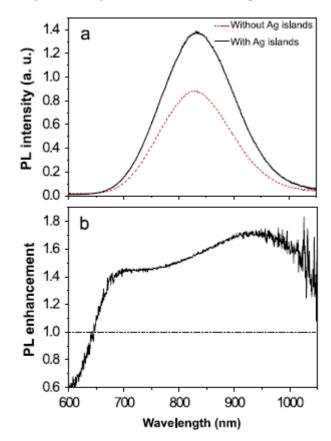
2.1 Scope

There is an unmistakable requirement for advancements that prompt better light absorption in thin solar based cells with a specific end goal to permit higher efficiencies and subsequently bring down general expenses of power creation. Plasmonics can possibly upset the photovoltaic business and convey high efficiency, minimal effort sunlight based cells. Light catching and centralization of light utilizing the modest metal nanoparticles

can open roads for a scope of sun powered cell outlines specifically for the third era photovoltaic innovation including quantum dabs and quantum wells and furthermore up-transformation process. Since the consolidation of the particles with the present approach is at the final phase of gadget handling for Si-based cells, no real interruption to the current manufacture process would be included.

Thus ebb and flow examine is focused at lessening the manufacture cost of the metal nanoparticles and furthermore empowering its creation on vast region gadgets. Displayt

lithographic procedures like ebeam lithography and focused particle beam lithography empower



DisplayFig. 3. (a) PL measured from a Si nanocrystal superlattice with (black solid line) and without (red dash line) silver metal islands and (b) corresponding relative s like e-enhancement in intensity (intensity with silver islands/intensity without silver islands). The X-axis scale is the same for both (a) and (b). (For interpretation of the focusedreferences to colour in this figure legend, the reader is referred to the web version of this article.)

manufacture of nanoparticles with high exactness however is costly and not reasonable for huge territory handling. Advancement of new strategies, for example, Nano-engraving or delicate lithography [5, 14] is picking up prominence as a vigorous commonsense creation process for plasmonic sun powered cells. This innovation in conjunction with existing testimony systems (like warm vanishing or sputtering) guarantees control of the size, shape and dissemination of the nanoparticles with precision at the nanoscale, permitting more opportunity for streamlining independent of the idea of the semiconductor used. Optimization of the different parameters specified before isn't a simple undertaking because of the numerous factors included. Henceforth it imagines the need to a decent comprehension of the innovation specifically the cooperation of light with the metal nanoparticles and the encompassing condition. Capable recreation devices which can give a more reasonable elucidation of results (representing the dielectric medium encompassing the particles and furthermore the impact for the neighboring particles) are expected to foresee the photocurrent improvements to empower creation of ideal nanoparticle exhibits for light catching applications.

2.1 MATERIAL SELECTION AND PROCESS PARAMETERS

2.1.1 IMPORTANCE: WHY CdTe?

The binary compound CdTe has been recognized as one of the promising thin film photovoltaic materials owing to its near optimum bandgap of 1.44 eV and high absorption coefficient over 10^{5} /cm. CdTe, therefore, absorbs over 90% of available photons (hv > 1.44 eV) in 1 µm thickness, and hence, films of only 1–3 µm are sufficient for solar cells.

2.1.2 PROCESS PARAMETERS

- 1) Since CdTe has high absorption coefficient hence thicknesses for CdTe thin films are limited within $1-10 \,\mu\text{m}$.
- 2) Among all the deposition methods, the highest efficient CdTe thin film solar cell was obtained by close-spaced sublimation (CSS). The substrate temperature is one of the crucial parameters for CdTe deposition as it could be observed that most of the deposition techniques demonstrated has substrate heating. Higher growth temperature not only enhances the deposition rate, but it also determines the quality of junction formation.

Substrate temperature	550 –6 20°C	🗣 Snippi
Source temperature	565–625°C	<u> N</u> ew
Pressure	1–2 Torr (Ar gas atmosphere)	Select a sr
Spacing	2 mm	DO COTA

TABLE 1.

Deposition conditions used in the CSS growth of CdTe films.

- 3) At low pressures, such as 1 Torr, the mean free path of the gaseous species in the reaction tube increases. In case of fixed source-substrate spacing, high thermal conductivity of the ambient gas tends to increase the substrate temperature, thus reducing the growth rate.
- 4) High deposition rate of CdTe films (up to 10 μ m/min) is therefore a special feature of the CSS

process that benefits the thin film growth in a short span of time.

CHAPTER III

EXPERIMENTAL TECHNIQUES

CLOSED SPACE SUBLIMATION (EQUIPMENT)

INTRODUCTION

Close space sublimation is a thin film deposition technique like many other deposition methods i.e. sputtering, vapor transport deposition etc. It is form of physical vapor deposition in which deposition occurs in vacuum to increase the process efficiency. Equipment used in this method is formed by assembling many parts like pumps, vacuum chambers etc. together to get the final result. And parameters used in this are controlled manually by operator, as they change according to the material used. It's a homemade invention which was brought into shape by PLANT, PV. In this technique materials are deposited on substrates in presence of pressurized atmosphere like vacuum, atmospheric pressures etc.

3.1 WORKING PRINCIPLE

This equipment works on the principle of deposition of materials on substrates in specific thickness range. It works on consideration to lower the foreign ambiguities effect on film deposition. For this purpose vacuum (space) is used in order to decrease the impurities effects. As direct phase change (between gas and solid) occurs while deposition and sublimation processes so following factors must be kept in to considerations:

- 1. Source surface sublimation
- 2. Vapor transport towards the substrate
- 3. Deposition on substrate surface

3.2 ASSEMBLY PARTS AND THEIR INTRODUCTION

As we know it is a home-made assembly so in order to control the vacuum and atmospheric pressures and to optimize many other parameters like temperature, time etc. different parts are assembled together to achieve the final goal.

Following are parts used in it:

- 2 Diffusion pump
- 3 Rotary pump
- 4 Main power supply
- 5 Vacuum chamber
- 6 Thermocouples
- 7 Pirani gauge
- 8 Vacuum and pressure valves

3.2.1 DIFFUSION PUMP

Diffusion pumps are used to create high vacuum while process is being run as they are extremely functional and stationary without any violent oscillations. It can create vacuum in range of mbar from10–10 to 10–2.

3.2.1.1 Working principle

Of this pump is based upon the vaporization of oil or fluid which is being boiled for molecules (air) entrapment. This liquid is then cooled down at different location where air molecules are allowed to liberate. These molecules are moved to pump lower (bottom) side as due to action of gravity and vapors downward direction. Diffusion pump made up of stainless steel chamber body can even be used in presence of various particles and reactive gases.

3.2.1.2 WORKING

As we can see from above diagram, oil or fluid is heated by means of heaters present at lower (bottom) side. Vaporization occurs when fluid is boiled enough and these vapors start moving toward the pump center while escaping through the nozzles at downward angle. These ring nozzles form vapor shield stretched towards the pump wall from nozzle.

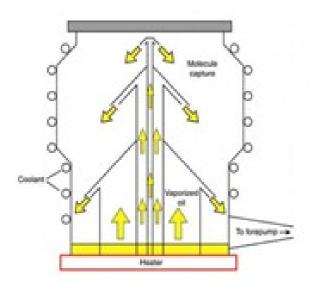


Fig. 4 diffusion pump working

These vapors entrap any air or molecules they encounter. When these vapors reach the pump walls (cooled by water continuously), they are cooled and condense back to oil while moving down to reservoir and by that time all captured molecules would be released. Cycle keeps on repeating. No molecule could escape in above direction and if it happens it is again captured by the vapor curtain above it which forces it to move in lower direction.

This downward movement of molecules will create regions of higher

pressure at lower side of each vapor shield so pressure at pump bottom would rise enough than rest pump region to pump all air outward. Some of fluid vapors could move upward but we can avoid this happening by using cold cap which helps condense the vapors.

3.2.1.1 CONSIDERATION

Following considerations must be kept in mind while using diffusion pump:

- 1. In order to increase the efficiency we should use high quality fluid or oil.
- 2. Oil or fluid used must match with vacuum level.
- 3. Water flow in cooling line, their inlet and outlet flow rates and temperatures must be checked.

3.2.2 ROTARY PUMP

Rotary pumps works on **principle** of basic straw in which we lower air pressure in it when we draw air by sucking. Air pressure in surroundings would then be higher and easily move the liquid upward.

In rotary pumps fluid is moved or displaced by pumping material rotary motions. Every rotation displaces the oil by its entrapment among the case or body and the pumping element. These pumping elements could be in form of rotatory pistons, gears etc. Rotary pumps facilitates the smooth flow of liquid because of its entrapment in closed body (casing). Speed to operate rotary pumps must be lower as to enhance the smooth flow if not then fluid motion inside the case would be difficult.

3.2.2.1 BENEFITS

Following are some benefits of rotary pumps:

 Able to pump all fluids as long as they do not contain hard or abrasive materials.
 They are able to withstand high differential pressures.

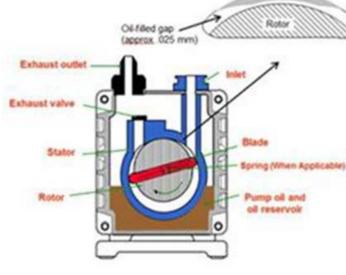
3. Give positive displacement of fluids.

4. As they clear airways and facilitate fluid pumping so they are self-priming.

Fig5: rotary pump working principle

3.2.2.2 DISADVANTAGES

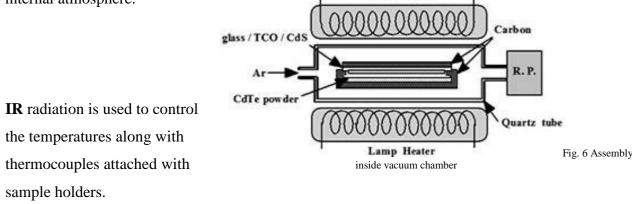
- 1. Discharge area must be not be closed otherwise it could wear out.
- 2. Fluids with abrasive particles cannot be used.



3.2.2 ACUUM CHAMBER

In this chamber deposition occurs by condensation and sublimation phenomenon. Inside the vacuum chamber assembly there is a quartz tube placed horizontally attached by a stainless steel reactor. There are holders where substrate and source are kept and they are apart from each other by approximately 1mm distance. This whole body is

enclosed in fused silica tube containing gas inlets and outlets in order to maintain the internal atmosphere.



Chamber is discharged many times and at 1.8 torr Ar gas to facilitate deposition process.

Fig 6 vaccum/ sample chamber

3.2.2.1 IMPORTANT PARAMETERS

Following are some important parameters that must be considered in vacuum chamber:

- 1. Atmosphere nature
- 2. Temperature of substrate and source.
- 3. Reaction tube internal pressure.
- 4. Source material composition.

All above mentioned parameters are related to one another in one way or other. As deposition rate is largely influence by the partial pressures inside the reaction tube which also depends upon temperature exponentially. At particular source temperatures the internal pressure drops to lower which results in increase in rates of sublimation.

Low pressures such as 1 Torr enhances the free mean path of gaseous bodies in reaction tube results in no limitation of condensation process between source and substrate. But if the

distance between the source and substrate remain constant and if the thermal conductivity, which is related to nature of gas, is high then substrate temperature would rise results in lower growth rates.

3.2.4 PIRANI GAUGE

This device is used for low vacuum pressure measurements from 0.5 to 10-4 torr. It is mostly preferred on thermocouples because it has wide uses and 10 times faster. This device need electrical supply to work which is considered its limitation.

It has 2 filaments made of tungsten, a power source and voltmeter or ammeter. One of filaments is open to atmosphere to measure pressure attached to gauge tube. Other filament is kept in reference sealed tube having stable or constant pressure. Heating source of these filaments is electric current. Heat is being carried away by gas molecules interaction with filament. In presence of high pressure more gas molecules interact with filament and carry away its heat.

3.3 SEQUENCE IN ON AND OFF PROCEDURE

Sequence we follow while starting the whole assembly is opposite to that we follow while shutting it. While starting the machine we follow the following steps:

- 1. First, we set the vacuum chamber and we feed the substrate and source temperatures as well.
- 2. Then we turn on the water circulation loop.
- 3. Then we turn on the diffusion pump.
- 4. And then check the outlet valve whether it is close or not. It must be closed otherwise vacuum would not be developed inside the chamber.

5. Then we turn on the main power supply and on the rotary pump button to facilitate the diffusion pump.

6. We can check the pressure changes from pirani gauge.

While shutting the equipment we will follow the same steps but in reverse sequence.

3.4 PRECUATIONS

Following precautions must be kept in mind while operating it:

1. Vacuum chamber must be cleaned with acetone before use.

- 2. Operator should be there for machine monitoring.
- 3. On and off sequence must kept in check.

3.5 ADVANTAGES

Following are some of the advantages of CSS equipment:

- 1. It is easy to handle.
- 2.No violent oscillations.
- 3.Not moving and produce effective results.
- 4. Easily available.
- 5.Homemade.

3.6 DISADVANTAGES

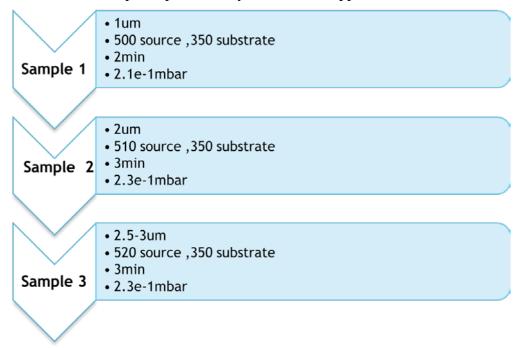
1.Can affect the results as operator dependent (manual).

- 2. Difficult to control the pressure flow.
- 3. Time consuming.
- 4. Parts need to be assembled not available as single body.

5.Difficult to repair.

Film growth

Thus we grow many films under varying conditions as it was difficult controlling its thickness and adhesion. Out of which we presented three samples that we're to be best opt for further characterization and other work. We obtained the thickness for op to 1 um calculated with optical profilemetry. There on as apparatus conditions are as such :



CHAPTER IV

CHARACTERIZATION TECHNIQUES : XRD

Characterization techniques are the methods by which we analyze our sample, learn about their morphological changes, crystal structures and their characteristics etc. In this chapter we will discuss in detail the parameters of xrd characterization technique, its formulas and how to analyze the results.

4.1 X-RAY DIFFARACTION

X-ray diffraction (XRD) is common technique for analysis of atomic spacing and crystal structure. X-ray diffraction based on constructive interference of monochromatic X-rays and a crystalline sample. And the X-rays generated by a cathode tube, filtered to produce monochromatic radiation, collimated to concentrate, and are directed toward the sample.

4.2 METHODOLOGY

The interaction of the incident rays and the sample produces constructive interference (and a

diffracted ray) when conditions satisfy Bragg's law:

$n\lambda = 2dsin\theta$ equation # 1

Where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle.

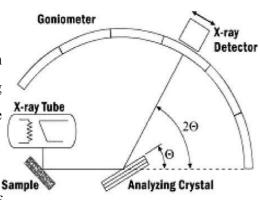


Fig. 7 x-ray diffractrometer

This law relates the wavelength of

electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted Xrays are then detected, processed, and are counted.

By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to dspacing allows identification of the compound because each compound has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, and Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction.

These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies Bragg's law, constructive interference occurs and a peak in intensity appears. A detector record processes this X-ray signal and converts the signal to account rate, which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X- rays and rotates at an angle of 2 θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data are collected at 2 θ from 5 to 70, angles that are preset in the X-ray scan.

4.3 XRD USES

•Phase Composition of a Sample –Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities

•Unit cell lattice parameters and Bravais lattice symmetry –Index peak positions –Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.

•Residual Strain (macrostrain)

•Crystal Structure –By Rietveld refinement of the entire diffraction pattern •Epitaxy/Texture/Orientation

•Crystallite Size and Micro strain –Indicated by peak broadening –Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

•We have in-situ capabilities, too (evaluate all properties above as a function of time, temperature, and gas environment.

SAMPLE CHARACTERISTICS

- A flat plate sample for XRPD should have a smooth flat surface –if the surface is not smooth and flat, X-ray absorption may reduce the intensity of low angle peaks (parallel-beam optics can be used to analyze samples with odd shapes or rough surfaces).
- Densely packed
- Randomly oriented grains/crystallites
- Grain size should less than 10 microns
- 'Infinitely' thick
- homogeneous

4.4 SAMPLE PREPARATION FOR XRD OF POWDERS

- The distribution of orientations should be smooth and equally distributed amongst all orientations.
- Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation.
- If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern.
- So crystallites should be $<10\mu$ m in size to get good powder statistics.

4.4.1 Preferred orientation

- If the crystallites in a powder sample have plate or needle like shapes it can be very difficult to get them to adopt random orientations –top-loading, where you press the powder into a holder, can cause problems with preferred orientation.
- in samples such as metal sheets or wires there is almost always preferred orientation due to the manufacturing process
- for samples with systematic orientation, XRD can be used to quantify the texture in the specimen

4.5 EXPERIMENTAL RESULTS:

SAMPLE #1

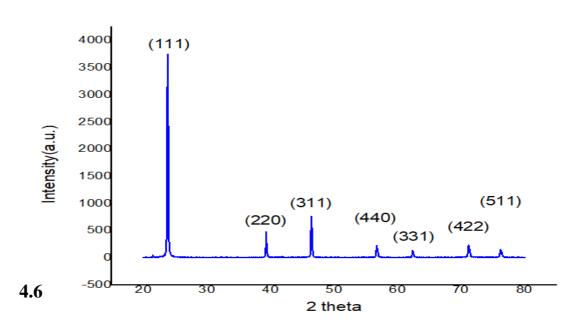
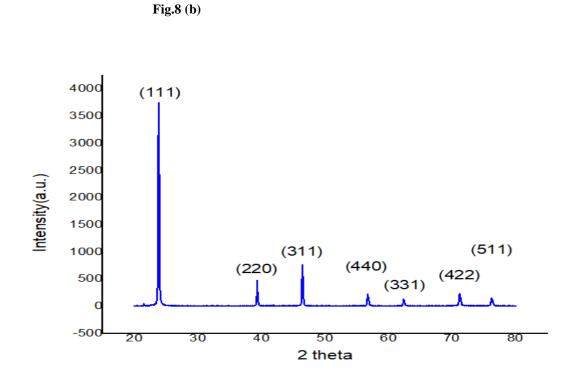


Fig.8 (a)

Wavelength: 1.541874 Cu-Ka

Peak list [Range 1: 2Theta = 23.669 76.064 0.040 IMAX = 1000]

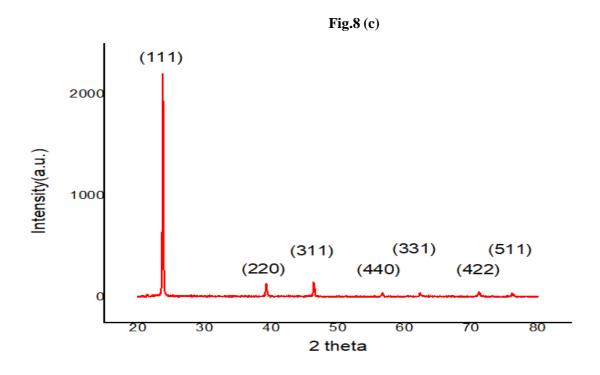
SAMPLE #2



Wavelength: 1.541874 Cu-Ka Peak list [Range 1: 2Theta = 22.433 71.138 0.040 Imax = 1000]

Table: 3

SAMPLE #3



Formula : n.a.

Wavelength: 1.541874 Cu-Ka

Peak list [Range 1: 2Theta = 22.259 78.241 0.040 Imax = 1000]

Table no. 4

	(111)	<u>FWHM(beta)</u> (211)	(311)	Crystallite size (nm)
Sample 1	0.167	0.228	0.251	51.57
Sample 2	0.168	0.11	0.135	50.4
Sample 3	0.197	0.213	0.230	43.06

The crystallite sizes and FMWH

D=K λ /(β cos θ)

K=0.89

Debye(D) scherrer's formula

Beta = Full width half maxima of longest peak

Theta = the angle of the selected peak

CONCLUSION:

Above are the xrd results of 3 samples of CdTe thin films before doping which shows its crystalline nature. Its crystal structure is FCC cubic. Difference in I(rel), I(abs) and I(int) and the values of FWHM are very important in acquiring crystallite size and also to find band gap for studying samples optical properties.

CHARACTERIZATION TECHNIQUES: UV-VIS SPECTROSCOPY

5.1 What is uv-spectroscopy?

Ultraviolet (UV) spectroscopy is a physical technique of the optical spectroscopy that uses light in the visible, ultraviolet, and near infrared ranges. UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm.) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. The energy of the ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states (delta E=hf). Generally, the most favored transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). Some of the important transitions with increasing energies are: nonbonding to pie^{*}, nonbonding to sigma^{*}, pie to pie^{*}, sigma to pie^{*} and sigma to sigma^{*}.

5.1.1 The Beer-Lambert law

States that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. It means that thickness is directly proportional to the absorbance. Thus, for a fixed path length, UV/VIS spectroscopy is being used to determine the concentration of the absorber in a solution. So we need to know how rapidly the absorbance changes with concentration.

5.2 WHY UV_VIS?

Because of following:

- □ Simplicity
- □ Versatility
- □ Speed
- $\hfill\square$ Accuracy and
- □ Cost-effectiveness. (spectroscopy.).

5.3 Instrumentation of UV spectroscopy

Most of the modern UV spectrometers consist of the following sections:

1. Light Source: Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source. Tungsten filament lamps are rich in red radiations, they

emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium falls below 375nms.

- 2. Monochromators: these are generally composed of prisms and slits. The most of the spectrophotometers are **double beam spectrophotometers**. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording.
- 3. Sample and reference cells: One of the two divided beams is passed through the sample solution and second beam is passé through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz.
- 4. Detector: Generally two photocells serve the **purpose of detector in UV spectroscopy**. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.
- 5. Amplifier: The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servometer. The main purpose of amplifier is to amplify the signals.
- 6. Recording devices: Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.

5.4 Principle of u-v spectroscopy

A molecule or ion will exhibit absorption in the visible or ultraviolet region when radiation causes an electronic transition within its structure. Thus, the absorption of light by a sample in the ultraviolet or visible region is accompanied by a change in the electronic state of the molecules in the sample. The energy supplied by the light will promote electrons from their ground state orbitals to higher energy, excited state orbitals or antibonding orbitals. Potentially, three types of ground state orbitals may be involved:

- 1. σ (bonding) molecular
- 2. π (bonding) molecular orbital
- 3. n (non-bonding) atomic orbital

In addition, two types of antibonding orbitals may be involved in the transition:

 $(I)\sigma^*$ (sigma star) orbital

ii) π^* (pi star) orbital

The greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption.

$A = \log (I_0/I) = \epsilon cl$ for a given wavelength

Where,

A = absorbance/Optical density

 I_o = intensity of light incident upon sample cell I = intensity of light leaving sample cell

c = molar concentration of solute l = length of sample cell (cm)

 $\varepsilon = molar absorptivity$

Absorptions arise from a charge transfer process, where electrons are moved from one part of the system to another by the energy provided by the visible light.

PURPOSE:

We are using this process for the characterization of our sample. In order to find the band gap from absorption and transmission data.

5.6 EXPERIMENTAL RESULTS:

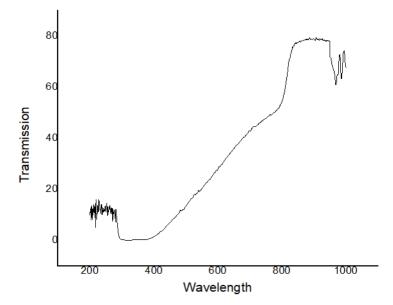


Fig.9 (a) Transmission vs wavelength . For sample 1.

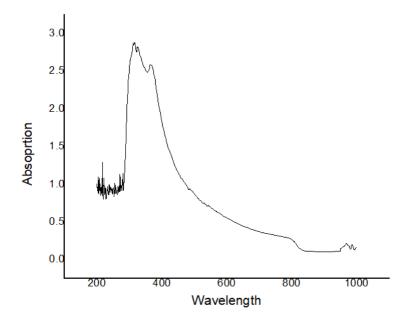


Fig.9 (b) absorption vs wavelength

CONCLUSION:

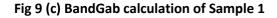
Above both graphs shows the relation between wavelength and transmission in fig.9 (a) and relation between wavelength and absorbance in fig.9 (b). In first graph we can see that as wavelength (nm) changes from smaller to larger values the amount of transmission

increases. While in second graph we can see by higher values of wavelength absorbance decreases. By finding absorption coefficient alpha then drawing a graph between hv on X axis and (alpha hv) square on y axis then draw linear fitting tangent to your curve to interact y axis in energy band gap value

Band Gap Energy (E) = h^*C/λ

2.00E-014 (1.50eV) 0.00E+000 1.4 (hv)

h = Planks constant = 6.626 x 10-34 Joules sec



CHARACTERIZATION TECHNIQUES: SEM

SEM (INTRODUCTION)

Scanning electron microscopy is used for inspecting topographies of specimens at very high magnifications using a piece of equipment called the scanning electron microscope. SEM magnifications can go to more than 300,000 X but most semiconductor manufacturing applications require magnifications of less than 3,000 X only. SEM inspection is often used in the analysis of die/package cracks and fracture surfaces, bond failures, and physical defects on the die or package surface.

PRINCIPLE

During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected.

PARAMETERS

Following are some parameters we need to keep in mind while working on SEM characterization technique:

- The energy of the primary electrons determines the quantity of secondary electrons collected during inspection.
- The emission of secondary electrons from the specimen increases as the energy of the primary electron beam increases, until a certain limit is reached. Beyond this limit, the collected secondary electrons diminish as the energy of the primary beam is increased, because the primary beam is already activating electrons deep below the surface of the specimen. Electrons coming from such depths usually recombine before reaching the surface for emission.
- Aside from secondary electrons, the primary electron beam results in the emission of backscattered (or reflected) electrons from the specimen. Backscattered electrons possess more energy than secondary electrons, and have a definite direction. As such, they cannot be

collected by a secondary electron detector, unless the detector is directly in their path of travel. All emissions above 50 eV are considered to be backscattered electrons.

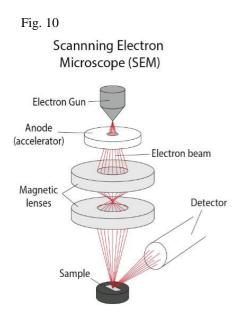
Backscattered electron imaging is useful in distinguishing one material from another, since the yield of the collected backscattered electrons increases monotonically with the specimen's atomic number. Backscatter imaging can distinguish elements with atomic number differences of at least 3, i.e., materials with atomic number differences of at least 3 would appear with good contrast on the image.

INSTRUMENTATION AND WORKING

In a scanning electron microscope, an emitted primary electron beam is diverted by an angle of at least about 45 degrees prior to incidence with a specimen. The beam may be bent by a magnetic separator. The separator may also serve to deflect secondary electron and back scattered electrons. As the angle of emissions and reflections from the specimen is close to the angle of incidence, bending the primary electron

beam prior to incidence, allows the electron source to be located so as not to obstruct the travel of emissions and reflections to suitable detectors. Scanning electron microscopes are highly versatile electron beam instruments that can provide images over 100 times more magnified than

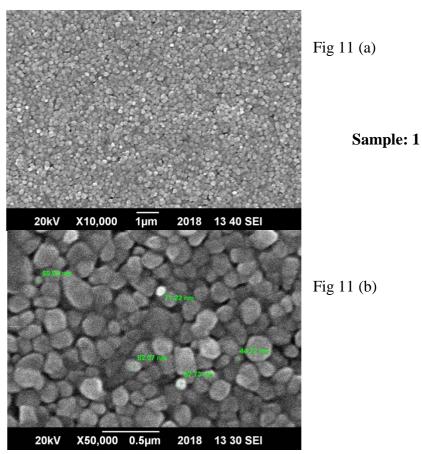
commercial optical microscopes.



A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.

PURPOSE:

We used this characterization technique in order to learn about the morphology, topography of our samples.



EXPERIMENTAL RESULTS:

SAMPLE 2

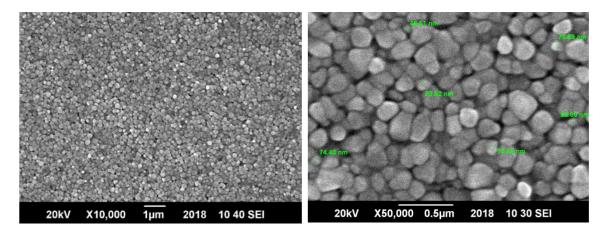


FIG11(d)

FIG11 (e)

SAMPLE 3

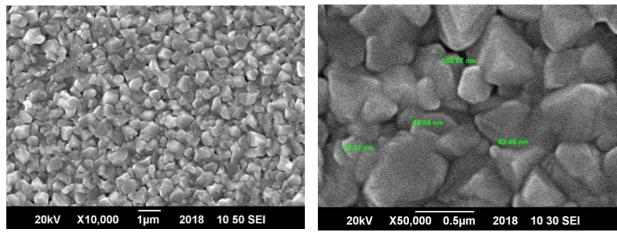


FIG 11 (g)

FIG 11(h)

RESULTS CONCLUSION:

Above obtained results from SEM shows the morphological changes of different samples of CdTe thin films at different magnifications before doping. We can also analyze phase transformations in these samples. We can distinguish between the grain sizes and grains uniformity in above samples at different magnifications. It is showing that at higher temperature grain sizes are somewhat larger than at lower temperatures.

CHAPTER V

DOPING

INTRODUCTION

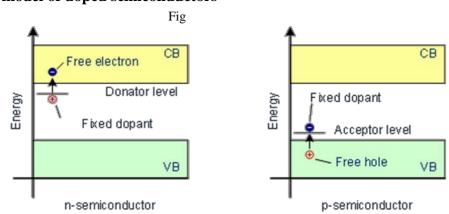
Doping means the introduction of impurities into a semiconductor crystal to the defined modification of conductivity. Two of the most important materials silicon can be doped with, are boron (3 valence electrons = 3-valent) and phosphorus (5 valence electrons = 5-valent). Other materials are aluminum, indium (3-valent) and arsenic, antimony (5-valent).

The dopant is integrated into the lattice structure of the semiconductor crystal, the number of outer electrons define the type of doping. Elements with 3 valence electrons are used for p-type doping, 5-valued elements for n-doping. The conductivity of a deliberately contaminated silicon crystal can be increased by a factor of 10^6

Electronic band structure in doped semiconductors

By the introduction of a dopant with five outer electrons, in n-doped semiconductors there is an electron in the crystal which is not bound and therefore can be moved with relatively little energy into the conduction band. Thus in n-doped semiconductors the donator energy level is close to the conduction band edge, the band gap to overcome is very small.

Analog, through introduction of a 3-valent dopant in a semiconductor, a hole is available, which may be already occupied at low-energy by an electron from the valence band of the silicon. For p-doped semiconductors the acceptor energy level is close the valence band.



Band model of doped semiconductors

MATERIAL SELECTION FOR DOPING

In our project we are purposely doping and embedding the silver nanoparticles for

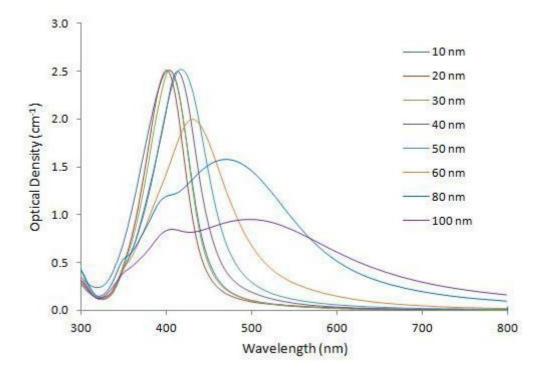
- (1) To improve the photovoltaic application and enhancing its efficiency by means of doping.
- (2) Some undoped or embedded form of metallic Nps at the range of 50-200nm can produce localize plasmon effect that enhance the light absorption and increasing overall photon efficiency to minimize the loses that cause by light scattering in dielectric medium.

Significance of silver nanoparticles

Silver nanoparticles (colloidal silver) have unique optical, electronic, and antibacterial properties, and are widely used in areas such as bio sensing, photonics, electronics, and antimicrobial applications.

Most applications in bio sensing and detection exploit the optical properties of silver nanoparticles, as conferred by the localized surface plasmon resonance effect. That is, a specific wavelength (frequency) of incident light can induce collective oscillation of the surface electrons of silver nanoparticles. The particular wavelength of the localized surface plasmon resonance is dependent on the silver nanoparticle size, shape, and agglomeration state.

Figure 12 shows the plasmon resonance spectra of different sizes of Cyto-diagnostics silver nanoparticles, as measured with UV-visible spectroscopy. As the particle size increases from 10 to 100 nm, the absorbance peak (lambda max) increases from 400 nm to 500 nm, and broadens in width. For particles of greater size, especially above 80 nm, a secondary peak at lower wavelength becomes apparent, which is a result of quadrupole resonance, in addition to the primary dipole resonance.

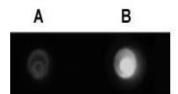




The aggregation state of silver nanoparticles also has significant effect on their optical properties. This fact can be used to monitor the stability of silver nanoparticles, both over time, and upon addition of salt-containing buffers, which at high enough concentrations cause particle aggregation. As shown in the absorbance spectra in Figure 2, aggregation is indicated by a decrease in the primary peak, and an increase in the red region.

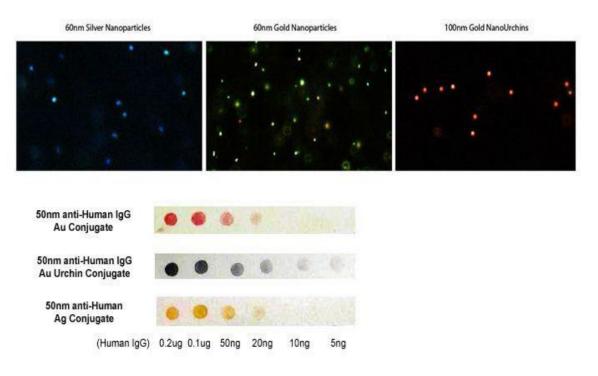
Comparison Gold Vs silver

Both silver nanoparticles and gold nanoparticles are commonly employed in optical detection for their surface plasmon resonance effect. The plasmon excitation efficiency of silver nanoparticles is known to be even more pronounced than that of gold nanoparticles, as shown in their stronger, sharper plasmon resonance peaks at the same particle concentration. Silver nanoparticles thus can render better sensitivity for some applications, such as localized surface plasmon resonance or surface enhanced Raman scattering detection. Silver nanoparticles may also be advantageous over gold nanoparticles, when used in combination with fluorescence emission detection. Most fluorophores emits at a wavelength above 500 nm. However, the Plasmon resonance absorbance of gold nanoparticles is primarily in the range of 500-600 nm, and hence can quench the detectable fluorescence to some extent, when the fluorescent dyes are close to the particle surface. This issue of fluorescence quenching is minimized for silver nanoparticles, as their Plasmon resonance absorbance is mostly below 500 nm, with little overlapping with the emission wavelength of most fluorescent dyes. Figure 14 shows images of fluorescent gold and silver nanoparticles, labeled with the same amount of Cyto633 fluorescent dye. The fluorescent signal from silver is about 4 times stronger than that of gold.



Gold (A) and silver nanoparticles (B) surface-modified with the same amount of Cyto633 fluorescent dye.

Fig. 15



Effect of size and distribution

SIZE EFFECT

Silver NPs SPR frequency w.r.t sizes:

As you can see in the table above the Plasmon frequency (i.e. wavelength of excitation) varies with

Diameter (nm)	Peak SPR Wavelength (nm)	NPS/ml	Wt. Conc (mg/ml)	Size Dispersity (+/-nm)	Particle Volume (nm3)	Surface Area (nm2)	Surface/ Volume Ratio	Particle Mass (g)	Molar Mass (g/mol)	Molar Concentration
10	390-405	~3.6E+12	2.0E-02	<18%	5.24E+02	3.14E+02	0.600	5.49E-18	3.31E+06	5.98E-09
20	390-410	~4.6E+11	2.0E-02	<15%	4.19E+03	1.26E+03	0.300	4.39E-17	2.65E+07	7.64E-10
30	400- <mark>41</mark> 0	~1.4E+11	2.0E-02	<15%	1.41E+04	2.83E+03	0.200	1.48E-16	8.93E+07	2.32E-10
40	405-425	~5.7E+10	2.0E-02	<15%	3.35E+04	5.03E+03	0.150	3.52E-16	2.12E+08	9.47E-11
50	410-430	~2.9E+10	2.0E-02	<12%	6.54E+04	7.85E+03	0.120	6.87E-16	4.13E+08	4.28E-11
60	425-450	~1.7E+10	2.0E-02	<12%	1.13E+05	1.13E+04	0.100	1.19E-15	7.14E+08	2.82E-11
80	440-480	~7.1E+09	2.0E-02	<12%	2.68E+05	2.01E+04	0.075	2.81E-15	1.69E+09	1.18E-11
100	480-520	~3.6E+09	2.0E-02	<10%	5.24E+05	3.14E+04	0.060	5.49E-15	3.31E+09	5.98E-12

sizes with having below 5 nm causes a blue shift in frequency while having ranges between 5-10 or 20 nm causes redshift in wavelength.

Effect of distribution:

For localized Plasmon effect the distribution of Nano particles contributes towards, the scattering and concatenating the enhanced abundance of photons that are excited at a particular Plasmon resonance. Not too much that it would shadow out the area for incoming light and neither less to bear any fruitful result.

DOPING BY USING Ion Exchange method under

For the purpose of studying effect of size and distribution of Nano-particles of silver, we're going to analyze this effect by the ion exchange of solution of Ag Nano particles. This would give us a nice spread of particles as the annealing of it make to embed them on the surface of film as well as diffused into the crystallites producing silver telluride which infact enhances the photovoltaics.

EXPERIMENTAL PROCESS AND PARAMETERS

We're using AgNO3 precursor solution that would evaporate, liberating us nanoparticles

(<20 nm). Then we will do spin coating to distribute or spread the nanoparticles to the surface of substrate. We selected only sample 1 as it has least thickness that we want and 72 % transmission

PARAMETERS

Parameters to adopt for spin coating is:

- Silver nitrate solution (300mg/100ml)
- Thin film immersed in solution for different intervals of time.
- 30 sec ~ sample 1
- 1 minute ~ sample 1
- 2 minute ~ sample 1
- Anealing for 1 hr

ION EXCHANGE

INTRODUCTION

It is a process in which the ionic solution is spread out and vacuum and heat is provided so that more stable ion can replace the atom on crystallite.

OPERATING PROCESS IN Ion Exchange method

- 1) Preparation first prepare the sample.
- 2) Degrease the sample: (Note: this step is optional depending on user preference and process

conditions.)

- 3) Immerse the sample in Acetone for 2-3 minutes, followed by Isopropanol for 2-3 minutes and rinse in DI H2O. Dry using N2.
- 4) Bake on a hot plate for 2-3 minutes at 120 to $130 \,^{\circ}$ C.
- 5) Place the sample on any metal surface (bench) to cool in air for at least 2-3 minutes.
- 6) Spread the silver nitrate solution on the film.
- 7) Place it under vaccum and heat it
- 8) The ions will diffuse into the film medium.
- 9) The evaporation of solvent causes some ions to re stabilize and form nucleats.
- 10) Such nucleats will create NPs and than they are embedded on the film surface.
- 11) Anealing for 1 hr gives sufficient time for ion exchange as well some deposite or secure embedding of clustered NPs.

FACTORS AFFECTING THE PROPERTIES OF THIN FILMS DURING

As more time is given the concentration of ions will increase. Since the annealing temperature is constant for all 3 cases hence the only difference in property would come from the drop concentration and the dewel time

CHAPTER VI

AFTER DOPING CHARACTERIZATION

After the doping of the sample 1. We break into 8 further pieces and performed the SEM and UV vis for the doped. We took the as Deposited as our **Refference** and compared the **30 sec, 1 Min & 2 Min** doped deposited films

<u>SEM</u>

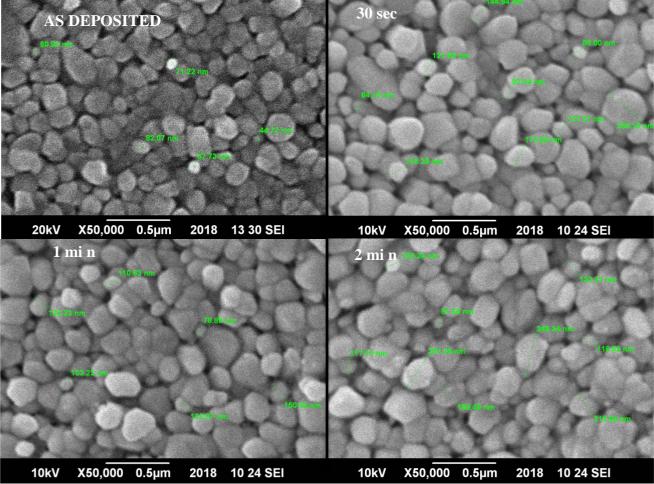


Fig 16 (a) as deposited ref of sample 1, b) 30 sec dwell time in doping, c) 1min dwell time, d) 2 min dwell time

As in figures above clearly shows that how the grains sizes are chains, and at some places are brighter than the other. As you increase the dwell time the diffusion and more rapidly evaporation of solvent takes place which induce recrystallization tha causes a decreases in grains sizes. As well as the film becomes more intact and the voids are closing which means the roughness is decreasing. As film is observed it was much more reflecting than previous hence its shows that, some of it has metallic form deposited on the films surface. The more brighter and shiner areas concern predominantly metallic form of silver in grains which would form the bases of plasmonic effect.

<u>UV-VIS</u>

No IV Transmission graph

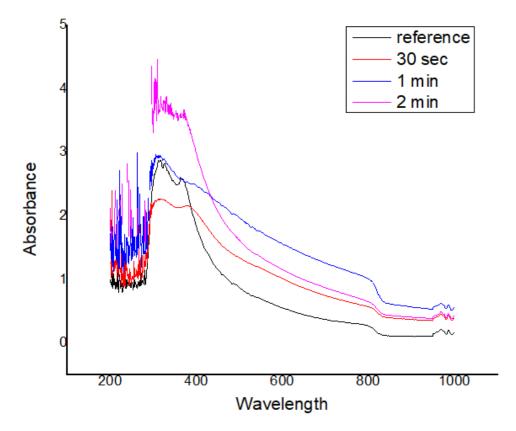
Transmission spectrum

We can clearly see as the density of dopend or embeds on surface increases and so the film thickness increases which reduces the transmission. This is the very reason for using the Sample 1 at first place with 72 % transmission. Otherwise the other films transmission would near to 7 - 5 % if we would have to dope them. There isn't really significant difference in their trend only which its magnitude of transmission had decrease from 72 to 25%.

FIG 17 Transmission graph

Adsorption Spectrum





Our main focus is on the hump that forms over a certain wavelength. With reference to our sample. Doping it with in near 30 secs makes the adsorption more linearly falloff and its hump had reduced at 300nm which is the UV region.

The one at for 1 min dwell doped film the hump had slightly raised and its fall off is even spread, that may be due to clustering of metallic silver particles that actually causing scattering.

And for the 2 min dwell doped, the hump had raised almost twice but a bit noises that shows that scattering is caused by metallic NPs. And the hump spread is over 410 NM which is the blue spectrum in visible region. Hence it may also indicates that at this wavelength plasmonic scattering and interferences is occurring.

As can be seen in this graph from literature

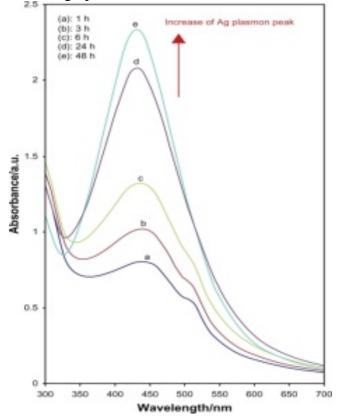


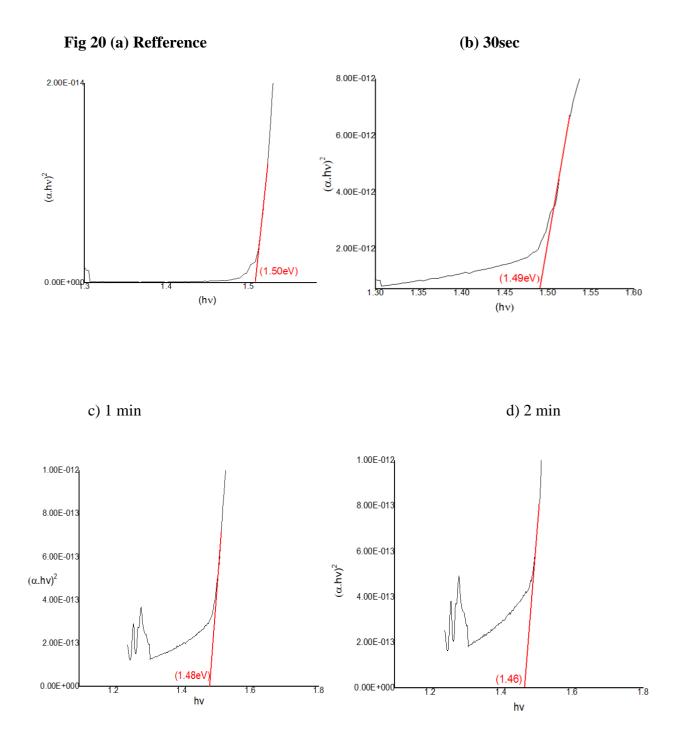
fig 19 The UV-vis absorption spectra of the colloidal Ag-NPs synthesized using glucose at different reaction times. Abbreviations: Ag-NPs, silver nanoparticles; UVvis, ultraviolet visible.

As the plasmonic interference increases the absorbance hump is greatly enhanced. So is in our case it is over 410 nm the hump spread as it increased from the reference. The only difference is of Noisiness in graphs which is due to the surface defects , impurities on film or insensitivity of instrument might have caused.

This somewhat identifies that there's some degree of Plasmonic effect is generated over the 400nm wavelength range.

To further confirm this we have to characterize our sample with Photolumineces (PL) technique to observe its optical density hump which further clarifies this effect nature. However with the formed silver telluride during ion exchange the photovoltaic efficiency increases as it helps reducing the photo voltaic loses during Recombining and increases the overall donor species.





As by doping and the interaction of silver with cdte it decrease its band gab from UV region (1.50-1.52) to the visible solar spectrum region (1.46 for 2 min). As for cdTe the direct band gap for optimized solar spectrum is 1.44. And so we have obtained it till 1.46. Which further states that we made our film functional and near optimum at visible range for photovoltaics applications.

As we also had observed the Plasmon interference at 410 nm for 2min sample, this

means our plasmonic resonance is acquired at the visible region too but for its further efficiency calculation we need to characterize it with PL technique which unfortunitaly couldn't due so due to lack of resources.

CONCLUSION

From this study it was revealed that the CdTe grow in cubic fcc phase and that the post-deposition treatment affects the crystallographic as well as the electrical properties strongly. A significant change in the shape and size of the CdTe grains were also observed. The transmission and absorption spectra showed an increase of transmission with an increase of wavelengths. A slight increase of the refractive indices of the films and a shift in the optical band gap.

Then the mutual comparision of the sample one and doped at different dwell conditions shows that the how drastically the transmission is decreased, where we also had observed the incread hump as we increase the dwell or allow the ions and particles to more deeply exchange and adsorb in place. The doped films also had appeared a bit more shiny and reflective which further states that silver in metallic form is also dispersed on the surface of film. Thereby the increase in films thickness change in optical n reflective index as well as the interaction of phase silver telluride causes its bandgab to decrease which we successfully brought it to visible region of CdTe. The decreas in bandgab to visble range and absorption hump at 410 nm shows that plasmonic interence had occurred for our film which needs to be further assed by more advance techniques which were un available at prior time. However it is on bay to future implementation and further advance study is to be done.

Future recommendations:

In this research study we found new ways of improving the over all efficiency for third gen solar cells (<1um thicknes) without actually increasing its surface area or other complex modulation. We can simply dope optimize the film growth to acquire the required bandgap and increase its over all photovoltaic efficiency.

The plasmon effect generated alongside by silver metallic particles can help reducing the energy loses in terms of light absorption and focusion such as the light that is wasted inside material can be re focused with the help of plasmon effect generated at the surface in our case is resonating at visible range.

The doping with silver can greatly enhance its photovoltaics more than its doping with copper as it greatly reduces the over all resistance in material and provides channeling for proper electron flow as well as during recombination reduces the energy loses.

So in our future study we will enhance it light absorption and selective wavelength efficiency by improving its surface plasmon effect.

Think about having solar cell giving almost 50% output even in dim sunlight or cloudy, it can really revolutionize the overall photovoltaic industry as you can amplify or subtract a particular wavelength by simply manipulating the size and shape of metallic nano particles

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