Summary and conclusions

In the future for various applications, basic research activities will be necessary, to increase understanding, knowledge and to develop projecting capabilities for relating fundamental chemical and physical properties to the nanostructure, microstructure and performance of thin films in various applications. A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors. A very thin film coating (less than a nanometer thick) is used to produce two-way mirrors. The performance of optical coatings (e.g. antireflective, or AR, coatings) are typically enhanced when the thin film coating consists of multiple layers having varying thicknesses and refractive indices. Similarly, a periodic structure of alternating thin films of different materials may collectively form a so-called superlattice which exploits the phenomenon of quantum confinement by restricting electronic phenomena to two-dimensions. It is also been applied to pharmaceuticals, via thin film drug delivery. Thin-films are used to produce thin-film batteries. Thin film application also be adopted on dye-sitizized solar cell. Ceramic thin films are in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude.

Research is being done on a new class of thin film inorganic oxide materials, called amorphous heavy-metal cation multicomponent oxides, which could be used to make transparent transistors that are inexpensive, stable, and environmentally benign. One of the widest applications of thin film is in photovoltaic solar cells. Initially appearing as small
strips powering hand-held calculators, thin-film PV is now available in very large modules used in sophisticated building-integrated installations and vehicle charging systems. Solar Cell operations depend mainly on: absorption of light to create electron-hole pairs (carriers), diffusion of carriers, separation of electrons and holes, collection of carriers. For this it requires Cheap, Simple and Abundant Material, integrated and large Scale manufacturability, high absorption coefficient greater than $10^{-5}$ cm$^{-1}$ with direct band gap $\sim$1.5 eV, junction formation ability, high quantum efficiency, long diffusion length, low recombination velocity, abundant, cheap and eco-friendly material, simple and inexpensive integrated processing with energy pack period about two year. Copper chalcogenides is one of most important binary alloys (compound) which fulfills all these properties.

Thin films of copper sulfide gives one of the simplest solar cell to produce with simple chemical conversion technique, up to now it got highest efficiency obtained $\sim$10 %. Large scale production of modules with $\sim$5% efficiency is demonstrated during 70’s. Stability of cells due to cuprous-cupric conversion remained an issue. Due to the emergence of higher efficiency Si cells, this cell lost the battle of survival. Revival of this cell with suitable modifications is a possibility. Room temperature deposition process can used to uniform coat with extremely large areas. The deposition technique and by-product of the technique are environmentally begin making it truly green manufacturing process. The optical band gap of these material lies in range of 1.7- 2.3 eV which is close to peak. Monolithic integration of individual cells is simple and done by selective electron irradiation allows for module voltage optimization. This material possesses the necessary electron and hole transport properties for p-type solar cells. This research describes a simple and efficient method suitable for the fabrication of nanorods by electrodeposition at
room temperatures. The results obtained are important since the production and modification of copper monosulfide, copper selenide, copper telluride nanostructures can be a key for the wide use of this material in the present day semiconductor devices. I believe the work will be interesting for the nanoscience and nanotechnology researchers.

The overall research objective is the development and modification in surface morphology, optical properties to discover an efficient, practical, and economically sensible material. We are exploring a shift in the research model from conventional serial chemical research approach featuring a systematic and conscious high-speed investigation of the masterpiece-structure-property relationships of new semiconductor based solid-state materials. Surface treatment with electron irradiation has been shown to improve the morphology, optical properties. In recent years, much effort has been focused on the self-assembly of lower dimensional inorganic nanostructures into three-dimensional (3D) ordered upper structures because of the complexity of the possible arrangements, such as multipods, fowflakes, dendritic structures, hollow spheres, nanorods, and hierarchical structures. Controlled organization of primary building units into ordered superstructures represents another interest for materials self-assembly. Such a capability is attractive not only in understanding the concept of self-assembly with building blocks but also due to the importance in its potential applications. Hollow microspheres, as a special kind of 3D curved microstructures with inner cavities are also important in many fields due to their unique properties of low density, high specific surface area, and good permeation.

Also hollow spheres have attracted considerable attention because of their unique properties and widespread applications in drug delivery, catalysis, sensors, artificial cells, and photonic crystals, and so on. Various fabrication procedures for hollow structures have
been developed, such as hard templates, soft templates, as well as physical/chemical processes based on the Kirkendall effect, Ostwald ripening, chemically induced self-transformation, and so on. Here in our research simple method to obtain these fascinating structures with designed morphology, we use to irradiate the electrodeposited prepared thin films with highly energetic electron irradiation.

**Chapter I** describes the classification of various physical and chemical techniques of thin films deposition, advantages of electrodeposition, basics and working of electrodeposition technique, characterization techniques such as film thickness surface profiler, the various characteristics of as grown and irradiated thin films such as structural, compositional and optical properties of thin films were studied by various techniques. X-ray diffraction (XRD) study was done by a Rigaku Rint-2000 X-ray diffractometer using Cu/30kv/15mA radiation with a scan step of 0.001. The compositional analysis was find out by energy-dispersive X-ray analysis, using JEOL model, JSM-6300 (LA) The surface morphology were studied by using scanning electron microscopy (SEM) using JEOL model, JSM-6360 (LA). Raman spectra of the films were collected on a combination system including research grade FTIR model VERTEX 70 with model- Ram- II FT Raman spectrometer equipped with Nd-YAG laser at 1064 nm wavelength. The spectra were recorded at laser power 0- 450 mW, the wave number range from 200- 4000 cm\(^{-1}\). For study of Optical absorption the film deposited potentiostatically on ITO coated glass substrate is carried out using UV-VIS spectrophotometer is also included in this chapter.

**Chapter II** begins with general introduction about experimental set up to irradiate the as deposited thin films. This chapter also includes the literature survey on synthesis and characterization of copper chalcogenides materials, brief literature survey on
Summary and conclusions

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Chapter VII

Irradiation of as deposited copper chalcogenides and other material. It also includes the statement of choosing problem on irradiation to scope of science and technology.

Chapter III includes the introduction of copper sulfide material with literature survey. Copper sulfide thin films were deposited at room temperature due to which oxidation and corrosion of thin film is avoided. For deposited thin films CuSO$_4$ is taken as source of copper, Na$_2$S$_2$O$_3$ is taken as source of sulfate and triethanolamine as complexing agent which act as co-ordination polymer. All are dissolved in pure distilled water; 30 ml synthesized mixture is taken for electrodeposition. Cathodic potential is determined by potentiostat. The effects of preparative parameters such as deposition time and bath concentration on structural, morphological, optical properties are studied. The optimized values of preparative parameters; especially bath concentration and deposition time are given in the following Table 7.1

<table>
<thead>
<tr>
<th>Preparative parameters</th>
<th>Studied range</th>
<th>Optimized/ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition time</td>
<td>5 min -20 min</td>
<td>15 min</td>
</tr>
<tr>
<td>Electrolyte concentration</td>
<td>0.05-0.20M</td>
<td>0.15M</td>
</tr>
</tbody>
</table>

Comparison of measured and standard ‘d’ values confirms the deposited thin films of various concentration indicate the formation of polycrystalline copper sulfide and all of them can be indexed as the reported hexagonal copper sulfide. All samples show similar XRD pattern, it means growth of the film is in a particular direction. Diffraction peaks of other phases or impurities were not detected, further confirming that the precursors have been completely transformed into copper sulfide nanostructures. SEM images with revealing the general morphology of the as-synthesized rods. It is seen that for lower
concentration of sulfur hexagonal crystal structures are observed. At higher concentration of sulfur these hexagonal crystals are converted in rods of different length.

The compositional analysis of copper sulfide was carried out by Energy-Dispersive X-ray analysis, the ratio between the copper and sulfur peaks should be nearly equal to one. With increase in bath concentration of sulfur the atomic percentage of copper decreases and that of sulfur increases. This is due to cumulative effect of ionic transport, discharge, nucleation and growth at higher solution concentration of sulfur. The optical band gap energy of copper sulfide thin films estimated from the figures were 2.37 eV, 2.59 eV, 2.77 eV and 2.67 eV depending on the bath concentration. Copper sulfide shows band gap of 2.77 eV at 0.15M bath concentration and 15 min deposition time. There is a tendency that more copper rich thin films have a smaller band gap. This increase in band gap energy value of copper sulfide thin films with decrease in crystal size explaining the quantum size effect. To examine the effect of the products morphology on their optical property, the UV-VIS of the as-deposited copper sulfide nanomaterials with four different morphologies was investigated which shows some correlation between surface morphology and optical property. As deposited films shows two absorption shoulders in the regions of 400-425 nm and 500-600 nm, for bath (3); it shifts towards lower wavelength side. Raman shifts of sample are detected at almost the same wave number 473 cm\(^{-1}\). In the Raman spectra the high intensity peaks recorded at 473 cm\(^{-1}\) can be attributed to the formation of hexagonal copper sulfide.

**Chapter IV** provides the preparation and characterization of copper selenide thin films in which crystal structure is determined with XRD patterns and crystallite size vary from 11 nm to 17 nm is determined according to Scherrer’s formula. XRD patterns indicate
the formation of polycrystalline copper selenide and all of them can be indexed as the reported hexagonal copper selenide. Diffraction peaks of other phases or impurities were not detected, further confirming that the precursors have been completely transformed into copper selenide nanostructures. All of the diffraction peaks (107), (108), (110) and (213) can be well indexed to those of hexagonal copper selenide and peak intensity goes on decrease with increase in bath concentration and deposition time. This is due to change in local structure order of thin films.

From the SEM and FESEM images, it is seen that hexagonal grains are clearly observed. The grain size increases by increasing bath concentration and these crystal structure changes into different shapes. These structures are uniformly distributed over smooth homogenous background. The average grain size increases with the increase in at % of copper in the film. Larger the concentration of copper larger is the grain size. For films with higher concentration of copper ions, the growth occurs with multiple nucleation centres resulting in a higher grain size, while for lower concentration of Cu ions; comparatively lower nucleation centres give lower grain. By energy dispersive analysis chemical composition is determined in which it is observed that with increase in concentration and deposition time at % of copper increases and that of selenide decreases.

The absorption coefficient is calculated from transmission data. Band gap energy was calculated from the classical relation for direct-band optical absorption. With bath concentration 0.15M of CuSO₄·5H₂O, 0.10M of SeO₂ and deposition time of 20 min copper selenide thin films show band gap of 2.55 eV. This increase in the optical band gap energy and appearance of second band gap with increases in bath concentration implies the creation of additional energy levels. Such additional levels could be mostly due to the
creation of deep trap states. The first absorption range is 350-380 nm, Second absorption range is 420-520 nm. There is a shift in the absorption edge at lower wavelength with higher deposition time and concentration. This shift of absorbance to edge of lower wavelength is attributed to the quantum size effect due to higher deposition time. A Raman shift of sample is detected at almost the wave numbers 1014, 1035, 1074 and 1151 cm\(^{-1}\) respectively.

This attributes to the formation of copper selenide, by correlation with Berzelianite RRUFF ID: R060260 \(\text{Cu}_2\text{x}_\text{Se} (\text{x}\sim0.12)\). Raman spectra of copper selenide thin films deposited at 20 min shows the shift at higher wave number values; this may be linked with the vacancies in the copper selenide lattice, induced during the film growth.

**Chapter V** deals with the preparation and characterization of copper telluride films using different quantities of solution by electrodeposition technique. The film thickness increases with deposition time from 526 to 685 nm due to supply of more number of ingredient ions with increase in deposition time. It is found that the films are polycrystalline in nature with a hexagonal crystal structure having orientation along the (103) and (201) planes. Onion flower like structure appear in the SEM and FE-SEM images. The average grain size increases with increasing deposition time. These micro grains possess over whole surface, these micro grains are different in diameter. These results indicate that the chemical reaction of copper foils and telluride can selectively produce various copper telluride structures. For films with higher telluride ions, the growth occurs with multiple nucleation centres resulting in a onion flower like structure.

Atomic percentage of telluride increases with increase in deposition time from 24.77 to 35.63 % and grain increases with increases in at% telluride. This is due to
cumulative effect of ionic transport, discharge, nucleation and growth of telluride at higher deposition time. Optical band gap increase with decrease in crystal size from 2.52 eV to 2.90 eV with deposition time this is due to quantum size effect. Blueshift will be observed for copper telluride thin films with increase in deposition time. Peak that appears at 255 cm\(^{-1}\), which is only Raman active, is assigned to the A\(_1\) mode. Three peaks at 288, 327, 351 cm\(^{-1}\), probably having the E symmetry are also observed. Peaks at 380, 423 cm\(^{-1}\) are due to Metal–ligand vibrations of chelate compounds such as TEA. Intermolecular coupling between Cu and Te due to increase in deposition time can give rise shift in the peak (frequency) and band splitting.

Chapter VI explains the effect of electron beam irradiation on copper chalcogenide thin film. Structural analysis indicates that optimized thin films irradiated upon 7 MeV with the electron flux was \(\sim 3 \times 10^{12}\) electrons/cm\(^2\). The thin films were irradiated by the electron pulses at a repetition rate of 12 pulses per second for about 6.5 s, accounting for a cumulative dose of about 10, 20, 30, 40, 50 kGy. The peak intensity increases upon electron irradiation with dose rate of 10-40 kGy and decreases for dose of 50 kGy. In two of the material i.e. copper sulfides, copper telluride crystal size increases with electron irradiation upto 40 kGy and at higher electron dose of 50 kGy it decreases. While for copper selenide crystal size increases with electron irradiation upto 30 kGy and at higher electron dose of 40, 50 kGy it decreases. No more change is observed in chemical composition of copper chalcogenides by electron irradiation. The XRD pattern of the irradiated (electron dose rate of 50 kGy) copper sulfide samples for different bath concentration with deposition time of 15 min shows the formation of polycrystalline copper sulfide and all of them can be indexed as the reported hexagonal copper sulfide.
The crystal sizes vary from 9 nm to 5 nm according to Scherrer’s formula. All rods are converted into hollow spheres with increased grain size. Surface treatment with electron irradiation has been shown to improve. Band gap energy of copper sulfide for different bath concentration increase with electron irradiation from value 2.54 to 2.89 eV, hence absorption region becomes narrower with electron irradiation, 500-550 nm, which is in accordance with the characteristic absorption of copper sulfide. Intermolecular coupling between Cu and S due to electron beam irradiation can give rise shift in the peak (frequency) and band splitting. Decrease in peak intensity is revealed in XRD. Following table shows the change in dose rate with crystal size and optical band gap energy of as-deposited and irradiated copper sulfide thin film.

<table>
<thead>
<tr>
<th>Electron dose rate (kGy)</th>
<th>As-deposited</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size (nm)</td>
<td>7</td>
<td>92</td>
<td>78</td>
<td>41</td>
<td>19</td>
<td>5</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>2.77</td>
<td>2.45</td>
<td>2.57</td>
<td>2.62</td>
<td>2.67</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Similar results are observed with copper selenide, copper telluride thin films in which grain size increases and crystal size decrease with high electron irradiation dose of 50 kGy. All hexagonal crystals of copper selenide are converted into small crystals of size from 10 to 6 nm, while in case of copper telluride the crystal size decreases from 11 to 6 nm. SEM micrographs of the copper selenide film deposited with 20 min deposition time shows relatively rough surface morphology. The copper telluride film with 15 min deposition time shows morphology with increase in grain size like onion flower like
structure is converted into cauliflower like structure with electron irradiation. Optical band gap energy value of copper selenide and copper telluride increases with electron irradiation from 2.47 eV to 2.62 eV and 2.67 eV to 3.01 eV respectively. Also in case of copper selenide and copper telluride thin films with different bath concentration crystal size decrease with electron dose of 50 kGy. Crystal structure remains unchanged upon electron irradiation for copper chalcogenides. There is drastic change in surface morphology is observed with electron irradiation. Composition remains unchanged upon electron irradiation. Following table shows the change in dose rate with crystal size and optical band gap energy of as-deposited and irradiated copper selenide thin film.

<table>
<thead>
<tr>
<th>Electron dose rate (kGy)</th>
<th>As-deposited</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size (nm)</td>
<td>11</td>
<td>63</td>
<td>44</td>
<td>24</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>2.55</td>
<td>2.32</td>
<td>2.45</td>
<td>2.50</td>
<td>2.58</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Following table shows the change in dose rate with crystal size and optical band gap energy of as-deposited and irradiated copper telluride thin film

<table>
<thead>
<tr>
<th>Electron dose rate (kGy)</th>
<th>As-deposited</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size (nm)</td>
<td>9</td>
<td>45</td>
<td>32</td>
<td>25</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>2.90</td>
<td>2.52</td>
<td>2.67</td>
<td>2.76</td>
<td>2.86</td>
<td>3.01</td>
</tr>
</tbody>
</table>

The increase in the optical band gap energy and appearance of second band gap with electron irradiation implies the creation of additional energy levels. Such additional
levels could be mostly due to the creation of deep trap states. It is a tendency that, more telluride-rich films have a higher band gap in copper telluride thin films. The change in the band gap with crystal size shows the blueshift in copper telluride thin films which can be attributed to the quantum size effect in cauliflower like structure. Optical absorption is narrower for copper selenide and copper telluride films with electron irradiation. This is important in understanding the optoelectronic properties of semiconducting materials. No more change in chemical composition with electron irradiation for copper selenide and copper telluride films. Raman peak intensity decreases with shift in peak takes place with electron irradiation for copper selenide and copper telluride films. This is due to intermolecular coupling between Cu and Se and also Cu and Te.

Copper sulfide, copper selenide, copper telluride thin films exhibit an increasing trend in optical band gap with dose rate of 50 kGy. This incline in optical band gap with electron fluence has been discussed on the basis of electron irradiation induced modification in copper chalcogenides. The XRD pattern of copper chalcogenides shows the decreasing intensity of peak positions with increasing in fluence, which suggest that semicrystallinity of copper chalcogenides changes slightly to amorphous phase after irradiation. At low dose, crystallinity was found to increase but at higher dose, it decreased which could be ascribed to electron- induced defects in the copper chalcogenides samples. Crystallite size calculated using Scherrer formula indicates a change and reflects the formation of disordered system in the irradiated copper chalcogenides samples. The EDAX spectra show no more change with electron irradiation.
These studies have help to arrive at following conclusions for as-deposited and irradiated copper chalcogenide thin films,

- In the present study it is observed that, the copper chalcogenide films shows polycrystalline in nature.
As bath concentration and deposition time increases, shows decrease in crystallite size.

For copper chalcogenide thin film, grain size and film thickness increases with deposition time attains maximum growth at 15 min.; for copper sulfide and copper telluride, 20 min.; for copper selenide. It decreases with higher deposition time.

Compositional analysis of copper chalcogenide thin films shows; increase in at% of sulfur, copper and telluride respectively, with increase in bath concentration and deposition time up to 15 min. for copper sulfide, copper telluride and 20 min. for copper selenide. It decreases with higher deposition time.

Optical band gap energy of copper chalcogenide thin films increases with increase in bath concentration and deposition time 15 min. for copper sulfide and copper telluride. Copper selenide thin films shows decrease in band gap energy with higher deposition time at 20 min.

Irradiated Copper chalcogenide thin films shows polycrystalline in nature. However, for copper sulfide and telluride shows, increase crystallinity at electron dose of 10, 20, 30, 40-kGy , further it decreases by higher electron dose of 50-kGy. Similarly, for copper selenide thin films, it increases up to 30-kGy and shows decrease with 40, 50-kGy.

Copper chalcogenide thin film after irradiation shows, substantial change in surface morphology upon absorbed electron doses. No compositional variation is observed.

The optical band gap energy is concern for irradiated, copper sulfide and copper telluride thin films at dose rate 10-40-kGy, shows decrease in band gap energy but at 50-kGy shows increase in band gap energy. After irradiation copper selenide thin
films, its band gap energy increase up to 30-kGy dose and decreases at 40 and 50-kGy doses.

- Irradiated Copper chalcogenide thin films shows decrease in Raman intensity.