ज्ञान-विज्ञान विमुक्तये

ANNEXURE III

UNIVERSITY GRANT COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI-110 002.

Annual/Final Report of the work done on the Major/Minor Research Project. (Report to be submitted within 6 weeks after completion of each year).

1. Project report No. 1st /2nd/3rd/final : Final
2. UGC reference no. : 36-209/2008 (SR)
3. Period of report : from 02/05/2009 to 01/05/2012
4. Title of research project : "Studies on effect of electron irradiation on electrodeposited silver chalcogenide thin films by holographic interferometry".
5. (a) Name of the Principal Investigator : Dr. Fulari Vijay Janardhan

   (b) Dept. and University/college where the work has progressed : Department of physics, Shivaji University, Kolhapur- 416004. (Maharashtra)
6. Effective date of starting of the project : 02/05/2009
7. Grant approved and expenditure incurred during the period of the report:

Sr. no.	Items	Total amount of approved for 3 years in Rs.	Total expenditure in periods 02/05/2009 to01/05/2010 in Rs.	Total expenditure in periods 02/05/2010 to 01/05/2011 in Rs.	Total expenditure in periods 02/05/2011 to01/05/2012 in Rs.
1.	Equipments	2, 00,000.00	Nil	1,75,702.00	23,388.00
2.	Project fellowhip@8000 per month	2,88,000.00	70,451.00	88,000.00	1,06,477.00
3.	Books and journals	32,800.00	Nil	Nil	23,977.00
2.	Contingency	20,000.00	10903	Nil	8,770.00
3.	Consumable	20,000.00	4632.00	452.00	14,687.00
4.	Travel and field work	20,000.00	2460.00	4192.00	11,819.00
5.	overhead Charges @ Rs.10% approved recurring Grant (Except travel & Field Work)	32,800.00	10,933	Nil	21,866.00
	Total	**Rs. 6,10, 800/-**	**Rs. 99379/-**	**Rs. 268346/-**	**Rs. 210984/-**
Total Amount Received Rs. 4,36,800/-			**Total Expenditure Rs. 5,78,709/-**		

Report of the work done: (Please attach the separate sheet)

(i) Brief objective of the report:

A separate sheet is attached. Please see **Annexure A**

(ii) Work done so far and results achieved and publications, if any, resulting from the work (Give details of the papers and names of the journals in which it has been published or accepted for publication)

A separate sheet is attached. Please see **Annexure B**

(iii) Has the progress been according to original plan of work and towards achieving the objective? If not, state reasons: **Yes**

(iv) Please indicate the difficulties, if any, experienced in implementing the project: **No.**

(v) If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission a separate sheet: **Not applicable**

(vi) If the project has been completed, please enclose the summary of the findings of the study. Two bound copies of the final report of the work done may also be sent to the Commission: Yes. Please see **Annexure C.**

(vii) Any other information which would help in the evaluation of the work done on the project. At the completion of the project, the second report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of the results (d) Other impact if any: **Annexure D**

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

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Principal Investigator (U.G.C. Scheme)
Holography & Material Research Lab.
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REGISTRAR / PRINCIPAL

Registrar,
Shivaji University, Kolhapur.

Annexure A

Brief objective of the report

1. Using chemical methods, namely Electrodeposition method, deposition of nanocrystalline large area (>3 cm^2) Silver Sulphide, Silver Selenide, and Silver telluride thin films will be carried out.
2. Deposition of Silver Sulphide films onto conducting substrate such as fluorine doped tin oxide coated glass and Stainless steel substrate will be carried out and optimisation of deposition parameters such as the pH of bath, deposition temperature, deposition potential, bath concentration and deposition time etc will be optimised to get large area deposition for good quality thin films. These films are deposited by different concentration and different time.
3. Deposition of Silver Selenide films onto conducting substrate such as fluorine doped tin oxide coated glass and Stainless steel substrate will be carried out and optimisation of deposition parameters such as the pH of bath, deposition temperature, deposition potential, bath concentration and deposition time etc will be optimised to get large area deposition for good quality thin films. These films are deposited by different concentration and different time.
4. Deposition of Silver Telluride films onto conducting substrate such as fluorine doped tin oxide coated glass and Stainless steel substrate will be carried out and optimisation of deposition parameters such as the pH of bath, deposition temperature, deposition potential, bath concentration and deposition time etc will be optimised to get large area deposition for good quality thin films. These films are deposited by different concentration and different time.
5. Holographic study of the electrodeposited Silver Sulphide, Silver Selenide, and Silver telluride thin films for different concentrations and deposition times.
6. Irradiation of the deposited thin films of Silver Sulphide, Silver Selenide, and Silver telluride with 7MeV electron beam.
7. Characterization of as deposited and electron irradiated thin films of Silver Sulphide, Silver Selenide, and Silver telluride with the techniques such as XRD, SEM, Optical absorption, Wettability and FT-Raman spectroscopy etc.

Annexure B

Work done so far

I. Synthesis of Silver chalcogenides

1] Synthesis of Ag_2S thin films by Electrodeposition method

The Silver sulphide thin films were deposited cathodically using 0.02M $AgNO_3$ and 0.06M $Na_2S_2O_3$ with Ethylene Diamine Tetra acetic Acid (EDTA) as complexing agent dissolved in double distilled water. The uniform and well adherent thin films have been deposited at room temperature using electrodeposition method. The stainless steel plates and fluorine doped tin oxide (FTO) coated glasses were used as substrates. The films were prepared for different time of intervals.

Electrodeposition was carried out on the area ($3cm^2$) of the substrates at potentiostatic mode in an unstirred bath. Electrochemical studies and films deposition were made using a three electrodes configuration. The reference electrode was a Saturated Calomel Electrode (SCE) Graphite plate of area 5cm × 2cm was used as an anode. Stainless steel and FTO coated glass substrates were used as working electrodes.

The history of electroplating, experimental set up for deposition, mechanism of electrodeposition with its several attractive features. We have deposited Silver sulphide thin films onto stainless steel substrate in potentiostatic mode. Good quality Ag_2S thin films were obtained from aqueous acidic bath containing 0.02 M $AgNO_3$, 0.06 M $Na_2S_2O_3$, and 0.01 M EDTA in the same volumetric proportion. The pH of the bath lies between 4-5. We have estimated the value of deposition potential for Ag_2S film and it is -0.65 V versus SCE.

Table 1: Optimized parameters for deposited Ag_2S thin film

Cationic precursor	Silver Nitrate (0.02M AgNO3)
Anionic precursor	Sodium Thiosulphate (0.06M Na2S2O3)
Complexing Agent	Ethylene Diamine Tetra acetic Acid

Bath	Aqueous acidic
Deposition temperature	Room temperature
Substrate	Stainless steel and FTO
Deposition potential	- 0.65 V
pH	4-5
Deposition time	20-60 sec.

2] Synthesis of Ag_2Se thin films by Electrodeposition method

Silver selenide (Ag_2Se) films were cathodically electrodeposited from solution containing 5 mM $AgNO_3$, 2 mM SeO_2 were used as a precursor source of Ag & Se ions and EDTA was used as complexing agent. The electrolyte solutions were made up with double distilled water. Electrodeposition was carried out on the area ($3cm^2$) of the substrates at potentiostatic mode in an unstirred bath. Electrochemical studies and film deposition were made using three electrode configurations with a Saturated Calomel Electrode (SCE) as the reference electrode, graphite plate as the counter electrode. The stainless steel substrate and FTO coated glass plates were utilized as working electrodes. The films were deposited by varying the time of deposition.

We have deposited silver selenide thin films onto stainless steel substrate in potentiostatic mode. Nearly stoichiometric polycrystalline Ag_2Se thin films were deposited from aqueous acidic bath containing 5 mM $AgNO_3$, 2 mM SeO_2, and 0.05 M EDTA in the same volumetric proportion. The pH of the bath lies between 4-5. Thin films deposited at optimized preparative parameters were gray in color and well adherent to the substrates. We have estimated value of the deposition potential for Ag_2Se film and it is -0.2 to -0.4 V versus SCE for time of deposition 7-25 min.

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Table 2: Optimized parameters for deposited Ag_2Se thin film

Cationic precursor	Silver Nitrate (5mM $AgNO_3$)
Anionic precursor	Selenium dioxide (2mM SeO_2)
Complexing Agent	Ethylene Diamine Tetra acetic Acid
Bath	Aqueous acidic bath
Deposition temperature	Room temperature
Substrate	Stainless steel and FTO
Deposition potential	- 0.35 V
pH	4-5
Deposition time	7-20 min

3] Synthesis of Ag_2Te thin films by Electrodeposition method

Silver Telluride (Ag_2Te) films were catholically electrodeposited from solution containing $AgNO_3$, Na_2Te were used as a precursor source of Ag & Te ions and EDTA was used as complexing agent. Good quality Ag_2Te thin films were obtained from aqueous acidic bath containing 0.025 M $AgNO_3$, 0.025 M Na_2Te, and 0.025 M EDTA in the same volumetric proportion. The as deposited thin films were gray in color and well adherent to the substrates. From the Cyclic Voltammetry study, deposition potential was found to be -0.55V to -0.60 V. The electrolyte solutions were made up with double distilled water. The stainless steel substrate and FTO coated glass plates were utilized as working electrodes. All potentials are expressed versus SCE. The steel substrates were polished by smooth polish paper (zero fine grades) and cleaned with doubled distilled water. The uniform and well adherent films have been deposited at room temperature. The films were deposited by varying the time of deposition. From the Cyclic Voltammetry study, deposition potential was found to be -0.55V to -0.60 V.

Table 3: Optimized parameters for deposited Ag_2Te thin film

Cationic precursor	Silver Nitrate (0.025M $AgNO_3$)
Anionic precursor	Sodium Telluride (0.025M Na_2Te)
Complexing Agent	Ethylene Diamine Tetra acetic Acid
Bath	Aqueous acidic bath
Deposition temperature	Room temperature
Substrate	Stainless steel and FTO
Deposition potential	- 0.55 V
pH	4-5
Deposition time	10-30 min

II. Holographic study of silver chalcogenide thin films

1. Electrodeposition of Ag_2S Thin films

1.1 Cyclic Voltammetry

Cyclic Voltammetry (CV) is employed to study the kinetics of the electrochemical reactions in electrolytic bath. Fig. 1.1 (a)-(c) shows the cyclic voltammogram recorded on stainless steel substrate from electrolytic solutions containing the 0.02 M $AgNO_3$, 0.06 M $Na_2S_2O_3$ and 0.02 M $AgNO_3$+ 0.01 M EDTA + 0.06 M $Na_2S_2O_3$, in order to find the suitable reduction potentials of Ag, S and Ag_2S compound.

Fig. 1.1 (a) explains that the cathodic current increases gradually up to -0.5 V/SCE and increased rapidly up to -0.8V/SCE. This reduction peak indicates that the reduction of elemental Ag takes place at this particular reduction potential. The deposited film is silvery in color. A cyclic voltammogram of 0.06M $Na_2S_2O_3$ solution is shown in Fig.1.1 (b).The film deposited at reduction potential -0.6 V gives blackish sulphur layer. From Fig.1.1(c), it is seen that up to -0.35V/SCE, the cathodic current slowly increases. After this potential there is a rapid increase in cathodic current. The film deposited at -0.65 V reduction potential gives uniform and well adherent Ag_2S thin film

Fig. 1.2 shows the photographs of as-deposited Ag_2S thin films for the deposition 20-60 s. The deposited films are grayish –black in color.

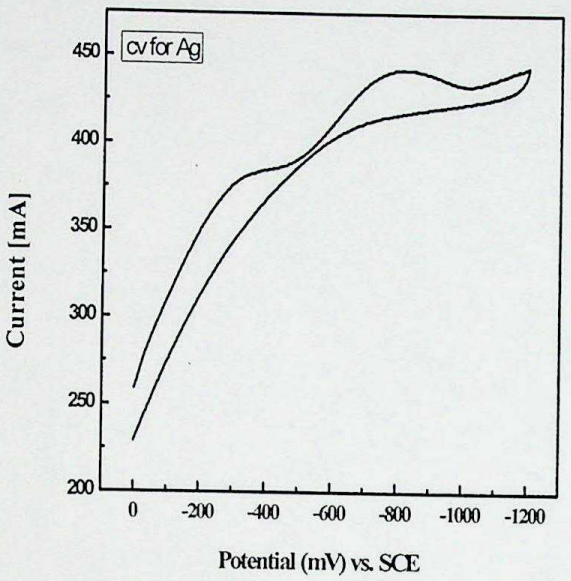


Figure 1.1 (a)

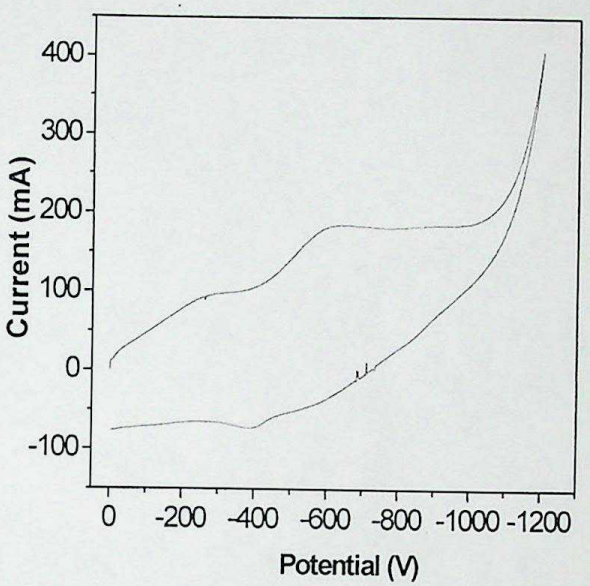


Figure 1.1 (b)

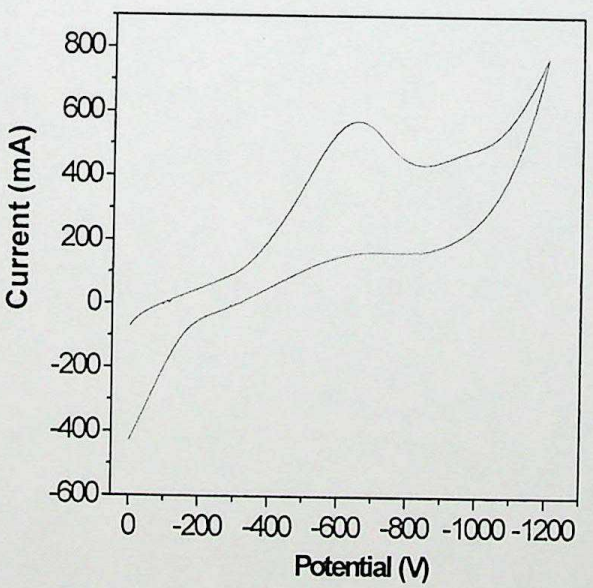


Figure 1.1 (c)

Figure 1.1 Cyclic Voltammogram (CV) on stainless steel substrate in the solution containing (a) 0.02M $AgNO_3$ (b) 0.06M $Na_2S_2O_3$ (c) 0.02M $AgNO_3$ + 0.01M EDTA + 0.06M $Na_2S_2O_3$

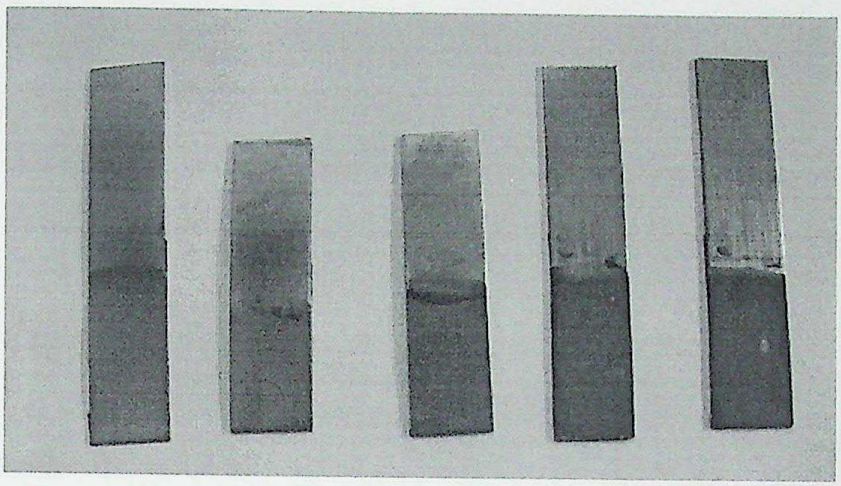


Figure 1.2 Photographs of electrodeposited Ag_2S thin films for various deposition times 20-60 s.

1.2 Reaction mechanism

The chemical reaction for the deposition of silver sulphide films taking place could be considered as below:

The aqueous solution of Sodium thiosulphate forms,

$$Na_2S_2O_3 + H_2O = 2Na^+ + S_2O_3^-$$

$$S_2O_3^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O$$

$$s + 2\bar{e} = s^{2-}$$

Silver ions, Ag^+, combine with S^{2-}

$$2Ag^+ + S^{2-} = Ag_2S$$

2. Electrodeposition of Ag_2Se Thin films

2.1 Cyclic Voltammetry

Fig 2.1 [a]-[c] shows the cyclic voltammogram recorded on stainless steel substrate from electrolytic solutions containing the 5 mM $AgNO_3$, 2 mM SeO_2 and 5 mM AgNO3 + 2 mM SeO_2+0.05 M EDTA, in order to find the suitable reduction potentials of Ag, Se, Ag_2Se compound.

Fig.2.1 [a] shows an examination of the solution containing 5 mM $AgNO_3$; the reduction peak at -0.5V to -0.8 V is associated with formation of Ag. The deposited film is silvery in color. A cyclic voltammogram of 2 mM SeO_2 is shown in Fig.2.1 [b]. From Fig.3.1 [c], it is seen that the cathodic current increases -0.2 V to -0.4 V. The reduction of Ag_2Se takes place at this particular reduction potential.

Fig. 2.2 indicates Photograph of as-deposited Ag_2Se thin films for deposition time 7-20 min.

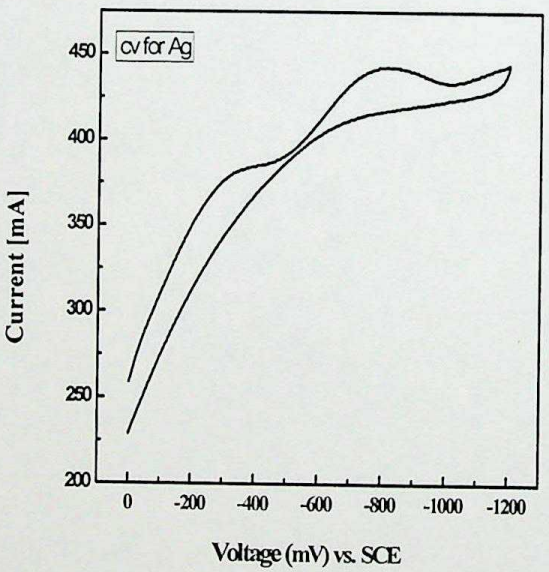


Figure 2.1 (a)

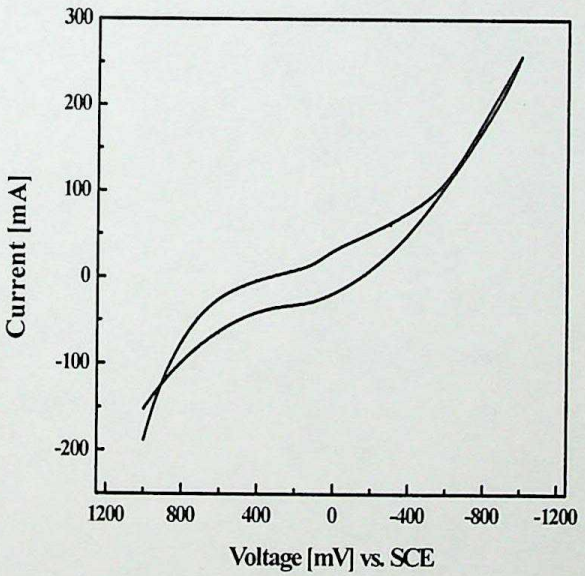


Figure 2.1(b)

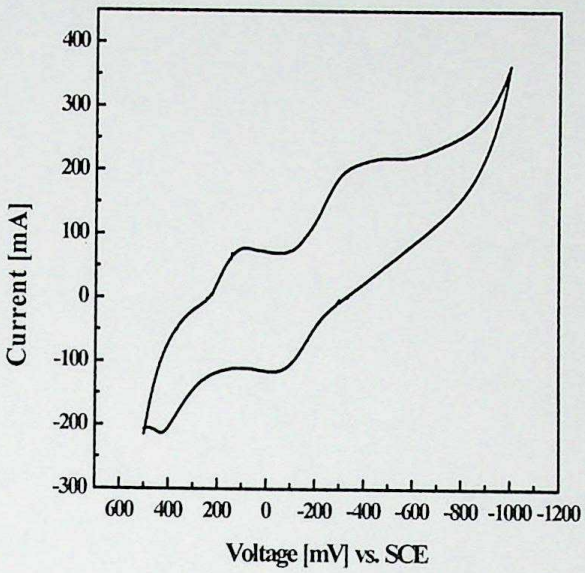


Figure 2.1(c)

Figure 2.1 Cyclic Voltammogram(CV) on stainless steel substrate in the solution containing (a) 5 mM $AgNO_3$ (b) 2 mM SeO_2 (c) 5 mM $AgNO_3$ + 2 mM SeO_2+0.05 M EDTA

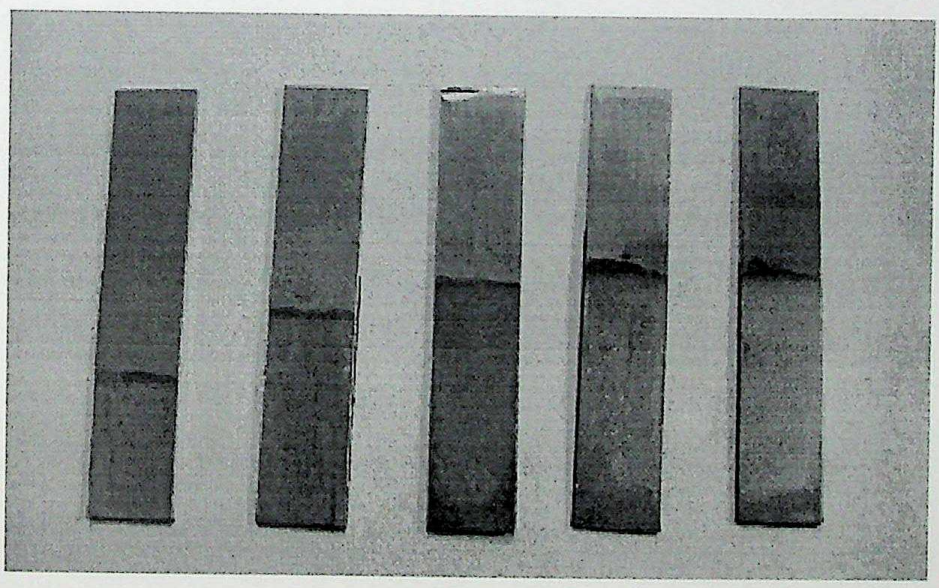


Figure 2.2 Photograph of as-deposited Ag_2Se thin films for deposition time 7-20 min.

2.2 Reaction mechanism

The chemical reaction for the deposition of silver selenide films taking place in bath could be considered as below:

The aqueous solution of Selenium dioxide forms,

$$SeO_2 + H_2O = HSeO_3^- + H^+$$

Silver ion Ag^+, combine with $HSeO_3^-$,

The final reaction takes place for the formation of Ag_2Se film

$$2Ag^+ + HSeO_3^- + 5H^+ + 4e^- = Ag_2Se + 3H_2O$$

3. Preparation of Ag_2Te Thin film

3.1 Cyclic Voltammetry

Cyclic Voltammetry (CV) is employed to study the kinetics of the electrochemical reactions in electrolytic bath. Fig. 3.1 (a)-(c) indicates the cyclic voltammogram recorded on stainless steel substrate from electrolytic solutions containing the 0.025M $AgNO_3$, 0.025M Na_2Te and 0.025M ($AgNO_3$+ Na_2Te + EDTA) in order to find the suitable reduction potentials of Ag, Te and Ag_2Te.

Fig. 3.1 (a) explains that the cathodic current increases gradually upto -0.5 V/SCE and increased rapidly up to -0.8V/SCE. This reduction peak indicates that the reduction of elemental Ag takes place at this particular reduction potential. The deposited film is silvery in color.

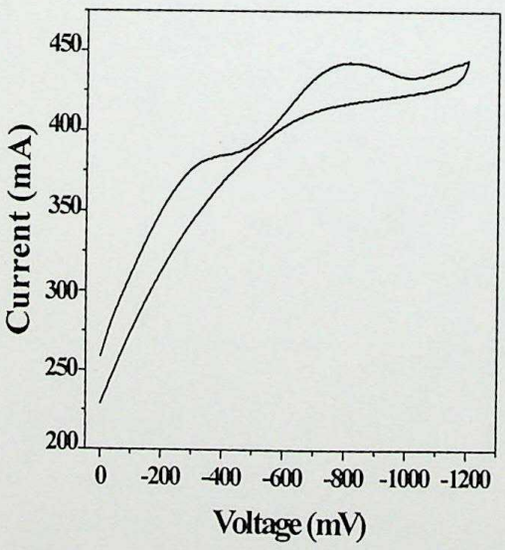


Figure 3.1 (a)

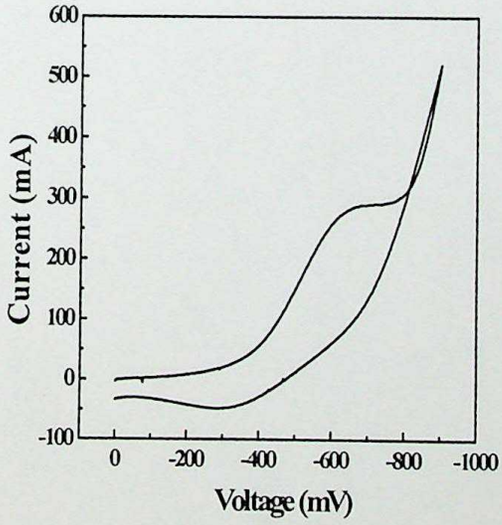


Figure 3.1 (b)

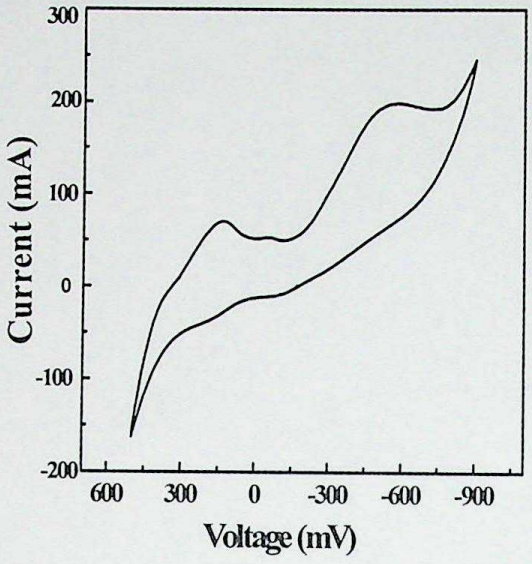


Figure 3.1 (c)

Figure 3.1 Cyclic Voltammogram (CV) on stainless steel substrate in the solution containing (a) 0.025M $AgNO_3$ (b) 0.025M Na_2Te (c) 0.025M [$AgNO_3$ + Na_2Te + EDTA]

A cyclic voltammogram of 0.025M Na_2Te solution is shown in Fig.3.1 (b).The film deposited at reduction potential -0.6 V. From Fig.3.1(c), it is seen that up to -0.55V/SCE, it is seen that the film deposited at -0.55 V reduction potential gives uniform and well adherent Ag_2Te thin film.

3.2 Reaction mechanism

The essential reaction mechanism is as follows

Silver nitrate dissolves in water and release Ag+

$$AgNO_3 = Ag^+ + NO_3^-$$

The sodium telluride forms,

$$TeO_3 + H_2O = HTeO_2 + H^+ + O_2$$

The final reaction occur to form silver telluride thin film is

$$2Ag^+ + HTeO_2 + 3H^+ + 2\bar{e} = Ag_2Te + 2H_2O$$

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4. Holographic Study

4.1 Holographic study of Ag_2S thin film

4.1.1 Recording of hologram

Recorded holograms of Ag_2S thin films by double exposure holographic interferometry method are displayed below. Recorded holograms of Ag_2S thin film for bath concentration N1 by varying time of deposition from 20 sec to 60 sec, the number of fringes increases from 2 to 4 are shown in Fig.4.1.1(a).For bath concentration N2 the recorded holograms of Ag_2S thin film for different deposition time are shown in Fig.4.1.1(b), the number of fringes varies from 3 to 5. For bath concentration N3 the recorded holograms of Ag_2S thin film for different deposition time are shown in Fig 4.1.1(c), the number of fringes varies from 4 to 8. Deposition time Vs Fringe Number plot shows that there is increase in fringe number with increase in deposition time (Fig.4.1.1 (d)).

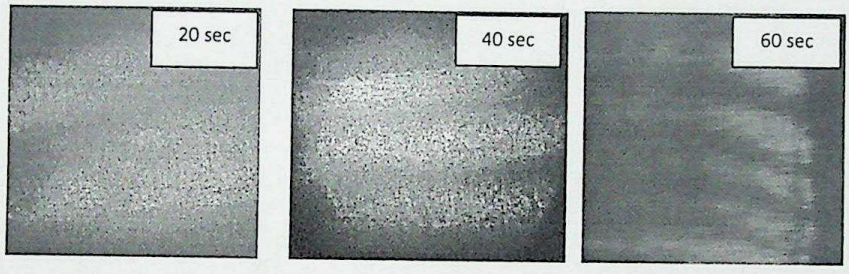


Fig.4.1.1(a): Holograms of Ag_2S thin films for N1 bath concentration

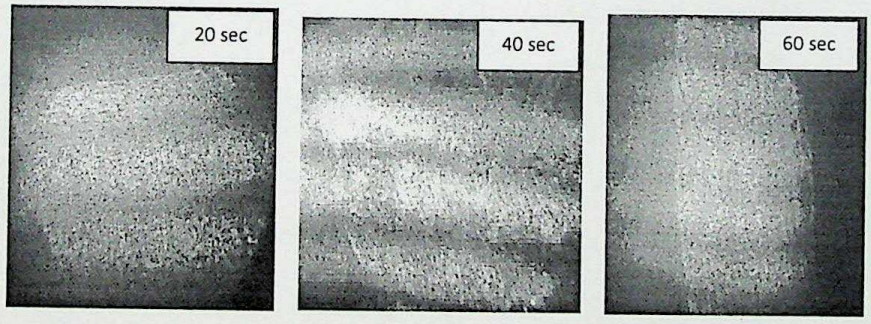


Fig.4.1.1(b): Holograms of Ag_2S thin films for N2 bath concentration

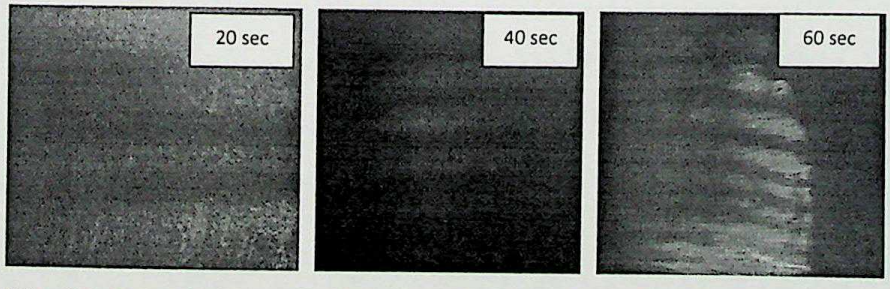


Fig.4.1.1(c): Holograms of Ag_2S thin films for N3 bath concentration

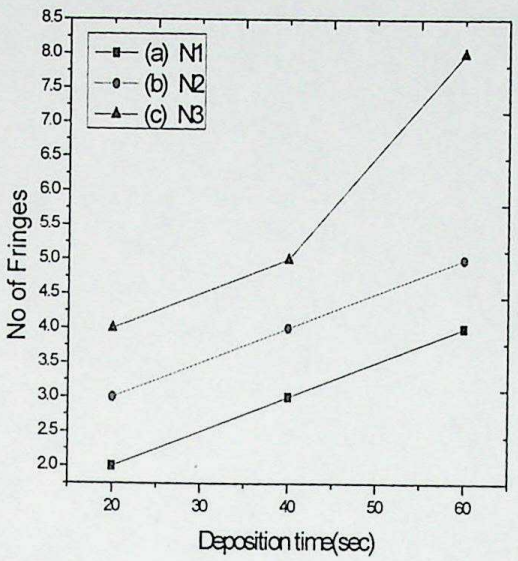


Fig 4.1.1(d) Deposition time Vs Fringe Number for Ag_2S thin film

4.1.2 Calculation of thickness of the Ag_2S thin films

The double exposure holographic interferometry technique used to study electrodeposited Ag_2S thin films reveals that as deposition time increases, number of fringes on substrate increases causing increase in thickness of the film. Thickness can be calculated using relation,

Calculated values of thickness of thin films of as deposited thin films for bath concentration N1, N2 and N3 are specified in table 4.1.Thickness of film varies from 0.6328 to 1.2656 μm for bath concentration N1 and time varies from 20 to 60 sec. For bath concentration N2 the thickness of Ag_2S thin films varies from 0.9492 to 1.5820 μm for various deposition times. For N3 bath concentration the thickness of thin film increases from 1.2656 to 2.5522 μm. From the study it is clear that increase in bath concentration increases the thickness of as-deposited films. Following graph shows there is increase in thickness as deposition time increases for N1, N2 & N3 concentrations.

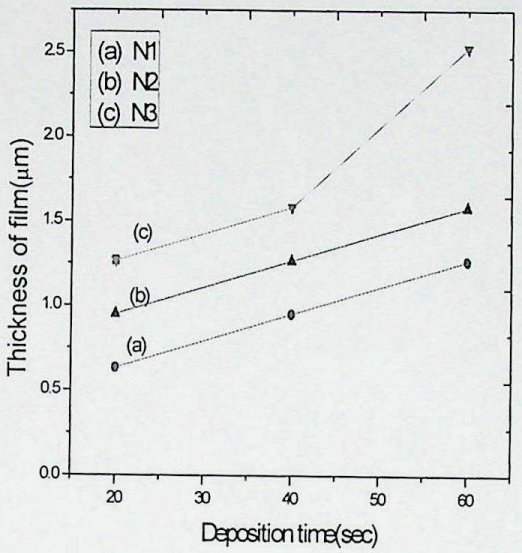


Fig 4.1.2 Deposition time Vs Thickness of Ag_2S thin films

4.1.3 Measurement of mass deposited on the stainless steel substrate

The calculated values of Ag_2S thin films depicted in table 4.1, express that mass of as-deposited Ag_2S thin films increases from 1.38905 to 2.7769 mg for bath concentration N1 by increasing deposition time from 20 to 60 sec. For bath concentration N2 and N3 the mass of as-deposited Ag_2S thin films increases from 2.08227 to 3.47122 mg and from 2.7769 to 5.55 mg with increasing deposition time. Deposition time Vs mass deposited on thin film plot shows that there is increase in mass of thin film deposited with increase in deposition time.

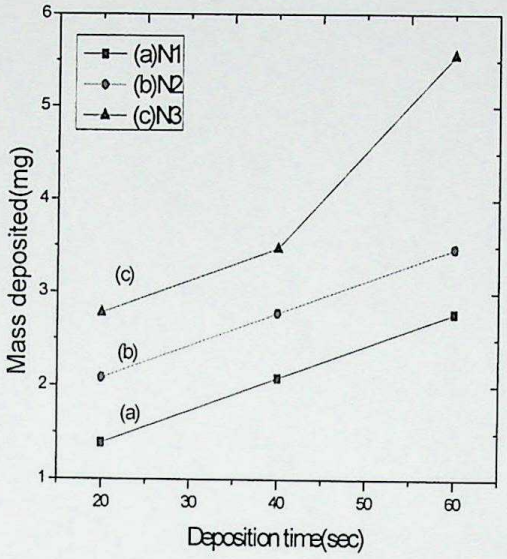


Fig 4.1.3 Deposition time Vs mass deposited of Ag_2S thin film

4.1.4 Determination of stress to substrate by DEHI

The value of stress to substrate of Ag_2S thin films was calculated. It is seen that as the time of deposition increases from 20 to 60 sec stress to substrate decreases from 1.330 $x10^9$ to 0.667 $x10^9$ dyne/cm^2 for N1bath concentration. By increase in deposition time from 20 to 60 sec, stress to substrate of Ag_2S thin films decreases from 0.888 $x10^9$ to 0.610 $x10^9$ dyne/cm^2 for bath concentration N2. For bath concentration N3 the stress to substrate of Ag_2S thin films decreases from 0.661 $x10^9$ to 0.333 $x10^9$ dyne/cm^2 Deposition time Vs stress to the substrate plot shows that there is decrease in stress of thin film deposited with increase in deposition time.

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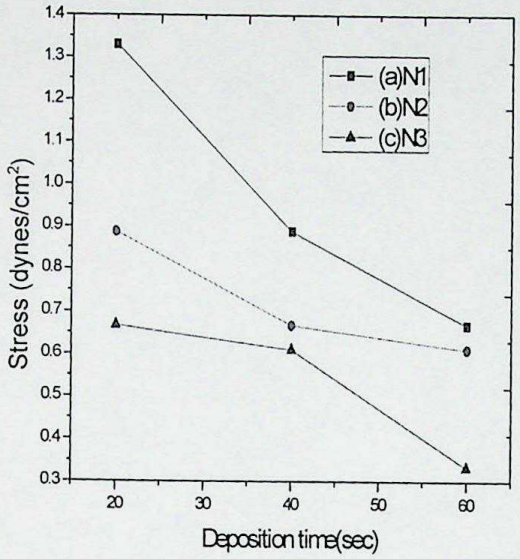


Fig 4.1.4 Deposition time Vs stress to the substrate of Ag_2S thin film

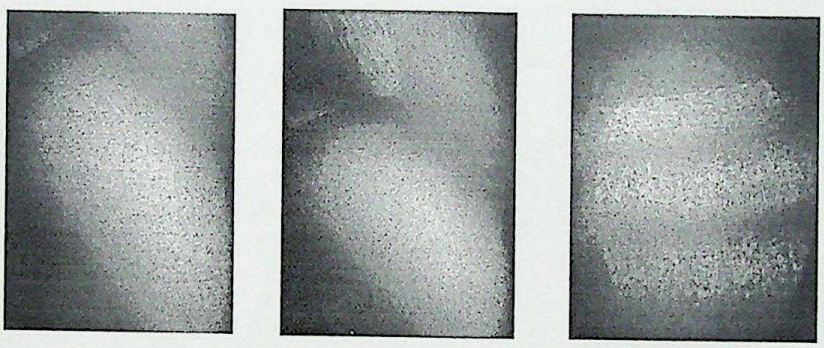
Table 4.1: Mass, stress, thickness, fringe width and number of fringes of Ag_2S films

Bath Conc.	Deposition Time(sec)	Fringe numbers	Thickness of Ag_2S film (μm)	Mass deposited (mg)	Stress$\times 10^9$ (dyne/cm^2)
N1	20	2	0.6328	1.38905	1.330
	40	3	0.9492	2.08227	0.888
	60	4	1.2656	2.77697	0.667
N2	20	3	0.9492	2.08227	0.888
	40	4	1.2656	2.77697	0.667
	60	5	1.5820	3.47122	0.610
N3	20	4	1.2656	2.77697	0.667
	40	5	1.5820	3.47122	0.610
	60	8	2.5312	5.55395	0.333

4.2 Holographic study of Ag_2Se thin film

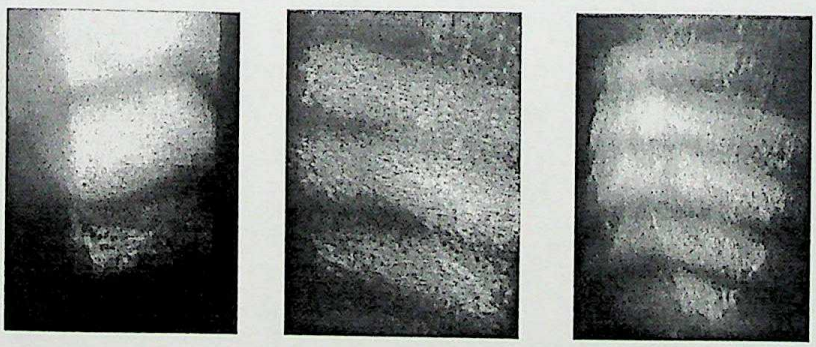
4.2.1. Recording of hologram

Recorded holograms of Ag_2Se thin films by double exposure holographic interferometry method are displayed below. Recorded holograms of Ag_2Se thin film for bath concentration U1 by varying time of deposition from 05 min. to 15 min., the number of fringes increases from 2 to 4 as shown in fig.4.2.1(a). For bath concentration U2 the recorded holograms of Ag_2Se thin film for different deposition time are shown in fig.4.2.1(b)., the number of fringes varies from 2 to 5. For bath concentration U3 the recorded holograms of Ag_2Se thin film for different deposition time are shown in fig.4.2.1(c)., the number of fringes varies from 3 to 7 . Deposition time Vs Fringe Number plot shows that there is increase in fringe number with increase in deposition time fig.4.2.1(d).



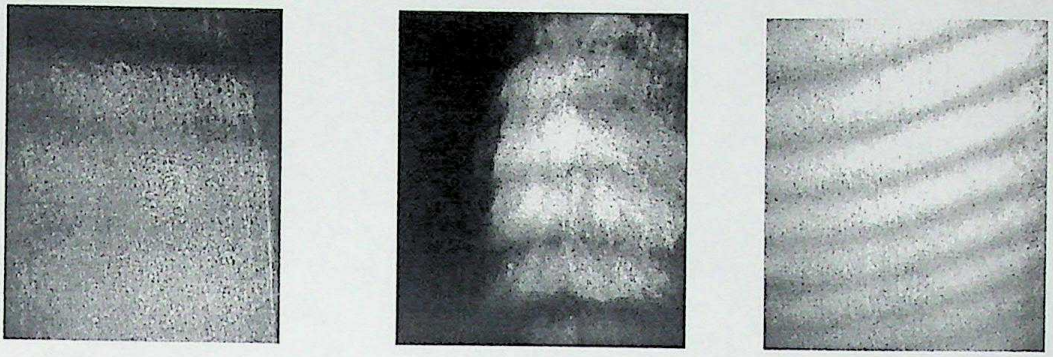
5 min. 10 min. 15 min.

Fig.4.2.1(a): Holograms of Ag_2Se thin films for 0.03M (U1) bath concentration for different time



5 min. 10 min. 15min.

Fig.4.2.1(b): Holograms of Ag_2Se thin films for 0.04M (U2) bath concentration for different time



5 min 10 min 15 min

Fig.4.2.1(c): Holograms of Ag_2Se thin films for 0.05M (U3) bath concentration for different Time

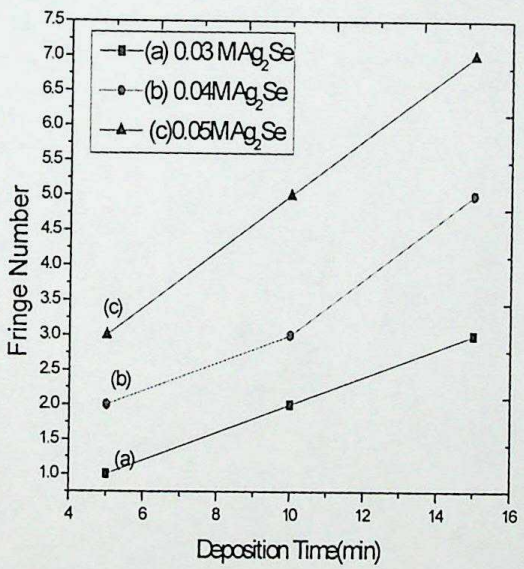


Fig 4.2.1(d) Deposition time Vs Fringe Number for Ag_2Se thin films.

4.2.2 Calculation of thickness of the Ag_2Se thin films:

The double exposure holographic interferometry technique used to study electrodeposited Ag_2Se thin films reveals that as deposition time increases, number of fringes on substrate increases causing increase in thickness of the film. Thickness can be calculated using relation

$$d = \frac{n\lambda}{2}$$

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Calculated values of thickness of thin films of as deposited thin films for bath concentration U1, U2 and U3 are specified in table 4.2.Thickness of film varies from 0.6328 to1.2656 μm for bath concentration U1 and time varies from 05 to 15 min. For bath concentration U2 the thickness of Ag_2S thin films varies from 0.6328 to 1.582 μm for various deposition times. For U3 bath concentration the thickness of thin film increases from 0.9492 to 2.2148 μm. From the study it is clear that increase in bath concentration increases the thickness of as-deposited films. Deposition time Vs Thickness thin film plot shows that there is increase in thickness of thin film with increase in deposition time.

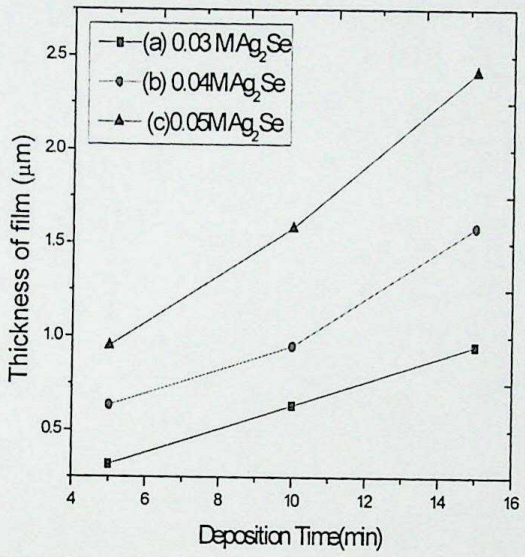


Fig 4.2.2 Deposition time Vs Thickness of Ag_2Se thin film

4.2.3 Measurement of mass deposited on the stainless steel substrate

The calculated values of Ag_2Se thin films depicted in table 4.2, express that mass of as-deposited Ag_2Se thin films increases from 1.56 to 3.119 mg for bath concentration U1 by increasing deposition time from 05 min to 15 min. For bath concentration U2 and U3 the mass of as-deposited Ag_2Se thin films increases from1.56 to 3.899 mg and from 2.34 to 5.460 mg with increasing deposition time. Deposition time Vs mass deposited on thin film plot shows that there is increase in mass of thin film deposited with increase in deposition time.

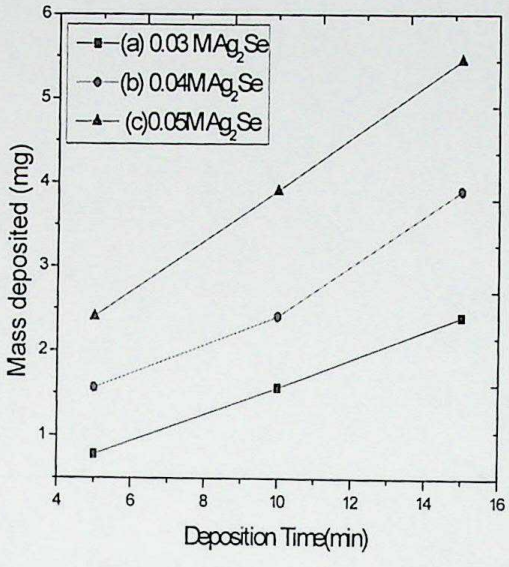


Fig 4.2.3 Deposition time Vs mass deposited of Ag_2Se thin films

4.2.4 Determination of stress to substrate by DEHI

The value of stress to substrate of Ag_2Se thin films was calculated. It is seen that as the time of deposition increases from 05 min. to 15 min. stress to substrate decreases from 1.33×10^9 to 0.667×10^9 dyne/cm^2 for U1bath concentration. By increase in deposition time from 05 min. to 15 min, stress to substrate of Ag_2Se thin films decreases from 1.33×10^9 to 0.533×10^9 dyne/cm^2 for bath concentration U2. For bath concentration U3 the stress to substrate of Ag_2Se thin films decreases from from 0.889×10^9 to 0.380×10^9 dyne/cm^2 Deposition time Vs stress to the substrate plot shows that there is decrease in stress of thin film deposited with increase in deposition time.

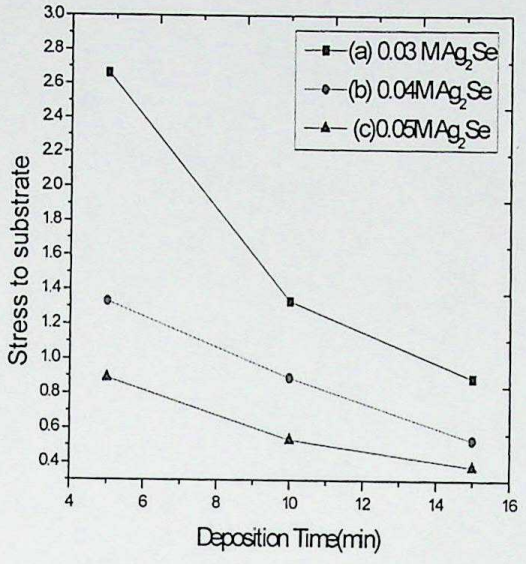


Fig 4.2.4 Deposition time Vs stress to the substrate of Ag_2Se thin film

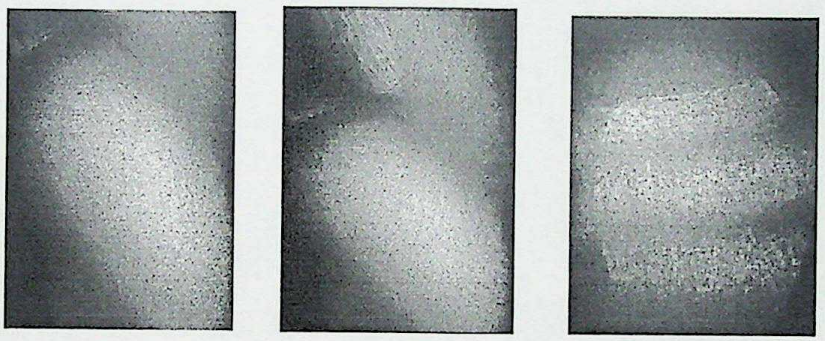
Table 4.2 : Mass, stress, thickness, fringe width and number of fringes of Ag_2Se films

Bath Conc.	Deposition Time(min)	Fringe numbers	Thickness of Ag_2Se film (μm)	Mass deposited (mg)	Stress$\times 10^9$ (dyne/cm^2)
U1(0.03 M)	05	01	0.3164	0.779	2.66
	10	02	0.6328	1.560	1.33
	15	03	0.9492	2.399	0.889
U2(0.04 M)	05	02	0.6328	1.560	1.330
	10	03	0.9492	2.399	0.889
	15	05	1.582	3.899	0.533
U3(0.05M)	05	03	0.9492	2.399	0.889
	10	05	1.582	3.899	0.533
	15	07	2.4148	5.460	0.380

4.3 Holographic study of Ag_2Te thin film

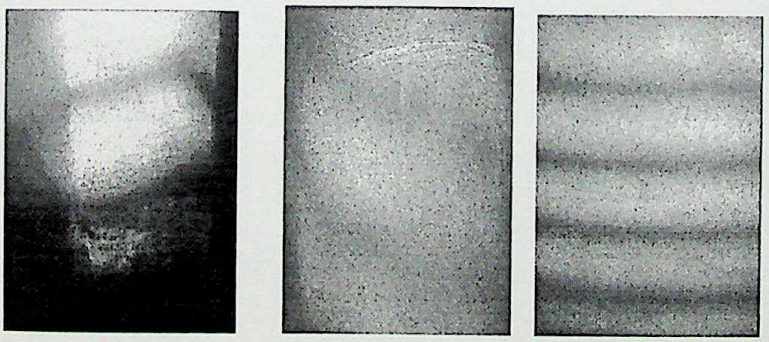
4.3.1. Recording of holograms

Recorded holograms of Ag_2Te thin films by double exposure holographic interferometry method are displayed below. Recorded holograms of Ag_2Te thin film for bath concentration T1 by varying time of deposition from 05 min. to 15 min., the number of fringes increases from 2 to 4 are shown in fig.4.3.1(a). For bath concentration T2 the recorded holograms of Ag_2Te thin film for different deposition time are shown in fig.4.3.1(b)., the number of fringes varies from 2 to 5. For bath concentration T3 the recorded holograms of Ag_2Te thin film for different deposition time are shown in fig.4.3.1(c).,the number of fringes varies from 3 to 7 . Deposition time Vs Fringe Number plot shows that there is increase in fringe number with increase in deposition time fig. 4.3.1(d).



5 min. 10 min. 15 min.

Fig.4.3.1(a): Holograms of Ag_2Te thin films for 0.03M (T1) bath concentration for different time



5 min. 10 min. 15min.

Fig.4.3.1(b) : Holograms of Ag_2Te thin films for 0.04M (T2) bath concentration for different

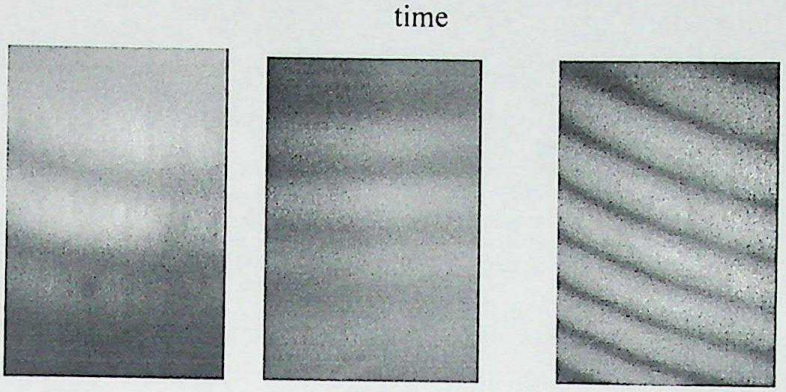


Fig.4.3.1(c): Holograms of Ag_2Te thin films for 0.05M (T3) bath concentration for different time.

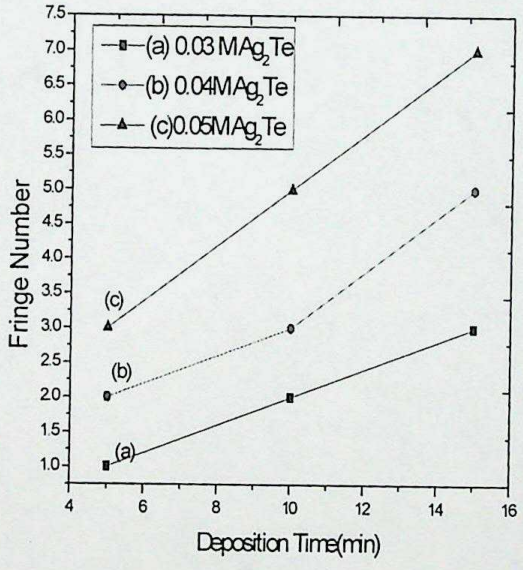


Fig.4.3.1(d). Deposition time Vs Fringe Number for Ag_2Te thin film

4.3.2 Calculation of thickness of the Ag_2Te thin films:

The double exposure holographic interferometry technique used to study electrodeposited Ag_2Te thin films reveals that as deposition time increases, number of fringes on substrate increases causing increase in thickness of the film. Thickness can be calculated using relation $d = \frac{n\lambda}{2}$

Calculated values of thickness of thin films of as deposited thin films for bath concentration T1, T2 and T3 are specified in table 4.3.Thickness of film varies from 0.6328 to1.2656 μm for bath concentration T1 and time varies from 05 to 15 min. For bath concentration T2 the thickness of Ag_2Te thin films varies from 0.6328 to 1.582 μm for various deposition times. For T3 bath concentration the thickness of thin film increases from 0.9492 to 2.2148 μm. From the study it is clear that increase in bath concentration increases the thickness of as-deposited films. Deposition time Vs Thickness thin film plot shows that there is increase in thickness of thin film with increase in deposition time.

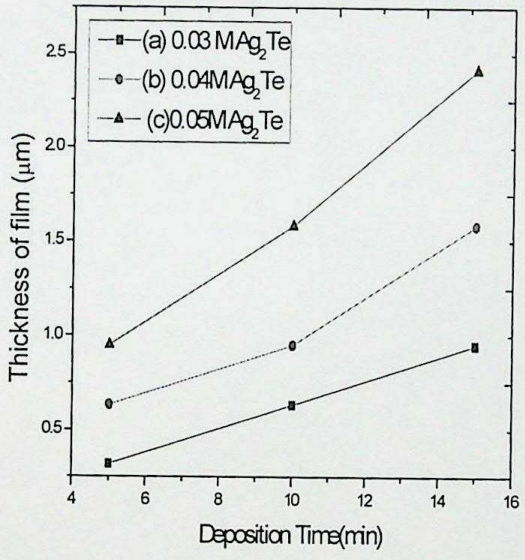


Fig 4.3.2 Deposition time Vs Thickness of Ag_2Te thin film

4.3.3 Measurement of mass deposited on the stainless steel substrate:

The calculated values of Ag_2Te thin films depicted in table 4.3, express that mass of as-deposited Ag_2Se thin films increases from 1.56 to 3.119 mg for bath concentration T1 by increasing deposition time from 05 min to 15 min. For bath concentration T2 and T3 the mass of as-deposited Ag_2Te thin films increases from1.56 to 3.899 mg and from 2.34 to 5.460 mg with increasing deposition time. Deposition time Vs mass deposited plot shows that there is increase in mass of thin film deposited with increase in deposition time.

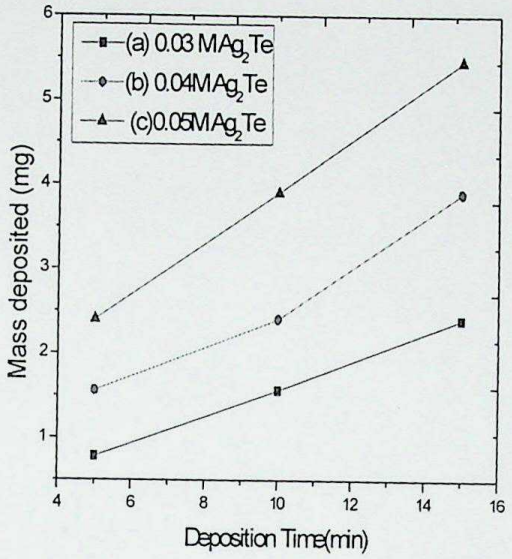


Fig 4.3.3 Deposition time Vs mass deposited of Ag_2Te thin film

4.3.4 Determination of stress to substrate by DEHI:

The value of stress to substrate of Ag_2Te thin films was calculated. It is seen that as the time of deposition increases from 05 min. to 15 min. stress to substrate decreases from 1.33×10^9 to 0.667×10^9 dyne/cm^2 for T1bath concentration. By increase in deposition time from 05 min. to 15 min, stress to substrate of Ag_2Te thin films decreases from 1.33×10^9 to 0.533×10^9 dyne/cm^2 for bath concentration T2. For bath concentration T3 the stress to substrate of Ag_2Te thin films decreases from from 0.889×10^9 to 0.380×10^9 dyne/cm^2. Deposition time Vs stress to the substrate plot shows that there is decrease in stress of thin film deposited with increase in deposition time.

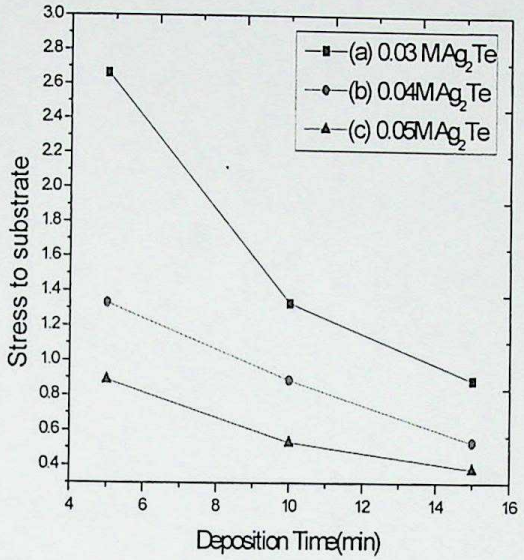


Fig 4.3.4 Deposition time Vs stress to the substrate of Ag_2Te thin film

Table 4.3: Mass, stress, thickness, fringe width and number of fringes of Ag_2Te films

Bath Conc.	Deposition Time(min)	Fringe numbers	Thickness of Ag_2Te film (μm)	Mass deposited (mg)	Stress$\times 10^9$ (dyne/cm^2)
T1(0.03 M)	05	01	0.3164	0.779	2.66
	10	02	0.6328	1.560	1.33
	15	03	0.9492	2.399	0.889
T2(0.04 M)	05	02	0.6328	1.560	1.330
	10	03	0.9492	2.399	0.889
	15	05	1.582	3.899	0.533
T3(0.05M)	05	03	0.9492	2.399	0.889
	10	05	1.582	3.899	0.533
	15	07	2.4148	5.460	0.380

5 Irradiation of thin films

Irradiation is a process in which electrons of high energy are used to treat an object for a variety of purposes. This may takes place under elevated temperatures and nitrogen atmosphere. Electron irradiation possibly used for sterilization and to cross-link polymers. Electron energies typically vary from the KeV to MeV range, depending on the depth of penetration required. The irradiation dose is usually measured in Gray (unit). The effect of irradiation may also include changes in crystallinity as well as microstructure. Every day irradiation is helping to save lives, maintain health and protect the environment.

The films of different concentrations were prepared by electrodeposition and irradiated by electron beam. The irradiation experiments were carried out at the 7MeV linear electron accelerator set up at Bhabha Atomic Research Center (BARC), Mumbai, India. The thin film samples are kept in front of the exit slit of the LINAC at a distance of 12 cm. The sample cell dimensions are 10 mm x 10 mm x 50 mm and are kept for the pulse radiolysis study. The dose absorbed by films per pulse was determined by a chemical dosimeter, an aerated aqueous solution containing 5 x 10-2 mol dm-3 potassium thiocyanate (KSCN). This dose value was used to calculate the total dose delivered in a sample under a repetitive irradiation condition. Electron pulses of 2 μs time duration with a peak current, 70mA were used for the irradiation of the samples. The electron flux was about 3 × 1012 electrons / 2μs / cm2. The samples were irradiated by these electron pulses at a repetition rate of 12 pulses per second for about 6.5 seconds, accounting for a cumulative dose of about 10 kGy

6. Effect of electron beam irradiation on thin films

6.1 Effect on Silver Sulphide Thin Films

6.1.1 Preparation of Ag_2S thin films

Silver sulphide (Ag_2S) thin films have been deposited on to stainless steel substrates by the electrodeposition process, in potentiostatic mode using silver nitrate ($AgNO_3$), sodium thiosulphate (Na_2S_2O3) as a precursor sources and Ethylene Diamine Tetra Acetic Acid (EDTA) was used as a complexing agent.

Ag2S thin films were prepared with bath containing following concentrations listed in Table 6.1.

Table 6.1 Bath composition for preparation of Ag_2S thin films

Film Name	Bath composition
A_1	0.02 M $AgNO_3$ + 0.06 M $Na_2S_2O_3$ + 0.01 M EDTA
A_2	0.03M $AgNO_3$ + 0.1 M $Na_2S_2O_3$ + 0.01 M EDTA
A_3	0.04 M $AgNO_3$ + 0.15 M $Na_2S_2O_3$ + 0.01 M EDTA

6.1.2 Characterization of as deposied and electron irradiated Ag2S thin films

I. X-Ray diffraction

The effects on the polycrystallinity of the as-deposited and irradiated Ag2S thin films are analyzed using glancing angle X- ray diffraction. Fig. 6.1(a) shows the XRD pattern of the as-deposited and electron irradiated A1 films. It indicates monoclinic phase with Argentite structure. All peaks belonging to monoclinic phase of Ag2S films were matched with database in JCPDS [11-0688]. It is noteworthy to mention here that crystallite size of the films calculated from the Scherer's formula for as-deposited and electron irradiated have exhibited 11.76 and 12.86 nm respectively. The particle size increases after irradiation.

Fig. 6.1(b) gives you an idea about the XRD pattern of the as-deposited and electron irradiated A2 films. The peak intensity increases after electron beam irradiation. Fig. 6.1(c) explains the XRD pattern of the as-deposited and electron irradiated A3 films.

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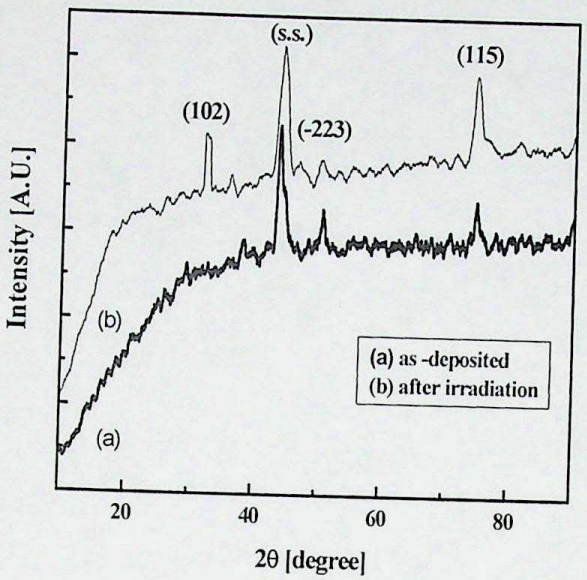


Figure 6.1 (a) X-Ray Diffraction patterns of A_1 films

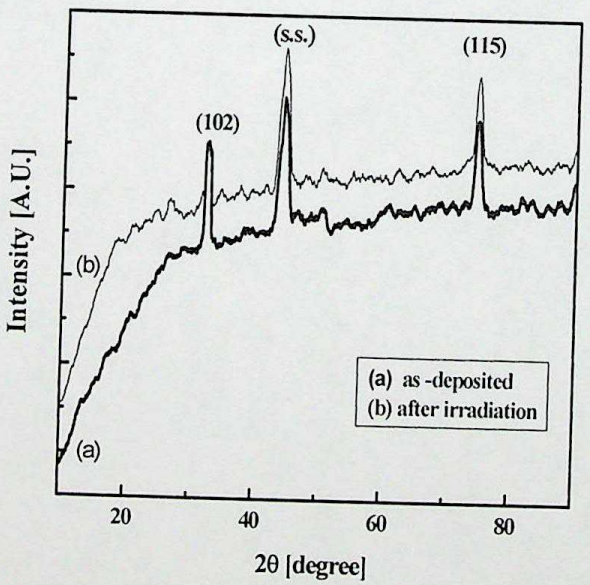


Figure 6.1 (b) X-Ray Diffraction patterns of A_2 films

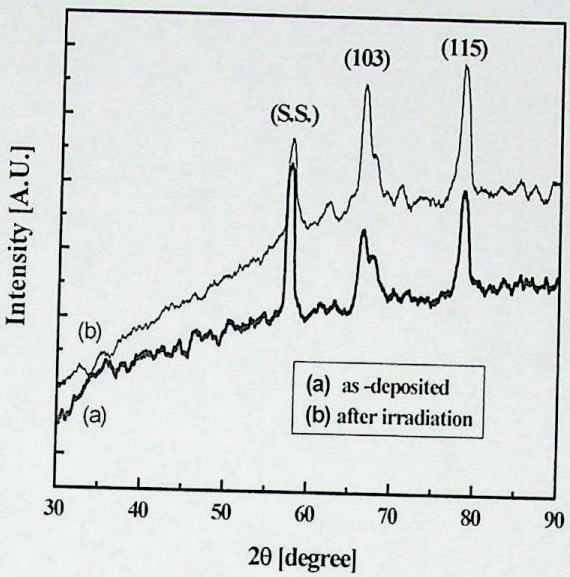
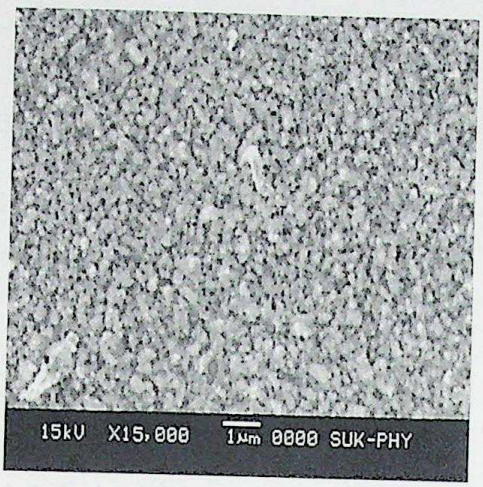


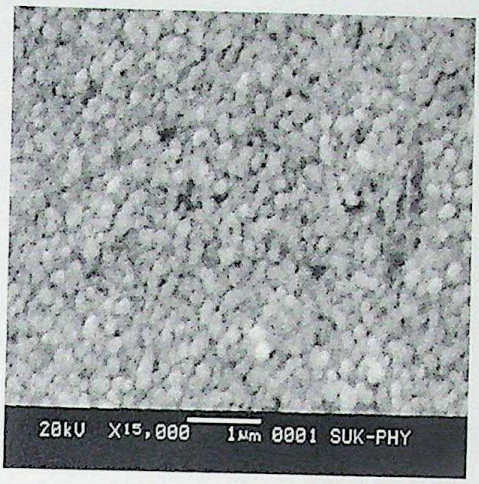
Figure 6.1 (c) X-Ray Diffraction patterns of A_3 films

II. Surface Morphology

The surface morphology of as-deposited and irradiated Ag_2S films was determined using Scanning Electron Microscope (SEM). Fig.6.1(d), Fig.6.1(e), and Fig.6.1(f), point toward SEM micrograph of (a) as- deposited and (b) irradiated A1, A2, A3 thin films, respectively. It is observed that the films are with spherical shaped grains, uniform. It is observed that, electron irradiation resulted in the increase in grain size. The SEM images clearly indicate that films have very good coverage without any crack.

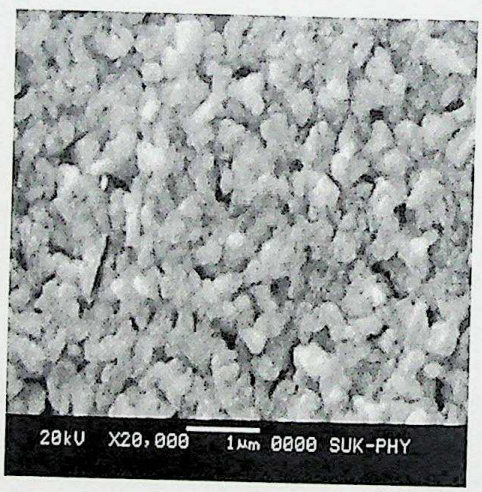


(a)

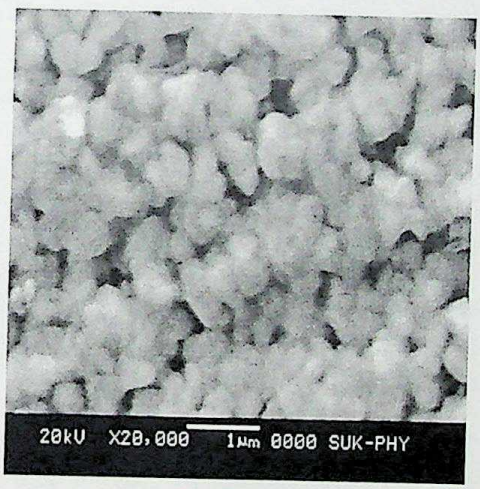


(b)

Figure 6.1(d) SEM images of A_1 thin films (a) as- deposited (b) after irradiation

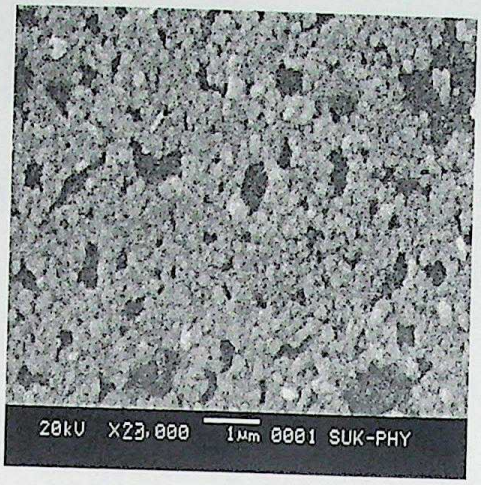


(a)

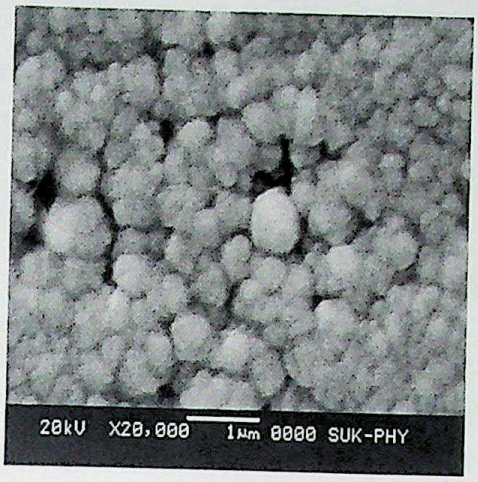


(b)

Figure 6.1(e) SEM images of A_2 thin films (a) as- deposited (b) after irradiation



(a)



(b)

Figure 6.1(f) SEM images of A_3 thin films (a) as- deposited (b) after irradiation

III. Optical absorption study

According to the theory of optical interband transition (direct and indirect) in solids, near the absorption edge, the absorption coefficient varies with photon energy hυ which is given by the following expression,

$$\alpha = \frac{A\left(h\nu - E_g\right)^n}{h\nu}$$

Where,

A - constant

Eg - optical band gap energy.

n - depends on the kind of optical transition.

Fig. 6.1(g) represents a plot of (αhυ) 2 versus hυ of A1 films. From this graph direct allowed transition energy was estimated by extrapolating the linear portion to intercept on the energy axis. The band gap energies estimated from the graphs are found to be 1.1 eV for as deposited thin films and 0.9 eV for irradiatedA1 thin film , 0.95 eV for as-deposited A2 thin film and it decreases 0.85 eV for irradiated A2 film Also band gap energy decreases from 0.9 eV to 0.76 eV after irradiation of A3 thin film. Electron beam irradiation resulted into decrease in the band gap energy.

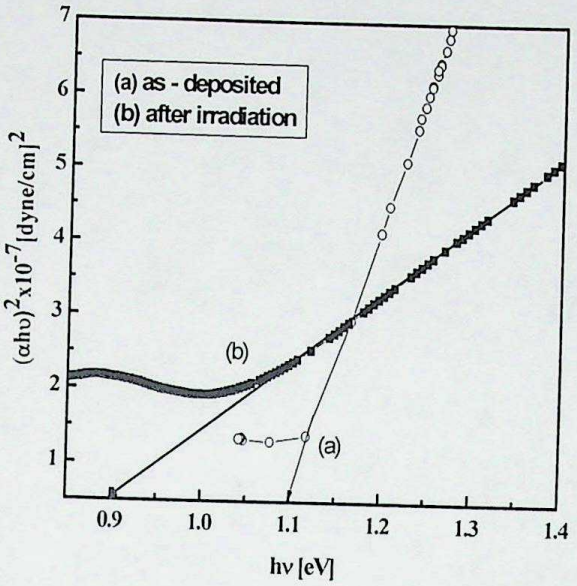


Figure 6.1(g) Plots of $(\alpha h\nu)^2$ versus hν for A1 thin films

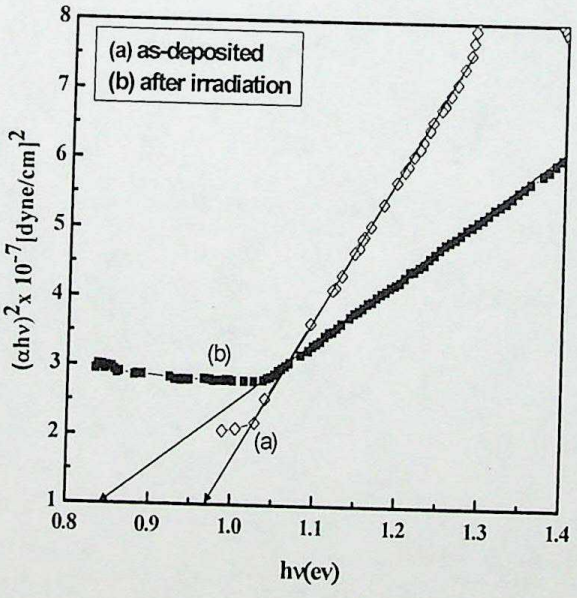


Figure 6.1(h) Plots of $(\alpha h\nu)^2$ versus hν for A2 thin films

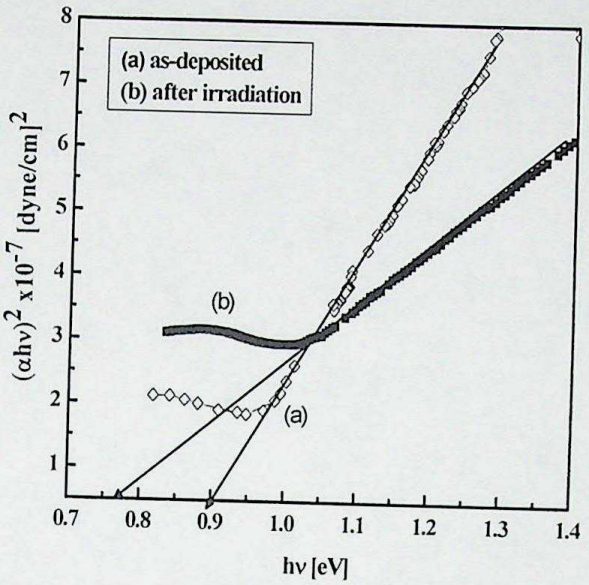


Figure 6.1(i) Plots of (αhν) 2 versus hν for A3 thin films

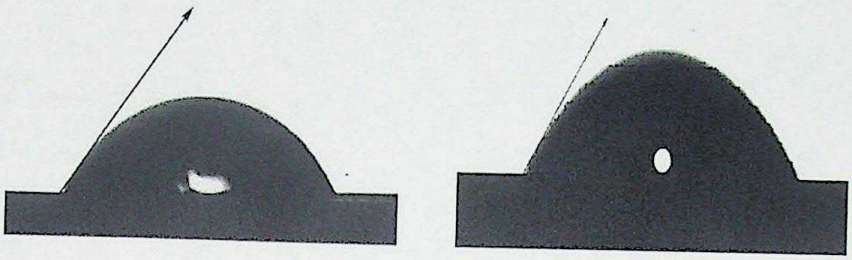
IV. Surface wettability

Wettability involves the interaction between a liquid and a solid in contact. The wetting behavior is characterized by the value of the contact angle, a microscopic parameter. If the wettability is high, contact angle (θ), will be small and the surface is hydrophilic. On the contrary, if the wettability is low, θ will be large and the surface is hydrophobic. The method involves the measurement of contact angle between water and the semiconducting electrode. The contact angle is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface energies and for evaluation of surface wettability. The contact angle is expected to depend upon local inhomogeneities, chemical composition and the surface morphology of the semiconducting electrodes.

Fig. 6.1(j) [a] and [b] shows the systematic presentation of measurement of contact angles for as-deposited and electron beam irradiated A1 thin films. These are 52° and 59° respectively, indicating that Ag2S is a hydrophilic material. Fig. 6.1(k) [a] and [b] shows the contact angles for as-deposited and electron beam irradiated A2 thin films are 65° and 70°.

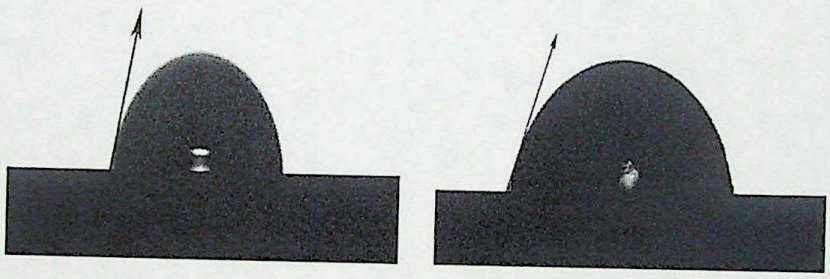
The contact angles are 75° and 87° of A3 thin films for as-deposited and electron irradiated is point out in fig.6.1(l) [a] and [b] respectively.

Slight increase in contact angle after irradiation is attributed to little enhancement in grain size. All the films have hydrophilic nature.



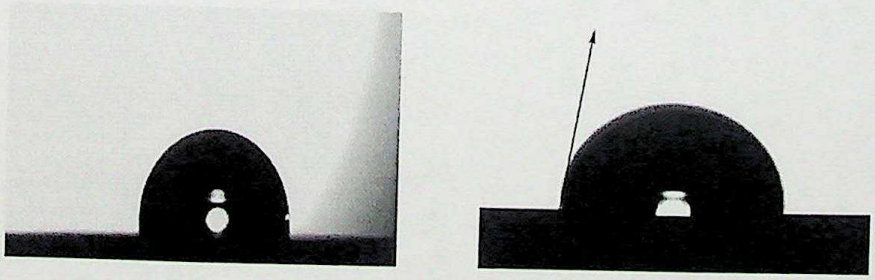
(a) Contact angle 52° (b) Contact angle 59°

Figure 6.1(j) Contact angles of A_1 thin films (a) as-deposited (b) after irradiation



(a) Contact angle 65° (b) Contact angle 70°

Figure 6.1(k) Contact angles of A2 thin films (a) as-deposited (b) after irradiation



(a)Contact angle 75° (b) Contact angle 87°

Figure 6.1(l) Contact angles of A3 thin films (a) as-deposited (b) after irradiation

V. FT-Raman spectroscopy

Raman spectrum was recorded on a 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 FT-Raman spectra of as- deposited and irradiated A1 films are known in fig.6.1 (m). The Raman band of as-deposited thin film observed at around 179 cm^{-1}. It shows broad band (around 212 cm-1) after irradiation.

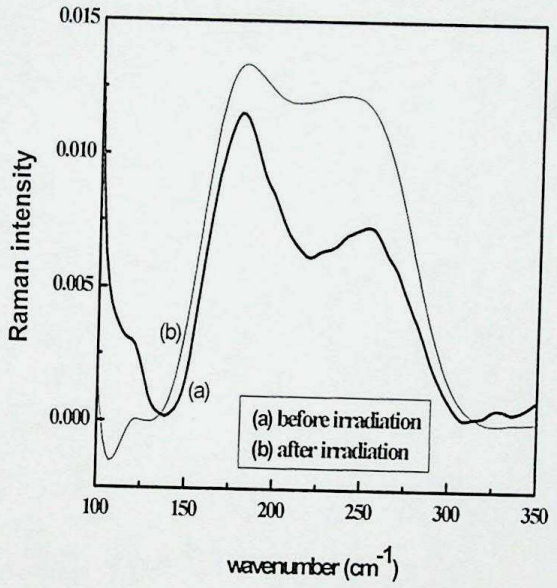


Figure 6.1(m) FT-Raman spectrum of A_1 thin films

6.2 Silver selenide thin films

6.2.1 Preparation of Ag_2Se thin films

Silver selenide (Ag_2Se) thin films have been deposited on to stainless steel substrates by the electrodeposition process, in potentiostatic mode using silver nitrate (AgNO3), selenium dioxide (SeO2) as a precursor sources and Ethylene Diamine Tetra Acetic Acid (EDTA) was used as a complexing agent. Ag_2Se thin films were prepared with bath containing following concentrations listed in Table 6.2.

Table 6.2 Bath composition for preparation of Ag_2Se thin films

Name	Bath composition
B1	3 mM $AgNO_3$ + 2 mM SeO_2 + 0.05 M EDTA
B2	4 mM $AgNO_3$ + 2.5 mM SeO_2 + 0.05 M EDTA
B3	5 mM AgNO3 + 3 mM SeO2 + 0.05 M EDTA

6.2.2 Characterization of electron irradiated Ag_2Se thin films

I. X-Ray diffraction

To evaluate the structure of the deposited thin films, X-ray diffraction (Philips PW-3710 diffractometer) technique with Cu target CuKα (λ=1.5406 Å) has been employed. XRD patterns obtained for the B_1, B_2, B_3 thin films for three different concentrations, with both as-deposited and electron irradiated have been shown in fig.6.2 (a), fig.6.2 (b) and fig.6.2(c) respectively. Both the films have exhibited the formation of orthorhombic crystal structure phase of Ag_2Se. All peaks belonging to Naumannite phase of Ag_2Se well matched with database in JCPDS (24-1041). The average crystallite size of the films (calculated from the Scherrer's equation) exposed to electron irradiation and as-deposited have 13.78 nm and 12.65 nm, respectively. After electron irradiation peak width decreases but peak intensity increases.

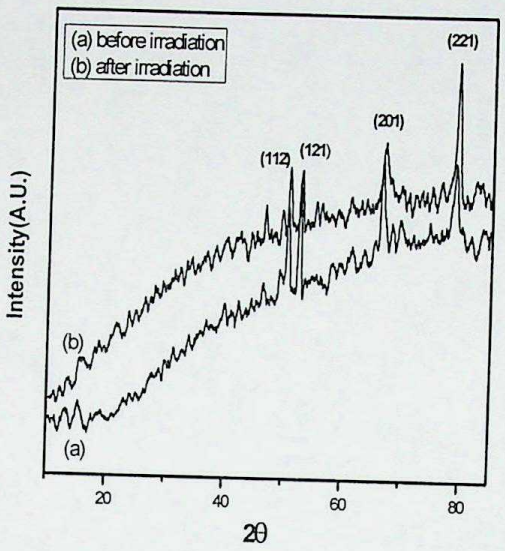


Figure 6.2(a) X-Ray Diffraction patterns of B1 thin films

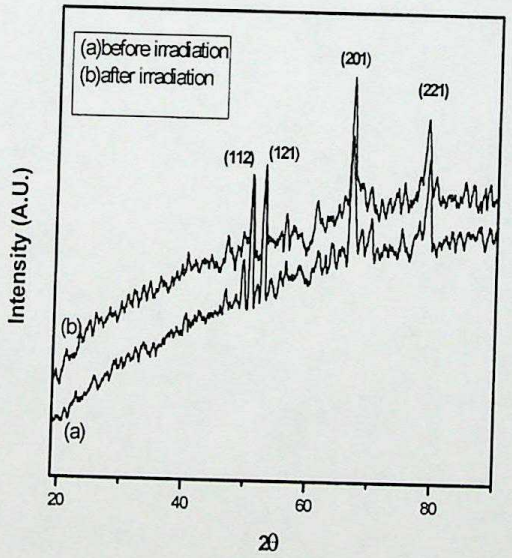


Figure 6.2(b) X-Ray Diffraction patterns of B2 thin films

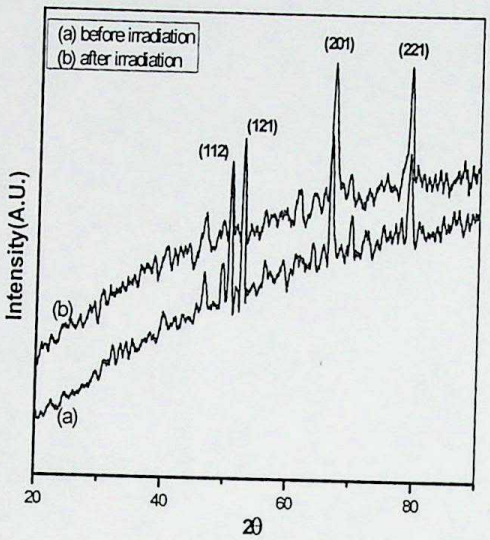


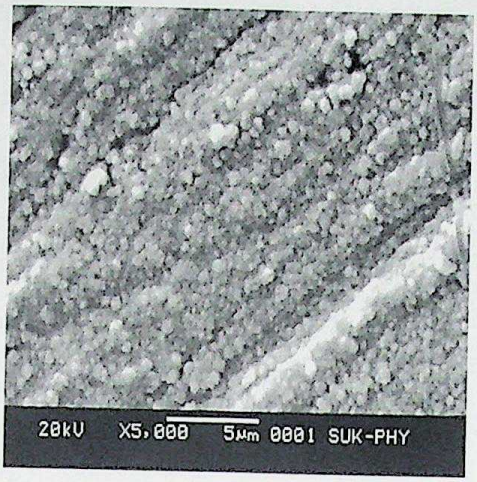
Figure 6.2(c) X-Ray Diffraction patterns of B3 thin films

II. Surface morphological study

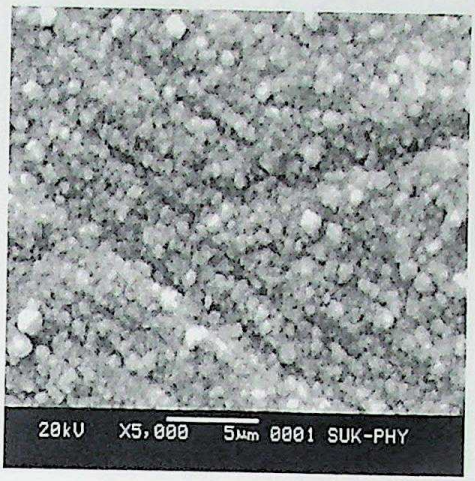
The fig.6.2 (d) (a) and (b) indicates the surface morphology of as-deposited and electron irradiated B1 thin films. The morphology shows granular crystals obtained by as-deposited and electron irradiated B2 thin films in fig.6.2 (e) (a) and (b) respectively.

The fig.6.2 (f) (a) and (b) indicates the surface morphology of as-deposited and electron irradiated B3 thin films. Increase in the grain size due to agglomeration of particles observed after electron irradiation.

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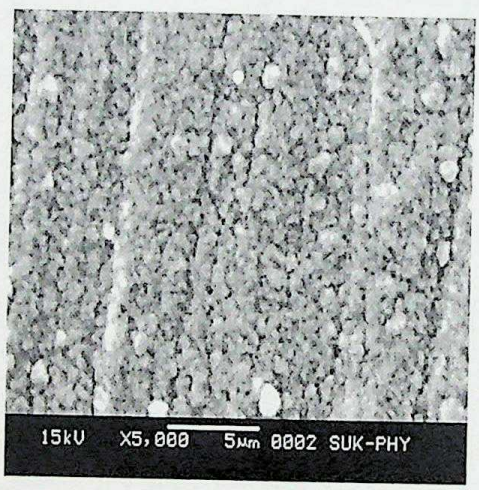


(a)



(b)

Figure 6.2(d) SEM images of B1 thin films (a) as-deposited (b) after irradiation



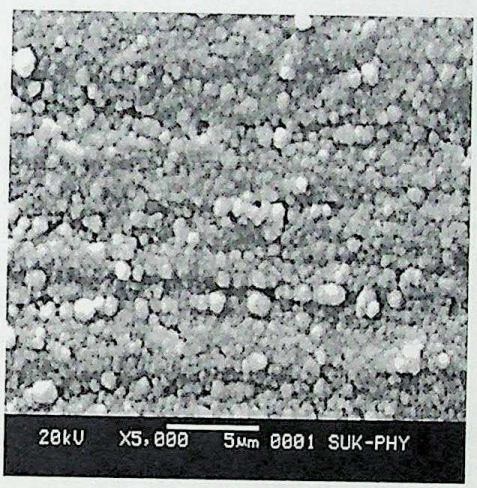
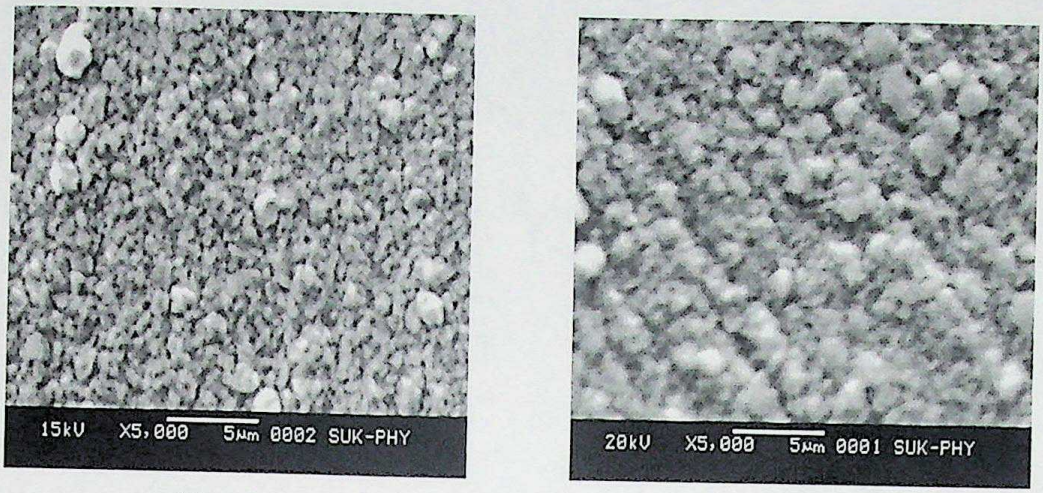


Figure 6.2(e) SEM images of B2 thin films (a) as-deposited (b) after irradiation



(a) (b)

Figure 6.2(f) SEM images of B3 thin films (a) as-deposited (b) after irradiation

III. Optical analysis

The optical absorption of these films has been studied in the wavelength range 350-1200 nm, without accounting for reflection and transmission losses. Fig.6.2 (g),(h) and (i), represents a plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ before and after electron irradiation of B1, B2 and B3 thin films respectively. From this graph direct allowed transition energy was estimated by extrapolating the linear portion to intercept on the energy axis. The band gap energies estimated from the graphs are found to be 1.13 eV for as deposited and 1.06 eV for irradiated B1 thin film for, 1.10eV for as deposited and it decreases 1.0 eV for irradiated B2 thin film. The band gap energy decreases from 0.96 eV to 0.88 eV after irradiation for B3 thin film. Band gap energy decreases, after electron irradiation.

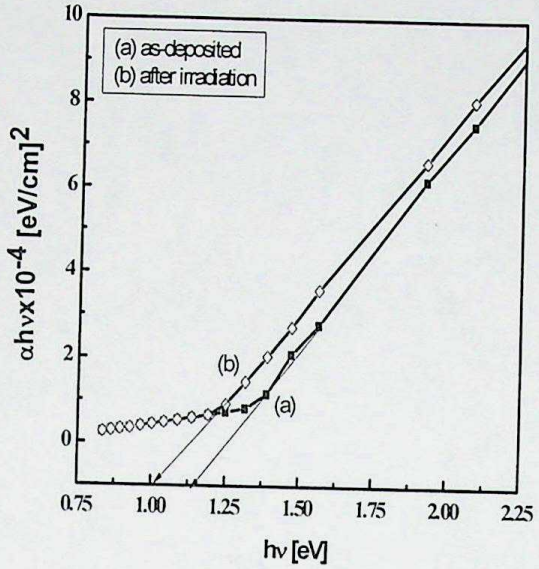


Figure 6.2(g) $(\alpha h\upsilon)^2$ Vs $h\upsilon$ of B1 thin films

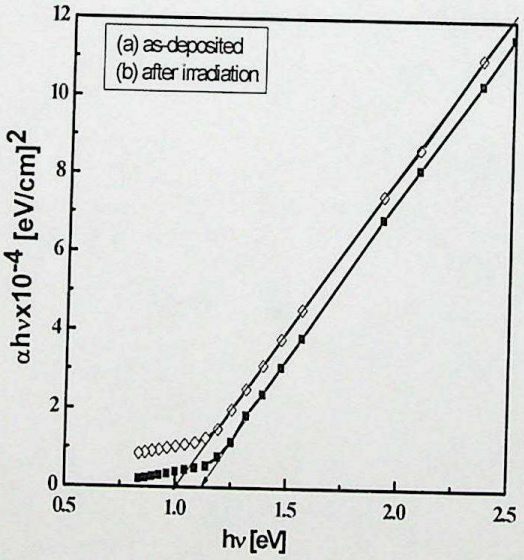


Figure 6.2(h) $(\alpha h\upsilon)^2$ Vs $h\upsilon$ of B2 thin films

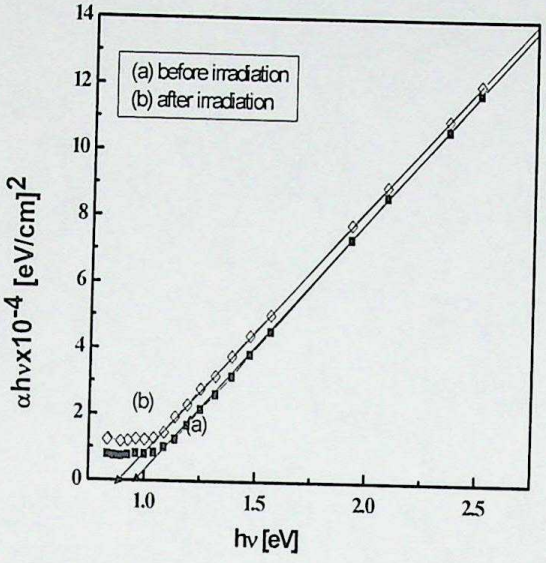
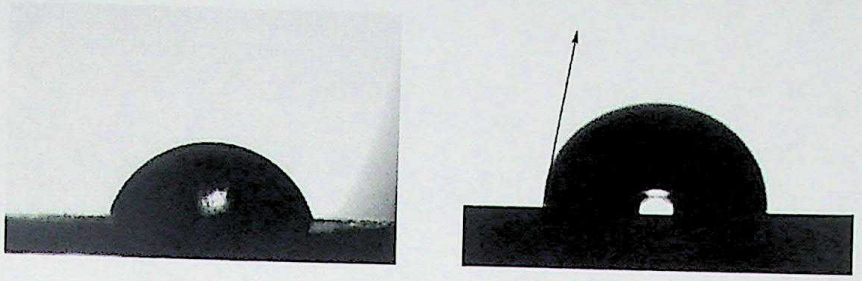


Figure 6.2(i) $(\alpha h\upsilon)^2$ Vs $h\upsilon$ of B_3 thin films

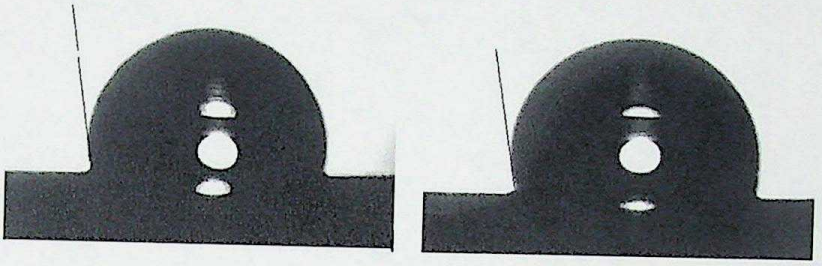
IV. Surface wettability test

An empirical diagnostic method for evaluation of thin film property is the measurement of water contact angle on its surface. The presence of local inhomogeneities, chemical composition and surface morphology in thin films are directly related to the surface water contact angle. Fig.6.2 (j), (a) and (b) shows the schematic representation of contact angles of B_1 thin films. The contact angles for as–deposited and electron irradiated Silver selenide films, were 63° and 84° respectively. It was confirmed that the nature of the silver selenide film shows hydrophilic surface. Fig.6.2 (k), (a) and (b) demonstrate contact angles of B2 thin films. The contact angles for as–deposited and electron irradiated Silver selenide films, are 82° and 98° respectively. These films become hydrophilic after irradiation. Fig.6.2 (l) (a) and (b) explains the schematic representation of contact angles for as -deposited and irradiated B3 thin films; it was 115° and 124° respectively. It was confirmed that the nature of the silver selenide films became hydrophobic after irradiation.



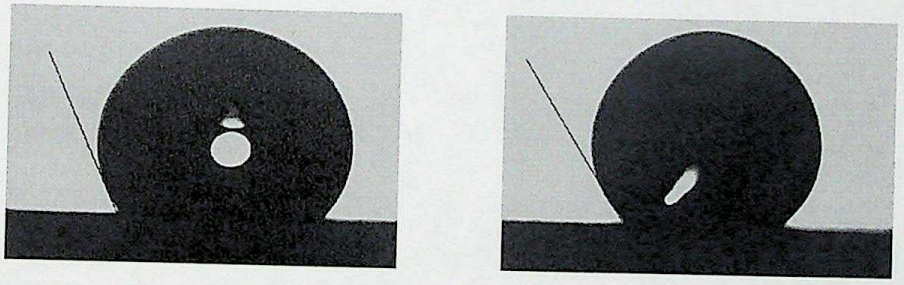
(a) Contact angle 63° (b) Contact angle 84°

Figure 6.2(j) Contact angles of B1 thin films (a) as-deposited (b) after irradiation



(a) Contact angle 82° (b) Contact angle 98°

Figure 6.2(k) Contact angles of B2 thin films (a) as-deposited (b) after irradiation



(a) Contact angle 115° (b) Contact angle 124°

Figure 6.2(l) Contact angles of B3 thin films (a) as-deposited (b) after irradiation

V. FT-Raman Spectroscopy

The FT-Raman spectra for as-deposited and irradiated B1 thin films are shown in fig. 6.2 (m) The Raman bands of as-deposited and irradiated thin films are observed at around 3249 cm-1. It is found that, the peak intensity and width increases after irradiation. The ion bombardment increases the crystallinity of films due to induced defects and therefore

the Raman bands whose intensity depends on the crystallinity also get increased, correspondingly.

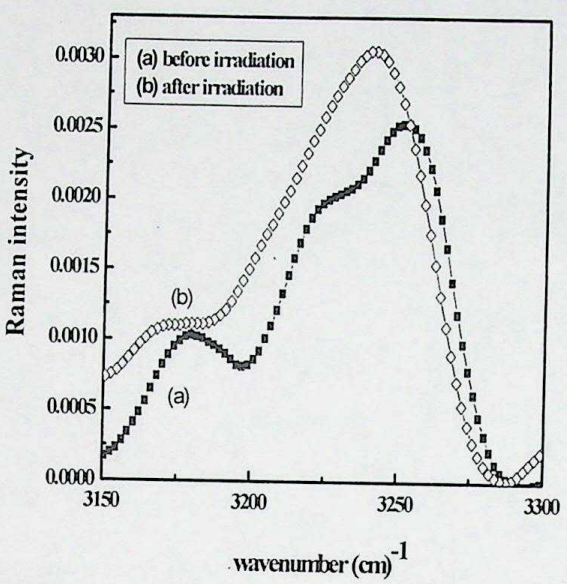


Figure 6.2(m) FT- Raman spectra of B1 thin films

6.3 Effect on Silver telluride thin films

6.3.1 Preparation of Ag_2Te thin films

Silver telluride (Ag_2Te) thin films have been deposited on to stainless steel substrates by the electrodeposition process, in potentiostatic mode using silver nitrate ($AgNO_3$), sodium telluride (Na_2Te) as a precursor sources and Ethylene Diamine Tetra Acetic Acid (EDTA) was used as a complexing agent. Ag_2Te thin films were prepared with bath containing following concentrations listed in table 6.3.

Table 6.3 Bath composition for preparation of Ag_2Te thin films

Film No.	Bath composition
C1	0.02 M $AgNO_3$ + 0.02 M Na_2Te + 0.02 M EDTA
C2	0.03 M $AgNO_3$ + 0.03 M Na_2Te + 0.03 M EDTA

C3	0.04 M $AgNO_3$ + 0.04M Na_2Te + 0.04 M EDTA

6.3.2 Characterization of irradiated Ag_2Te thin films

I. X-Ray diffraction

The XRD patterns of as-deposited and electron-irradiated films of C1, C2 and C3 thin films are shown in fig.6.3(a), fig.6.3(b) and fig.6.3(c). The pattern reveals that Ag_2Te films are polycrystalline. The planes indicate the monoclinic structure of the material. The average grain size calculated by using the Scherer's formula and was found to be 10.80 nm and 12.00 nm for as-deposited and irradiated films, respectively. It is found that after irradiation, there occurs increase in grain size.

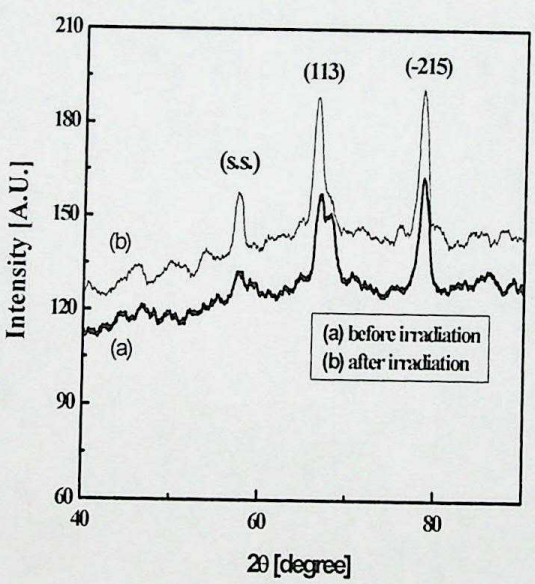


Figure 6.3(a) X-Ray Diffraction patterns of C1 thin films

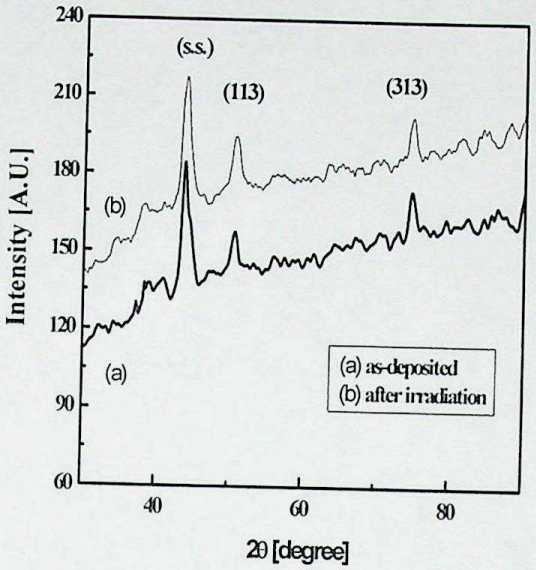


Figure 6.3(b) X-Ray Diffraction patterns of C2 thin films

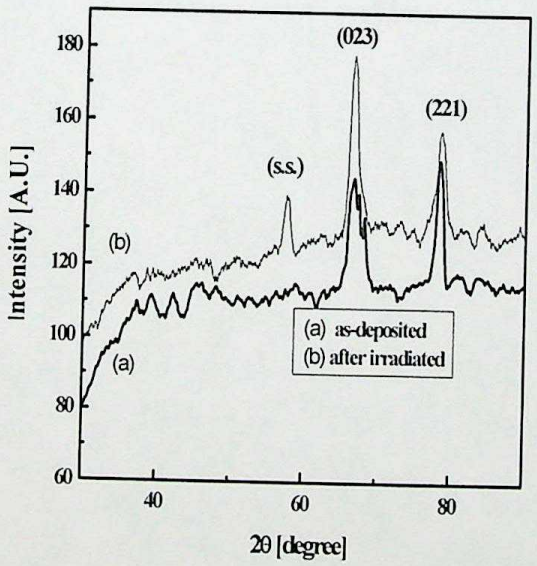
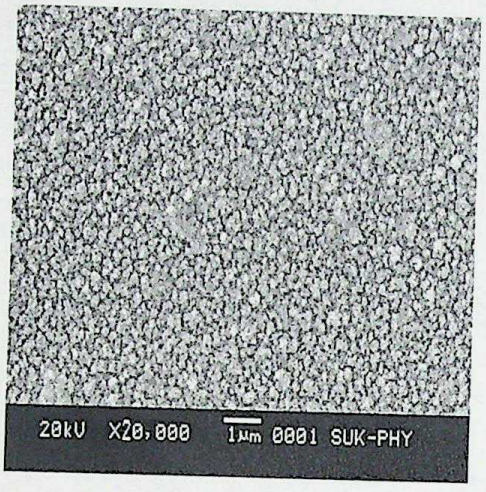


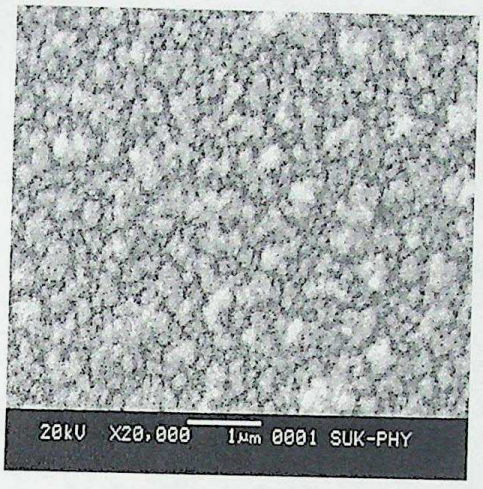
Figure 6.3(c) X-Ray Diffraction patterns of C3 thin films

II. Surface morphology

The surface micrographs of the(a) as-deposited and (b) electron irradiated of C1, C2 and C3 thin films are shown in Fig. 6.3(d), (e) and (f) respectively. It is an evidence for fine grains with almost smooth surface. It is observed from the micrographs that the Ag_2Te films were homogeneous and without cracks and covered the steel substrate well.

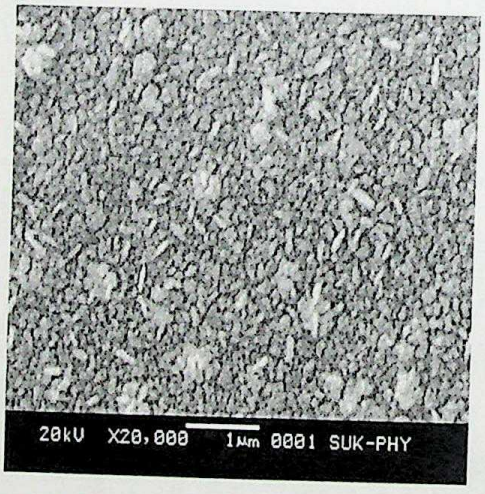


(a)

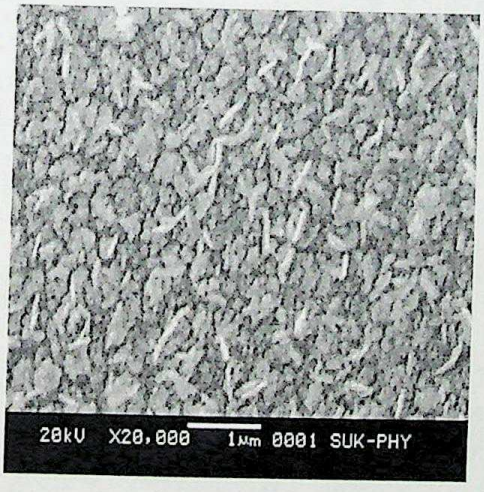


(b)

Figure 6.3(d) SEM micrographs of C1 thin films (a) before irradiation (b) after irradiation

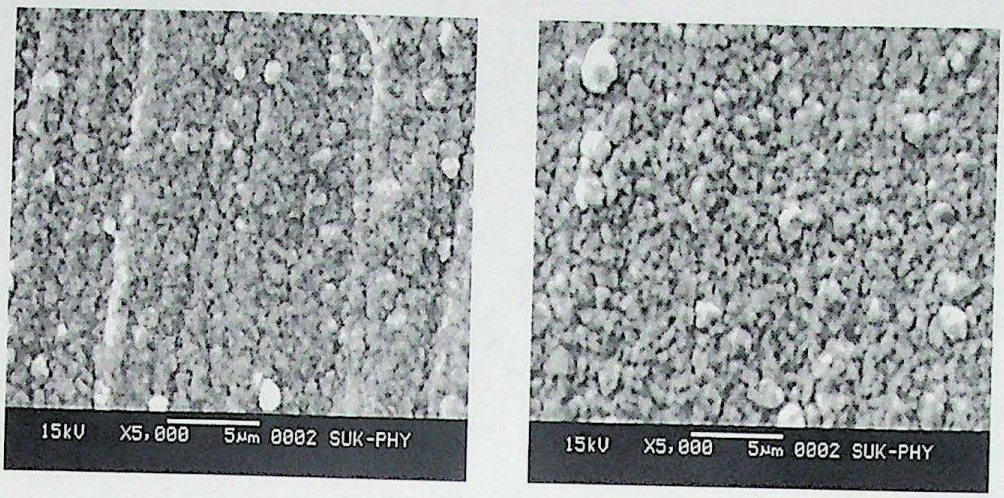


(a)



(b)

Figure 6.3(e) SEM micrographs of C2 thin films (a) before irradiation (b) after irradiation



(a) (b)

Figure 6.3(f) SEM micrographs of C3 thin films (a) before irradiation (b) after irradiation

III. Optical absorption study

Optical absorption spectra for as-deposited and electron-beam irradiated Ag_2Te films have been recorded over the range 350-1200nm. The variation of $(\alpha h\nu)^2$ versus $h\nu$ of C1, C2 and C3 thin films [Fig.6.3(g), Fig.6.3(h) and Fig.6. 3(i)] are linear, which means that the mode of transition in these films is of direct nature. Extrapolation of the curves on an energy axis for zero absorption coefficient value gives the optical energy gap (Eg). Band gap energies of as-deposited, irradiated films are found to be 1.57 eV and 1.15 eV respectively. The decrease in band gap is attributed to the increase in the crystallinity of irradiated samples. The decrease in the band gap is also attributed to the bond breaking or ionization of atoms, which leads to change in the local structure order of film, as well as induced lattice damage.

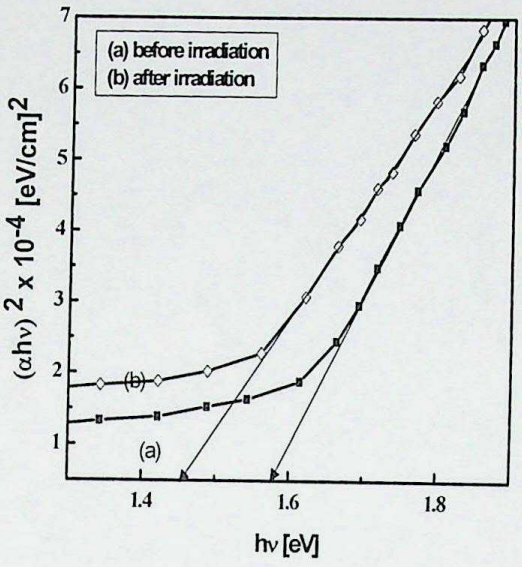


Figure 6.3(g) Plot of $(\alpha h\nu)^2$ versus hν of C1 thin films

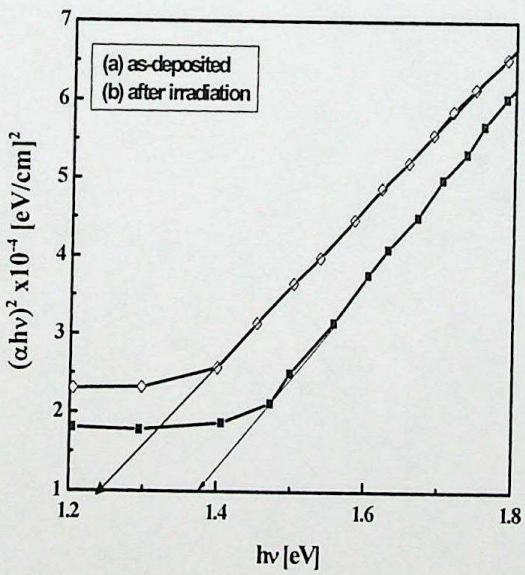


Figure 6.3(h) Plot of $(\alpha h\nu)^2$ versus hν of C2 thin films

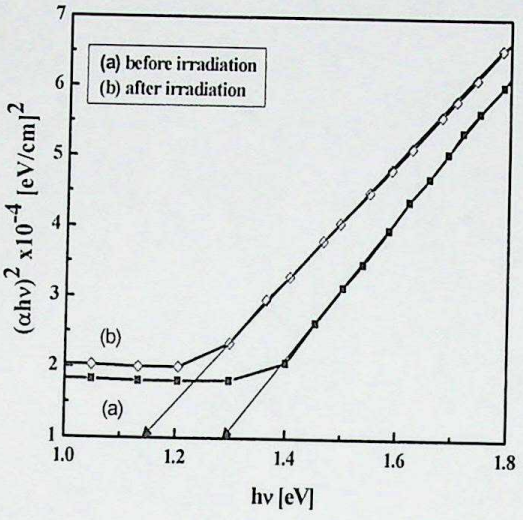
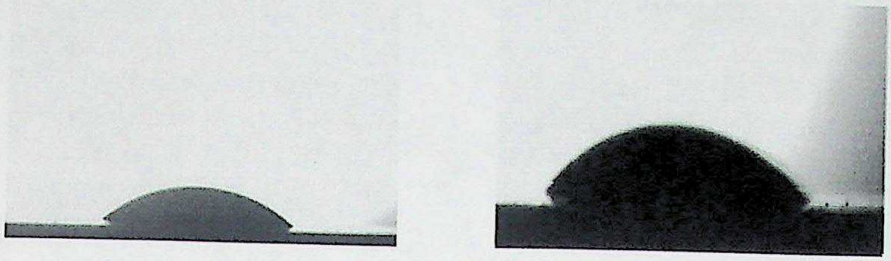


Figure 6.3(i) Plot of $(\alpha h\nu)^2$ versus hν of C3 thin films

IV. Surface wettability

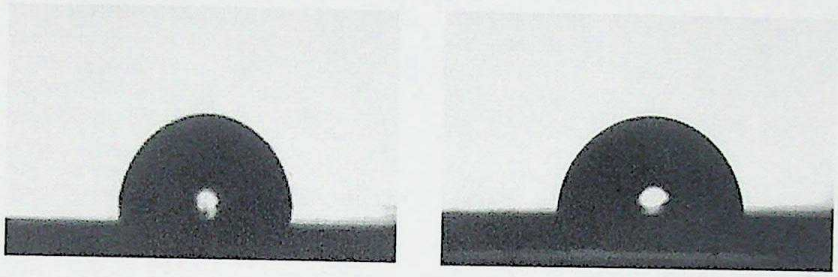
If the wettability is high, contact angle will be small and the surface is hydrophilic. On the contrary, if the wettability is low, contact angle will be large and the surface is hydrophobic. The contact angle is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface energies. Fig. 6.3(j) (a) and (b) shows the measurement of contact angles for as deposited and irradiated C1 thin films, it is 30° and 45°, respectively.

Fig. 6.3(k) (a) and (b) represents contact angles of C2 thin films for as-deposited and irradiated it is found to be 65° and 80°, respectively. The nature of the films indicated hydrophilic in both cases. Fig. 6.4(l) (a) and (b) gives contact of C3 thin films for as-deposited and irradiated, found to be 69° and 85° respectively.



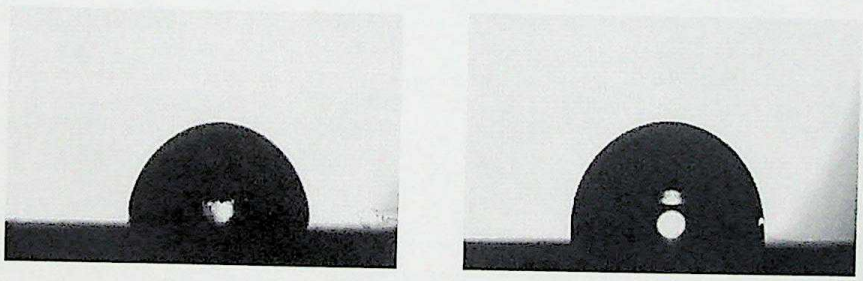
(a) Contact angle 30° (b) Contact angle 45°

Figure 6.3 (j) Water contact angles of C1thin films (a) as-deposited (b) electron irradiated



(a) Contact angle 65° (b) Contact angle 80°

Figure 6.3 (k) Water contact angles of C2 thin films (a) as-deposited (b) electron irradiated



(a) Contact angle 69° (b) Contact angle 85°

Figure 6.3 (l) Water contact angles of C3 thin films (a) as-deposited (b) electron irradiated

V. FT-Raman Spectroscopy

The FT-Raman spectra of as-deposited and irradiated C1 thin were shown in fig.6.3 (m) The Raman bands of as-deposited and irradiated thin films are observed at 722, 711 cm^{-1} respectively. The peak intensity and width increases after irradiation of electron beam. The ion bombardment increases the crystallinity of films due to induced defects and therefore the

Raman bands whose intensity depends on the crystallinity also get increased, correspondingly.

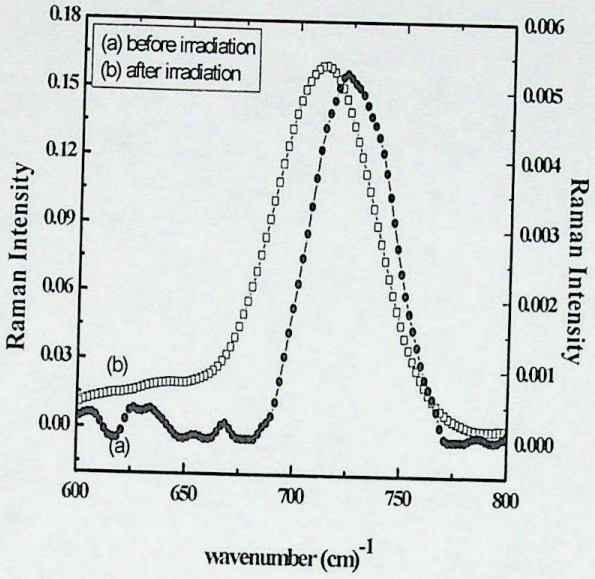


Figure 6.3(m) FT-Raman spectra of C1 thin films

Annexure C

Summary of the findings of the study:

The present research work is devoted for the study of Silver chalcogenide thin films, which have wide applications in various fields of science and technology as well as in semiconducting thin film physics. Therefore we have undertaken structural, morphological and HI studies on these films that have helped to arrive at following conclusions:

- Among the various deposition techniques, electrodeposition technique is less expensive and easy technique for deposition of silver chalcogenide thin films. The holograms are recorded in situ; hence it is feasible for DEHI technique.
- As bath concentration increases, the particle size and contact angle of Ag_2S, Ag_2Se and Ag_2Te thin films increases where as bandgap energy decreases.
- FT-Raman spectroscopic study of silver sulphide, silver selenide and silver telluride thin films show peaks at wavenumber 179, 3240 and 715 cm^{-1} respectively.
- Surface morphology study of silver chalcogenide thin film reveals that the films are good covered to the substrate. Silver selenide thin films show dendritic crystal structure.
- It is found that as time of deposition increases the number of fringes increases, fringe width decreases.
- Thickness of the thin films and mass of the deposited films increases, but stress to substrate decreases.
- Due to electron beam irradiation the intensity of the peaks as well as crystallite size of Ag_2S, Ag_2Se and Ag_2Te thin films increases.
- The bandgap energy of Ag_2S, Ag_2Se and Ag_2Te thin films are decreases after electron beam irradiation.
- The surface wettability testing of Ag_2S, Ag_2Se and Ag_2Te thin films are confirmed by an increase in contact angle after irradiation.
- FT-Raman spectroscopic study of Ag_2S, Ag_2Se and Ag_2Te thin films showed increase in peak intensity due to electron beam irradiation.

Annexure D

- **Details of the Publications resulting from the project work**

Sr No.	Name
1.	Preparation and characterization of electrodeposited silver selenide thin films and its holographic study. P.M.Kulal, S.H.Han, V.J. Fulari, journal of material science (submitted)
2.	"Modification of structural, optical, surface wettability and FT-Raman spectroscopy of nanostructure silver sulphide thin film using electron beam irradiation, V. J. Fulari, P. M. Kulal, V. B. Prabhune*, M. C. Rath, National Conference on Nanomaterials and Nanotechnology Dec. 21-23 (2009) University of Lucknow, Uttar Pradesh. ISBN 978-93-80043-61-6.
3.	Effect of Precursor Concentration in Electro Synthesis of Nanocrystalline Ag_2Se Thin Films U.M. Chougale, P.M. Kulal, J.V. Thombare, S.H. Han, V. J. Fulari, Physica E: Low-dimensional Systems and Nanostructures (submitted).
4.	On The 7MeV Electron Irradiation of Electrodeposited Silver Chalcogenide Thin Films U.M. Chougale, P.M. Kulal, J.V. Thombare, M. C. Rath, V. J. Fulari, Material Science: An Indian Journal(Submitted).

- **Other publication during project**

[1]	"Single Step Electrochemical Synthesis of Sb_2Se_3 Thin Films: Effect of Molarities of Precursor Solution" P. M. Kulal, D. P. Dubal, V. J. Fulari Journal of material science (accepted) 2010.
[2]	"Chemical synthesis of Fe2O3 thin films for supercapacitor application" P. M. Kulal, D. P. Dubal, C. D. Lokhande, V. J. Fulari Journal of alloys and compound509 (2011) 2567-2571.
[3]	Synthesis of Bi2Se3 Thin Films By Electrodeposition and its Holographic Study. P. M. Kulal, S. D. Kamat, S. A. Gangawane, V. J. Fulari. Bulletin of Materials Science Journal.(submitted)

➢ **Papers presented in the conference during the period of project**

SrNo.	Name
1.	"Electochemical synthesis of Sb_2Se_3 thin films and its holographic study using he-ne laser", P. M. Kulal, V.P. Malekar, V. B. Prabhune, S. J. Pawar, V. J. Fulari , Bionano Frontier, International Society of Science and Technology, ISSN 0974 – 0678 (2010)184.
2.	Electrochemical synthesis of polycrystalline Bi2Se3 cabbages, P. M. Kulal, H. D. Dhaygude, S.S.Dhasade, J.S.Patil, M.B.Dongare, V. J. Fulari Conference on Nanomaterials and Nanotechnology Dec. 21-23 (2009) University of Lucknow, Uttar Pradesh. ISBN 978-93-80043-61-6.

➢ **Other papers presented in the conference during the period of project**

1	Electrochemical Synthesis of Bi_2Se_3 Thin Film and Its Holographic Study, P. M. Kulal, S.D.Dhasade, S. A. Gangavane, V. J. Fulari, ASMFM- 2009 Shivaji University, Kolhapur, Maharashtra.
2	Electrochemical Synthesis of Cauliflower Network of ZnS Thin Films, P.M.Kulal, V.B.Prabhune, S. A. Gangavane, J. S. Patil, V. J. Fulari NTAFM-2009National Chemical Laboratory, Pune (M.S.)
3	Electrochemical Synthesis of Sb_2Se_3 Thin Films; P. M. Kulal , V. J. Fulari, National Seminar on Advanced Materials, March 19-20 (2010), Shivaji University, Kolhapur, Maharashtra.
4	Synthesis of Bi2Sse3 Thin Films by Electodeposition and Its Holographic Study P. M. Kulal, S. D. Kamat, S. A. Gangawane, V. J. Fulari IWSSCGGC-2010, Centre for materials for Electronics Technology, Pune.
5	Electrochemical Synthesis of undoped and Al doped Iron Oxide Thin Films J. V. Thombare, R. M. Jadhav,A. V. Raut,P. M. Kulal,U. M. Chougale, V. J. Fulari, ICPM-MDF-2012, January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra

6	Synthesis and Characterization of Cu doped Cadmium Sulphide Thin Films by Electrodeposition Method V. J. Fulari , A. S. Powar, S. V. Tikone, U. M. Chougale, S. K. Shinde,G. M. Lohar, J. V. Thombare. ICPM-MDF-2012, January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra
7	Preparation and Characterization Iron doped Zinc Selenide Thin Film by Electrodeposition G. M Lohar, J. V. Thombare, S. K Shinde, U. M Chougale, V. J. Fulari, ICPM-MDF-2012 January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra
8	Characterization and Surface Deformation Study of Electrodeposited Polyaniline Thin Films, V.J. Fulari , U.M. Chougale, S.K. Shinde, G.M. Lohar, J.V. Thombare, ICPM-MDF-2012 January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra
9	Preparation and Characterization of CdSe0.6Te0.4 Thin Films by Electrodeposition Method, S.K. Shinde, J.V. Thombare, G.M. Lohar, U.M. Chougale, V.J. Fulari, ICPM-MDF-2012 January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra.
10	Studies on copper oxide thin films by Double Exposure Holographic Interferometry, S.R. Patil, A.A. Patil, S. K. Shinde, J.V. Thombare, G.M. Lohar, U.M. Chougale, V.J. Fulari, ICPM-MDF-2012 January 17-19 (2012), Shivaji University, Kolhapur, Maharashtra.

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ज्ञान-विज्ञान विमुक्तये

ANNEXURE –IV

UNIVERSITY GRANT COMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI-110 002.

Utilization Certificate

Certified that out of **Rs. 6, 10, 800/- (Rupees Six Lakhs Ten Thousands Eight Hundred only)** of grant-in-aid sanctioned during the year 02/05/2009 to 01/05/2012 in favor of Dr. V. J. Fulari under the scheme of support for Major Research Project entitled "Studies on effect of electron irradiation on electrodeposited silver chalcogenide thin films by holographic interferometry", vide UGC letter No. F. 36-209/2008(SR) dated 26th March, 2009 only **Rs. 4,36,800/-(Rupees Four Lakhs Thirty Six Thousands Eight Hundred only)** are received and has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission. The total expenditure is of **Rs.5,78,709/- (Rupees Five Lakhs Seventy Eight Thousands Seven Hundred and Nine only)**. The excess expenditure of **Rs. 1,41,909/- (Rupees One Lakh Forty One Thousands Nine Hundred and Nine only)** incurred from the university fund and yet to be received from University Grants Commission.

For Sankpal Kulkarni & Associates
Chartered Accountants

(A. N. Sankpal)
Partner, M. No. 104718
F R N 121256W

SIGNATURE OF THE PRINCIPAL INVESTIGATOR

Dr. V. J. Fulari
Principal Investigator (U.G.C. Scheme)
Holography & Material Research Lab.
Department of Physics,
Shivaji University Kolhapur - 416 004 (India.

REGISTAR/PRINCIPAL

Registrar,
Shivaji University, Kolhapur

STAUTORY AUDITOR

SANKPAL KULKARNI & ASSOCIATES
Chartered Accountants
KOLHAPUR

30 JUN 2012

ज्ञान-विज्ञान विमुक्तये

ANNEXURE -V

UNIVERSITY GRANT COMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI-110 002
STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR/MINOR RESEARCH PROJECT

1. Name of the Principal Investigator Dr. V. J. Fulari
2. Deptt. of University/ College: Shivaji University, Kolhapur (Maharashtra)
3. UGC approval No. and date: 36-209/2008 (SR) dated 26 March 2009
4. Title of the Research Project: "Studies on effect of electron irradiation on electrodeposited silver chalcogenide thin films by holographic interferometry"
5. Effective date of the starting of the project: 02/05/2009
6. (a) Period of the expenditure from 02/05/2009 to 01/05/2012.
7. Details of the expenditure

Sr. No.	Item	Amount Approved Rs.	Total Expenditure incurred in periods 02/05/ 2009 to 01 /05/2010 in Rs.	Total expenditure incurred in periods 02/05/2010 to 01/05/2011 in Rs.	Total expenditure incurred in periods 02/05/2011 to 01/05/2012 in Rs
i.	Books and Journals	30,000/-	0/-	NIL	23,977/-
ii.	Equipment	2,00,000/- (For 3 years)	0/-	1,75,702.00	23,388/-
iii.	Contingency	20, 000/-	10903/-	Nil	8,770/-
iv.	Field Work/ Travel (Give details in the perform at the Annexure IV)	20, 000/-	2460/-	4192.00	11,819/-

v.	Hiring Services/consumable	20,000/-	4632/-	452.00	14,687/-
vi.	Chemicals and Glassware	NIL	NIL	Nil	NIL
vii.	Overhead @ 10% approved recurring Grant (Except travel/ Field Work)	32,800/-	10933/-	Nil	21,866/-
viii.	Project Fellowship @ Rs. 8, 000/-p.m	2,88,000/-	70,451/-	88,000.00	106,477/-
Total		**Rs.6,10,800/-**	**Rs.99379/-**	**Rs.2,68,346/-**	**Rs.2,10,984/-**
Total Amount Received Rs. 4,36,800/-			**Total Expenditure Rs.5,78,709/-**		

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. It as a result of check or audit objective, some irregularly is noticed, later date, action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the grant of Rs. **Rs. 4,36,800/-(Rupees Four Lakhs Thirty Six Thousands Eight Hundred only)** received from the University Grants Commission under the scheme of support for Major Research Project entitled "Studies on effect of electron irradiation on electrodeposited silver chalcogenide thin films by holographic interferometry", vide UGC letter No. F. 36-209/2008(SR) dated 26th March, 2009 has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission. The excess expenditure of **Rs. 1,41,909/- (Rupees One Lakh Forty One Thousands Nine Hundred and Nine only)** incurred from the university fund and yet to be received from University Grants Commission.

SIGNATURE OF PRINCIPAL INVESTIGATOR

Dr. V. J. Fulari
Principal Investigator (U.G.C. Scheme)
Holography & Material Research Lab,
Department of Physics,
Shivaji University Kolhapur - 416 004 (India.

REGISTRAR/PRINCIPAL

Registrar,
Shivaji University, Kolhapur

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ज्ञान-विज्ञान विमुक्तये

ANNEXURE -VI

UNIVERSITY GRANT COMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI-110 002.

STATEMENT OF THE EXPENDITURE INCURRED ON FIELD WORK

Name of the Principal Investigator: Dr. Fulari Vijay Janardhan

Name of the Place visited	Duration of the visit		Mode of Journey	Expenditure incurred (Rs)
	From	to		
Solapur University, Solapur	26/05/2009	26/06/2009	Traveling by Bus	615.00/-
Institute of Science Mumbai	06/07/2009	08/07/2009	Traveling by Car	1845.00/-
Solapur University Solapur	06/06/2010	07/06/2010	Traveling by Car	4192.00/-
Subject Expert from Karnataka University, Dharwad	05/09/2011	05/09/2011	Travelling by Bus	1540.00/-
Kuvempu University, Shimoga.	18/02/2012	20/02/2012	Travelling by Car	7,301.00/-
Karnataka University, Dharwad	03/03/2012	03/03/2012	Travelling by Car	2978.00/-
			Total	**Rs.18471.00/-**

Certified that the above expenditure is in accordance with the UGC norms for the Major Research Projects.

SIGNATURE OF PRINCIPAL INVESTIGATOR

Dr. V. J. Fulari
Principal Investigator (U.G.C. Scheme)
Holography & Material Research Lab.
Department of Physics,
Shivaji University Kolhapur - 416 004 (India)

REGISTRAR/PRINCIPAL

Registrar,
Shivaji University, Kolhapur