Chalcogenide Letters Vol. 16, No. 9, September 2019, p. 457 - 464

STUDY OF MIXING BEHAVIOR OF Cu-Sn-Se PRECURSORS USING ANNEALING PROCESS TO PREPARE Cu_2SnSe_3 THIN FILMS

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Cu_2SnSe_3, a ternary semiconductor has emerged as a suitable material for photovoltaic application and can be used as a precursor for $Cu_2ZnSnSe_4$ thin films. This paper reports the study of mixing behavior of Cu-Sn-Se precursor thin films. These thin films were grown by employing RF sputtering and thermal evaporation methods by maintaining substrate temperature at 100ºC. These were further annealed in Vacuum for 30 minutes at 200ºC and 500ºC. The structure of as- deposited and annealed stacked layer of constituents Cu, Sn and Se is analyzed by X-ray diffraction technique which revealed that the as-deposited and annealed sample possess secondary phases along with formation of Cu_2SnSe_3. AFM results confirmed that sample annealed at 500ºC revealed better surface having higher smoothness. The variation in electrical properties of the various thin films has been reported.

(Received June 5, 2019; Accepted September 25, 2019)

Keyword: Cu_2SnSe_3 thin films, XRD, AFM, Annealing

1. Introduction

Ternary compounds $A_{2\,I}B_{IV}C_{3VI}$ are of significant interest because of low band-gap, having low melting points 1). A lot of studies on the thin films of ternary semiconductor compound Cu_2SnSe_3 (CTSe) have been reported by various workers. This is due to the wide applicability of this compound in the fields like photovoltaic solar cells, opto-electronic devices etc.2). Important factors which have been investigated are optical band gap, radiation tolerance, absorption coefficient (from solar cell point of view) and price of large-scale production 1). A study of crystal structure refinement of this compound by Delgado et al shows that CTSe has unit cell parameters of a=6.9670Å, b=12.0493 Å, c=6.9453 Å crystallizing in the monoclinic space group *Cc* (C_s^4, No. 9) having Z=4 4). CTSe exhibits diamond structure with low thermal conductivity and high specific heat 5). Thin films of CTSe have been developed by using various deposition techniques like RF-DC sputtering method 6, 7), thermal evaporation method 8) etc. Marcano et al studied the crystal growth and structure of CTSe prepared by vertical Bridgman–Stockbarger technique and obtained the chemical composition in 2:1:3 ratios having the monoclinic structure with Cc space group. They have observed a secondary phase of $SnSe_2$ due to a eutectic reaction 9). Kang et al studied the effect of growth temperature on the CTSe thin films prepared by using thermal evaporation method and observed that at 400ºC single phase CTSe structure was attained. Growth temperature was varied between 325º–425ºC for which the band gap was varying from 0.84 to 2.1 eV.10).

Zeguo et al studied the formation of secondary phases like $Cu_{2-x}Se$ and SnSe in CTSe thin films. It was concluded that the increment in Cu/Sn ratio caused increment in $Cu_{2-x}Se$ phase. Higher carrier concentration was attributed to the formation of $Cu_{2-x}Se$ phase 11). Naji et al studied the influence of annealing temperature and thickness on the physical properties of CTSe thin films. Grain size was found to be increased with increasing the thickness, which decreased on increasing the annealing temperature 12). This work presents the preparation of Cu-Sn-Se precursor in the form of CTSe thin films employing RF sputtering and thermal evaporation method. During deposition ratio of elemental precursors was controlled to obtain the desired stoichiometry at a constant temperature of 100ºC.

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2. Experimental

Stacked layers containing Cu-Sn-Se were grown on Si-wafer and Soda lime glass substrates by means of RF sputtering and thermal evaporation methods. The substrates were immersed firstly in acetone and ultrasonically cleaned for 10 minutes. Afterward the substrates were kept in hot bath for 10 minutes and then were cleaned by using DI water. Thin films of Cu of thickness 127.4 nm was fabricated by RF sputtering method with maintaining the base pressure of the chamber 1.73×10^{-5} mbar using Argon as sputtering gas with flow rate of 15.0 sccm. The sputtering power was 70 watt during the deposition of Cu and deposition rate was 1.2 Å/sec at substrate temperature of 100ºC. Then the samples were cooled to room temperature in vacuum and shifted to thermal evaporation set- up where Sn and Se were deposited by employing the thermal-evaporation method (Model BC-300 HHV). The chamber was evacuated to the pressure of 1.5×10^{-5} mbar. The deposition rate for Sn (109.6 nm) was 0.9 Å/sec while for Se (236.9 nm) it was 9.2 Å/sec while the substrate temperature was again maintained at 100ºC. To obtain the uniform deposition the substrate plate was rotated at constant rate of 10 rpm throughout the deposition process. These as-deposited stacked layer of thin films were annealed in vacuum (Cast n’ Vac 1000 (Buehler)) at two different temperatures of 200ºC and 500ºC with holding time of 30 minutes and heating rate of 10ºC/min.

3. Results

3.1. XRD data analysis

X-ray diffraction data analysis was carried out using X’pert Pro X-ray Diffractometer model XPERT-PRO, with CuK$_\alpha$ radiation (1.540598Å) in the range of 2ϴ degree from 20.0150º to 89.9750º in the steps of 0.03º with a counting time of 0.7s. Working voltage and acceleration current were 45kV and 40mA, respectively.

XRD pattern of as-deposited stack of elemental precursor of Cu, Sn and Se is presented in Fig. 1. Five main peaks at 2ϴ=27.15º, 37.12º, 40.16º, 43.79º and 55.99º corresponding to d-spacing values of 3.2819Å, 2.4198Å, 2.2438Å, 2.0657Å and 1.6412Å were observed and attributed to the (20-2), (025), (31-2), (224)and (40-4) planes belonging to Cu_2SnSe_3.13) However, appearance of peak at (110) is due to Se with d- spacing of 1.9107 Å.14).

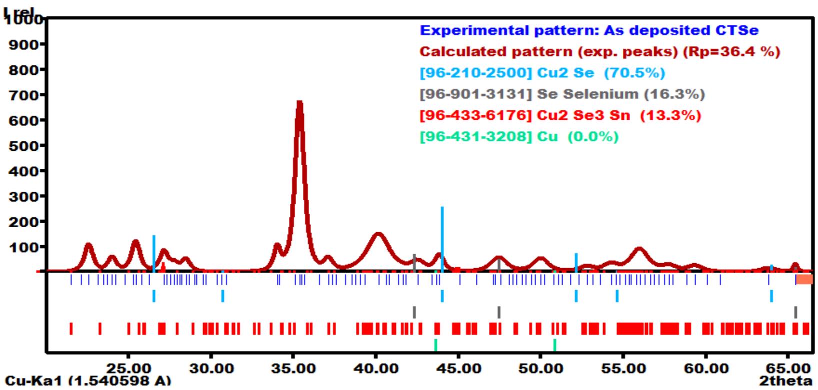


Fig.1. XRD pattern of as –deposited stacked layers of Cu-Sn-Se.

Cu_2SnSe_3 is formed of 13.3% in the as deposited stacked layers containing Cu-Sn-Se. Some other phases like Cu_2Se, Cu and Se are also formed during the deposition of stacked layers. Se is founded in the as- deposited sample in 16.3%. Cu_2SnSe_3 is found in monoclinic structure in the as-deposited sample while Cu_2Se is found in cubic structure. It is observed from the XRD analysis that Cu_2Se phase is found in maximum percentage of 70.5 % in the as- deposited sample.

Table 1 lists the unit cell dimensions and other structural information studied from the XRD curve plotted above.

Table1. Structural parameters of as-deposited stacked layers of Cu-Sn-Se.

Empirical formula	Crystal system	Space Group	Unit Cell dimension (Å)	I/I_c	c/2a	Density gm/cm^3	Wyckoff positions			
								X	Y	Z
Cu	Cubic	F m -3 m	a= 3.591	11.88	0.5	9.112	Cu	0.00	0.000	0.000
Se	Trigonal	R-3 m	a= 3.829 c= 2.790	10.29	0.36	11.100	Se	0.000	0.000	0.000
Cu_2Se	Cubic	F 2 3	a= 5.816	9.25	0.5	7.084	Cu Cu Se	0.33 0.67 0.00	0.33 0.67 0.00	0.33 0.67 0.00
Cu_2SnSe_3	Monoclinic	C1 c 1	a= 6.971 b= 12.078 c= 13.393 (β=99.96º)	6.563	0.96	5.770	Cu Cu Sn Se Se Se	0.23 0.74 0.25 0.05 0.04 0.30	0.082 0.086 0.250 0.425 0.082 0.2540	0.006 0.005 0.00 -0.051 0.058 0.190

XRD pattern of annealed stacked layers of Cu-Sn-Se at 200ºC has been shown in fig. 2. It can be profound from the study of XRD pattern that the sample annealed at 200º C exhibited various phases like Cu_2SnSe_3, SnSe, Se, Cu_3Se_2, Cu_2Se and $Cu_5Sn_2Se_7$.Peaks at 26.37º and 43.31º belongs to $Cu_{2.0}Se$ with hkl parameters (111) and (200) and d- spacing of 3.3771Å and 2.0874Å respectively. 15) A minor peak at 21.51º corresponds to SnSe with hkl plane of (021) 16). The most intense peak found at 35.59º belongs to $Cu_5Sn_2Se_7$ phase with d- spacing of 2.5208Å.17)

It could be shown that annealing of the as deposited stacked layers at 200º C reduced the amount of the phase of Cu_2SnSe_3 as comparing to the as deposited precurors. The dominating phase in the annealed stacked layer at 200º C is SnSe with 24.2 %.

Structural properties including the wyckoff positions of atoms of the phases present in annealed sample at 200ºC have been presented in Table 2.

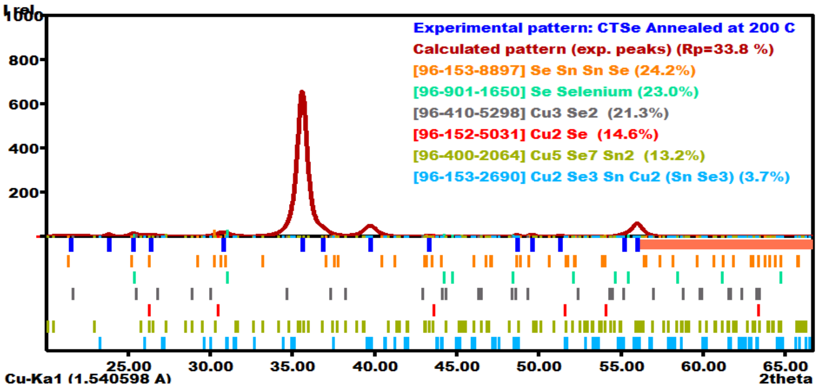


Fig.2. XRD pattern of stacked layer of Cu-Sn-Se annealed at 200º C.

Table 2. Structural parameters of stacked layers of Cu-Sn-Se annealed at 200º C.

Empirical formula	Crystal system	Space Group	Unit Cell dimension (Å)	I/Ic	c/2a	Density gm/cm^3	Wyckoff positions	X	Y	Z
SnSe	Orthorhombic	P n m a	a=11.570 b= 4.190 c = 4.460	9.35	0.192	6.072	Sn Se	0.855 0.118	0.250 0.250	0.479 0.103
Se	Trigonal	P 3121 (152)	a= 4.052 c= 5.038	9.90	0.624	5.491	Se Cu	0.237 0.370	0.000 0.418	0.333 0.116
Cu_2SnSe_3	Monoclinic	C 1 c 1	a= 6.967 b= 12.049 c= 6.945 β= 109.19º	6.45	0.498	5.822	Cu Sn Se Se Se	0.371 0.363 0.503 -0.026 0.000	0.257 0.091 0.259 0.078 0.409	0.616 0.107 -0.014 -0.015 0.00
Cu_3Se_2	Tetragonal	P- 4 2 1 m	a= 6.60 c= 4.102	3.96	0.310	6.362	Cu Cu Se	0.00 0.353 0.199	0.00 0.853 0.699	0.00 0.250 0.676
Cu_2Se	Cubic	F m- 3 m	a= 5.8707	6.49	0.5	6.764	Cu Se	0.30 0.00	0.30 0.00	0.308 0.00
$Cu_5Sn_2Se_7$	Monoclinic	C 1 2 1	a= 12.65 b= 5.664 c= 8.931 β= 98.125º	6.59	0.3530	5.807	Cu Cu Cu Sn Se Se	0.00 0.144 0.712 0.925 0.777 0.077	0.264 0.256 0.268 0.776 0.027 0.027	0.500 0.268 0.642 0.776 0.860 0.860

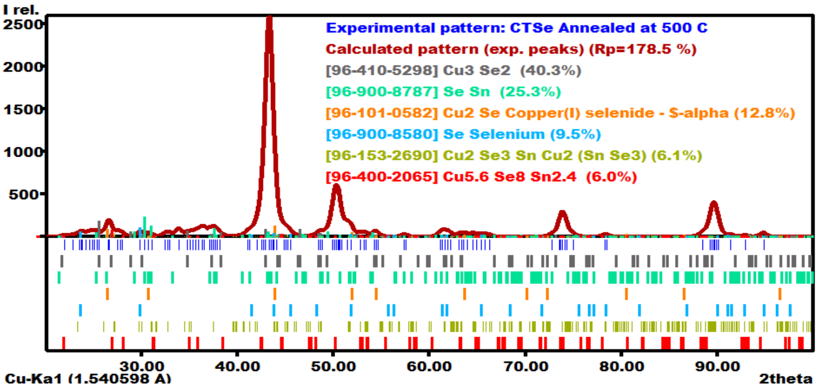


Fig.3. XRD pattern of stacked layer of Cu-Sn-Se annealed at 500° C.

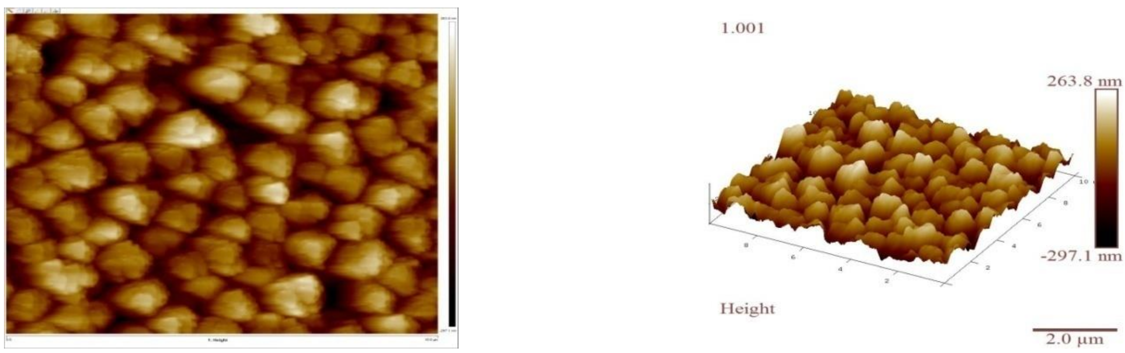
Table. 3. Structural parameters of stacked layer of Cu-Sn-Se annealed at 500° C.

Empirical formula	Crystal system	Space Group	Unit Cell dimension(Å)	I/Ic	c/2a	Density gm/cm^3	Wyckoff positions			
								X	Y	Z
SnSe	Orthorhombic	P b n m	a = 4.460 b= 11.570 c = 4.190	8.08	0.500	6.073	Sn Se	0.103 0.479	0.118 -0.145	0.250 0.250
Se	Trigonal	P 32 2 1	a= 4.355 c= 4.949	8.67	0.567	4.832	Se	0.217	0.000	0.167
Cu_2SnSe_3	Monoclinic	C 1 c 1	a = 6.967 b= 12.049 c= 6.945 β= 109.19°	6.45	0.498	5.822	Cu Cu Sn Se Se Se	0.370 0.371 0.363 0.503 -0.026 0.000	0.418 0.257 0.091 0.259 0.078 0.409	0.116 0.616 0.107 -0.014 -0.015 0.000
Cu_3Se_2	Tetragonal	P- 4 2 1 m	a= 6.60 c= 4.102	3.96	0.310	6.362	Cu Cu Se	0.000 0.353 0.199	0.000 0.853 0.699	0.000 0.250 0.676
Cu_2Se	Cubic	F 2 3	a= 5.840	8.48	0.5	6.872	Cu Cu Se	0.33 0.667 0.00	0.33 0.667 0.000	0.33 0.667 0.00
$Cu_{5.6}Sn_{2.4}Se_8$	Tetragonal	I – 4 2 m	a= 5.747 c= 11.455	11.28	0.996	5.583	Cu Cu Cu Sn Sn Se	0.000 0.000 0.000 0.000 0.000 0.257	0.000 0.000 0.500 0.000 0.500 0.257	0.000 0.500 0.250 0.500 0.250 0.372

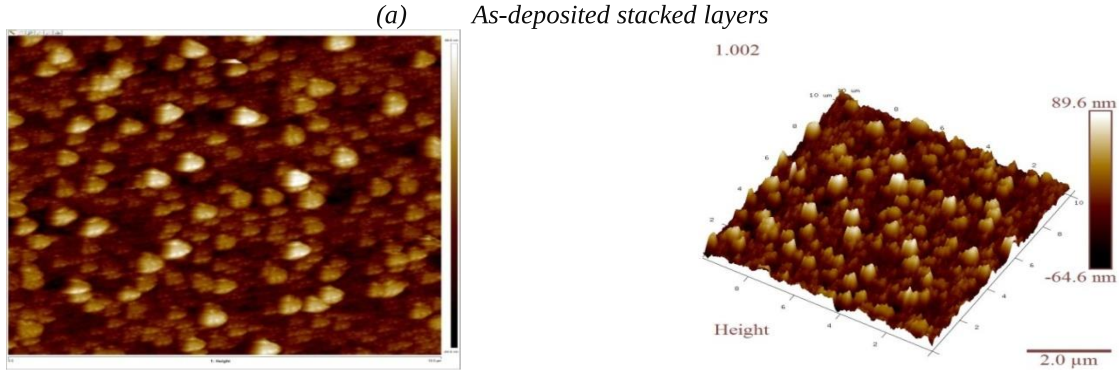
Fig. 3 represents the X-ray diffraction pattern of stacked layers annealed at 500° C. Sample annealed at 500°C exhibited the phases of Cu_3Se_2, SnSe, Se, Cu_2Se, Cu_2SnSe_3 and $Cu_{5.6}Se_8Sn_{2.4}$. Main peaks at 2ϴ= 35.88° and 42.49° belongs to $Cu_{5.6}Se_8Sn_{2.4}$ 17). $Cu_{5.6}Sn_{2.4}Se_8$ is found in tetragonal structure of space group of I-42 m. Wyckoff positions of atoms are shown in table 3. However appearance of peaks at 43.45° confirmed the formation of SnSe exhibiting d-spacing of 2.0810 Å of (hkl) planes (002) 18). Table 3 accounts the unit cell dimensions and Wyckoff positions of atoms of different phases present in the sample annealed at 500°C. It can be concluded that stacked layers of Cu-Sn-Se annealed at 500º C consist of a mixture of amorphous and crystalline phases. The stacked layer annealed at 500º C exhibited Cu_2SnSe_3 in monoclinic structure with C 1 c 1 space group and it is formed in 6.1%. 19)The dominating phase found after annealing at 500º C is Cu_3Se_2.

3.2. Analysis of AFM results

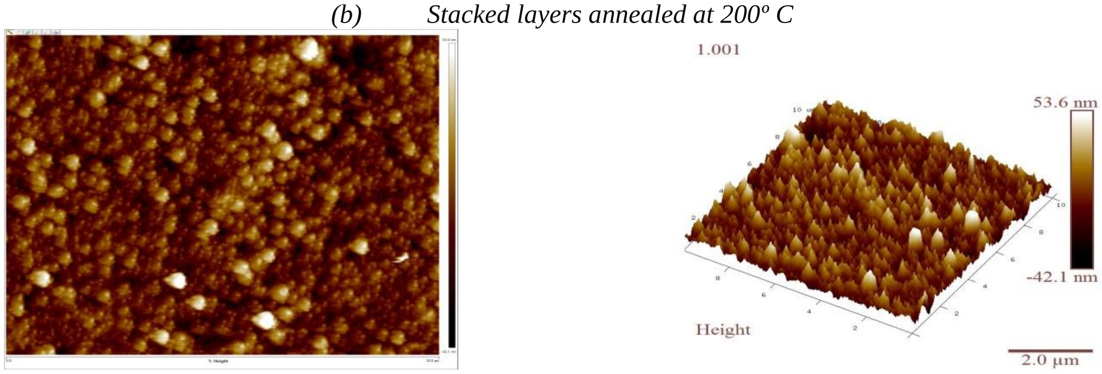
Surface features have been analyzed using the atomic force microscopy (AFM) images shown in Figs.4 (a-c). These show that the surface of the film annealed at 500ºC is exhibiting the smoother surface than others (represented by average roughness R_a values). This is because with increment in annealing temperature particles achieve enough energy to consolidate and distribute homogenously in all directions. Table 4 shows various parameters obtained from AFM results, which are as (i) Stress fracture: described by kurtosis parameter (R_{ku}) which represents the distribution of spikes about the mean line. Roughness kurtosis R_{ku} is more than 3 for spiky surfaces while it is less than 3 for bumpy surfaces; it is exactly equal to 3 for perfectly smooth surfaces. R_{ku} is found to be more than three for CTSe films annealed at 200°C and 500°C which shows that the sample exhibited the spiky surface as the distribution has relatively higher numbers of highest peaks and lowest valleys 20, 21). (ii) Average Roughness R_a which shows the mean height with respect to reference plane is found minimum for sample annealed at 500ºC revealing it a better surface than the other samples.



(a) As-deposited stacked layers



(b) Stacked layers annealed at 200º C



(c) Stacked layers annealed at 500º C

Fig.4. 2-D and 3-D AFM images of stacked layers containing Cu-Sn-Se.

(iii)The skewness is enumerated by R_q (root mean square roughness) which outlines the square root of the distribution of surface height and the finish of optical surface. As deposited sample exhibited the value of R_q as 80.5 nm which reduced with the increment in annealing temperature.(iv) The difference between five highest peaks and lowest peaks in surface profile is symbolized by R_z (Ten- points mean height roughness). The value of R_z for the as-deposited sample is found 583 nm and a decrement in this parameter has been observed with the increment in annealing temperature. (v) R_{sk} (Roughness skewness) represents symmetry of surface about the mean line plane, found maximum for the sample annealed at 200ºC which is the measurement of porosity and load carrying capacity 1, 2).

Table 4. Comparative analysis of AFM parameters of stacked layers with respect to annealing temperature.

	R_a (nm)	R_q (nm)	R_z (nm)	R_q/R_a	R_{ku}	R_{sk}
As deposited	64.3	80.5	583	1.251	2.93	-0.275
Annealed at 200º C	16.8	21.7	198	1.2916	3.81	0.850
Annealed at 500º C	10	13	190	1.3	4.34	0.694

3.3. Hall Effect analysis

Electrical properties of the stacked layers containing Cu, Sn and Se were investigated at room temperature by Hall Effect measurements. In a four probe technique current is applied across two probes while potential difference is measured across two another probes, as shown in Fig.5.

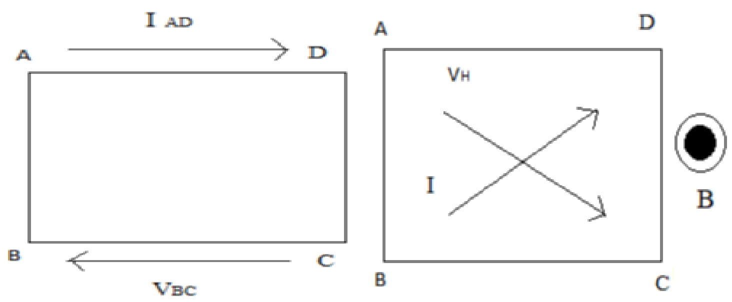


Fig. 5. Current node arrangement for Hall measurement 20).

A constant magnetic field is applied perpendicular to the direction of flow of current in the sample and variation in hall voltage is measured between the contacts 22).Hall measurements were performed by applying magnetic field of 0.5T strength. These measurements shows that n- type Cu_2SnSe_3 has been obtained having, resistivity and mobility of $3.1263\times 10^{-3}\Omega\cdot$cm and 1.4841 $cm^2/(V.s)$, respectively.

Table 5. Comparison of electrical parameters with respect to annealing temperature

Sample	Resistivity (Ω.cm)	Mobility ($cm^2/(V. s)$)	Carrier Concentration (cm^{-3})
As deposited	3.1263×10^{-3}	1.4841	5.3230×10^{21}
Annealed at 200° C	3.457×10^{-3}	3.8745	5.3258×10^{21}
Annealed at 500° C	2.9295×10^{-3}	4.1187	6.1820×10^{22}

The resistivity varied from 2.93×10^{-3} to 3.457×10^{-3} Ω.cm showing minimum for the sample annealed at 500º C. Mobility varied in the range from 1.4 to $4.1cm^2/(V.s)$. Carrier concentration has been found $5.3230\times 10^{21}cm^{-3}$ for as deposited which increased upto 6.1820×10^{22} cm^{-3} for the sample annealed at 500º C. These parameters have been shown in table 5.

From the results shown in aforementioned table 5, it could be revealed that the sample annealed at 500ºC exhibited the lowest value of electrical resistivity, this drastical change and decrement in the value of electrical resistivity shows the presence of some other phases which could be said as impurity making it a extrinsic semiconductor 23).

4. Conclusion

The effect of annealing temperature on structural and electrical properties of multilayer structure Cu-Sn-Se has been studied in this work. The XRD results revealed that with the annealing of the multilayer structure at two different temperatures, some secondary phases have been developed, along with the Cu_2SnSe_3 phase. Cu_2SnSe_3 phase is formed in monoclinic structure with the space group of C 1 c 1.While the AFM results revealed that roughness is minimum for stacked layers annealed at 500º C having spiky surface. Hall measurements showed that the carrier concentration increased with the increment in the annealing temperature.

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