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Review Article

Structural and Optical Properties of Nanocrystalline Cu_xS Solid Thin Films

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Abstract

Copper sulphide thin films were deposited by chemical bath deposition method at 65°C. These were then annealed at 100°C and 200°C. All films exhibit nanocrystalline nature, having Chalcosite low phase, with grain size ranging from a minimum of 5.71nm to maximum of 30.67nm. Effect of annealing shows increased grain size nano-thin film formation. Optical properties show that films can find application in optoelectronic devices as band gap ranging between minimum of Eg = 2.64 eV to highest of 2.92 eV. AFM studies shows that nanothin film formed has spiky and bumpy surfaces.

Keywords: Copper sulphide; Chemical bath deposition; Thermal annealing; XRD; Optical properties

Introduction

It is found that Cu_xS thin films act as p-type semiconductor material mainly due to that of copper vacancies occurring within the lattice [1,2] and its variable property exhibition depending upon the stoichiometry, $1 \leq x \leq 2$. Due to variable optical and electrical properties this found to have many potential applications in various fields as in solar cells, fluorescent devices [3-10], photo thermal conversion of solar energy, microwave shielding coatings, electro conductive electrodes, catalyst [11-14], selective radiation filters, photodetectors, as polarizers of infrared radiation [15], active absorbent of radio waves [16], semiconductors, electroconductive coatings, low temperature gas sensor applications [17], field emission [18], switching [19], sensing devices [20], themoreflecting coatings [21], eyeglass coatings, anti reflecting coatings [22], thermoelectric cooling materials [23], optical filters, optical recording materials, nanoscale switches, and superionic materials [24] etc. Copper sulphide at room temperature occurs in five stable phases namely: *covellite* ($Cu_{1.00}S$), *anilite* ($Cu_{1.75}S$), *digenite* ($Cu_{1.80}S$), *djurleite* ($Cu_{1.97}S$), and *chalcocite* ($Cu_{2.00}S$). Other phases that exist include *yarowite* ($Cu_{1.12}S$) and *spionkopite* ($Cu_{1.14}S$).

It has been found that $Cu_{2-x}S$ exists in four crystallographic modifications. The monoclinic phase, low-chalcocite (αCh) is stable up to temperatures between 90 - 104°C, depending on the chemical composition x's. Above 90°C, the hexagonal phase, high-chalcocite (βCh) is stable. At a composition close to $x = 0$, this phase is stable up to 435°C. The third, cubic phase called digenite (Dg-$Cu_{2-x}S$), stable between temperatures of 72 - 1130°C. The fourth crystallographic modification being orthorhombic phase denoted as djurleite (Dj), which is stable up to a temperature of 93°C. The compound Cu_7S_4 denoted as anilite (An) is stable up to 75°C. The copper sulfide, CuS (covellite, Cv), is stable up to a temperature of 507°C. Several phases of copper sulfides are metastable, but these may convert to the thermodynamically more stable ones. For example, after a few hours, the high digenite ($Cu_{1.80}S$) began to convert into the low digenite ($Cu_{1.765}S$), which in turn, converts to anilite ($Cu_{1.75}S$) [25,26]. At 41°C, anilite decomposes into CuS and low digenite, whereas low digenite transforms into high digenite around 82°C [25,27].

For reproducing copper sulphide thin films, chemical bath deposition method is being opted, because it is a low cost simple method, a large area of deposition is available which can occur at a low temperatures. Principle of CBD method follows a controlled chemical reaction which eventually leads to deposition of thin film by precipitation. CBD method involves specified reaction conditions, which generally involves substrates immersed in a beaker having an alkaline solution containing chalcogenide source ions, metal ions and added base, where complexing agent is being added to control release of metal ion. This process itself depends on various parameters like ionic product, solubility product, super saturation, type of precipitation etc.

In the present paper, an attempt is made to deposit nano crystalline thin film of copper sulphide on glass substrates by chemical bath deposition method. Effect of variation in chemical bath composition on the structural and optical properties has been studied specifically for as-deposited and post deposited thermal annealed thin films.

Experimental Details

Preparation of Glass Substrate

For deposition of thin film, glass substrate (micro slides – 75mm L × 25 mm wide) were taken. Pretreatment of glass substrate follows:-

- Wash with normal water 2 - 3 times
- Soak them in chromic acid for 48 hrs. – 120 hrs.
- Boil them for one hour in chromic acid itself.
- Wash by deionised water several times.
- Washing them with detergent solution.
- Then Micro slides cleaned with tap water and further by deionised water.
- Degreased with ethanol, washed with deionised water in ultrasonicator and air dried.

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- Eventually preheat the slides in the oven before use.

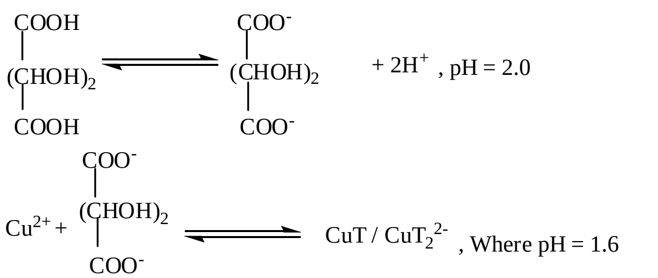
Preparation of CuS thin film

To prepare Copper sulphide thin films, 10 ml of 0.1 M $CuSO_4.5H_2O$ (Cu^{2+} ion source) and 10 ml of 0.1 M $C_4H_6O_6$ (being used as complexing agent) were taken in 50 ml beaker. After constantly stirring for 5 min, add 1 ml NH_3 and 3ml or 4ml of TEA concentration, to obtain reaction pH maintained 9.2 ± 0.1. Other than for maintaining optimum pH for reaction bath, the concentration of TEA was varied over a wide range and optimized condition was found to be 3 ml and 4 ml for adherent and uniform thin film deposition. This followed by addition of 10 ml of 0.1 M $(NH_2)_2CS$ (S^{2-} ion source). Stir the solution for 20 to 25 min. Keep the reaction mixture in a water bath at 65°C with vertically placed slides in it. After 180 mins, slides were taken out from reaction bath (the temperature and deposition time being controlled over for good deposition of thin film on glass substrate and optimum condition found for stable adherent film deposition). The slides which were taken out washed with deionised water and air dried. Out of two sets of slides (three slides each), one slides restored as-deposited slides, other two annealed at 100°C, 200°C for an hour in the oven. The slides, S1 and S4 being as-deposited / 180 min for 1:3 and 1:4 ratio of NH_3: TEA, S2 and S5 are being their annealed samples at 100°C and S3 and S6 annealed sample at 200°C.

Mechanism of thin film formation

The growth mechanism is proposed by the following reaction steps:

$$CuSO_4.5H_2O \longrightarrow Cu^{2+} + SO_4^{2-} + 5H_2O \text{ , Where pH = 4.1}$$



With addition of NH_3 and TEA, pH of chemical bath was maintained at 9.2 ± 0.1. When the pH increases, there is an increasing tendency for the formation of mixed ligand complexes or hydroxyl complexes. With copper cations, this equilibrium can be expressed by the following equilibriums:-

$$Cu^{2+} + 2\,OH^- + 2\,T^{2-} \rightleftharpoons CuT_2(OH)_2^{4-}$$

Other than above complex, TEA and NH_3 form complex with availability of free copper ions present in reaction bath, as both TEA and NH_3 have tendency to act as complexing agent also. Thus helps in reduced growth phase of the thin film or controlling the concentration of free Cu^{2+} ions.

$$Cu^{2+} + 4\,(NH_3) \longrightarrow [Cu(NH_3)_4]^{2+}$$

$$Cu^{2+} + n\,(TEA) \longrightarrow [Cu(TEA)_n]^{2+}$$

Therefore tartaric acid, TEA and NH_3 results in the coexistence of different copper complexes in the bath.

Eventually with addition of thiourea in the reaction mixture, can result in following reactions:-

$$(NH_4)_2CS + OH^- \longrightarrow CH_2N_2 + HS^- + H_2O$$

$$HS^- + OH^- \longrightarrow S^{2-} + H_2O$$

This result in following cases of copper sulphide thin film formation:-

$$CuT + S^{2-} \longrightarrow CuS + C_4H_4O_6^{2-}$$

$$CuT_2^{2-} + S^{2-} \longrightarrow CuS + 2T^{2-}$$

$$[CuT_2(OH)_2]^{4-} + CS(NH_2)_2 \longrightarrow Cu_xS + 3H_2O + OC(NH_2)_2 + \text{By Products}$$

$$[Cu(NH_3)_4]^{2+} + CS(NH_2)_2 + 2OH^- \longrightarrow CuS + NH_3 + CN_3H_5 + H_2O$$

$$[Cu(TEA)_n]^{2+} + CS(NH_2)_2 + OH^- \longrightarrow Cu_2S + (NC\text{-}NH_2) + 2H_2O$$

$$[Cu(TEA)_n]^{2+} + CS(NH_2)_2 + OH^- + H_2O \longrightarrow CuS + OC(NH_2)_2 + nTEA + 3H_2O$$

Characterization of thin film

The X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the thin films using a Bruker D8 advance X ray diffractometer with CuKα radiation (40 kV and 40 mA) with λ = 1.54 Å for 2θ° values over 20°–80°. The surface morphology and topography of CuS thin film were examined using atomic force microscopy (AFM) having details as AFM model-NSE (Nano scope-E), AFM mode-Contact mode AFM, Tip Material-Si_3N_4 (Silicon Nitride). Optical absorption data were obtained with a Cary Bio 50 Varian UV–Vis spectrophotometer at normal incidence of light in the wavelength range of 200-1000 nm. Thickness measurements of thin film were done by surface profiler.

Results and Discussion

XRD Studies

The X-ray diffraction was carried out for six samples, respectively, as-deposited and annealed (at 100°C, 200°C) of thin films and their diffractograms being shown respectively in Figure I (a) and (b). Sample S1 shows orthorhombic Cu_2S phase of copper sulphide, but shows very small peaks, but two peaks clearly identified. The peaks at angles 2θ°, reflection from crystal peaks from corresponding standard 2θ° as from JCPDS card being shown in Table I. From this it's been found that annealing effectively increases crystalline nature of thin films. Table II shows the average grain size calculated by:-

$$D = 0.9\lambda / \beta \, Cos\, \theta \qquad \ldots (1)$$

Average Micro strain

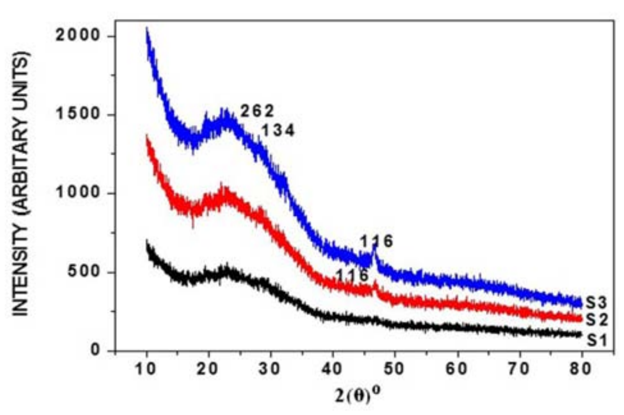


Figure 1 (a): XRD pattern of as-deposited, annealed (100°C, 200°C) copper sulphide thin films with 3 ml TEA, 180 min deposition time.

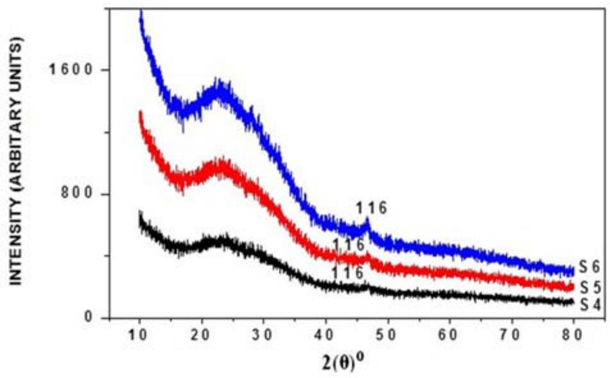


Figure 1(b): XRD pattern of as-deposited, annealed (100°C, 200°C) copper sulphide thin films with 4 ml TEA, 180 min deposition time.

Table I: Comparison of observed XRD data of thin films with the JCPDS cards (Cu_2S: 23-0961).

S.No.	Sample	Obs. 2θ°	Std.2θ°	*hkl planes*	*Phase and System*
1	S 1	*28.333* *37.452*	*28.309* *37.506*	*421* *1 11 1*	*Cu_2S Orthorhombic*
2	S 2	*46.111*	*46.559*	*116*	*Cu_2S Orthorhombic*
3	S 3	*28.014*	*28.026*	*262*	*Cu_2S Orthorhombic*
		32.375	*32.472*	*134*	
		46.314	*46.559*	*116*	
4	S 4	*46.341*	*46.559*	*116*	*Cu_2S Orthorhombic*
5	S 5	*46.503*	*46.559*	*116*	*Cu_2S Orthorhombic*
6	S 6	*46.588*	*46.559*	*116*	*Cu_2S Orthorhombic*

Table 2: Showing 2θ°, d-spacing, average crystallite size, dislocation and micro strain of sample S 1 – S 6 thin film.

I	II	III	IV	V	VI	VII
Sample. No.	**Obs 2-theta**	**Standard 2-theta**	**d-spacing**	**Grain Size D (nm)**	**Dislocation density (δ) ×10^{14} Line's m^{-2}**	**Microstrain (ε) ×10^{-3}**
S1	-	-	-	-	-	-
S2	*46.111*	*46.559*	**1.95**	**11.82**	**7.16**	**7.41**
S3	*28.014*	*28.026*	**1.96**	**7.15**	**19.58**	**12.33**
S3	*32.375*	*32.472*	**3.18**	**14.59**	**4.7**	**9.81**
S3	*46.314*	*46.559*	**5.53**	**5.71**	**30.67**	**21.77**
S4	*46.341*	*46.559*	**1.96**	**3.15**	**7.1**	**28.06**
S5	*46.503*	*46.559*	**1.95**	**30.60**	**1.07**	**2.89**
S6	*46.588*	*46.559*	**1.95**	**36.97**	**7.3**	**2.37**

$$\xi_{Strain} = \beta / 4\tan\theta \qquad \ldots (2)$$

Dislocation density (lines m^{-2}) by Williamson Smallman's formula

$$\delta = 1/D^2 \qquad \ldots (3)$$

D-Spacing by Bragg's equation

$$n\lambda = 2d\ Sin\ \ \theta \qquad \ldots (4)$$

Optical Studies

From Figure II (a) and (b) absorbance decreases in order of *S 2 > S 1 > S 3* and *S 4 > S 5 > S 6* respectively, while % transmittance decreases in order of *S 3 > S 2 > S 1* and *S 6 > S 5 > S 4.* The optical band gap has been found to be 2.92eV, 2.8eV, 2.64eV, 2.9eV, 2.94eV, 2.9eV as for S 1- S 6 samples individually as shown in Figure II (c) and (d), having thickness of film 150 nm, 20 nm, 15 nm, 200 nm, 70 nm, 20 nm in the order of samples for S 1, S 2, S 3, S 4, S 5, S 6 respectively. On the basis of absorbance variation the annealed samples can be effective in reducing solar reflectance side by side helps in increasing transmittance, and can prove to be an effective material for AR coatings. The decrease in value of band gap shows the transition of poor crystallinity towards polycrystalline nature that is annealed sample being more crystalline as compared to as-deposited samples.

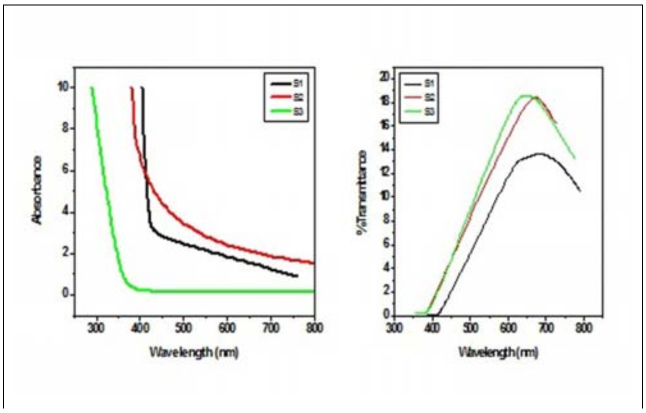


Figure2 (a): Absorbance and % transmittance of S 1-S 3 copper sulphide thin films.

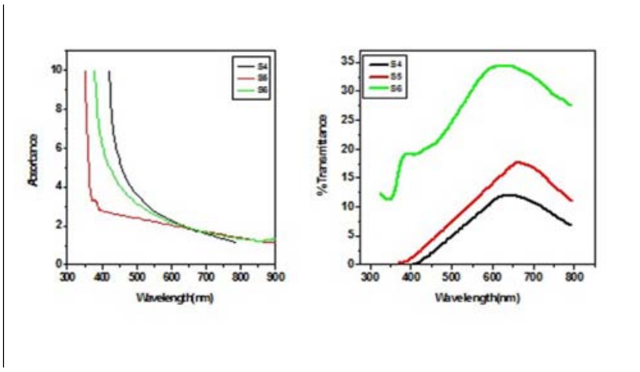


Figure 2 (b): Absorbance and % transmittance of S 4 -S 6 copper sulphide thin films.

AFM Studies

AFM studies reveal that annealed samples have greater surface quality as compared to their as-deposited samples as shown in Table III, RMS roughness of thin film increases on annealing showing that grain size increases after annealing process [28,29]. S1 and S2 have spiky surface as $R_{ku} > 3$, while on greater annealed temperature film shows the bumpy surface as $R_{ku} < 3$ i.e S3. The surface profile picture of S1, S2, S3, shows that size of particles is nanoparticles. S4 sample having good bearing surface as have negative skewness, while S5 sample has a large number of spikes all over the surface also been cleared by value of R_{ku} being 16.82, as well from 3D picture also $R_{sk} > 3$ [30], while S6 has highest RMS roughness, has the best surface quality

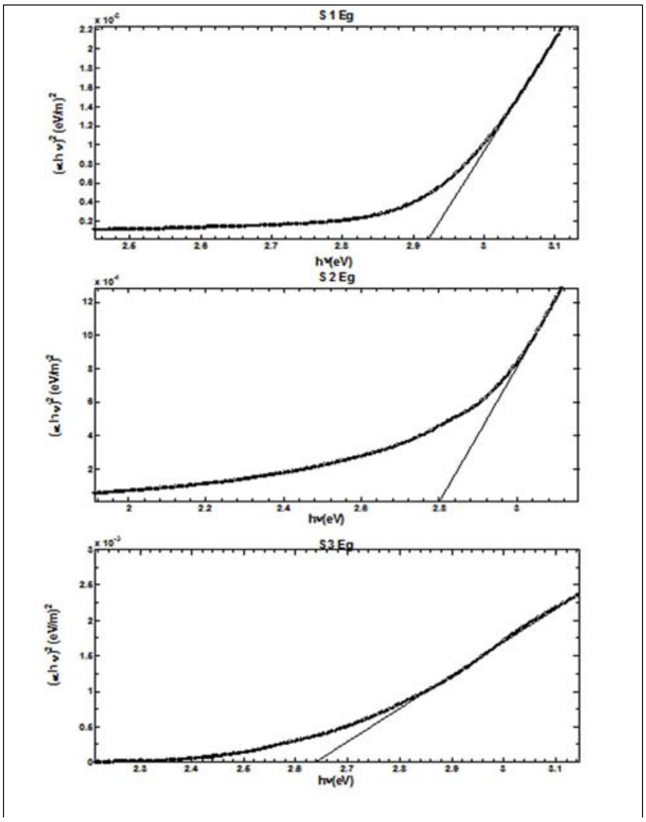


Figure 2(c): Optical Band Gap (Eg) for S 1 – S 3 copper sulphide thin films.

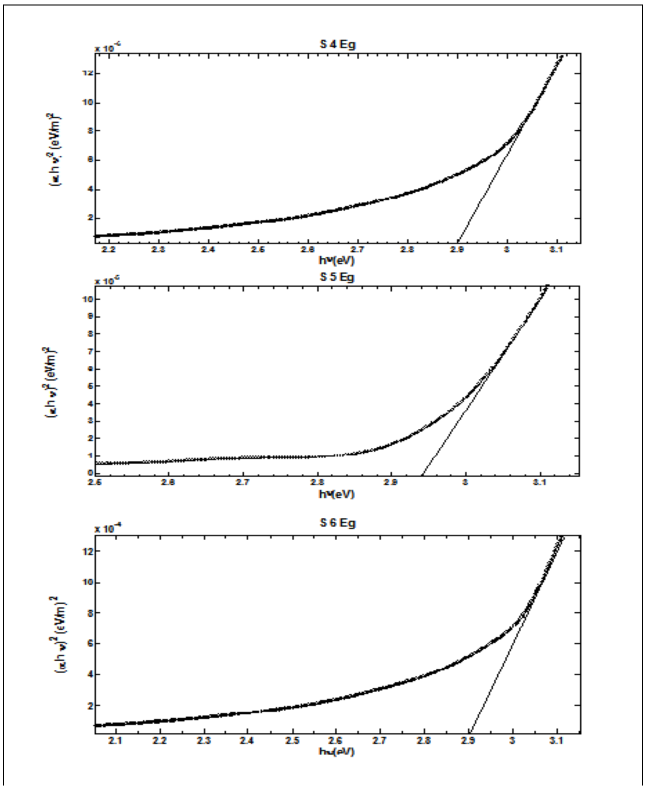


Figure 2 (d): Optical Band Gap (Eg) for S 4 – S 6 copper sulphide thin films.

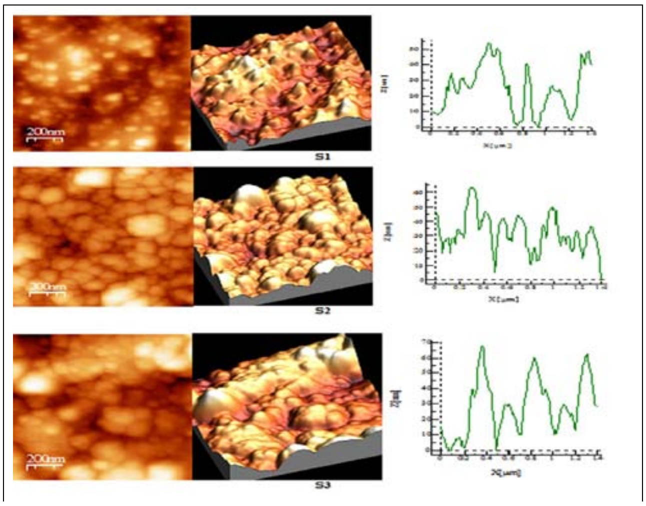


Figure 3 (a): AFM study of S 1-S 3 copper sulphide thin films.

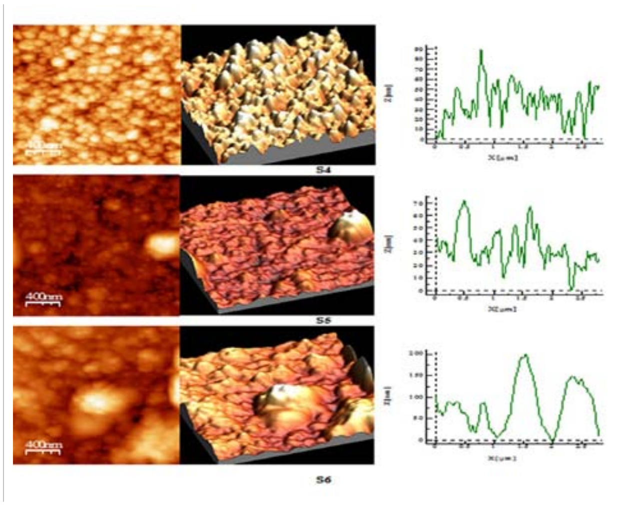


Figure 3 (b): AFM study of S 4-S 6 copper sulphide thin films.

Table 3: Showing RMS roughness, surface skewness and surface kurtosis of sample S 1 – S 6.

I	II	III	VI	V
S. No.	**Sample**	**RMS (root mean square) Roughness**	**Surface Skewness ($R_{sk)}$**	**Surface Kurtosis ($R_{ku)}$**
1	S 1	14.97	0.59	3.08
2	S 2	18.72	0.67	3.69
3	S 3	26.85	0.37	2.47
4	S 4	18.84	-0.005	2.84
5	S 5	28.60	3.15	16.82
6	S 6	44.62	0.86	3.76

among all, having spiky surface $R_{ku} > 3$.

Conclusion

It is seen that bath composition effectively help in increasing the band gap, and that annealing also help to improve the structural and optical properties of thin film. Here it also been observed that concentration ratio of NH_3: TEA effect deposition of thin film on substrate. Higher concentration of NH_3 more than 1ml, and TEA concentration more than 4- 5 ml result in poor deposition of thin film on glass substrate.

As compared to the as-deposited thin films, annealed samples showed increased crystallinity. The AFM study shows that on annealing, the surface roughness increases, which explain that coalescence of grain, occur after annealing at higher temperatures. The band gap decreases on annealing in some samples which shows that on annealing crystallinity of thin film increases.

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