OPTICAL CHARACTERIZATION QUATERNARY THIN FILM OF COPPER CHROMIUM TIN SULPHIDE

PRESENTED By

Oyiogu Agatha Uju; PROF AARON EZE; PROF M.N. NNABUCHI.

NIP 44TH ANNUAL CONFERENCE LAGOS

11TH MAY, 2023

ABSTRACT

- Copper zinc tin sulfide (Cu_2ZnSnS) is emerging as an alternative light absorbing material to the present thin film solar cell technologies such as cu,In,ga)Se2 and cdte. All the elements in CZTS are abundant, environmentally friendly, and inexpensive. In addition, CZTS has a band gap of ~1.5 eV, the ideal value for converting the maximum amount of energy from the solar spectrum into electricity. CZTS has a high absorption coefficient (>10^4 cm-1 in the visible region of the electromagnetic spectrum) and only a few micron thick layer of CZTS can absorb all the photons with energies above its band gap. A single-stage process of CuCrSnS thin film synthesis is presented, the chemical bath deposition technique was used to synthesize this film under a constant temperature of 68^0C, while varying the concentration and deposition time of chromium to see its effect in the optical property of the film under annealing temperature of 280^0C. It was observed that the film has high absorbance in the visible region and good energy band gap of 1.27 – 1.55 eV which is optimal for solar energy conversion to electricity. The film has high absorption coefficient at a photon energy of 1.49eV which is the maximum energy needed for solar energy conversion.

- Keyword: concentration, deposition time, band gap, optical properties

INTRODUCTION

fabrication and application of modern semiconductor devices involves thin film technology and most of the devices includes thin film as essential operational parts (ibach and luth, 2004).according to chopra and das (1983), thin films are fabricated by atom by atom molecule by molecule, ion by ion, or by cluster of species by clusters of species condensation process. some applications of thin films are as follows:

- microelectronic
- semi-conductors
- optics
- solar cell etc.

MATERIALS

- Glass slide
- A thermostatic blast resettable oven of 50^0C – 1000^0C temperature
- Magnetic stirrer
- Digital hot plate
- Digital weighing balance
- Oven, tapes, hand dryer, beakers, measuring cylinder, syringe, spatula, thermometer, pot, retort stand, stop watch, annealing dish, petri dishes.

LIST OF CHEMICALS

For the deposition of cucrsns

- Thioacetamide ($CH_3CS.NH_2$) as source of sulphur
- Copper (11) sulphate pentahydrate as source of copper
- Chromium sulphate cr $(SO_4)_3$ as source of cr
- Tin (11) chloride as source of Sn.
- hydrochloric acid
- Acetone
- Distill water
- Methanol.

METHODS

- **Preparation of substrate and measuring instrument**
- The microslide used as substrate were first soaked in hydrochloric acid for 1 hour and the dipped in acetone for 45minutes the were then removed and washed in methanol with sponge and then rinsed with distill water, there where placed in a beaker and dried in oven at 30^0C for 1 hour, after which there were brought out and allowed to cool to room temperature and them were places in film rack.
- The beakers, measuring cylinder, syringe were similarly degreased and dried in the oven 30^0c for 30 minutes and allowed to cool under room temperature before use.

Deposition of CuCrSnS

Solution was prepared by dissolving in 100ml of distilled water masses of 0.02M of copper II sulfate, different moles/concentration of chromium sulphate (0.02,0.03,0.04,0.05m), 0.05M of tin chloride and 0.02M of thiacetamide as sources of sulfur in different beaker it was first dissolved in methanol to stabilize it to prevent it forming precipitate with the precursor (subramanian et al, 2014). Each beaker was placed on a magnetic stirrer for 10minutes to ensure complete dissolution of the salt. During stirring, it was observed that the salt particles dissolved and formed a colourless solution. To grow the film, four beakers were used, beaker one had 0.02M of chromium sulphate mixed in equal volume of 20ml with other precursor solution. To beaker two 0.03m of chromium sulphate with equal volume of 20ml of other precursor beaker three 0.04M of chromium sulphate and beaker four with 0.05M of chromium sulphate with 20ml each of other precursor solution of 0.05M copper sulfate, 0.05M tin chloride, 0.02M of thiacetamide. Then cleaned glass substrates were immersed one each into each of the beaker containing the precursor solution. The beaker was then placed the chemical bath set up and thereafter heated for two hours maintaining maximum temperature of 68^0C. The same procedure was followed to prepare the solution again and allowed for 12hours under the same temperature. The samples where air dried after which it was annealed for one hour at a temperature of 280^0C. A complexing agent was not used because most of the precursor contains sulphur, so adding ammonia will make it form precipitate and the film will not deposite on the substrate.

SUMMARY OF MASSES TO BE DESOLVED IN 100ML OF WATER

REAGENTS	CONCENTRATION (Molarities) (M)	QUANTITY REQUIRED/ 100ml
copper(ii)sulphate pentahydrate	0.05	0.99 grams
Tin (ii) chloride	0.05	0.2ml
$[Cr_2(SO_4)_3.H_2O]$	0.02, 0.03, 0.04, 0.05	0.78g, 1.18g, 1.57g, 1.96g
$CH_3CS.NH_2$	0.1	0.75g

- The possible reaction mechanism for the formation of CuCrSnS is as follow:
- $CuSo_4$ —> $Cu^+ + SO_4^-$
- $Cr_2(So4)_3$ —> $2Cr^{3+} + 3SO_4^-$
- $SnCl_2$ —> $Sn^+ + Cl^{-2}$
- CH_3cCSNH_2 —> $NH_4^- + 2C^+ + H^+ + S^+$
- The overall ionic reaction is
- $Cu^+ + 2Cr^{3+} + Sn^+ + S^+$ —> $CuCr_2SnS$
- Hence the $CuCr_2SnS$ formation is according to the equation

EXPERIMENTAL OBSERVATIONS

- The deposition thickness increased with increase in deposition time.
- The colour of the annealed substrates deepens with increase in the thickness of deposited thin films.

OPTICAL CHARACTERIZATION

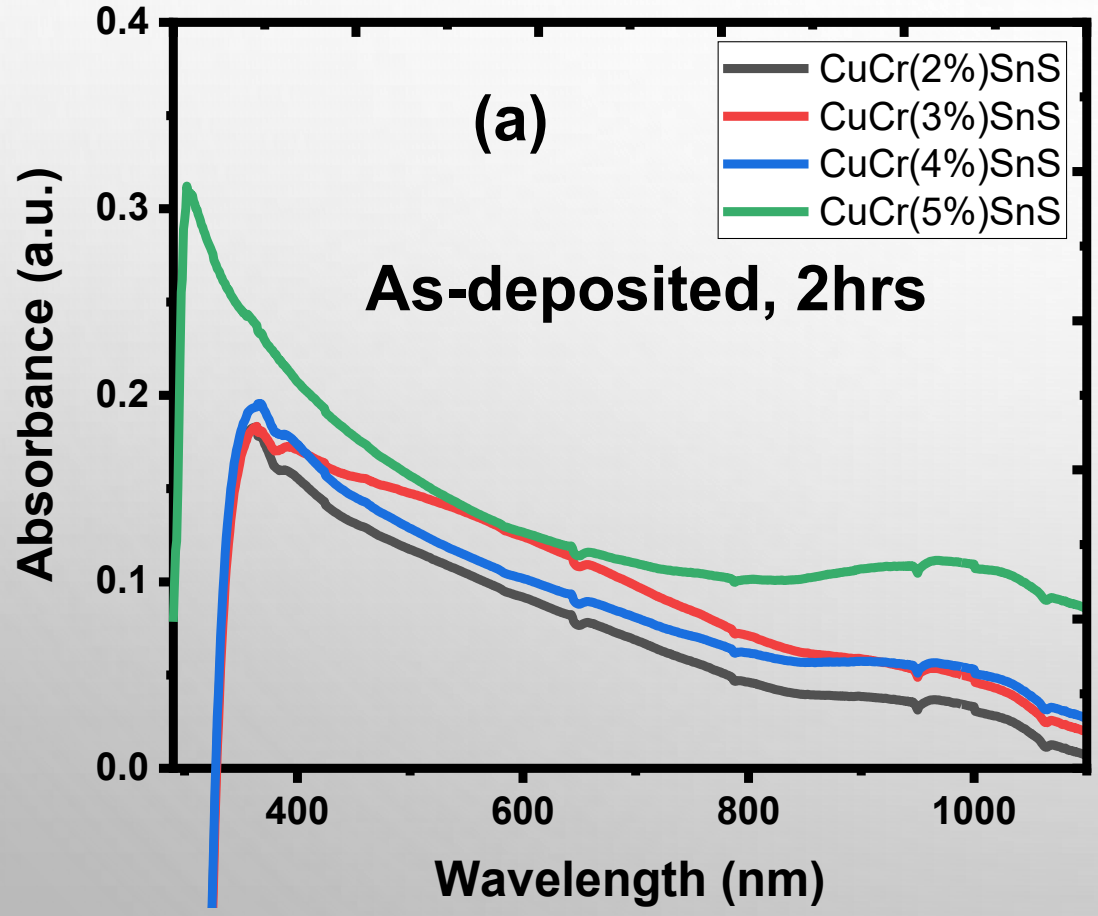
- **Absorbance**
- Absorbance A, is defined as a number that measures the attenuation of the transmitted radiant power in a material. If i_o and I be the incident and transmitted intensities, then
- $A = \log_{10}(i/i_o) = \log_{10}(1/T)$
- Where T is the transmittance given as
- $T = 10^{-a}$
- **Transmittance:** $t = i/i_o$
- **reflectance:** this is the fraction of incident electromagnetic power that is reflected at an interface. . From the law of conservation of energy; r+a+t=1 therefore r = 1-a-t
- **Absorption coefficient:** it is the decrease in the intensity of a beam of photons or particles as it passes through substances or medium.

$$A = -\frac{[InT]}{d} = [\ln 1/T]/d$$

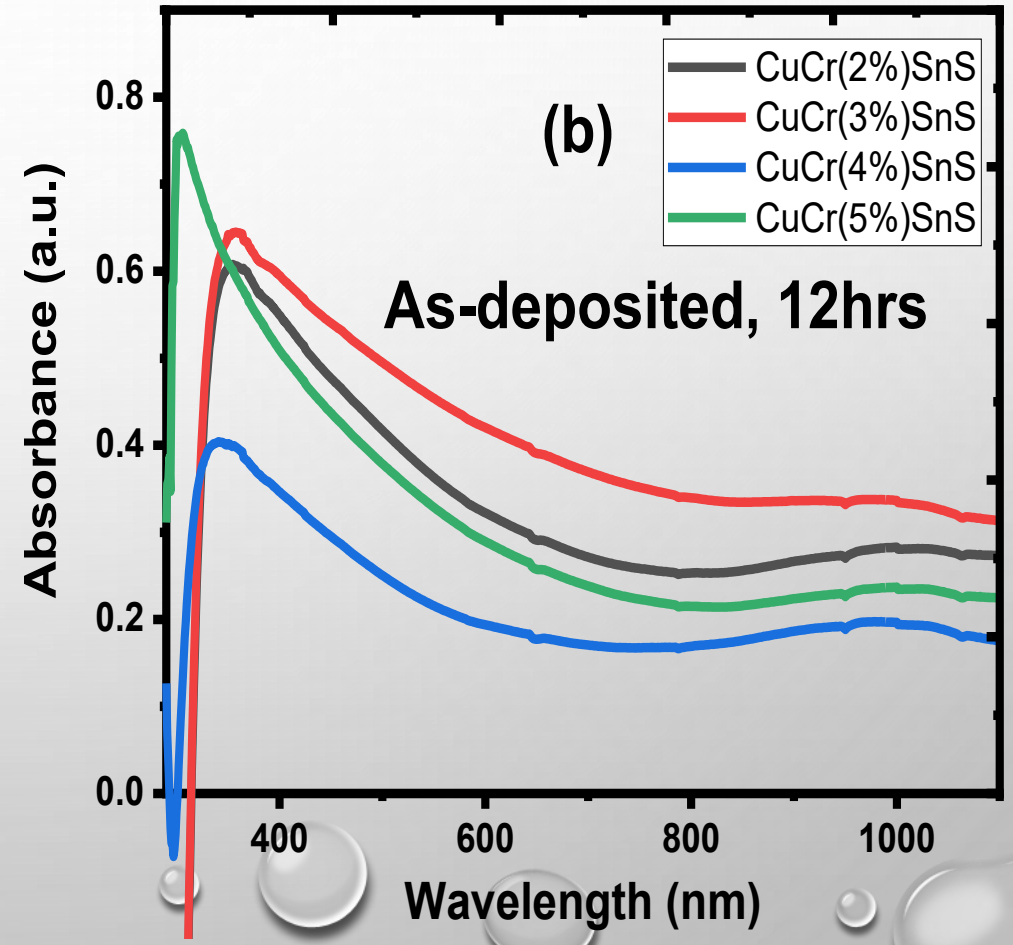
- **Band gap energy:** band gap (e_g) is the energy needed to move valence electrons into the conduction band given by $\alpha^2 = (hv-eg)$

OPTICAL ANALYSIS FOR CuCrSnS ABSORBANCE

AS DEPOSITED FOR 2HRS

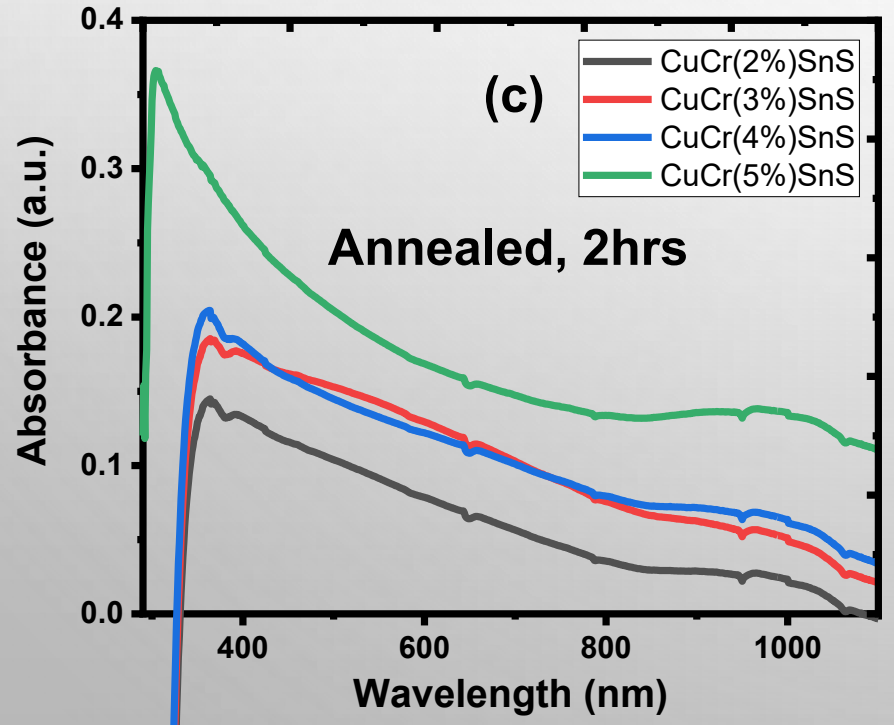


AS DEPOSITED FOR 12HRS

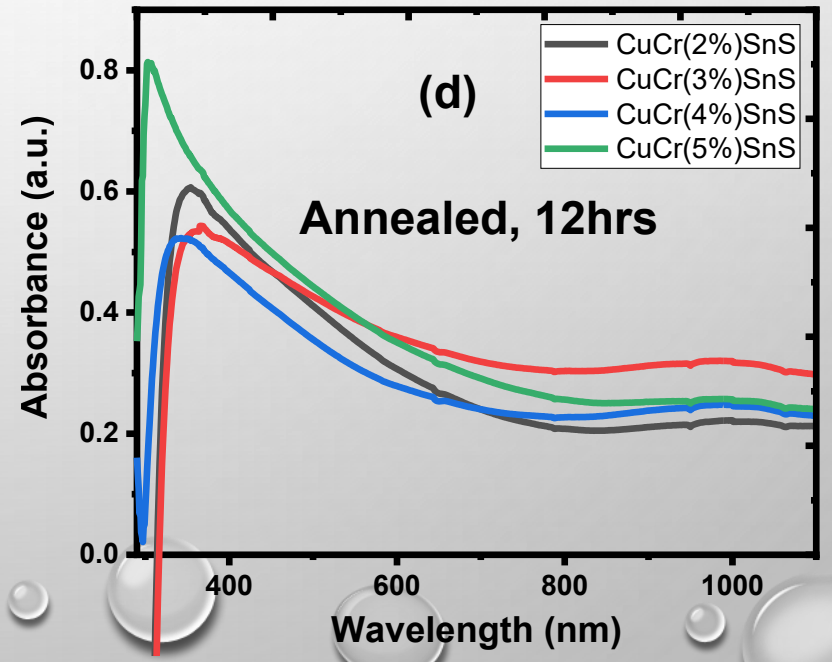


- In terms of deposition time, absorbance increased with increase in deposition time and concentration as seen after 2hours as compared to 12 hours. After 2hours there is high absorbance of 0.31 au at concentration of 3% and this is effected as the deposition time increases to 12 hours with increase in concentration of 5%. Which is in line with beer lambert law. Absorbance is also seen to reduce with increase in wavelength of incident radiation at the visible region.
- Annealing enhanced absorbance as seen from 0.31au of as deposited 2hours for 3% to 0.38au for annealed 2hours and 0.78au of as deposited 12hours of 5% to 0.81au annealed 12hours
- For absorbance purpose this film requires high deposition time. It is observed that film with 5% cr has highest absorbance in comparism to the ones grown with 2%, 3%, and 4% cr

ANNEALED SAMPLE

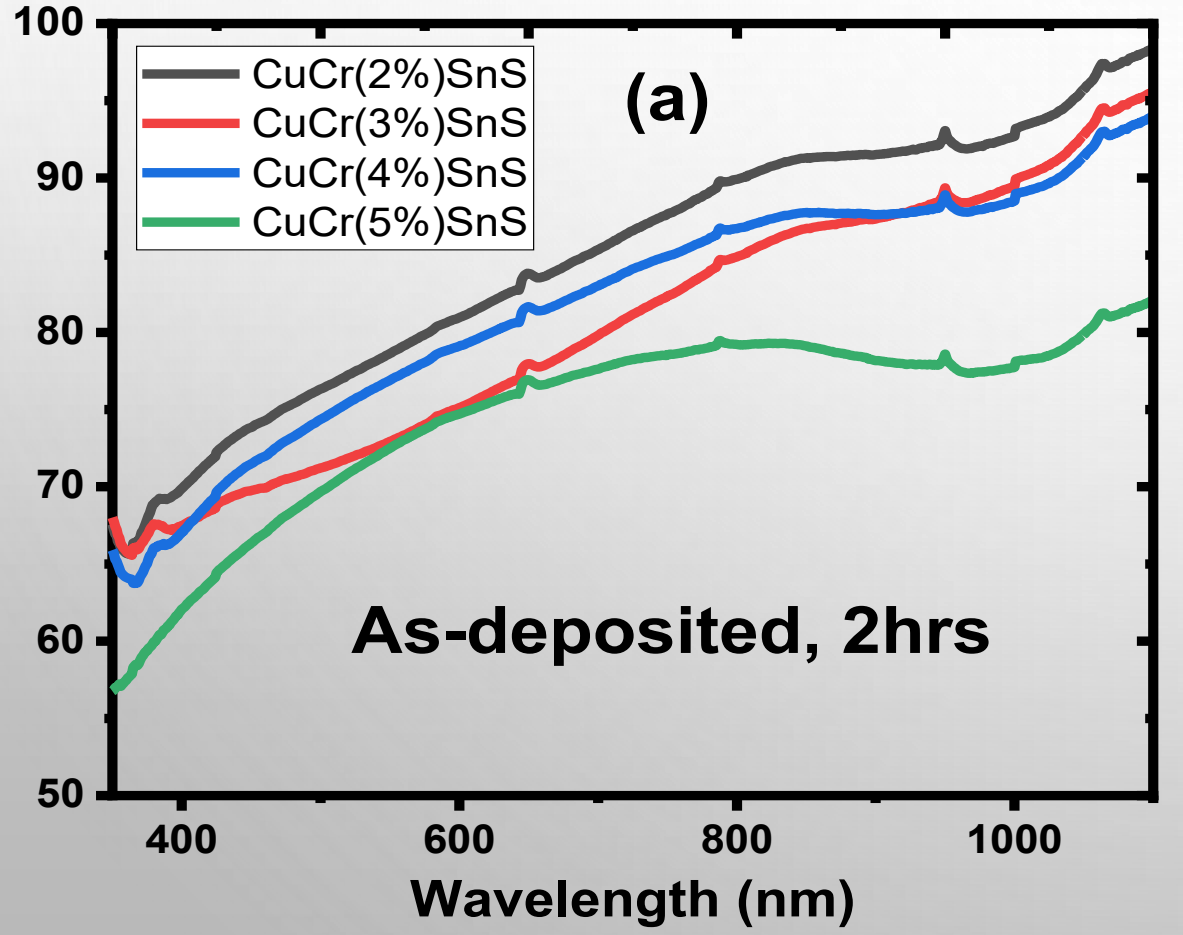


ANNEALED SAMPLE

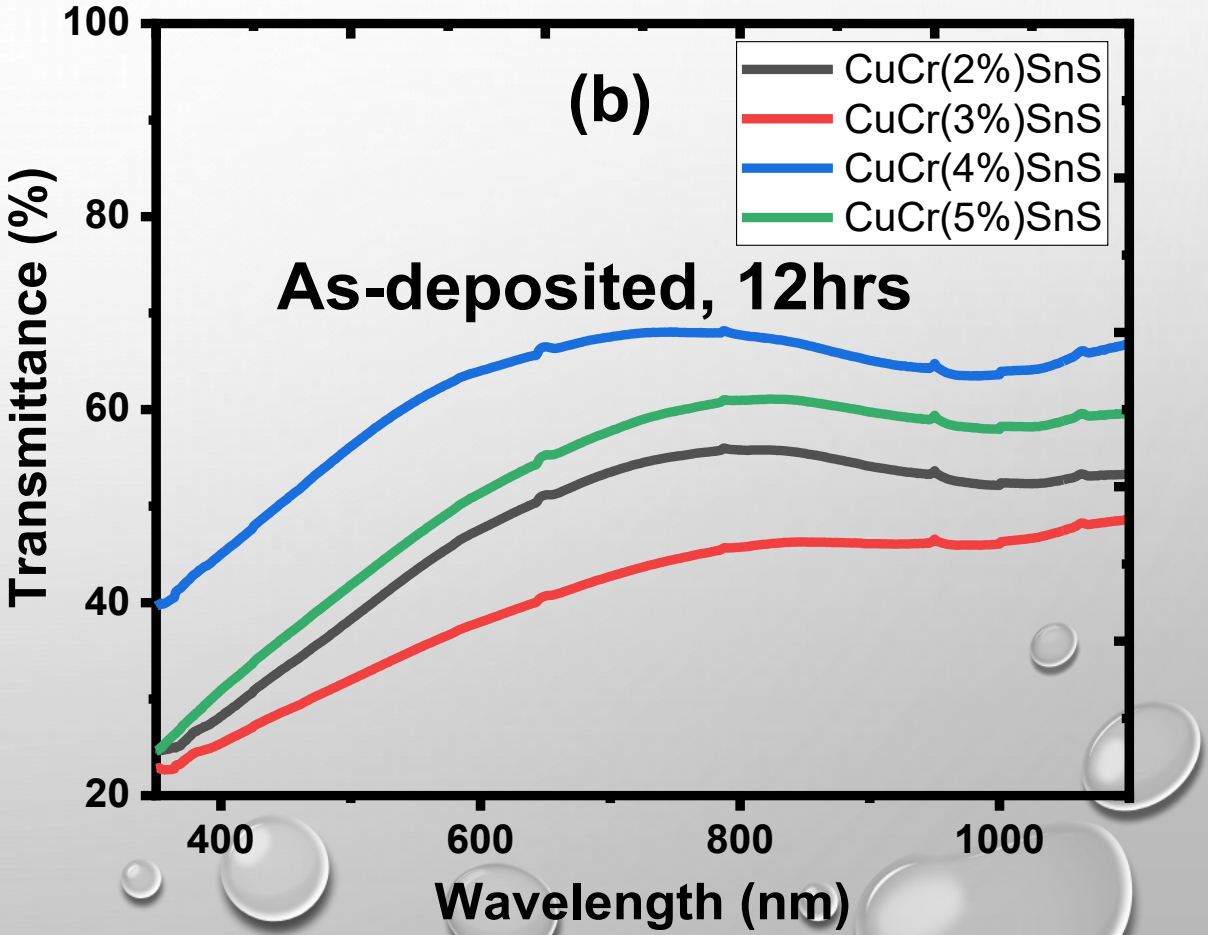


TRANSMITTANCE

AS DEPOSITED 2 HRS

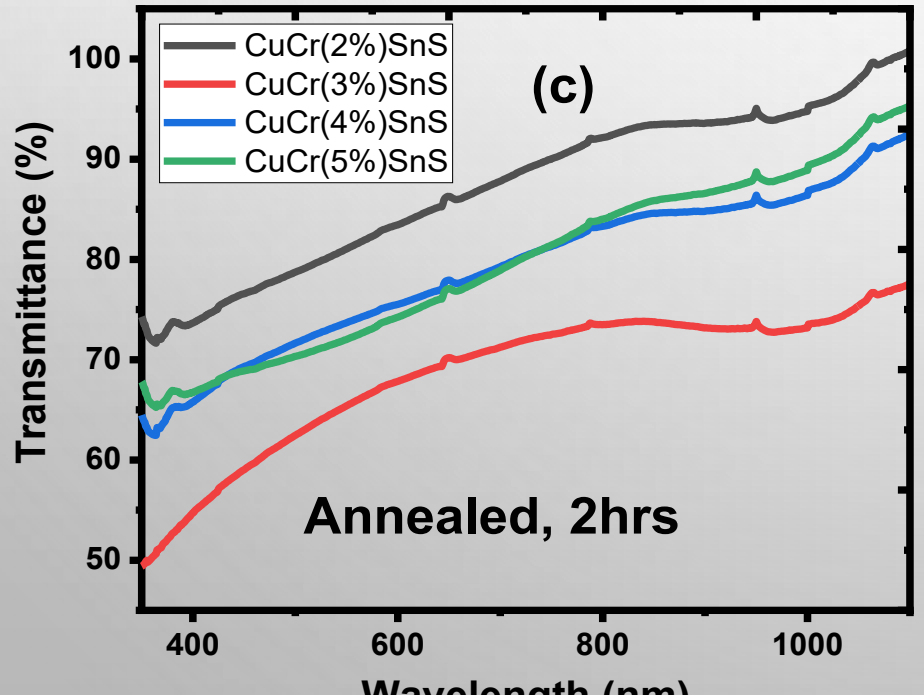


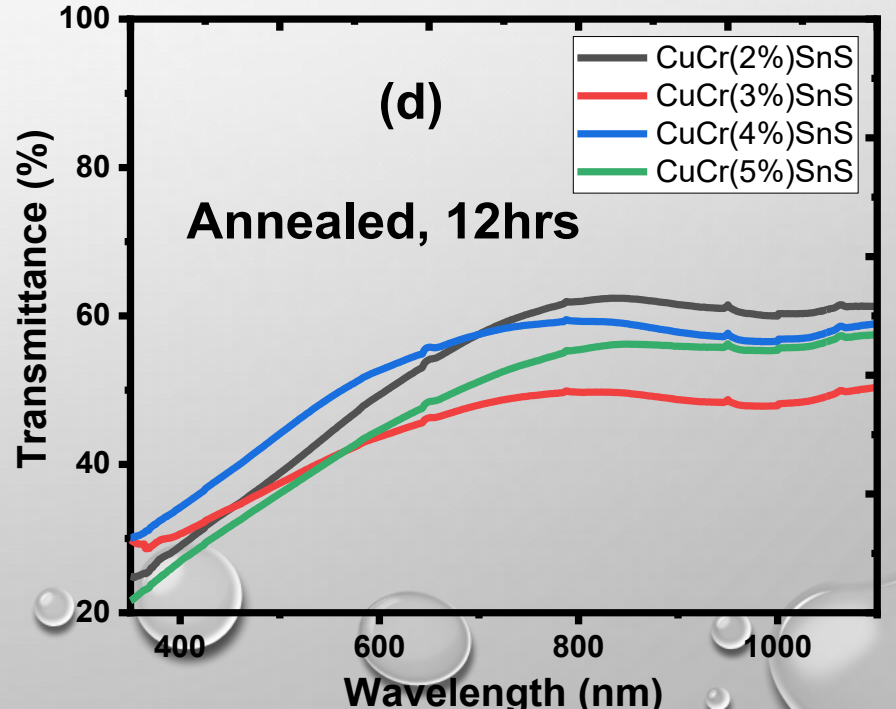
AS DEPOSITED 12HRS



ANNEALED FOR 2 AND 12 HRS

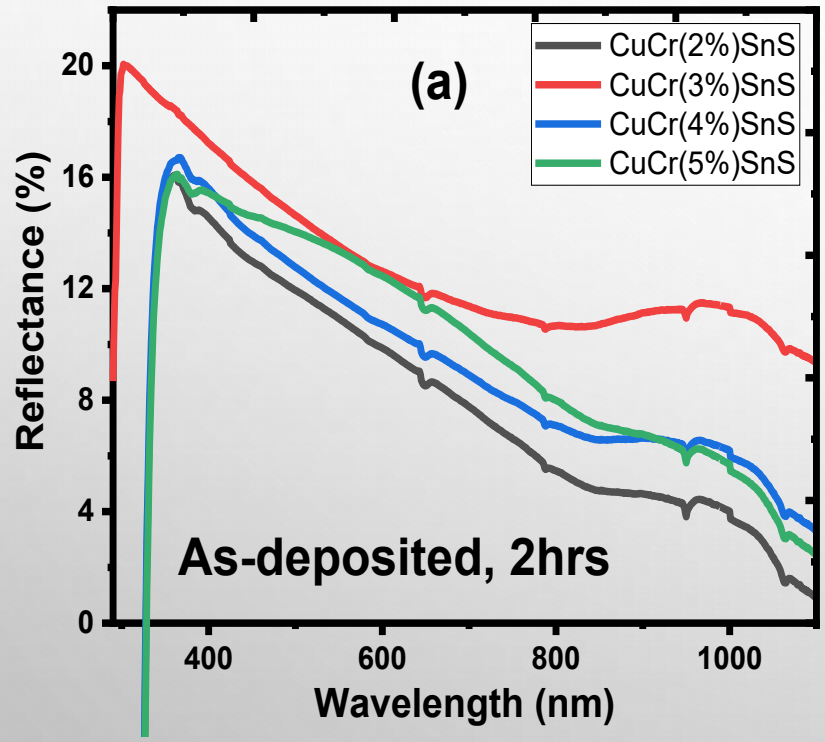
- Transmittance is seen to increase with increase in the incident radiation. Comparing the as deposited and annealed for 2hours, is observed that transmittance increased at a lower concentration of 2% from 67% to 74% with increased wavelength of incident radiation
- Now increasing the deposition time and concentration for 12 hours showed a decrease in transmittance for 4% concentration from 40% to 30%.



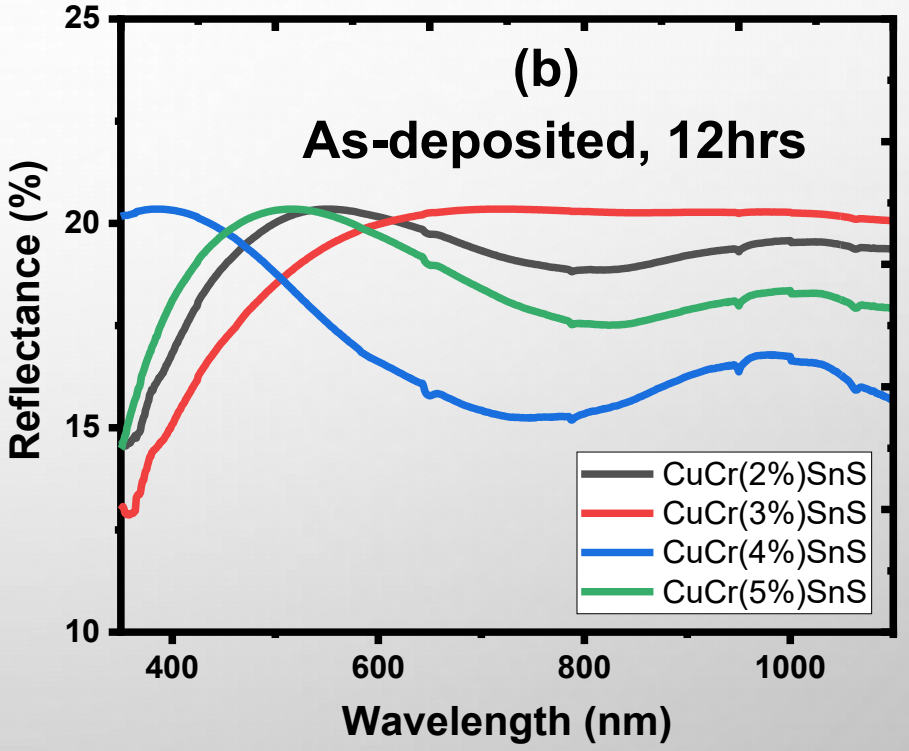


REFLECTANCE

UNANNEALED 2HR

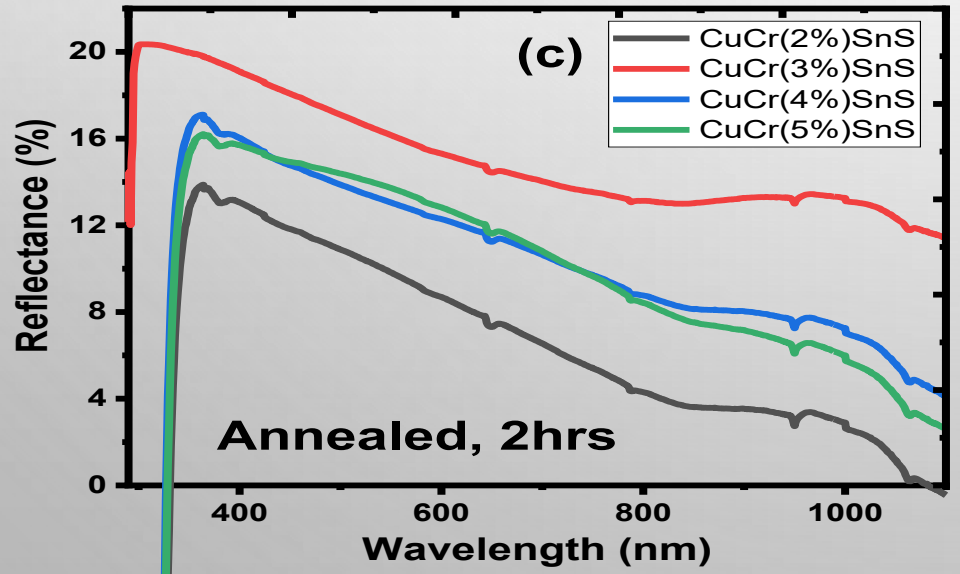


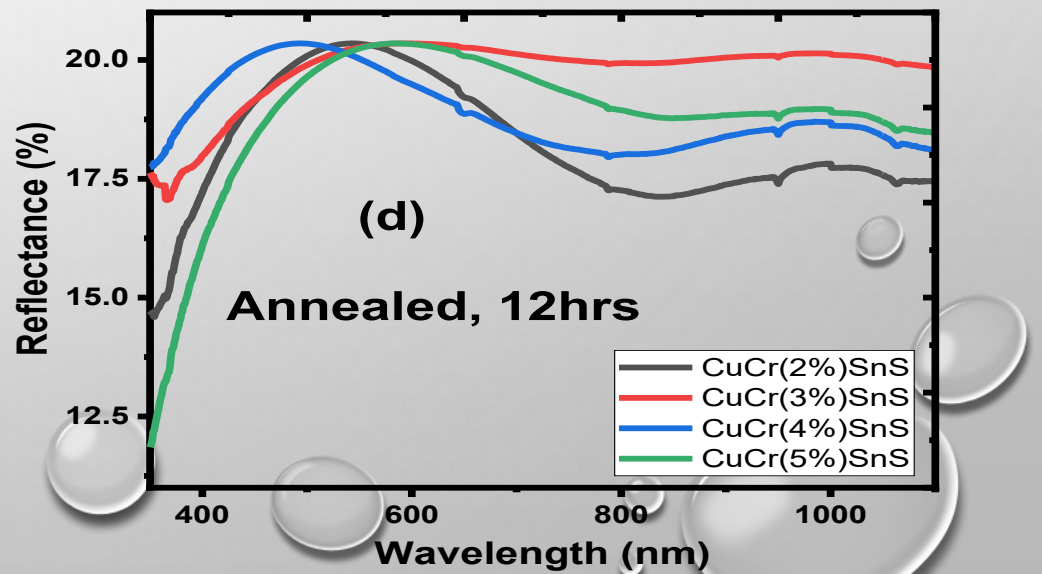
UNANNEALED 12 HRS



ANNEALED FOR 2 AND 12 HRS

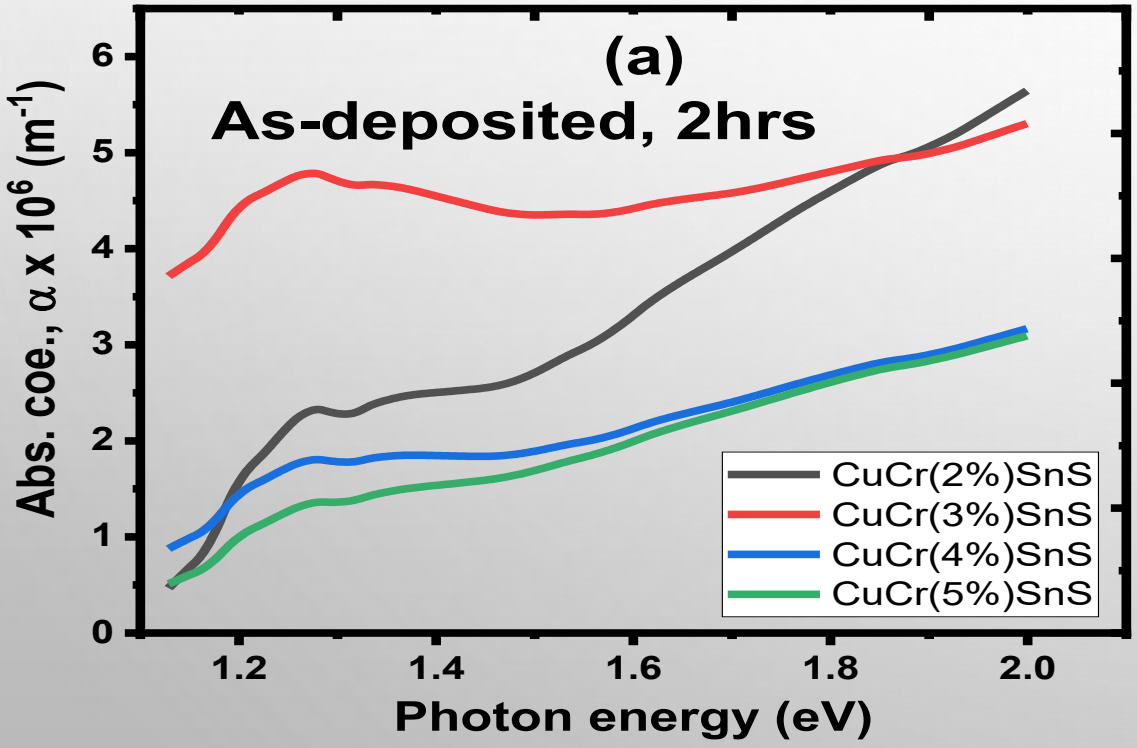
- the best reflectance was observed at a concentration of 3% cr. is observed that at 2hours reflectance decreased drastically with increase in wavelength of the incident radiation but as the deposition time increased reflectance increased with wavelength up to 550nm by approximately 3%. is also observed that at 3% concentration is continuous reflectance of 20% at the visible region.
- for reflectance purpose this film requires high deposition time and a lower concentration of 3%



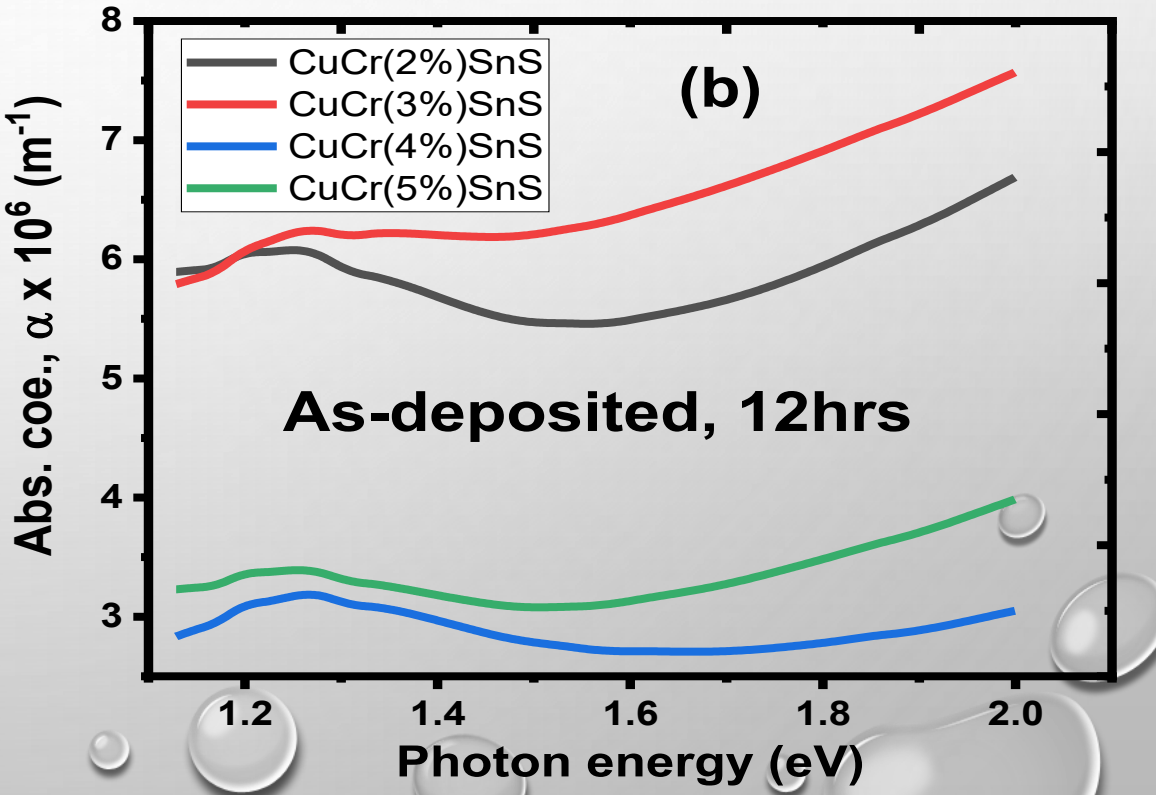


ABSORPTION COEFFICIENT

UNANNEALED 2HRS

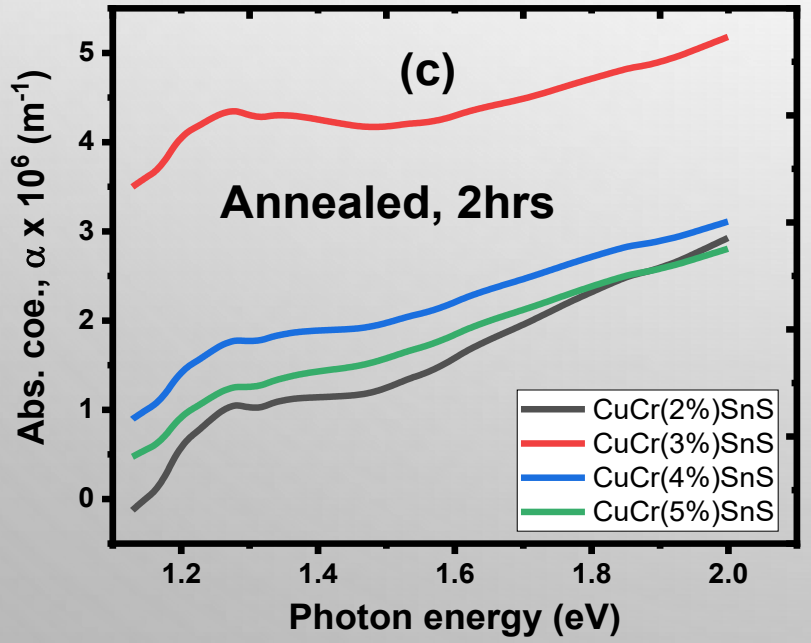


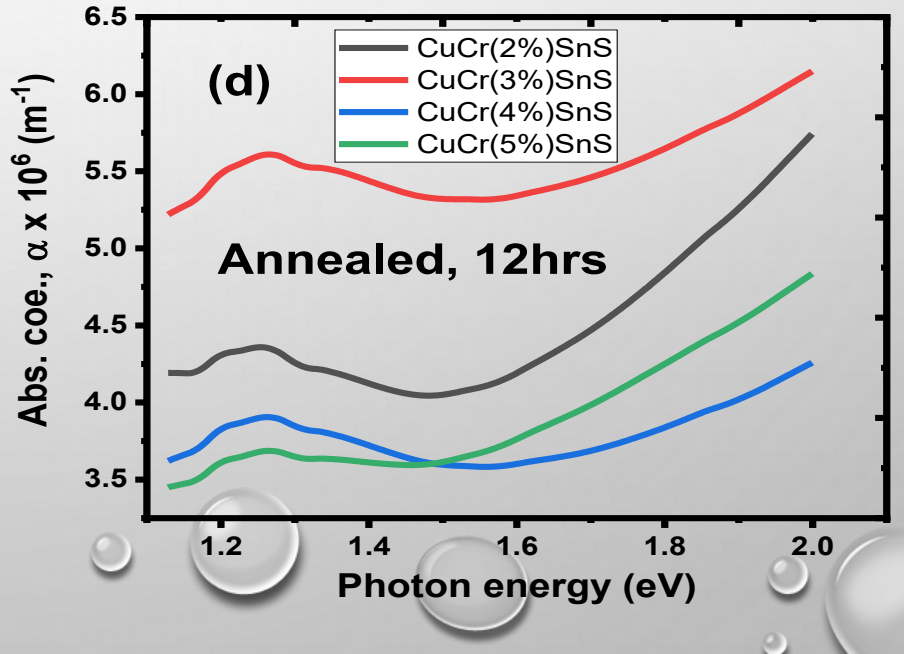
UNANNEALED 12 HRS



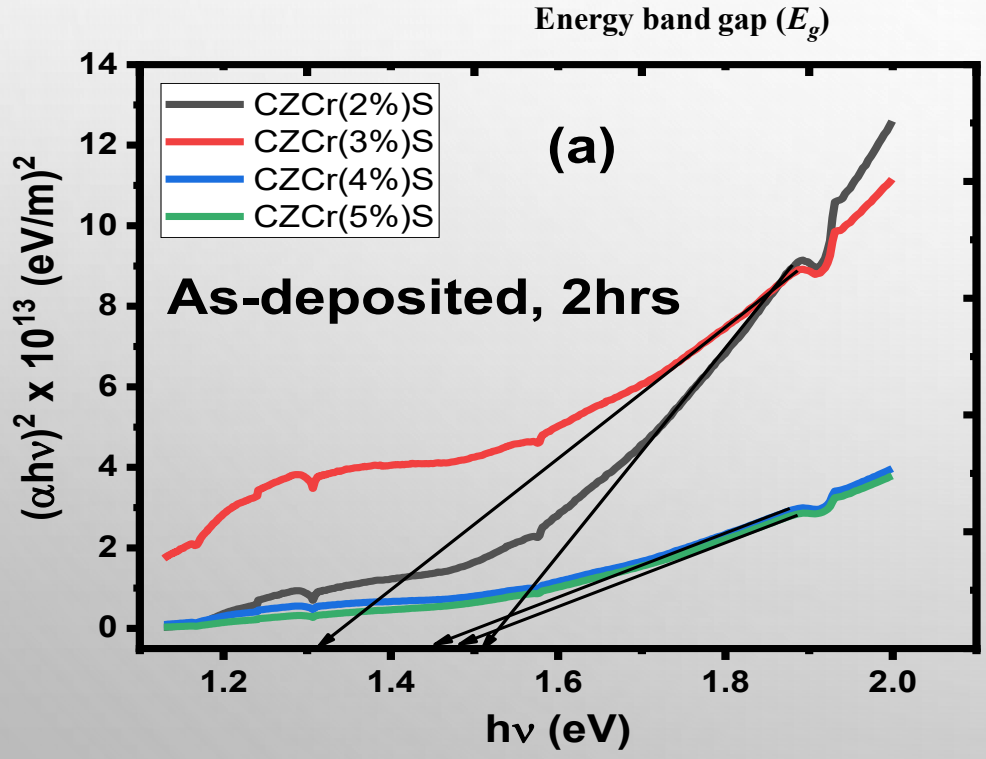
ANNEALED FOR 2 AND 12 HRS

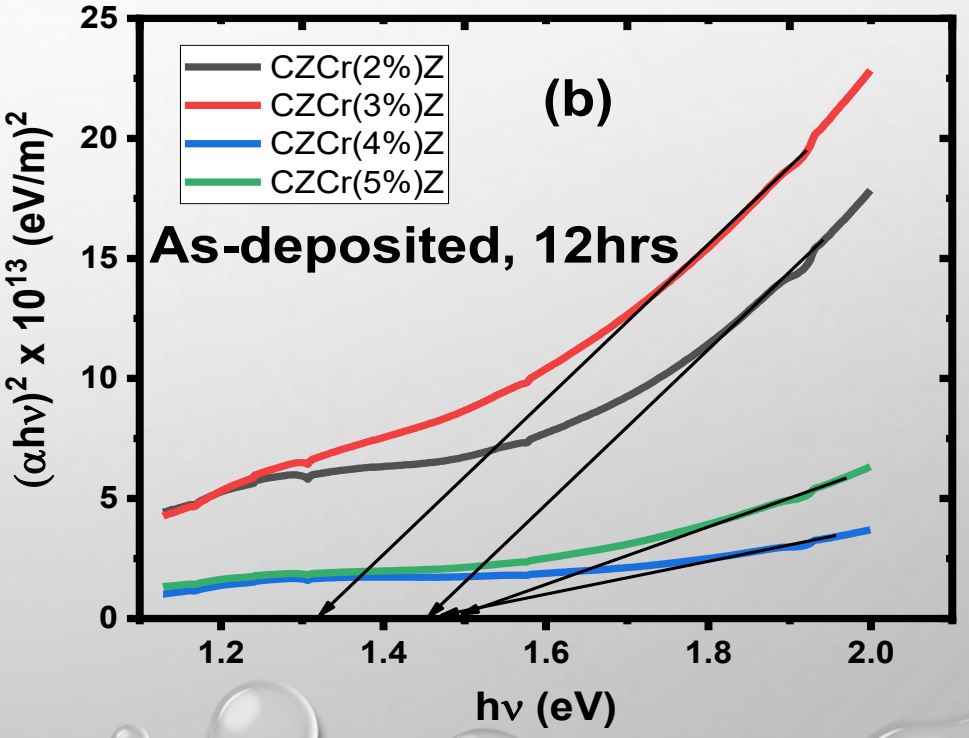
- Con of 3%low absorption coefficient means high absorption of light. The film has high absorption coefficient at a concentration of 3%. Increase absorption coefficient increased with increase in deposition time at a photon energy of 1.5ev there was a drastic decrease in absorption coefficient and from 1.5 to 2.0ev the coefficient increased by 1.5ev. This film is observed to be a good absorber of photon energy at at 3% conc of Cr
-





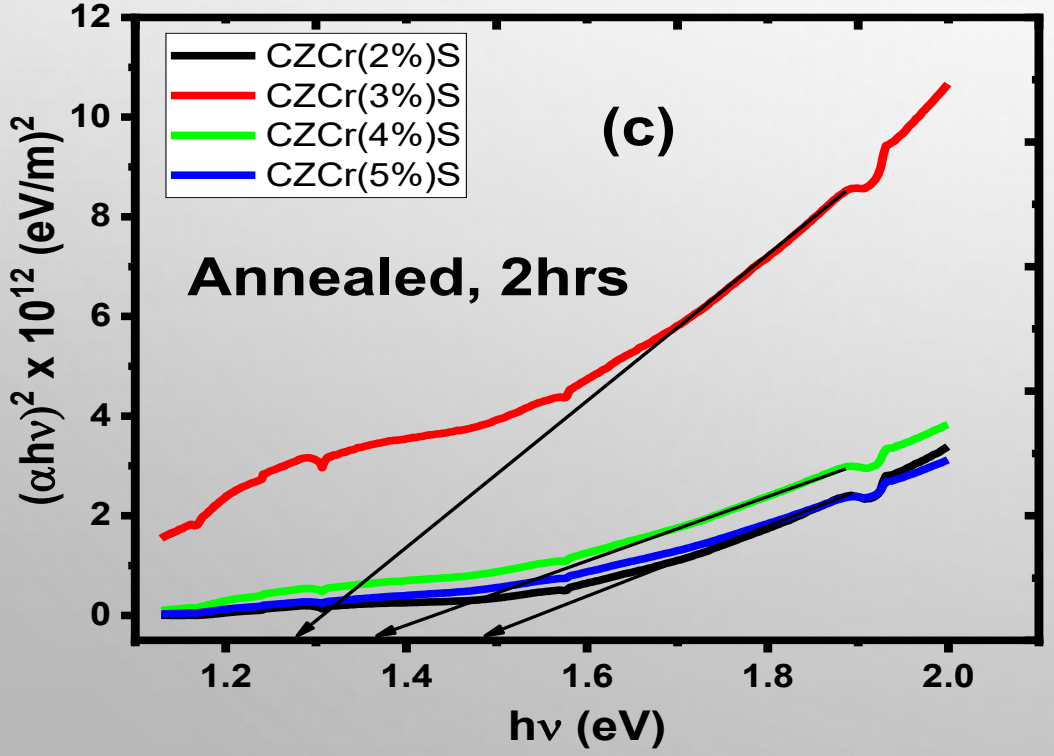
ENERGY BAND GAP

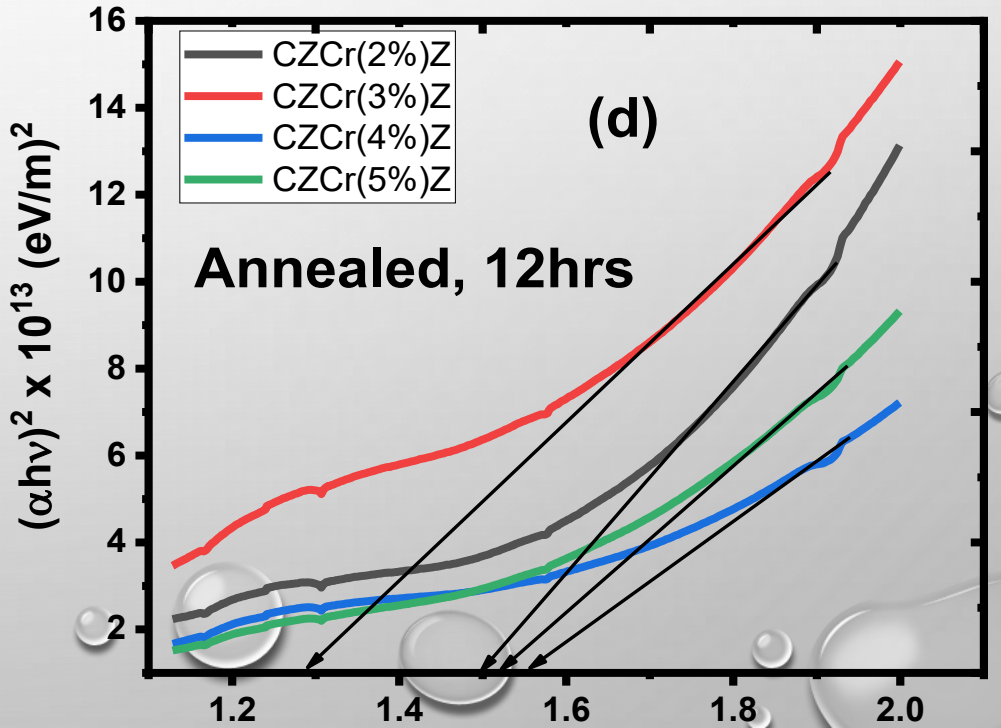




ANNEALED FOR 2 AND 12 HRS

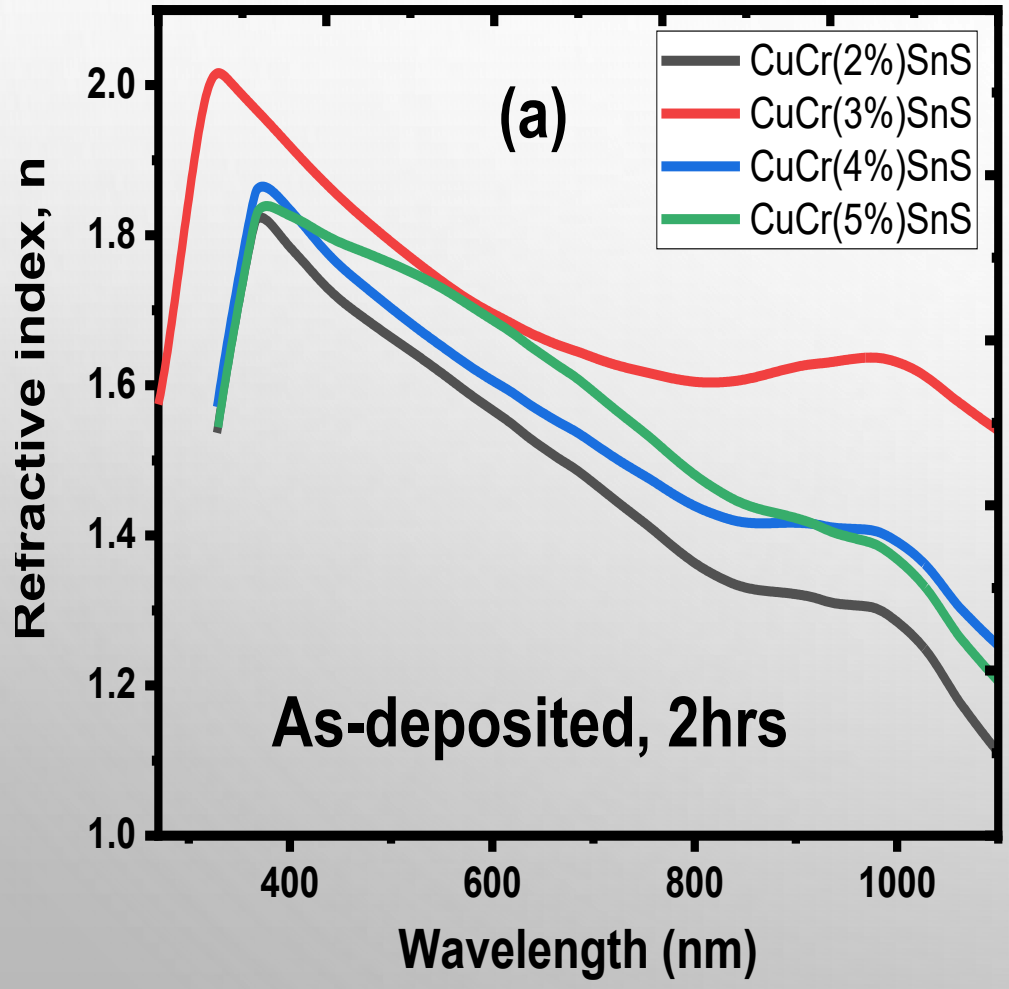
- It can therefore be seen that annealing reduced the magnitude of the band gap for the deposited films which implies a reduction in the magnitude of work needed to take an electron from the conduction to the valence band. Therefore, annealing is of great advantage to the band gap energy of the film. The best band gap is obtained at concentration of 3% CuCrSnS thin. 1.32 – 1.28eV



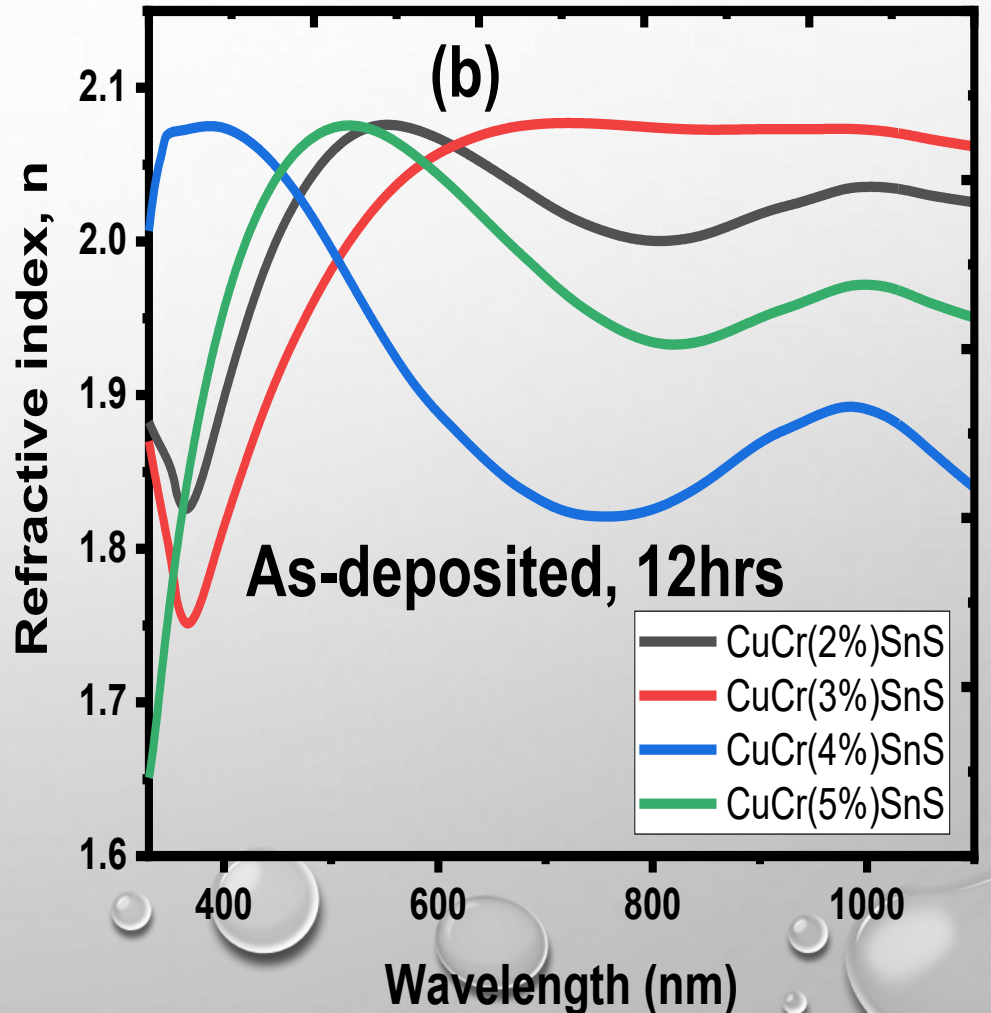


REFRACTIVE INDEX

UNANNEALED FOR 2HRS

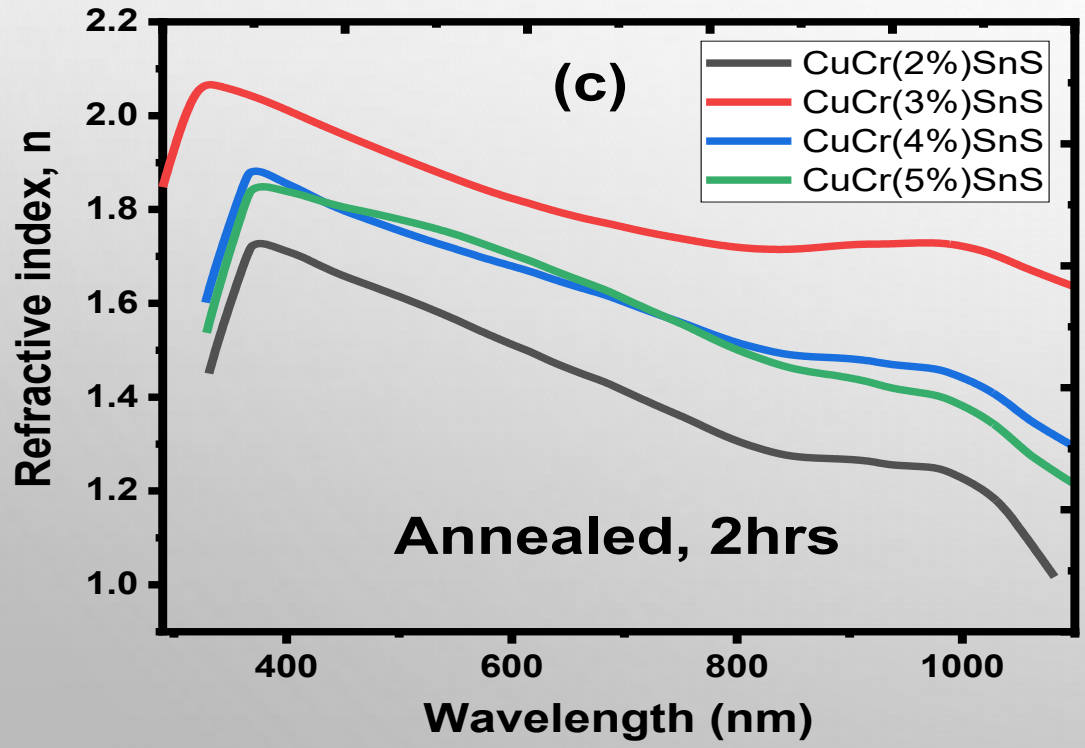


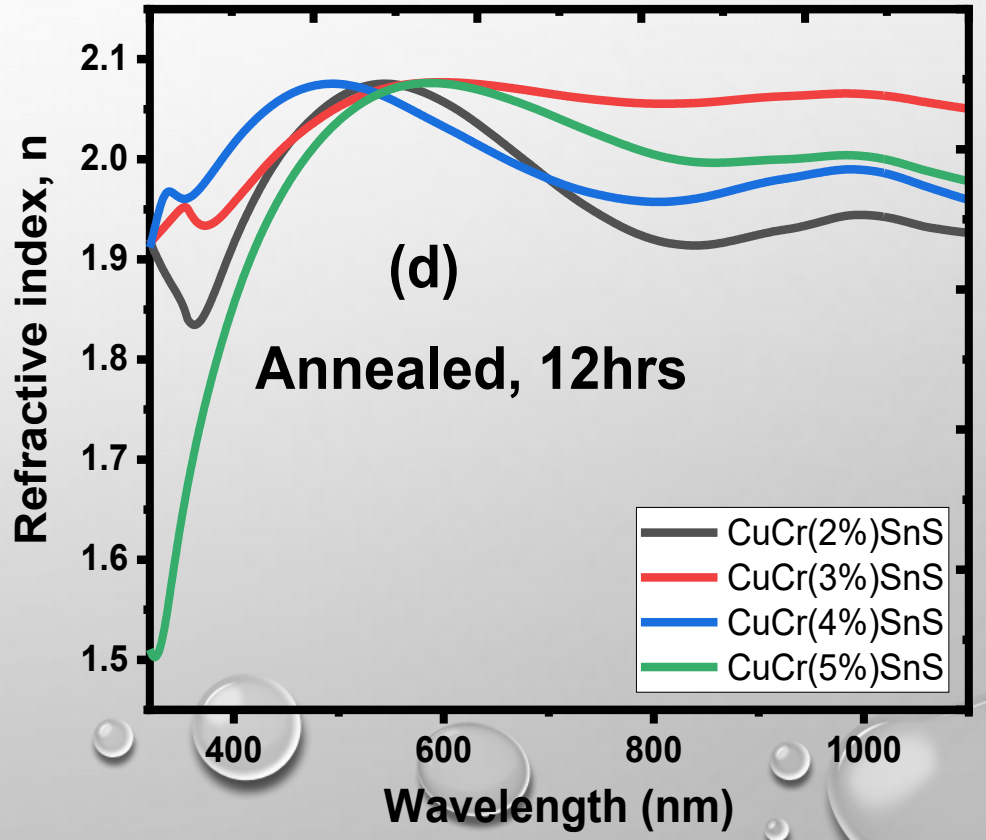
UNANNEALED 12HRS



ANNEALED FOR 2 AND 12 HRS

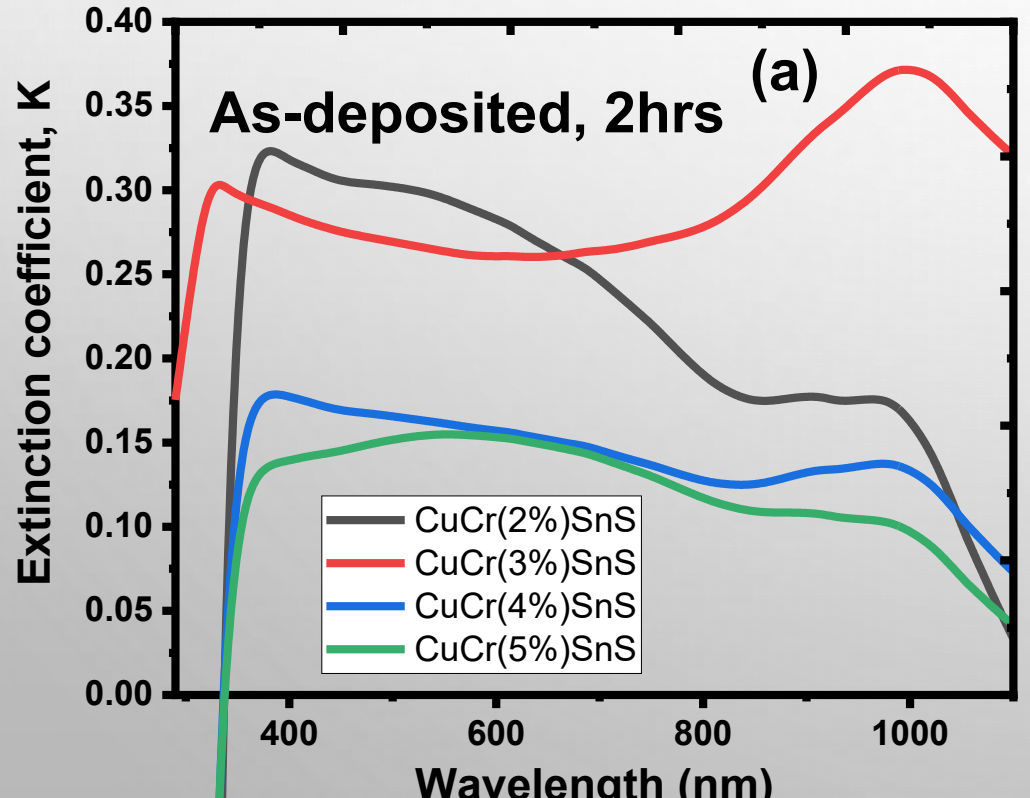
- The film shows refractive index with varying concentration of chromium for as- deposited 2hrs, is 1.3, 1.6, 1.4, 1.43 after annealing it was observed to be 1.28, 1.7, 1.47, 1.5 increasing the deposition time to 12 hrs with the varying concentration it was observed that refractive index increased to 2.0, o , 1.94, 1.82 for as-deposited and 1.9, 0, 1.98, 1.95 after annealing under 250^{0}C which is in line with the reflectance of the film.



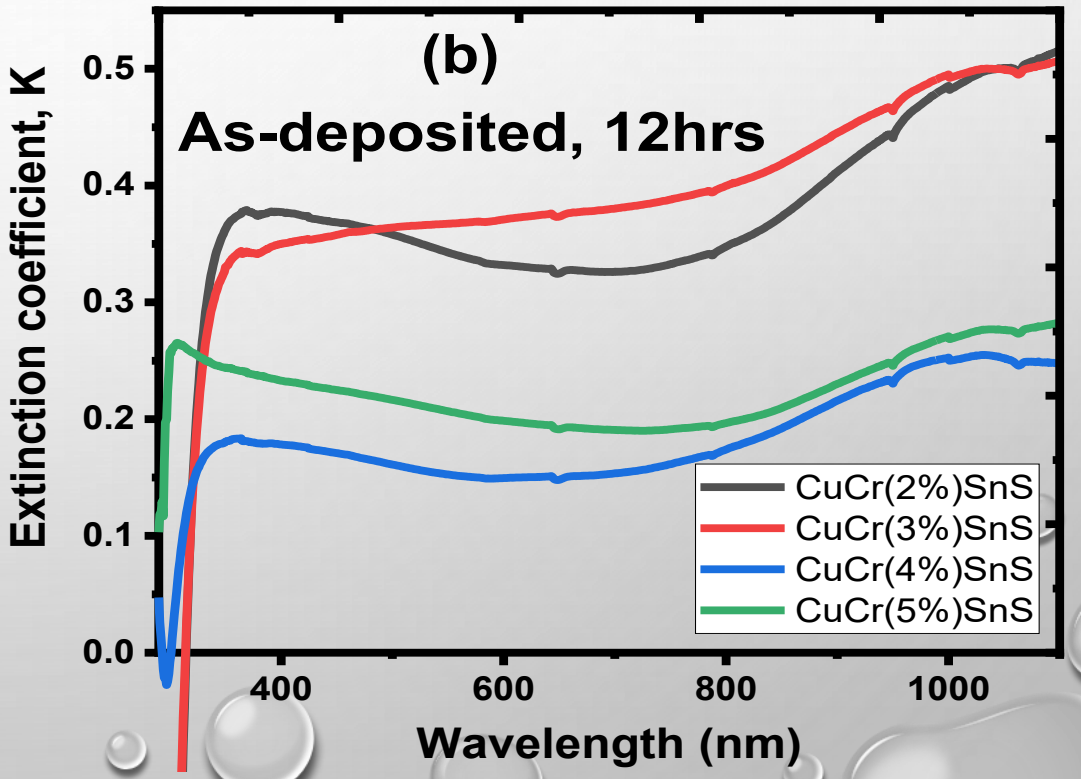


EXTINCTION COEFFICIENT

UNANNEALED 2HR



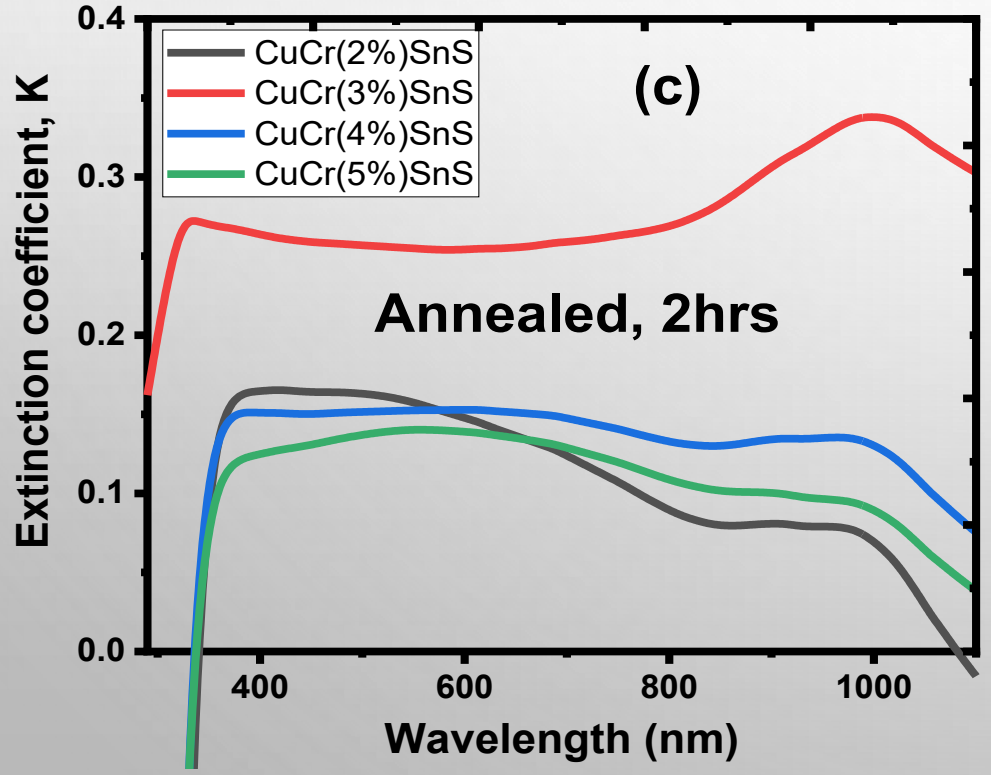
UNANNEALED 2HR

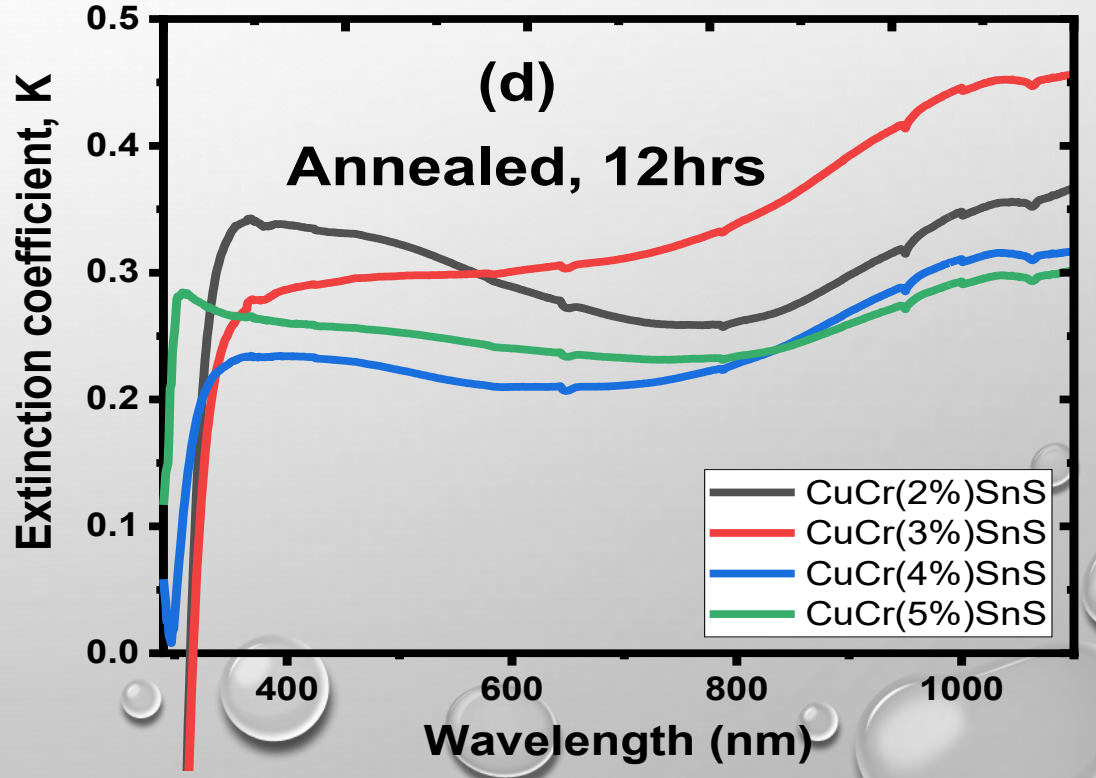


light.

ANNEALED FOR 2 AND 12 HRS

- Extinction coefficient decreased with increase in wavelength at the visible region for as-deposited for 2hrs with optimal observed at 3% cr annealing improved this by just 1% but as the deposition time increased extinction coefficient increased with optimum observed at 2% cr this also decreased with increase in wavelength.

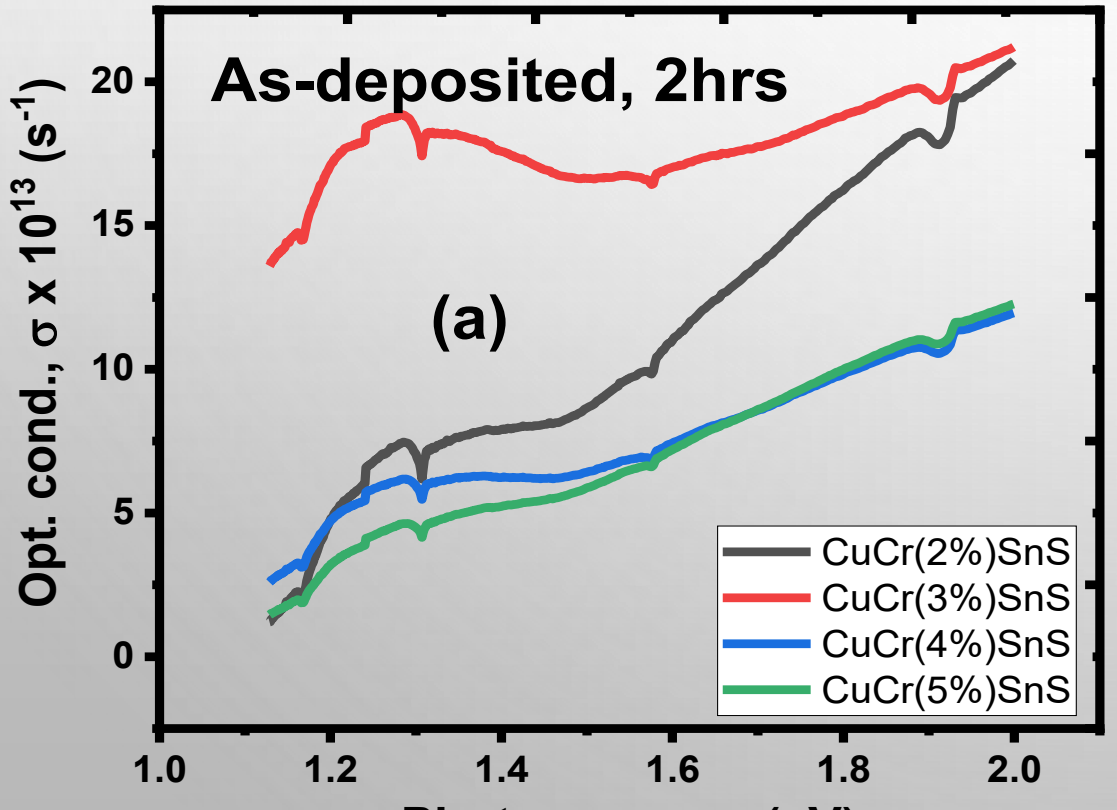


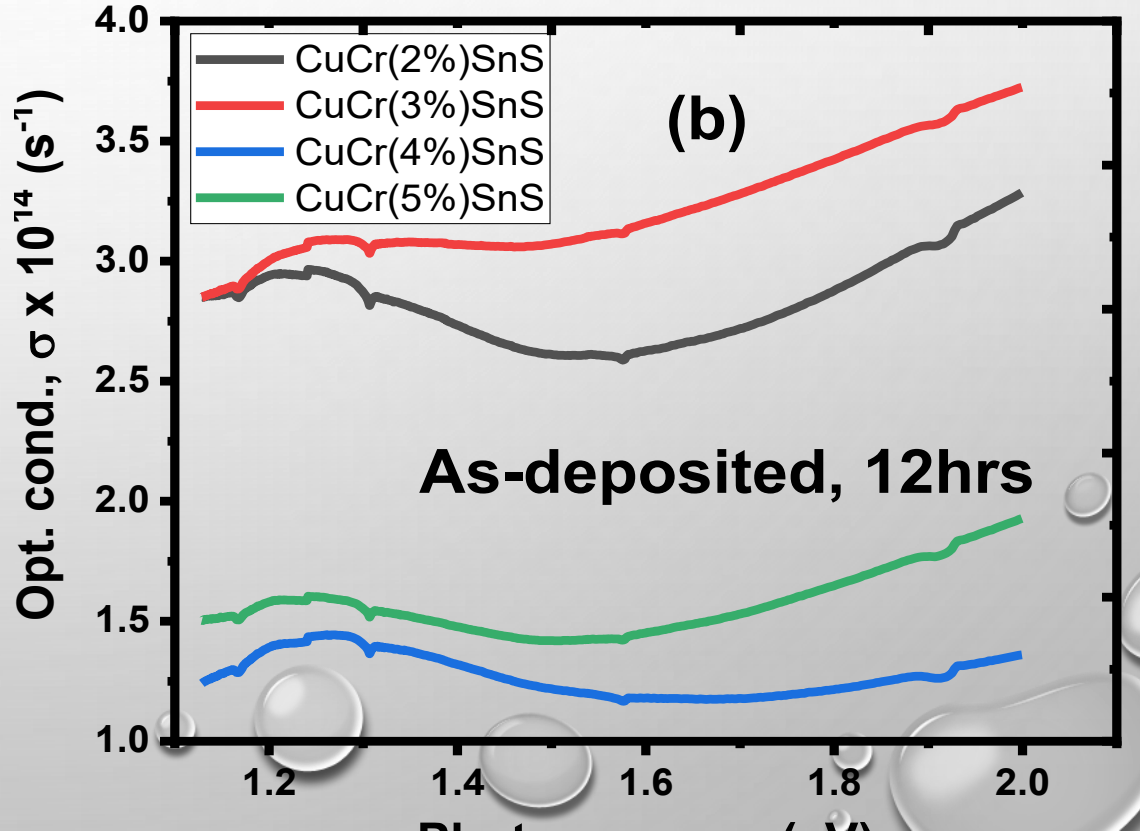


OPTICAL CONDUCTIVITY

UNANNEALED FOR 2 HRS

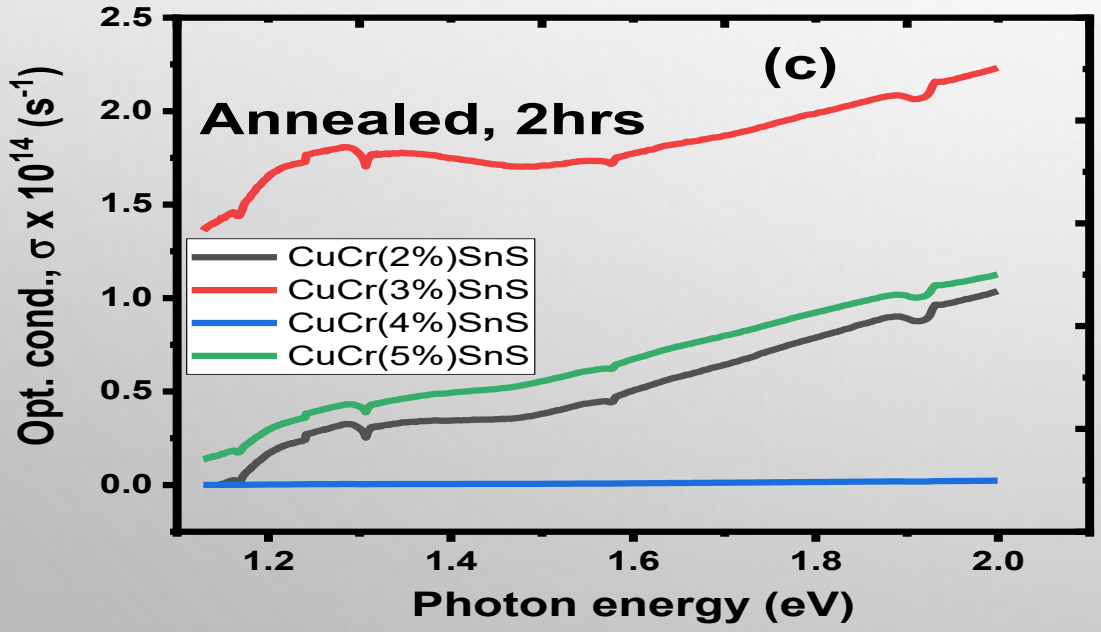
UNANNEALED FOR 12 HRS

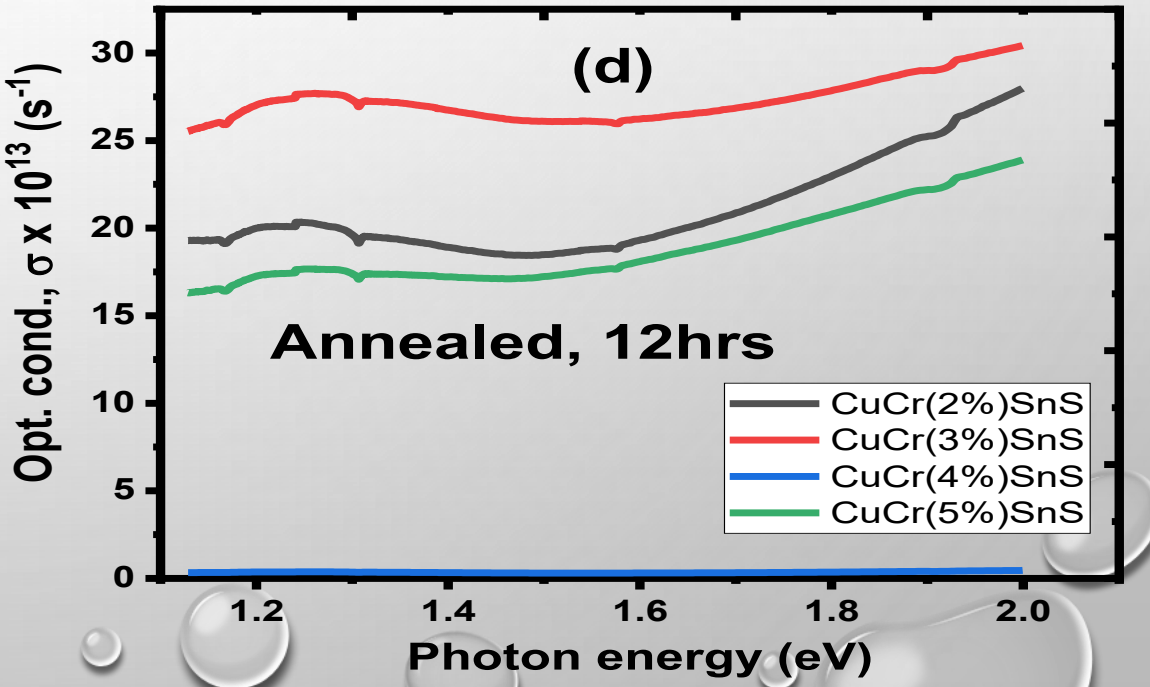




ANNEALED FOR 2HRS AND 12 HRS

It is observed that optical conductivity increases inversely with photon energy of the film absorbance is high in regions with low photon energy. It is observed that the film has high conductivity at 3% cr in the low region of the photon energy. Annealing was seen to reduce conductivity slightly as observed for as-deposited 2hrs from1.8(s/1) to 1.6(s-1) and for as- deposited 12hrs from3.1(s-1) to 2.7(s-1). Also increase in deposition time was observed to improve conductivity as the film absorb photon energy. At 4%cr it was observed that the film had 0% conductivity.





CONCLUSION

- Almost every property of the deposited thin film was affected by annealing in a positive way
- The CuCrSnS thin film showed a high absorbance in the area of the visible region, this makes the deposited film suitable in the designing of solar cells.
- This film does not require high concentration for absorption purpose
- For reflection purpose, CuCrSnS thin films may not be very appropriate since it exhibits very low reflection properties.
- The energy band gap for deposited chemical bath CuCrSnS thin film was in the range of 1.27 - 1.49ev for annealed sample indicating that they are suitable for use as absorber layers in solar cell device.

THANK YOU