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# Development of Novel Ultra-Light Absorber for Remote Distributed Energy Applications

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**Abstract:** Thin films of copper (Cu) doped antimony suliphide $SbS_2$ have been deposited on glass substrates at different doping concentrations (0.1, 0.2 and 0.3M) using the chemical bath deposition method. The filmswere characterized using various instrumental techniques including ultraviolet-visible spectroscopy (UV-Vis) and scanning electron microscopy (SEM). The optical energy bandgap is found in the range of 1.50-1.24 eV which are suitable for absorbing sunlight in the visible regtion of electromagnetic spectrum. The results of the study showed that the transmittances of the film were quite high and reached peak of 90 %. The results also showed that both the extinction coeffificient (k) and refractive index (n) increased with wavelength at all Cu concentrations. The variations of both high frequency dielectric constant and static dielectric constant with doping concentrations followed the same trend as that of refractive index. The SEM results of the films showed that films are polycrystalline and almost uniform throughout the substrate. Cu-$SbS_2$ is a potential demanding candidate for UV absorbing coatings in solar cell.

***Keywords:*** *Antimony Sulphide ($SbS_2$); Copper; Thin Film; SEM Chemical Bath Deposition method*

## 1. Introduction

Energy sector is very crucial to the development and stability of the economy of any nation. The present instability in the economics of developing countries is strongly related to the epileptic nature of power supply in the country. Most of these countries are naturally blessed with vast sources of renewable (clean) and non-renewable energy source but the uses of these energy sources have been largely skewed in favour of hydro-power and crude oil, with the other sources either untouched or poorly harnessed, leading to "energy scarcity" in these countries. Research in clean energy is a step in the right direction toward achieving energy sustainability and availability in both developed and developing nations.

Thin film solar cells have been established as the only way forward to produce solar cells with increased efficiency at reduced costs. The most advanced thin film solar cells: CdTe (cadmium telluride), CIGS (copper indium gallium diselenide), and α-silicon are known to be saddled with some issues. In CdTe, the environmental acceptability of cadmium is still uncertain in some countries and the abundance of tellurium is in doubt while for CIGS, the constituent elements (indium and gallium) are rare (Peccerillo *et al.*, 2018; Onah et al., 2021; Pal *et al.,* 2019; Nazligul *et al.,* 2020; De Souza Lucas *et al.,* 2018). For α-silicon, the cost of production is still high. Cu-Sb-S (copper antimony sulphide) have been largely ignored as PV materials until the past decade due to lack of awareness of its potential optical qualities or properties.

For light absorber or detectors (semiconductors) photons incidents upon them generate extra carriers. Examples of these materials include CdS, PbS, InSb, nickel-dopde germanium (Ge-Ni), phosphorus-doped silicon (Si-P). They are cost effective and can also be easily deposited or constructed using simple deposition techniques or methods (Tauc *et al.,* 1966; Zang., 2018). The applications of halide thin films have been reported by many scholars. CdS, CdSe, GaSe, CuS and ZnS have been proved to be excellent materials for electroluminescent devices and photo-detectors (Ornelas-Acosta *et al.,* 2015), (Banu *et al.,* 2016). Many deposition methods such as successive ionic layer adsorption and reaction (SILAR), chemical bath deposition (CBD) or solution growth techniques and sol-gel process, have been used to deposit semiconductor thin films on glass substrates (Hamberg *et al.,* 2021; Xue *et al.,* 2006; Dutková *et al.,* 2021; Zhang *et al.,* 2016).

In this study, we deposited thin films of antimony sulphide doped with copper using chemical bath deposition method. We studied the optical, electrical and morphological properties of copper-doped antimony sulphide (Cu-$SbS_2$) thin films. Here, our interests were particulaly on the effects of the concentrations of the dopant on the properties of the films. The applications of the studied thin films were determined based on the film's characterization and properties.

## 2. Methodology

### *2.1 Sourcing of materials*

The materials used are; soda lime glass substrates, synthetic foam, beakers, thermometer, digital (PH meter) type (Inolab PH720), automatic magnetic stirrer, distilled water, antimony trichloride ($SbCl_3$), Thiorea ($SC(NH_2))_2$, aqueous ammonia ($NH_4OH$), Copper II Sulphate pentahydrate ($CuSO_4.5H_2O$), sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$), hydrochloric acid, acetone, and other materials such as beakers, stirrers, stop watch, and therometers. All the source chemicals used for the growth of the $Sb_2S_3$ thin films and the dopant was of analytical grade, obtained from Testbourne Chemical Limited, and Sigma Aldrich, all from UK through local suppliers.

### *2.2 Experiments*

Substrate cleaning is a critical step in thin film deposition. In this study, the substrates were first e with detergent and then degreased with acetone. The soda lime glasses were further cleaned ultrasonically to make the substrates completely dirt-free. Substates cleaning involved the removal of contaminants without damage to these substrates. In this way, the substrate film interface, morphology, nucleation and electronic properties were not affected by contaminants (Uguru *et al.,* 2017). In the synthesis and deposition of Cu-$SbS_2$ thin films, the chemical bath deposition (CBD) techniques or method was used. The solution was obtained by dissolving `1.5 g of $SbCl_3$ in 1.5 ml of acetone in a beaker and 150 ml of $Na_2S_2O_3$ and distilled water were also added to this beaker. A magnetic stirrer was used to stir the solution for 15 minutes. This solution in acidic range of 5.2 was distributed equally into other 4 beakers labelled SX, SX1, SX2, and SX3, respectively. The different molarities of copper dopant ranging from 0.1-0.3 M were prepared from $CuSO_4.5H_2O$ salt in another beaker. A 10 ml each of the different molarities of the dopant was introduced into SX1 to SX3 accordingly and stirred, keeping SX as control. The previously cleaned glass slides were then immersed into each beaker (SX – SX3). The substrates were held vertically through synthetic foam and the deposition time was fixed for 15 min. After the end of the deposition time, the films were removed and rinsed with distilled water and then dried. The films were further stored in a vacuum environment prior to characterisation.

### *2.3 Thin film characterization.*

The deposited Cu-$SbS_2$ thin films were characterized using various techniques and analysis. The optical properties of interest in this study were obtained within the UV, Visible and NIR regions using a Unico–UV-2102PC spectrophotometer. The surface morphological characterization was carried using a scanning electron microscopy. SEM images was obtained using a TESCAN Vega TS5136LM typically at 20 kV at a working distance of 20 mm. Film thickness is one of the fundamental and critical parameters that determines the behavior of most semiconductor thin film materials. In this study, the film thickness was deduced using Sem.Afore 5.2.1 software.

## 3. Results and Discussion

### 3.1 Optical properties of thin films

The absorbance (A.u), transmittance (T) and extinction coefficient (k) of the Cu-$SbS_2$ thin films were recorded at various of concentration of Cu impurity in the spectral range of wavelength 300-800 nm as presented in Figs. 1, 2 and 3. Figure 2 depicts the absorbance of as-grown and Cu doped $SbS_2$ thin films at different doping concentrations.

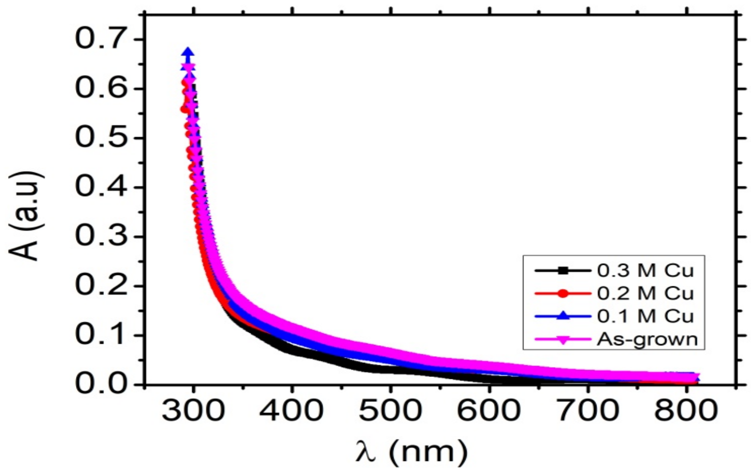


**Figure 1:** Absorbance (a.u) verus wavelength plots of as-grown and variation of Cu concentrations.

The absorption edge of the films shifted to lower wavelength from (342 to 300 nm) with increasing of Cu concentration associate with an increase of the carrier concentration in conduction band according to Burstein-Moss effect (Xie et al., 2012), (Sze, 1981). From Figure 1, the absorbance of the thin film samples reached the peak values within the ultrviolet region of electromagnetic spectrum. The clearly showed that the films are good candidates for UV absorbing coatings due to their high optical quality in UV region. This is in an agreement with the resullts of other scholars (Ugwu et al., 2015). Figure 2 depicts the optical transmittance spectra of as-grown and Cu-doped $SbS_2$ thin films at different doping concentration (0.1 M, 0.2 M, 0.3 M). The fringes associated with interference effects confirm the optical homogeneity and the excellent surface quality of deposited thin films, otherwise, the fringes should have been eliminated and shown as some smooth transmittance curves (Pathan et al., 2004; Uguru et al., 2017; Cho et al., 2017). As presented in figure, the films exhibit good transparency in the visible range a sharp fundamental absorption edge around a wavelength of 380-450nm wavelength, but a difference has observed in the near-IR region. The films were highly transparent and the transmittance increases when Cu doping decreases. The film doped with 0.3 M Cu shows low transmittance and this may be attributed to highest crystallite size of thin film. This indicates thatthat Cu species can be considered as suitable candidates for use as doped to fabricate $SbS_2$-based absorber material in solar cells applications.

The variation of the extinction coefficient(k) with wavelength for the $SbS_2$ thin films at different Cu concentrations (0.1 M, 0.2 M, 0.3 M) is presented in Figure 3. The results confirmed that the extinction coefficient (k) decreases with increasing the incident wavelength in the visible range of frequency due to normal dispersion of the films. Thus, increase the extinction coefficient (k) gradually with wavelength for different Cu doping concentration could be attribute to an increase of the carrier content after doping and creation of the scattering centers by Cu atoms. Similar behavior was found by Vishwas (2017) in Al-doped $TiO_2$ thin films prepared by spray pyrolysis technique.

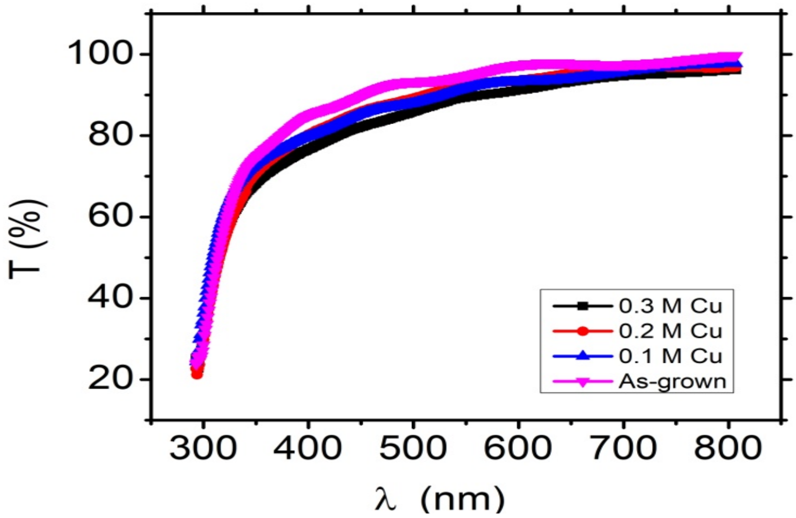


**Figure 2:** Transmittance verus wavelength plots of as-grown and variation of Cu concentrations.

### *3.4 Electrical properties of thin film*

The direct energy gap $E_g$ of the as-grown and Cu doped $SbS_2$ thin films was obtained by plotting $(\alpha h\nu)^2$ versus(hν) Figure 4. Then extrapolating the straight-line part of the plot to the photon energy axis. The relationship between the absorption coefficients α and the incident photon energy hν using the Tauc et al. (1966) relation:

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \quad \textbf{Egn 1}$$

where hν is the photon energy, and m is the constant, which varies with the probability of transitions, it takes values as 1/2 in this research and α is the absorption coefficient, From Figure 4, it is observed that the band gap (Eg) decreased with an increase in Cu doping concentration.

The value of band gap of pure film is about 1.50 eV lowered to 1.24 eV for 0.3 M Cu doped $SbS_2$ thin film. This is an agreement with the findings in the literature which confirmed that Cu-$SbS_2$ has a direct band gap and the band gap values changes according to the preparation parameters and conditions. The results showed that the presence of Cu impurities in the films effect in position and concentration of carrier, which lead to reduction in optical band gap of thin film materials. This is in line with other reserachers (Li et al., 2022; Tobbeche et al., 2019). AS direct bandgap materials, Cu-$SbS_2$ thin films are suitable electroluminescence devices. Fig. 5 gives the variation of the energy bandgap and doping conditions.

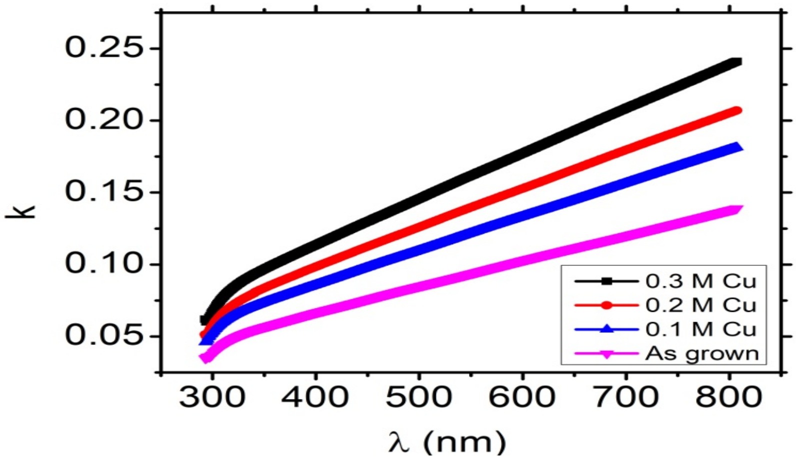


**Figure 3.** Extinction coefficient(k) verus wavelength plots of as-grown and variation of Cu concentrations.

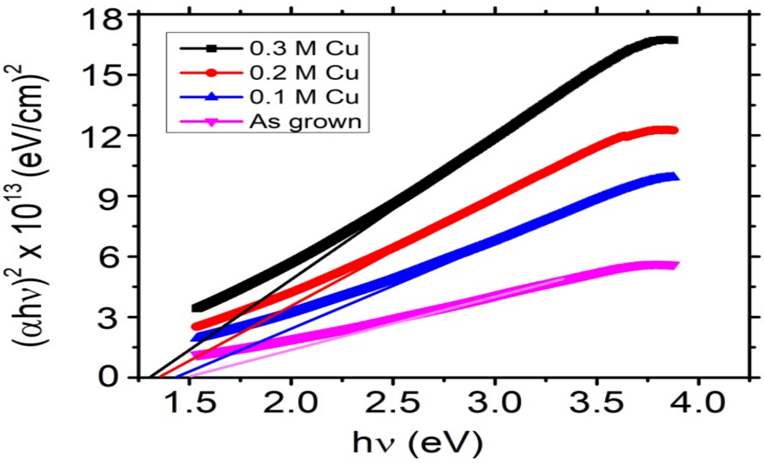


**Figure 4**. $(\alpha h\nu)^2$ plotted against hν for the films as-grown with variation of Cu concentration.

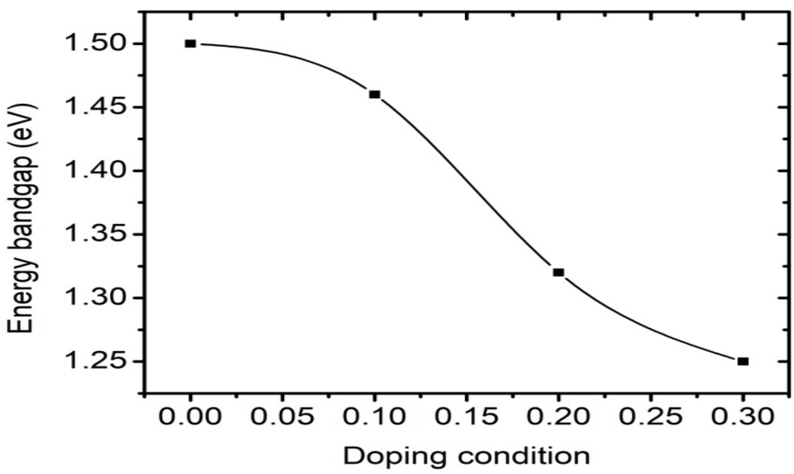


**Figure 5**. Plot of energy bandgap (eV) versus doping condition of Cu impurity.

The plot indicates that the direct bandgap energy decreased from 1.50 to 1.24 eV with increasing Cu concentrations. This band gap narrowing may be explained by the Burstein-Moss shift (Shariful et al., 2022), while the reduction of the band gap is usually caused by a shift in energy of the valence and conduction bands resulting from some known effect such as electron–impurity and electron-electron scattering (Zhao et al., 2021; Xu et al., 2021). In present study, energy band gap values decreased as the dopant concentration is higher than 0.3M

The variation of the refractive index (n), verus doping conditions of thin films is shown in Figures 6. It is apparent note that the refractive index of thin film increases with increasing doping conditions. It is also evident from Fig. 6 that Cu doping can improve the refractive index, and with the increase of Cu content. From the plot, we can see the refractive index of the as-grown found to be lower than other films this may related to the film crystallinity, film porosity, lattice point defect, which could change the structure and bonding arrangement.

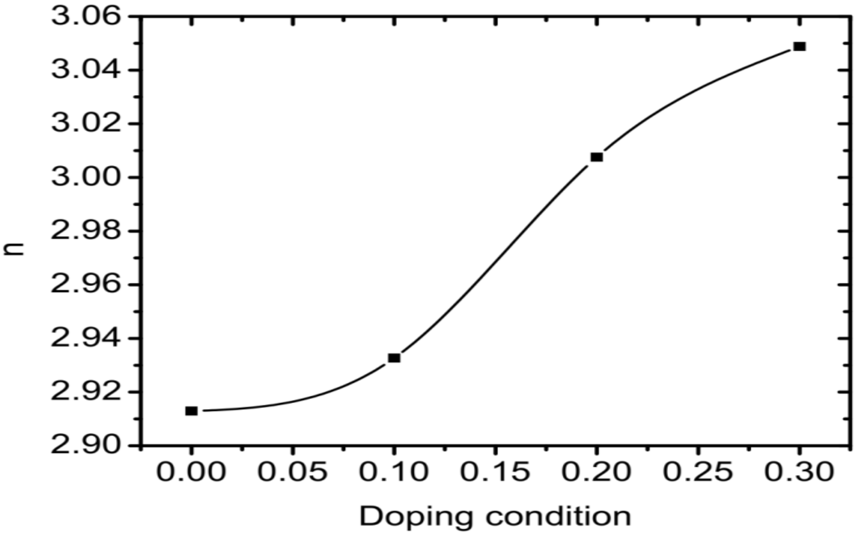


**Figure 6**. Plot of refractive index (n) versus doping condition of Cu impurity.

The variation of the high frequency dielectric constant and static dielectric constant, with doping conditions for the $SbS_2$ thin films at different Cu concentrations (0.1 M, 0.2 M, 0.3 M) is shown in figures 7and 8 respectively. It can be observed that both It is apparent that both the high frequency dielectric constant and static dielectric constant increase with increasing the doping condition of the thin films. This trend can be explained in the terms of the behaviour of the dipole movement and the permittivity related to free dipoles oscillating in the presence of alternating electric field.

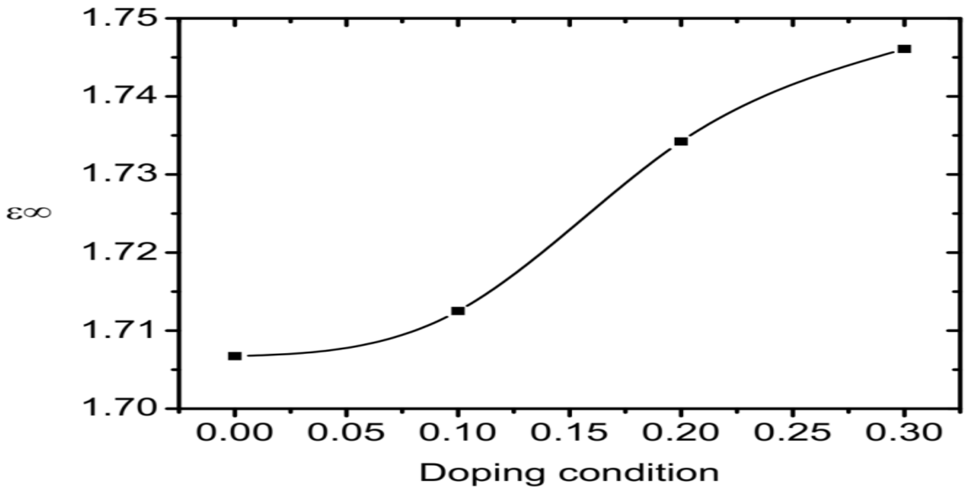


**Figure 7**. Plot of high frequency dielectric constant versus doping condition of Cu impurity.

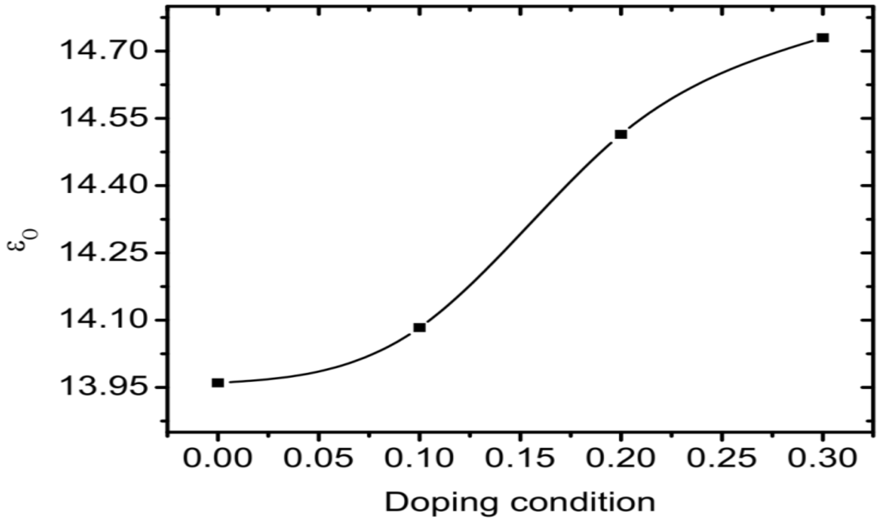


**Figure 8.** Plot of static dielectric constant versus doping condition of Cu impurity.

### *3.5 Scanning electron microscopy (SEM) analysis of thin films*

SEM micrographs for the $SbS_2$ films with different Cu concentrations are shown in Fig. 9A-D. The result from Fig. 9A showed that the film surface is smooth and the grains are evenly distributed on the substrates. It is clearly seen in Figures 9A-D that the grain size increased with the increase in Cu concentration and also no cracks were observed in these film samples. These films can therefore be used as gas sensor. It suggests that the Cu concentration has great influence on the crystallinity and grain size. Their size increase with Cu concentration in the produced nanocomposites. The results confirmed that the films processed with 0.1 M, 0.2 M and 0.3 M Cu, illustrating the trend of refinement with increasing additive concentration and for the highest Cu concentration of impurity applied (0.3 M Cu), the grain size is more pronounced in the film studied (Al-Shomar, 2020), (Alqahtani et al., 2021)

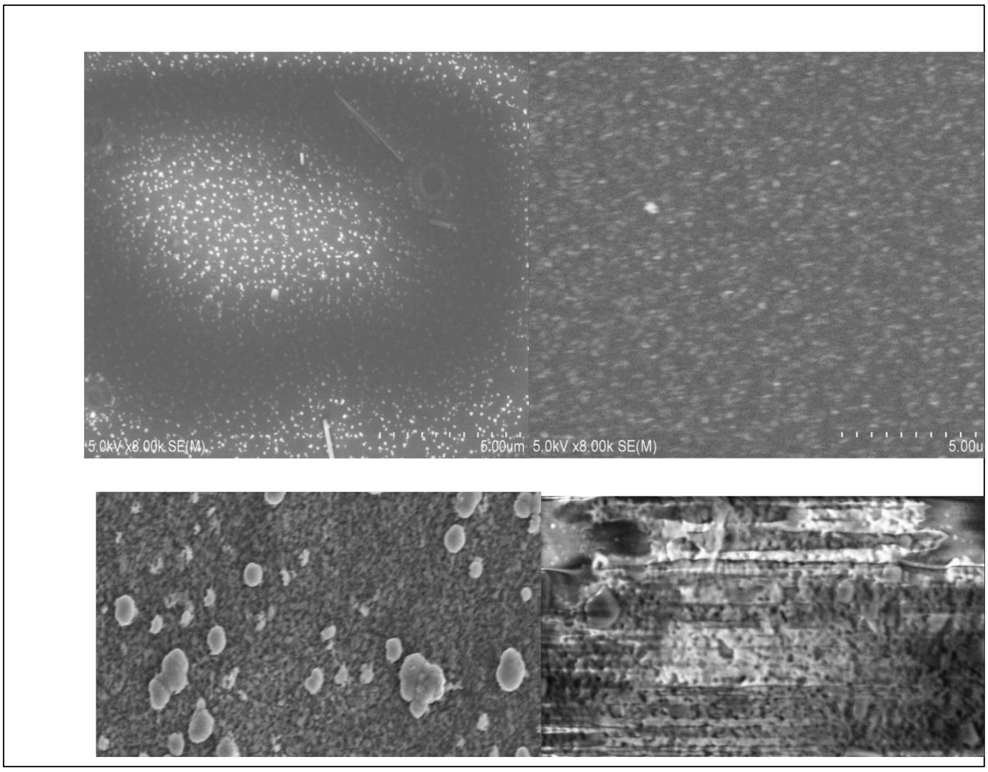


**Figure 9.** SEM images of (a) as-grown (b) 0.1 M Cu (c) 0.2 M Cu and (d) 0.3 M Cu.

## Conclusion

From the present work, chemical bath method was to deposit thin films of antimony sulphide ($Sb_2S_3$) and films were then doped using copper impurities at different concentrations in the range 0.1M to 0.3M. The optical and structural characterizations were done using UV–vis spectroscopy and scanning electron microscopy techniques. The following findings were deduced from the study as follows:

The transmittance spectra, band gap and optical constant of the as-grown and Cu doped $SbS_2$ thin films has obtained from UV–vis spectroscopy. The optical analysis showed that all the films had high transmittance in the visible region. The band-gap energy of the CuSbS2 thin films was estimated by extrapolation to lie between 1.50-1.24 eV, in good agreement with the values reported in the literature. The optical band gap of the as-grown film is higher than that of the Cu doped SbS2 due to enlarged charge carriers according to Burstein-Moss effect.

The extinction coefficient (k) and the refractive index values for all the films decrease rapidly for all doping concentration. The high frequency dielectric constant and static dielectric constant was increased with the increment of doping condition due to polarization enlargement.

The SEM results showed that the Cu concentrations has great influence on the crystallinity and grain size of thin films. As a conclusion, copper antimony sulphide ($CuSbS_2$) is easily available, inexpensive, abundant, and stable and also exhibit good properties of photoelectric materials, indicating their potential for application as light absorbers in future photovoltaic technologies.

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*Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.

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