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STRUCTURAL AND SPECTRAL ANALYSIS OF CHEMICAL BATH DEPOSITED COPPER SULFIDE THIN FILMS FOR SOLAR ENERGY CONVERSIONS

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Copper sulfide chalcogenide thin films have been successfully deposited on glass substrates using copper II chloride, thiourea, TEA and ammonium hydroxide in a solution bath. Structural and optical characterizations were carried out with the aid of X-ray Diffractometer and Unico–UV-2102PC spectrophotometer respectively. The effects of varying the annealing temperatures on the structural and spectral properties were also investigated. The presence of both chalcocite ($Cu_{1.96}S$) and digenite (Cu_9S_5) phases of the copper sulfide thin films with average grain sizes between 12.55nm and 14.22nm were confirmed by XRD analysis. The thermally treated Cu_xS thin films have very high transmittance, between 85% and 95%, and low reflectance, less than 21% at both the visible and the NIR regions of the electromagnetic spectrum. They have optical band gap energy between 2.1eV and 2.5eV. The refractive index, extinction coefficient, optical conductivity and the dielectric properties were also studied. The analysis show that the thin films could serve as good materials for the fabrication of solar cell and other optical devices.

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1. Introduction

Copper sulfides belong to the I-IV compound semiconductor materials [1] and are among the chalcogenide compounds with several applications in Nanosciences. They have been found very useful in coating solar energy conversion systems and solar control devices. The chalcogenides are also used in the fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor applications [2-4]. Moreover, ternary copper chalcogenides like copper indium diselenide, and copper indium gallium selenides, in recent times, are now widely used in the fabrication of solar photovoltaic cells [5-6]. At least five stable phases of the copper-sulfur system are known to exist in nature among which include *covellite* ($Cu_{1.00}S$), *anilite* ($Cu_{1.75}S$), *digenite* ($Cu_{1.80}S$), *djurleite* ($Cu_{1.97}S$), and *chalcocite* ($Cu_{2.00}S$) [1,7]. Other phases that exist include *yarowite* ($Cu_{1.12}S$) and *spionkopite* ($Cu_{1.14}S$) [8]. The crystal structures of the Cu_xS such as hexagonal, orthorhombic, pseudo cubic and tetragonal is determined by the value of x. XRD spectra has shown that varying the deposition temperature for the films grown by spray pyrolysis significantly affects both the phase and the crystallite sizes of the Cu_xS thin films [9]. The special attention given to the study of copper sulphide thin films is due to the discovery of the CdS/Cu_xS heterojunction solar cell [1].

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Among the different techniques for the deposition of high quality transition chalcogenides, the chemical bath method has become more and more popular because of its cost effectiveness, advantage of large area of deposition and easy adaptability [10]. The technique is extensively used by researchers where affordability and availability of the highly sophisticated methods are challenging [11]. It is a low temperature process which in effect avoids the oxidation and corrosion of the substrate. In addition, as a slow process, it facilitates better orientation of the crystallites with improved grain structures [12,13]. Furthermore, the chemical deposition method offers minimal toxicity and less environmental hazards due to the fact that the vapour phase of the reactants are usually avoided as a result of the use of dilute solutions of the reacting compounds. Though the method is relatively inexpensive and less sophisticated, the key factor in solar cell development by CBD technique requires the optimization of the experimental parameters for the thin films fabrication. Thermal treatment of thin films, for instance, is necessary after their depositions in other to enhance their properties for optimal performance. Such treatments after deposition can give significant improvements due to grain boundary passivation, and clearly a deposition technique which gives large grains with minimum grain boundary states is advantageous [6]. We report in this work the spectral and structural characterization of copper sulfide thin films synthesized by the chemical bath deposition technique and deposited on glass substrates.

2. Experimental

2.1 Synthesis

The chemical bath solution was obtained by first preparing one molar solution of copper II dihydrate ($CuCl_2.2H_2O$), thiourea $(NH_2)_2SC$, 25% ammonium solution (NH_4OH) and triethanolamine (TEA) ($N(CH_2CH_2OH)_3$). 10ml each of TEA, thiourea and ammonium solution and 30ml of distilled water were added to 3ml of copper chloride solution in a 50ml beaker and then gently stirred at room temperature to obtain a homogenous solution. The complexing agent, TEA was used in order to obtain high quality films [14,15,16] by ensuring the slow release of the metallic ions in the solution and hence slow precipitation of the compound. As the state of the substrate's surface greatly affects the growth of the deposited films [17], the glass substrates with dimensions, 7.5mm x 2.6mm x 1.0mm, were washed with detergent solution and rinsed in distilled water. They were subsequently dipped into acetone and ethanol for 30 minutes respectively, rinsed in distilled water and allowed to dry. The substrates were then vertically suspended into the beaker; containing bath solution.

In a saturated bath solution, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product, the solution becomes supersaturated and precipitation occurs with subsequent combinations of ions on the substrate and in the solution to form nuclei. Therefore, for thin film deposition to occur successfully, the ionic product must exceed the solubility product. The optimal deposition temperature and dip time for the copper sulfide thin films were found to be 60°C and 2 hours 20 minutes respectively. The reaction mechanism for the deposition of the copper sulfide thin films involve Cu^{2+} and S^{2-} ions in the solution, which condensed onto the substrates. The possible mechanism for the reaction can be written as shown below.

$$CuCl_2.2H_2O + TEA \leftrightarrow Cu(TEA)^{2+} + 2Cl^- + 2H_2O$$
$$Cu(TEA)^{2+} \leftrightarrow Cu^{2+} + TEA$$
$$NH_4OH \leftrightarrow NH_4^+ + OH^-$$
$$(NH_2)_2SC + OH^- \leftrightarrow CH_2N_2 + HS^- + H_2O$$
$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$
$$Cu^{2+} + S^{2-} \rightarrow \downarrow CuS$$

At the end of the deposition, the glass slides were removed, rinsed with distilled water and allowed to dry in the air. It is common for the chemically-deposited samples to be contaminated with oxygen from the environment as the sample was exposed to the environment during preparation. Oxygen contamination is removed during the annealing process [18]. One of the samples, 40A was left as-deposited and the rest (40B, 40C and 40D) were annealed at 200^{o}C, 300^{o}C and 400^{o}C respectively in an oven.

2.2 Characterizations

The structural and spectral properties of the copper sulfide thin film samples were characterized with X-ray diffractometer and UV-VIS Spectrophotometer. The optical absorbance and transmittance of the chemical bath deposited thin films samples were measured at room temperature by using the Unico–UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1100nm. Based on the spectral theoretical relationships, the spectra data was employed to evaluate the reflectance, absorption coefficient, refractive indices and optical band gaps. The XRD data was used to determine the phases of the deposited copper sulfide thin films and to estimate their crystallite sizes.

3. Results and discussion

3.1 Structural Analysis

The XRD studies was carried out with the aid of Mini D10 Diffractometer, using the CuK_α radiation of wavelength $\lambda = 1.5405Å$. Figures 1 and 2 show the X-ray diffraction patterns of the as-deposited Cu_xS thin films and the films annealed at 400^{o}C respectively. A comparison of the observed XRD patterns for the as-deposited copper sulfide thin film with the standard JCPDS cards reveals that the films possess a structure that matches with the mineral *chalcocite*, (JCPDS file No. 29-0578), $Cu_{1.96}S$ with corresponding diffraction 2θ peak angles of 31.94^{o} and 70.77^{o}. The (*h k l*) planes responsible for the diffractions are (*0 0 4*) and (*1 0 8*) with respective full-width-at-half-maximum (FWHM) of 1.9000 and 1.0343. The XRD data for the Copper sulfide thin films annealed at 400^{o}C compares very well with the standard XRD data of the compound, *digenite,* Cu_9S_5 (JCPDS file No. 26-0476). Analysis for the sample annealed at 400^{o}C revealed that the standard diffraction angles are 26.29^{o}, 29.31^{o}, 32.20^{o} and 40.07^{o}. The (*h k l*) planes responsible for these diffraction patterns are (*1 0 1*), (*1 0 7*), (*1 0 10*) and (*1 0 16*) with respective FWHM of 1.0689, 1.0858, 1.0544 and 1.0351.

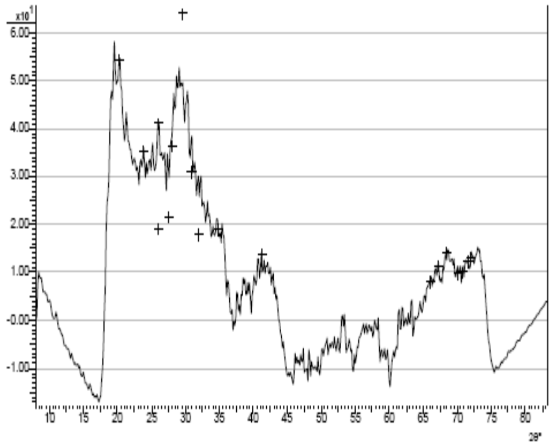

Fig. 1. XRD pattern of the as-deposited copper sulfide thin films

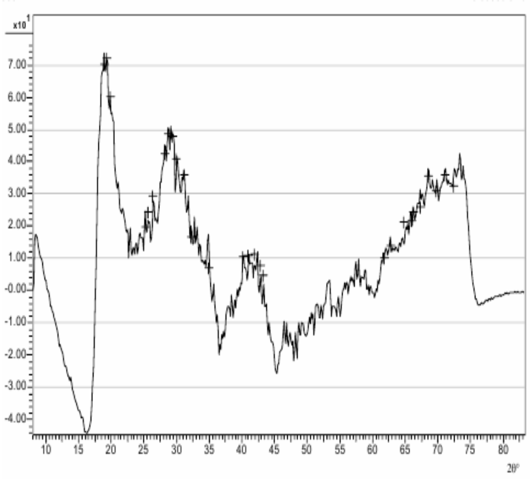

Fig. 2. XRD pattern of the copper sulfide thin films annealed at 400^{o}C

A close observation and comparison between the diffractograms shows peak broadening in the patterns due to the thermal treatment. This may be as a result of the formation of crystalline thin films [19]. The average grain sizes of the thin films were evaluated using the Scherrer's formula given by

$$D = \frac{k\lambda}{\beta \cos\theta} \quad , \tag{1}$$

where θ, β, k and λ represent the Bragg's angle, the FWHM, a constant (assumed to be 0.94) and the wavelength of the X-ray respectively. The above formula showed that there was an increase in the average crystallite sizes from 12.55nm for the as-deposited copper sulfide thin film to 14.22nm for the films annealed at 400^{o}C. The summary of the XRD results is displayed on table 1.

Table 1: Summary of the XRD results.

	AS-GROWN	**ANNEALED (400^{o}C)**
Mineral Structure (Phase)	Chalcocite	digenite
Chemical Symbol	$Cu_{1.96}S$	Cu_9S_5
Diffraction peak angles (2θ)	31.94^o and 70.77^o	26.29^o, 29.31^o, 32.20^o and 40.07^o
Diffraction planes (h k l)	(0 0 4) and (1 0 8)	(1 0 1), (1 0 7), (1 0 10) and (1 0 16)
FWHM	1.9000 and 1.0343	1.0689, 1.0858, 1.0544 and 1.0351
Average grain size (nm)	12.55	14.22
JCPDS ref. card number	29-0578	26-0476

3.2 Optical properties

The following relationships exist for a material with optical transmittance (T), refractive index (n), thickness (t), reflectance (R) and absorption coefficient (α) [5,6].

$$T = \frac{(1-R)^2 e^{-\alpha t}}{(1-R^2)e^{-2\alpha t}}. \tag{2}$$

The reflectivity of the material is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \tag{3}$$

The extinction coefficient k depends on the wavelength, λ of the photon and is related by the expression

$$k = \frac{\alpha \lambda}{4\pi}. \tag{4}$$

Absorption coefficient

The graph of absorption coefficient, α vs photon energy, $h\nu$ is shown in figure 3. This curve shows that α is not linearly related to $h\nu$. It can as well be seen that the thermally treated Cu_xS has lower value than the as-deposited sample. Maximum values of absorption coefficient are observed at shorter wavelengths.

Band gap study

The nature of the transition in both amorphous and crystalline semiconductors can be determined from the energy dependence of the absorption coefficient near the absorption edge. For direct transition in polycrystalline thin film, the band gap energy, E_g and absorption coefficient, α are related by the expression [5]:

$$(\alpha h\nu) = A(h\nu - E_g)^n. \tag{5}$$

The constant A is independent of the photons energy ($h\nu$) but depends on the effective masses of the electrons and holes in the semiconductor material [20]. For the allowed and the forbidden direct transitions, the selection rule gives that n = ½ and 3/2 respectively. The graph of $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) is plotted for direct allowed transition (n = ½). The approximately straight portion of the curve is extrapolated to the horizontal axis where the band gap energies are read. These are shown in Fig. 4. Extrapolations show that the Cu_xS thin films has direct band gap of 2.4eV for the as-deposited but 2.5eV, 2.1eV and 2.3eV respectively for samples annealed at 200°C, 300°C and 400°C. Indirect band gap energy between 1.0eV and 1.4eV (graph not shown) were also observed.

The direct band gaps of the Cu_xS thin films are in agreement as reported elsewhere [1,4,9,21] although Valentina and Mindaugasand [22] reported an indirect band gap of 1.25eV and 1.3eV for copper sulfide layers on a polyamide film. Materials with such indirect wide optical band gap energy may possibly be used in the fabrication of blue light emitting diodes as well as in electroluminescent display [20, 21, 23].

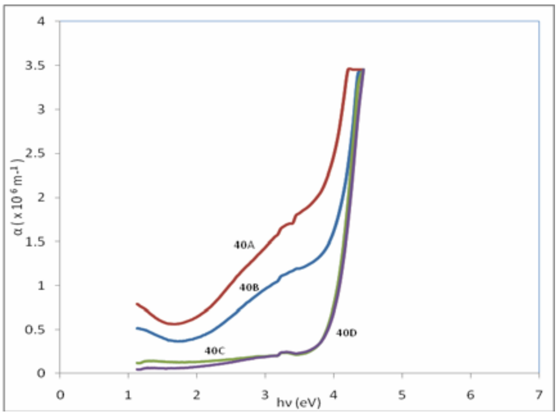

Fig. 3. Plot of α as a function of photon energy (hv) for copper sulfide thin films

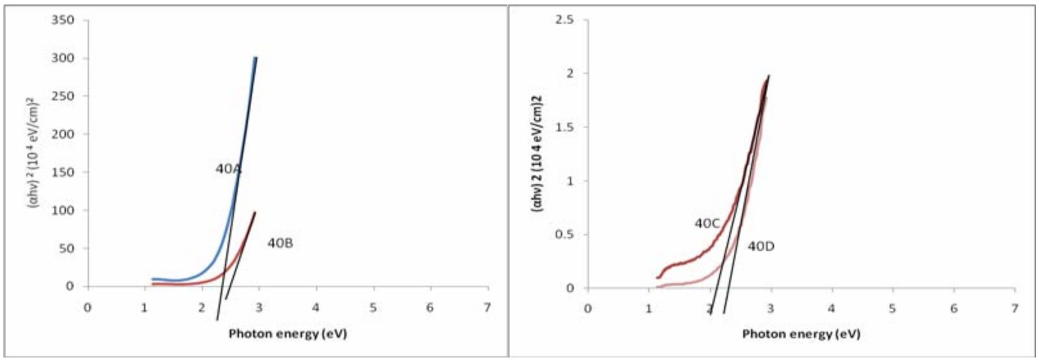

Fig. 4: Plot of $(\alpha h\nu)^2$ as a function of photon energy (hv) for copper sulfide thin films

Absorbance, transmittance and reflectance

Fig. 4 shows the plot of optical absorbance against the wavelength of electromagnetic spectrum. From the figure, we observe that all the deposited thin films exhibit high absorbance in the UV region of the electromagnetic spectrum which decreased towards the NIR region. However, while the absorbance of the as-deposited films is about 90%, the Cu$_x$S thin films annealed at 200^{o}C has absorbance of about 50%. The films treated at higher temperatures have very low absorbance (less than 20%) in all the regions of investigations. All the films show relatively low absorbance in the NIR regions of the spectrum (less than 35%).

Conversely, the thermally treated Cu$_x$S thin films (300^{o}C and 400^{o}C) have very high transmittance, between 85% and 95%, at both the visible and the NIR region of the electromagnetic spectrum. The plot of the transmittance against the wavelength of the incident photon is shown in figure 5. Figure 6 is the plot of the reflectance of the Cu$_x$S thin films with respect to the incident photon wavelength. The graph shows that all the samples have reflectance values which are less than 21%. Moreover, the thermally treated Cu$_x$S films exhibited the least reflectance of less than 10%.

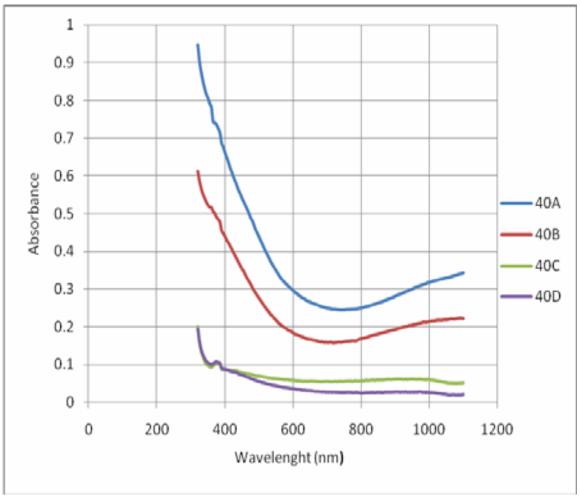

Fig. 4: Plot of absorbance against wavelength for the CuS thin films

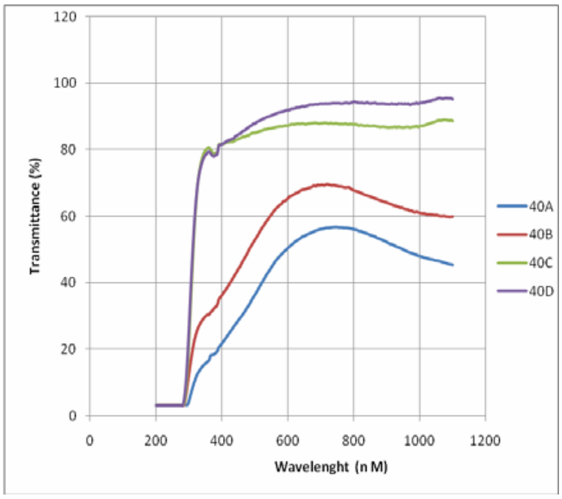

Fig. 5: Plot of transmittance against wavelength of the CuS thin films

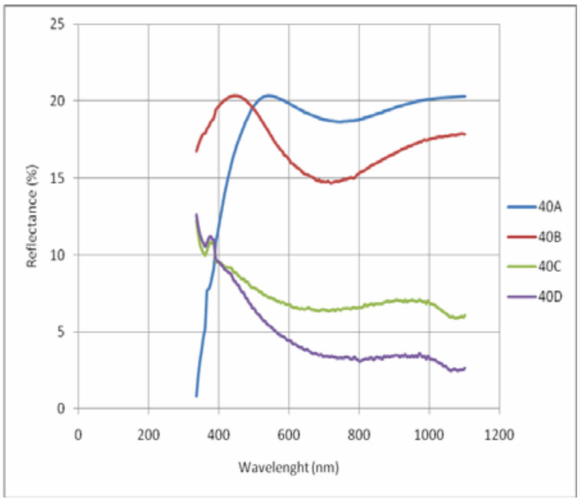

Fig. 6. Plot of reflectance against wavelength of the Cu_xS thin films.

The high transmittance and low reflectance properties of the Cu_xS thin films annealed at 300°C and 400°C make them good material for anti-reflection coatings which could as well be employed in solar thermal and other optical devices to reduce solar reflectance and enhance their transmittance [4]. In addition, the high absorbance of the as-deposited thin films also suggests that they may be used in solar cell fabrication.

Refractive index and dielectric constant

The real and the imaginary dielectric constants are related to the refractive index, *n*, and are respectively given by equations 8 and 9 [24].

$$\varepsilon_r = n^2 - k^2 \tag{6}$$

$$\varepsilon_i = 2nk \tag{7}$$

Plots of the refractive index and the extinction coefficient against the photon energy are displayed in figures 7 and 8 respectively. A decreasing trend in the refractive index (between 2.2 and 0.1) was observed for the as-deposited Cu_xS and the thin films annealed at 200°C with respect to the photon energy. However, the thin film annealed at 300°C and 400°C showed increasing trend from about 1.2 to 2.3. At photon energy between 1.0eV and 4.2eV, the average extinction coefficients fall between 0.005 and 0.070. It can also be observed that the as-deposited thin films and the films annealed at 200°C have relatively high values of k at all wavelengths. In addition, the k values decreased with increase in annealing temperatures.

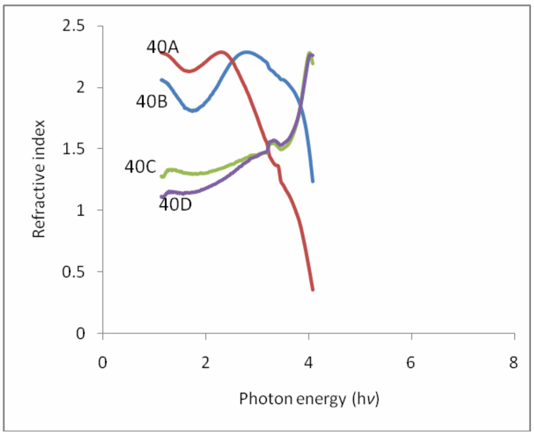

Fig. 7: Plot of refractive index against incident photon energy of the Cu_xS thin films

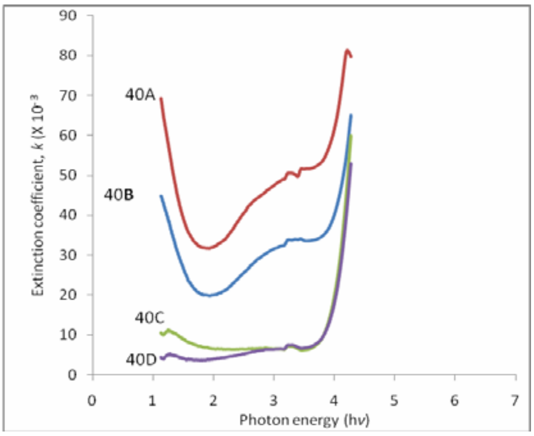

Fig. 8. Plot of extinction coefficient against incident photon energy of the Cu_xS thin films

Figs. 9 and 10 respectively show the plot of the optical conductivity and the real dielectric constant against the energy of the incident photons. The optical conductivity varies from 0.020 x $10^{14}s^{-1}$ to 0.600 x $10^{14}s^{-1}$. The values relatively increased with decreasing photon's wavelengths. However, the copper sulfide thin films annealed at 300°C and 400°C revealed lower optical conductivities. While the real dielectric constant of the thin films annealed at 300°C and 400°C increased from about 1.5 to about 6.0, the as-deposited thin films and the sample annealed at 200°C revealed a decrease from about 5.0 to about 0.20.

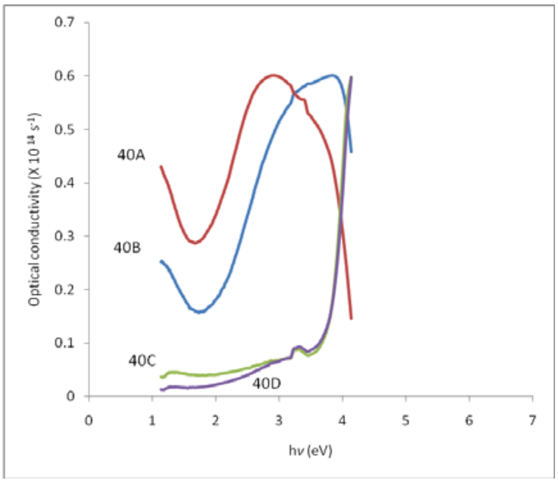

Fig. 9: Plot of optical conductivity against incident radiation energy

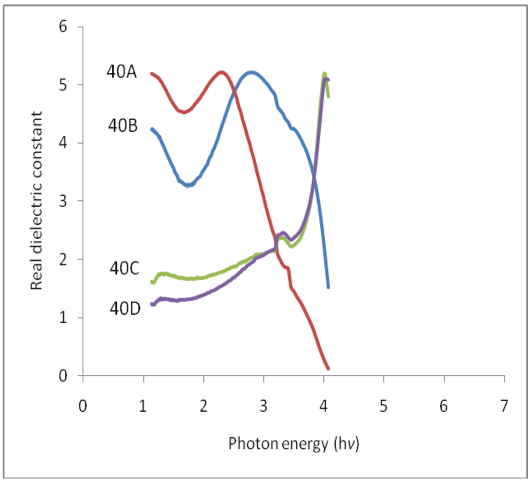

Fig. 10: Plot of real dielectric constant against incident radiation energy

4. Conclusion

Copper sulfide thin films were successfully deposited on glass substrate by chemical bath technique. The effects of post-deposition annealing on the structural, optical and solid state properties were studied. The structural studies revealed non stoichiometric copper sulfide compounds namely *chalcocite*, $Cu_{1.96}S$ and *digenite,* Cu_9S_5 for the as-deposited sample and the sample annealed at 400°C with respective average grain sizes of 12.55nm and 14.22nm. The optical studies show that the films annealed at 300°C and 400°C has very high transmittance and low reflectance as compared with the as-deposited sample and the samples annealed at lower temperatures. These are desired qualities of materials for anti-reflection coatings (in laminated glazing) and in solar photo-thermal conversions.

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