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Preparation of Copper Sulfide Films (CuS / Cu_2S) on Silicon by the Successive Ionic Layer Adsorption and Reaction Technique : Applications in Photo-conductivity

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Abstract:

The consecutive ionic layer adsorption and reaction approach was used to create CuS/Cu2S thin films on a silicon and glass substrate at room temperature. X-ray diffraction (XRD) and optical microscopy were used to examine the produced films' structural characteristics.

The obtained results show That all films have poly-crystalline structure and the average particle size as determined from Scherer's relation (140-180) nm. The electrical conductivity and optical energy gap of CuS / Cu_2S films were analyzed and the optical energy gap of these films (2.38- 2.4) eV.

Keywords: Thin film; **CuS / Cu_2S**; Chemical Technique; Growth of Crystalline; conductivity and Photovoltaic.

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Introduction

Thin crystalline silicon solar cells and accessible PV cells have several advantages. Using a polycrystalline Si film on a cheap substrate, such glass, is one potentially useful method. Excellent current densities (Jscs) that approached near-theoretical values were demonstrated in early attempts to fabricate cells using Si films with thicknesses ranging from 1 to 3 μm [1]. The p-n junction, an interface between a semiconductor's p-type and n-type regions, is the most basic semiconductor junction utilized in solar cells to separate photogenerated charge carriers. Therefore, before a material can be deemed a viable candidate for solar cells, it must first demonstrate its fundamental semiconductor property—the ability to modify its conductivity through doping.

To further enhance thin-film silicon solar cells, sophisticated ideas are still needed. Further advancements in thin-film silicon solar efficiency still need sophisticated ideas. Chemical techniques such spray pyrolysis [2], pulsed laser deposition [3], vacuum evaporation [4], electrode position method [5], electron beam evaporation [6], chemical bath deposition [7], and Atomic Layer Deposition (ALD) [8,9] can be used to create the CuxS films.

For silicon, this was the situation. were applied utilizing the SILAR technique on glass and single crystal Si wafer substrates. Covelite, CuS, aniline, Cu1.75S, jgenite, u1.8S, jurleite Cu1.95S, and chalcocite Cu2 S are the five stable phases that copper sulfide produces at normal temperature [10]. CuxS thin films have an intriguing array of uses due to their optical and electrical characteristics, including photothermal conversion, electroconductive electrodes, microwave shielding coatings, and solar control coatings [11]. One SILAR deposition cycle can be used to precisely control the film's development [12, 13]. Thin films of CdS, ZnS, PbS, ZnO, Sb2S3, and other elements have been deposited on a variety of substrates using the SILAR technique [14–16]. A review of the literature reveals that no attempt has been made to use the SILAR approach to deposit CuxS thin films [18]. Designing a low-cost, thin-film Si solar cell with high efficiency and creating a method for fabricating the cell utilizing a Si substrate are the goals of our effort. A novel single-junction, thin Si cell structure is described in this study along with several processing. The ultimate objective of this search is to produce CuxS thin films on glass at room temperature and standard pressure using the SILAR technology. The development and characteristics of CuxS thin films

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produced by SILAR on Si were examined as the initial step in this process [20].

II Experimental

As substrates, n-type single crystal Si wafers and 25 mm × 25 mm corning glass slides were employed. Corning glass slides were ultrasonically cleaned with hot distilled water after being boiled in concentrated chromic acid for 20 minutes. Immersion of the substrate in distinct cation and anion precursor solutions is the foundation of the SILAR technique. The CuxS precursor solution (1.4 M KOH) was made using deionized water.

By adding sodium thiosulphate ($Na_2S_2O_3$) to copper sulphate $CuSO_4$ solution until a bleach blue (dim blue) color results, thin films were created from a (0.08 M) $CuSO_4$ solution of copper thiosulphate complex. When adding sodium thiosulphate solution of a lower hue, one should pay attention to the color of the copper thiosulphate complex solution in order to prevent the formation of a copper oxide thin layer. Glass substrates were used to grow the films. The substrates were submerged in a hot KOH solution that was kept at 50 oC after first being dipped in a copper thiosulphate complex solution. As seen in figure 1, this cycle was repeated multiple times between 10 and 15 cycles, with a 5-second dipping duration in each bath. Dipping in both cationic and anionic precursors is one whole set of dipping. Silicon was also used to grow the Cu_2S/CuS films. The following is one SILAR process cycle:

(i) The substrate is immersed in the cation precursor solution - an aqueous solution of a soluble salt of the cation of the chemical to be produced. The cations are adsorbed on the substrate's surface in this stage.

(ii)The substrate is now immersed in the anion precursor solution — an salt of the anion of the chemical to be generated in an aqueous solution. The desired solid compound is created when the anions and adsorbed cations interact. It is possible to build thin films by repeating these techniques. CuXS thin film mechanism The process of preparation involves mixing thiosulphate ($Na_2S_2O_3$) with copper sulphate ($CuSO_4$) to create copper oxide (CuO) solution, which has a pale blue appearance. was submerged at 50°C in a (KOH) solution (0.1) gm./100 ml H2O.When the CuxS thin film appeared, the hue changed to a deep brown. In these reactions, potassium hydroxide (KOH) is utilized as a catalyst to produce $Cu(OH)_2$, and as soon as the final crucial result reacts with the sulfur ion (S-2), a product known as CuxS is formed on glass Substrate

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III RESULTS AND DISCUSSION

As seen in figure 1a and b, the photomicroscope image demonstrates that the growth of the CuxS thin film was caused by the SILAR method on both Si and glass substrates. In these cases, silicon acts as a seed to increase the crystallization, but when the CuxS thin film was deposited on glass substrates, it appeared as a forestation form.

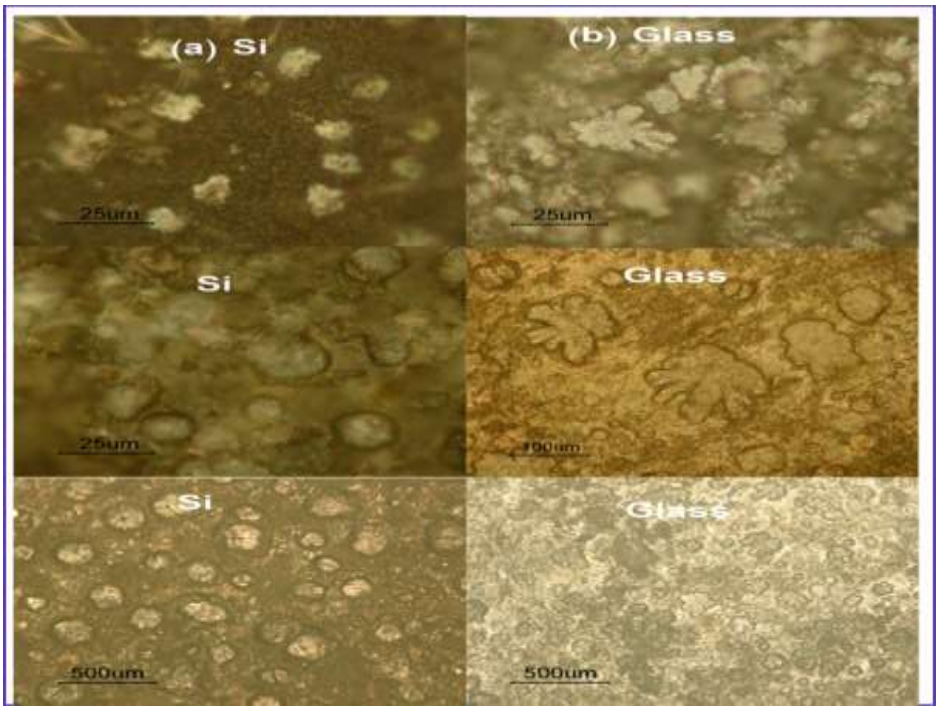


Fig.1 (a) The optical microscopy images of CuxS thin films deposited on a silicon, (b) On a glass substrates

In accordance with the joint committee on powder diffraction standard [N 1997 JCPDS prevalent] of CuS and Cu2S thin films, the XRD analysis of the CuS/Cu2S thin films formed on silicon and glass reveals that the thin films were nearly polycrystalline with a hexagonal structure. In this instance, the addition of hydrazine hydrate, which functions as a reducing agent and releases Cu+ ions rather than Cu+2 ions from the CuSO4 solution, may be

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the cause of the potential for Cu2S production. Table 1 presents a comparison between the observed and standard "d" values.

. The particle size of Cu_2S thin film was calculated by using the Scherrer's relation [17]. The average grain size was (140 - 160) nm. Show in fig. (2)

$$\boldsymbol{D = \frac{0.94\lambda}{\beta cos\theta}} \qquad (\mathbf{1})$$

D: is the grain size (G.S)
K: is a constant (0.94)
λ: is the wavelength of Cu Kα
θ: is the Bragg's angle and
β is full width half maximum (FWHM) of the preferential plane.

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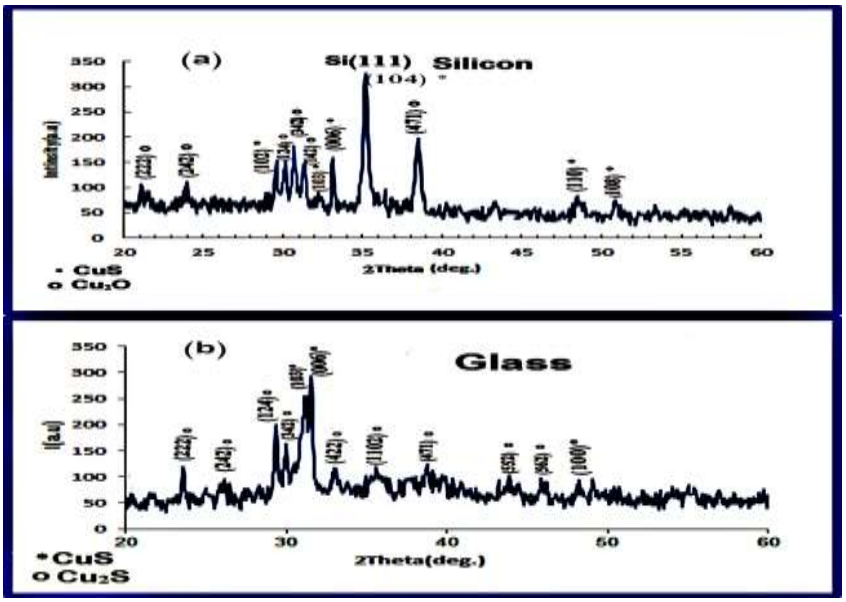


Fig. (2) An XRD pattern of a 400nm thickness CuS/Cu_2S film grown on (a) Si and (b) glass substrate.

Table N°1.Comparison of observed 'd'values with standard 'd'value for (CuS /Cu_2S) thin film deposited by modified chemical method.

Observed 'd' (A°)	**Standard 'd' (A°)**	**Plane(hkl)**	**Copper Sulphide**
Silicon and Glass			
4.097	4.24	(222)	Cu_2S
3.76	3.73	(242)	Cu_2S
2.39	2.40	(102)	CuS
3.14	3.15	(124)	Cu_2S
3.03	3.05	(342)	Cu_2S
2.97	2.94	(142)	Cu_2S

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2.83	2.82	(103)	CuS
2.64	2.61	(006)	CuS
2.5	2.4	(104)	CuS
2.319	2.325	(471)	Cu_2S
1.93	1.92	(110)	CuS
1.69	1.72	(108)	CuS
2.51	2.469	(1102)	Cu_2S
2.645	2.659	(422)	Cu_2S
1.97	1.97	(522)	Cu_2S
2.03	2.005	(562)	Cu_2S
3.4	3.37	(100)	CuS

Optical Properties

Fig. (4) shows the absorption spectrum of Cu_xS film was held in the wavelength range 200–900 nm at room temperature for the films deposited on glass substrate. Characterized high absorbency membranes, which makes a good base in solar cells, photovoltaic cells, selective absorption or location known as solar water heaters. Fig. (5) and fig. (6). absorption coefficient (α) against wavelength and photo energy ($h\nu$) for Cu_xS film on Corning glass substrate. The nature of the optical transition (direct or indirect) is determined by using the relation :

$$\alpha = A(h\nu - Eg)^n / h\nu \quad (2)$$

where $h\nu$ is the photon energy and Eg the optical band gap. A is the constant which is related to the effective masses associated with the valence and conduction bands. For allowed direct transitions, n=1/2 and allowed indirect transitions, n=2, as show in fig. (7). We found the variation of $(h\nu)^2$ with $h\nu$ is a linear which indicates that the direct transition is present. Extrapolating the straight line portion of the plot of $(\alpha\, h\nu)^2$ against $h\nu$ to energy axis for zero

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absorption coefficient give optical band gap energy value as 2.38 eV, which is which is comparable to the value reported earlier [18]. Fig. (5) shows the plot of optical absorption coefficient (α) against wavelength (λ) for Cu_xS film on glass substrate.

Fig.(6) shows the plot of optical absorption coefficient (α) against photo energy (hν) for Cu_xS film on glass substrate.

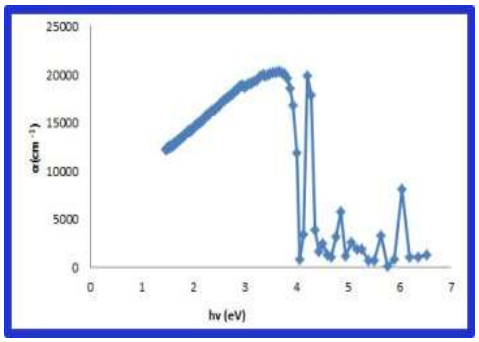


Fig.(4) Plot of optical absorptionfor the SILAR grown CuxS thin film on glass substrate.

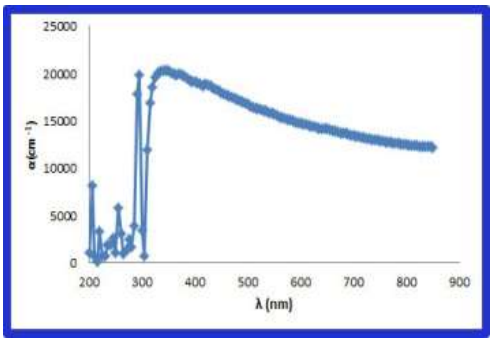


Fig. (5) Plot of optical absorption coefficient (α) against λ Cu_xS thin film on glass substrate.

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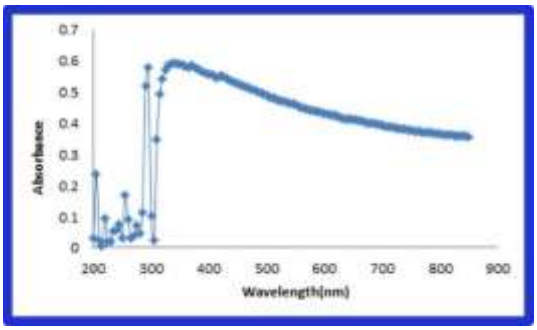


Fig.(6) Plot of optical absorption coefficient (α) against hν for the SILAR grown Cu_xS thin film on glass substrate.

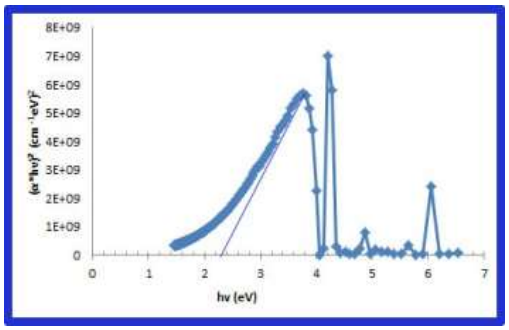


Fig. (7) Plot of $(\alpha h\nu)^2$ against hν for the SILAR grown Cu_xS thin film on glass substrate.

Electrical Properties

The resistive behavior, with charge transport but no charge transfer, characterizes all the films. There are two distinct domains in which the electric resistance varies. This is due to the presence of different (CuS/ Cu_2S) phases. In the first region where CuS is the dominant phase the values for resistance are lower than in the second region where Cu_2S is the dominant phases in the material. Figure (8) shows the variation of resistivity with reciprocal of temperature for the film on glass substrate. The resistivity increase with increase in temperature indicating the semiconducting behavior of the (CuS/ Cu_2S) film. In addition to enhances electrical contacts between the particles and, consequently, film resistivity increase It is also observed that the variation is non-linear. It was found that the conductivities σ in the core shell materials show Arrhenius-type behavior :

$\sigma = \sigma_\circ \exp [E_a/K_B T]$ (3)

Where, **$\sigma_\circ$:** constant represent to conductivity at high temperature
E :electrical conductivity activation for energy**,**
K_B: Boltasmans constant**.**
T: Temperatur

$\rho = \frac{R*A}{L} ...where\ A = (w.t), \sigma = \frac{1}{\rho}$

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w is Pole width , t is membrane thickness, L is distance between electrodes as shown in figure (7) the group of materials conform to the anti-Meyer–Neldel rule [19,20] (also called the compensation law):

$$\text{Ln } \sigma_{o} = \text{Ln } \sigma_{\infty} + (E_A / E_{MN}) \quad (4)$$

Where σ^{∞} and E_{MN} are the so-called Meyer–Neldel parameters (M–N pre factor and M–N characteristic energy). Conductivity of the (CuS/ Cu_2S) materials was calculated from the resistivity measurements. The conductivity initially increase with low temperature as shown in fig. (9). This was attributed to the increase in ionic conductivity, due to the charge dissociation induced by adsorbed water molecules.

The nature of the variation of conductivity with temperature suggests that more than one type of conduction is involved in (CuS/ Cu_2S). In the low temperature region it shows metallic behavior and the conductivity decreases with the increasing temperature as show in fig. (9).

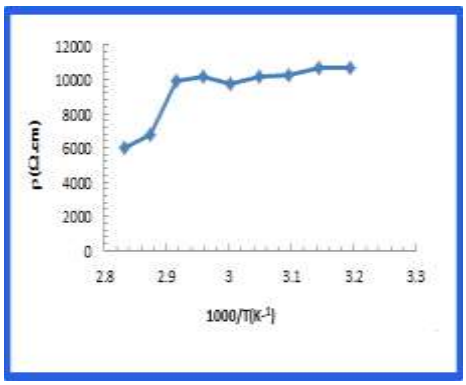


Fig.(8) The variation of electrical resistivity of Cu_xS thin film with

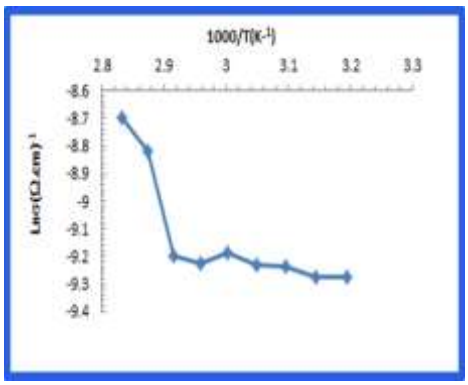


Fig (9). The variation of electrical conductivity of Cu_xS thin film as a function of working temperature

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IV. CONCLUSION

Deposit of CuxS thin films on the glass and Si substrates successfully by using the technique. The films were found to have polycrystalline, homogeneous structures and covered the substrates well. The films show p-type electrical conductivity, and band gap energy of 2.38 eV is used in solar cells.

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تحضير أغشية كبريتيد النحاس (CuS / Cu2S) على السيليكون باستخدام تقنية الامتزاز والتفاعل الطبقي الأيوني المتتالي: التطبيقات في التوصيل الضوئي

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ملخص:

تم تحضير أغشية رقيقة من CuS / Cu2S باستخدام طريقة الامتزاز والتفاعل الطبقي الأيوني المتتالي على ركيزة من الزجاج والسيليكون في درجة حرارة الغرفة. تم توصيف خصائص بنية الأغشية المحضرة بالمجهر الضوئي والحيود بالأشعة السينية (.(XRDأظهرت النتائج أن جميع الأغشية لها هياكل متعددة البلورات وأحجام جسيمات متوسطة، كما تم تحديدها من علاقة شيرر (140–180) نانومتر. تم تحليل الموصلية الكهربائية وفجوة الطاقة الضوئية لأغشية CuS / Cu2S وتم استخدام فجوة الطاقة الضوئية لهذه الأغشية (2.38– 2.4) إلكترون فولت في تطبيقات الخلايا الشمسية.

الكلمات المفتاحية: غشاء رقيق؛ النحاس / Cu2S؛ التقنية الكيميائية ; نمو بلوري. الموصلية والضوئية.