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Energy Band Diagram of CuS /Si Heterojunction

Sabah Salman Hamdi[1] ، HudaSaadiAli[2] ، Iftikhar Mahmood Ali[3]
[1-]University of Tikrit College of Computer Science and Mathematics
[2-]Department of Renewable Energy, College of Energy and Environmental Sciences, Al-Karkh University of Science, Baghdad, Iraq
[3-]University of Baghdad, College of Science, Physics Depart., Al-Jadiriyah, Iraq
Sabah.S.Hamdi@tu.edu.iq / Hudasaadi@kus.edu.iq
iftikhar.ali@sc.uobaghdad.edu.iq

Abstract:

This study prepared thin films of CuS, a p-type semiconductor, on n-type silicon substrates to create an n-p junction The temperature (200 °C) and the results of X-ray diffraction showed that CuS thin film has a polycrystalline nature of hexagonal (Hexagonal) and the preferred direction of growth (100). The optical properties proved the direct optical energy gap for the CuS thin film, which equals 2.58 eV ,and the thickness of the CuS film equals 228.4 n m measured by cross-section. Voltage-current illustrates diode behavior. Also, capacitance-voltage measurements were performed where the built-in voltage was determined. This study assumes a band diagram of the prepared heterojunction (pn).

Keywords: Chemical Spray Pyrolysis, copper Sulfide, thiourea, substrate temperature, band diagram.

مخطط حزم الطاقة للمفرق المتباين CuS /Si

صباح سلمان حمدي[1] ، هدى سعدي علي [2] ، افتخار محمود علي[3]
[1] قسم الرياضيات ، كلية علوم الحاسوب والرياضيات ، جامعة تكريت ، تكريت، العراق
[2] قسم الطاقة المتجددة ، كلية الطاقة وعلوم البيئة ، جامعة الكرخ للعلوم، بغداد، العراق
[3] جامعة بغداد ، كلية العلوم ، قسم الفيزياء ، الجادرية، العراق

مستخلص:

تم في هذا البحث تحضير اغشية رقيقة من كبريتيد النحاس CuS على ركائز وسليكونية نوع (n-type) للحصول على مفرق الهجين (n-Si/p-CuS) حيث ان كبريتيد النحاس هو شبه موصل نوع p. وتم استخدام طريقة الرش الكيميائي الحراري بدرجة حرارة (200 °C)، وأظهرت نتائج حيود الأشعة السينية أن غشاء CuS له طبيعة متعددة التبلور من النوع السداسي وان الاتجاه المفضل للنمو (100). لدراسة الخصائص البصرية فقد اظهرت النتائج ان قيم معامل الامتصاص للأغشية المحضرة كافة وهذا بدوره اثبت ان الانتقالات الالكترونية للأغشية كان من النوع المباشر المسموح وكانت قيمة فجوة الطاقة لغشاء CuS تساوي (2.58eV) وسمك غشاء يساوي (228.4 nm).. يوضح تيار الجهد سلوك الصمام الثنائي. أيضا، تم إجراء قياسات سعة-فولتية حيث تم تحديد الجهد الداخلي. تفترض هذه الدراسة مخطط حزم الطاقة للمفرق المتباين (np).

الكلمات الدالة: الانحلال الحراري بالرش الكيميائي، كبريتيد النحاس، الثيوريا ، درجة حرارة الركيزة، مخطط النطاق.

1- Introduction:

Copper sulfide (CuS) is a complex chemical compound consisting of sulfur (S) and copper (Cu), found in nature in the form of a dark powder or lumps [1]. Copper sulfide **is** an important class of semiconductor compounds called sulfide **is** a chalcogenide, which are formed by the reaction of one of the transition elements with one of the elements in the sixth column of the periodic table, such as sulfur, selenium, or tellurium. These compounds have gained significant attention because of their great diversity in their different properties and the high possibility of controlling these sulfides **is** with most of the compounds of chalcogenides, the compound (S) has many phases depending on the compound's ratio of copper to sulfur [2]. There is a compound (S) at room temperature with five known stable phases, starting from the phase of chalcocite The copper-rich phase has an orthorhombic system, the Digenite phase has a cubic system, and the anillite phase has a cubic system and ends with the sulfur-rich covellite phase (CuS) and has a hexagonal system [3,4] .Caprylate (CuS) is characterized by the fact that it crystallizes in a hexagonal form and is found in the form of mass, thin Layers, or granules spread in other copper metals, with a density of ((4.6-4.76) . The (CuS) thin films are of great importance in the field of industrial applications where photovoltaic applications are used in the manufacture of solar cells, which is an important source of new energy sources, these thin films were discovered in (1954) by the scientist (Reynolds)The most famous solar cells are the(CdS / The preferred phase in these cells is chalcocite as well as cells [4,5,6], and it is also used in thermal photovoltaic conversion (Photothermal) for solar energy and thin film (CuS) also work as absorbing coatings for sunlight, where they have a high absorption coefficient of visible wavelengths and are used as selective radiation filters on architectural windows (Architectural) for the control of solar radiation in warm climates, and good reflectivity of infrared wavelengths, it has been used in thermal mirror coatings, as well as these thin films can be used as electrically conductive coatings coated with organic polymers [7,8], as well as used in the manufacture of compounds involved in multi-device and multilayer structures (Multijunction Type Multilayer Heterojunction)[9] CuS thin films are used in the manufacture of gas sensors, especially ammonia [10].

2-Experimental work:

CuS thin films were prepared using the chemical pyrolysis spray method on glass and n-Si substrates from 0.005 M copper chloride ($CuCl_2.2H_2O$) and 0.01 M thiourea ($CS(NH_2)_2$) as starting materials for Cu and S ion sources, respectively. In addition, an equal volumetric ratio (1:1) of both solutions was used and mixed. The solutions were magnetically stirred for a period of (10 min) to obtain a homogeneous solution.

The thermochemical spraying method has been used because it is suitable for the preparation of oxides and sulfate materials, economical due to the low cost of the manufactured devices used in the preparation of these thin films, and can be prepared from the mixing of two or more materials with different melting points, the thin films are prepared under normal conditions. CuS solution was deposited on the glass and n-Si substrates at a temperature of (200. The distance between the nozzle and substrates is (28 cm) because more than that causes the material to evaporate before it reaches the bases.

Thin films were deposited on silicon bases where silicon type (n-type) with electrical resistivity (1-10 Ω.cm) with (111) orientation and thickness (500 were used, which were cut into pieces of dimensions $(1.25x1.25)^2$ then were cleaned with HF acid diluted with methanol in a ratio of (1:9), and left the slices with Si substrates inside this acidic solution for a minute then rinse with distilled water and repeated cleaning with distilled water for three times to ensure the disposal of the remnants of the solution after which the samples were dried well with pieces of cloth intended for cleaning glasses lenses, CuS films were deposited at a substrate temperature of 200 then samples were annealed at 300°C for half an hour, the thickness of the films was determined by cross section using SEM instrument. The structure of the films was examined by X-ray diffraction with a device with specifications) and the aluminum electrodes were deposited using a thermal evaporation system and under low pressure ($5x10^{-5}$ mpa) and thickness (200±20 nm). Optical measurements for all prepared films have been done using a spectrometer type (UV-Visible Spectra photometer-1800) for the wavelength range (180-1100nm), (I-V) characteristics are investigated using 2450 Keithley electrometer, and the LCR meter (HP-R2CC4274) was used to measure (C-V) characterizations.

3- Result and Discussion

3-1 Structure

The results of XRD for the CuS film at a substrate temperature of (200°C) annealed at 300 For half an hour, it showed a hexagonal system in the preferred growth direction (100 and Fig (1) shows the X-ray diffraction patterns of the film, Peak positions are at the angles (2θ~25.32,32.29, 39.39, 49.64, 68.26) corresponding to (100), (103), (105), (108) and (1011) respectively , and this is consistent with the results of the study [11], and when comparing the locations of the peaks with the standard card (ICDD) numbered (00-006-0464) for copper sulfide. Table 1 shows the structural parameters for standard peaks. The result shows that the average crystallite size decreases with more FWHM. The average crystallite size was calculated using the Scherer equation Equation No. (1) [12] and it was found that the measured crystallite size values fall within the range (6.8-27.0nm).

Table (1) Structural parameters of p-CuS/ n-Si

Sample	2Θ	Hkl	$d_{hkl}(A^{o})$	FWHM	D(nm)
CuS	**25.32**	(100)	3.49	0.3464	27.0
	32.29	(103)	2.77	1.056	6.8
	39.39	(105)	2.28	0.4224	18.6
	49.64	(108)	1.83	0.6336	12.3
	68.26	(1011)	1.37	0.6336	13.6

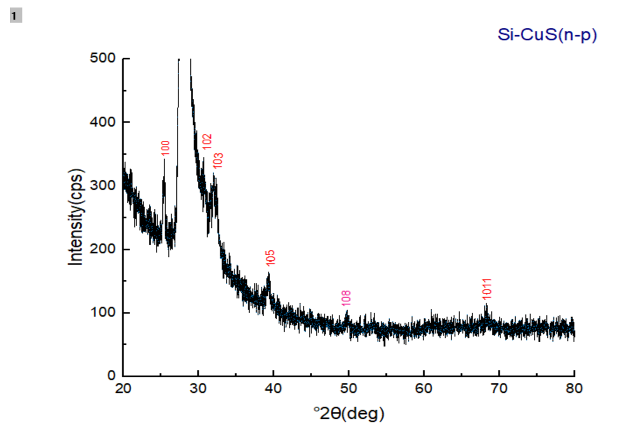
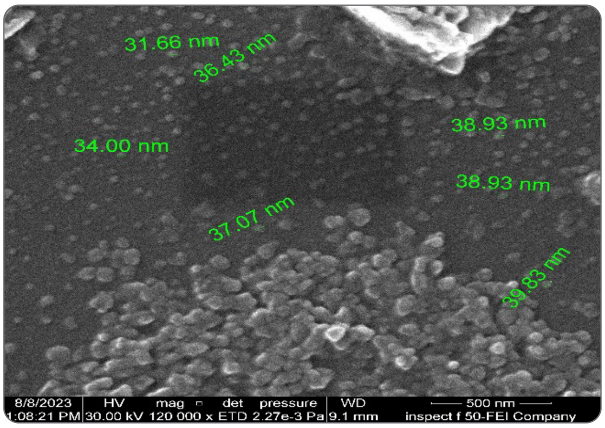


Fig. (1) XRD for CuS/Si

Through the study of surface morphology (scanning electron microscopy(FESEM)) of the prepared film, it is clear from Fig. (2) that the film structure consists of stone-like shapes of nanostructured very regularly and that the surfaces of the prepared films have a homogeneous distribution, are dense, and are free of spaces or characteristic islands, and this is consistent with [11,16]. Using the cross-section technique in the scanning electron microscope device, the thickness of the film was measured, and it was found that the film features are uniform and moderately deposited, and it was found that the thickness of the film is equal to 228.4 nm as shown in Fig. (3).

$$D_{ave} = 0.9\lambda/\beta\cos\theta \ldots\ldots\ldots\ldots(1)$$

Where =1.5406 Å is the x-ray wavelength (Kα -line), θ is the Bragg's diffraction angle, β (also called FWHM) is the full-width at half-maximum (in radians).



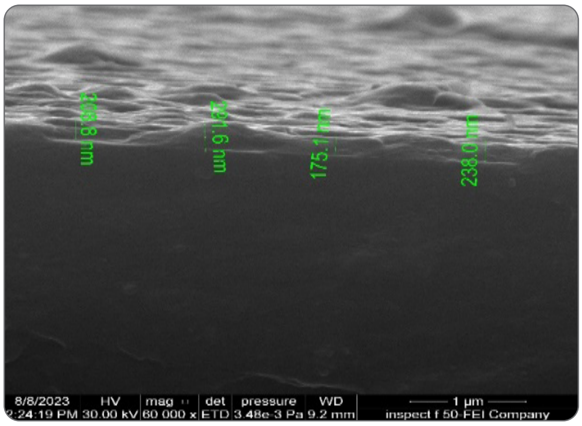


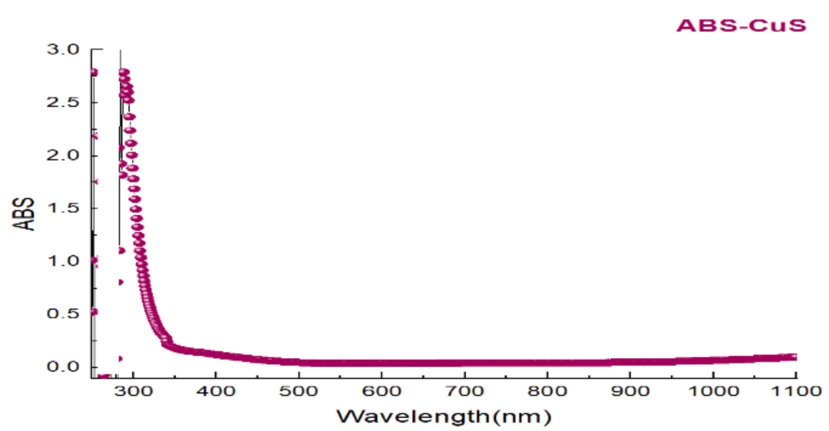
Fig. (2) FESEM for CuS/Si Fig. (3) Cross section of CuS deposited on n-Si

3-2- Optical properties:

The absorption coefficient of the prepared films was calculated through equation (2), and Fig (4-a) shows the absorption spectrum as a function of wavelength. The results showed that the best absorbance was within the visible area (300-700) nm of the electromagnetic spectrum, and on the other hand, its energy gap is more significant. This statement suggests that the film exhibits high permeability and finds applications in heterojunctions, reagents, and the fabrication of solar cells. [17]. Fig. (4-b) shows the absorption coefficient change as a function of the incident photon energy. The results showed that the absorption coefficient increases with the increase in photon energy of the prepared films, as the most significant values of the absorption coefficient are at high photon energies (4-4.3) eV, and this indicates the occurrence of the absorption process in this range (which includes the optical absorption edge) and the possibility of electronic transitions between the valence and conduction bands, this is consistent with the results of studies [13,14] The energy gap value was calculated to estimate the difference between the valence bands and the conduction bands, which can help determine the electrical, thermal and electronic properties of materials. The Tauc formula in equation (2) determines the direct energy gap. Since the transitions are of the direct type allowed, i.e., the value of the constant r = 1/2) and by drawing the relationship between ($(\alpha h\vartheta)^2$) and the energy of the incident photon , and through the extension of the straight part of the curve to determine the point of intersection $(\alpha h\vartheta)^2$ with the axis (X) of the photon energy where ($(\alpha h\vartheta)^2 = 0$), which represents the value of the optical energy gap and as shown in Fig. (5), where it was found that the optical energy gap value of copper sulfide with a thickness of (228.4nm) for these films was (2.58) eV represents the Tauc equation, and this is consistent with [17].

$$\alpha hv = \beta(hv - E_g)^r \text{......(2)}$$

Where is a constant, is the absorption coefficient, hv is the energy of an incident photon, E_g is the optical bandgap, and r=1/2 is the allowed direct transition.



Fig(4-a) The absorption of CuS

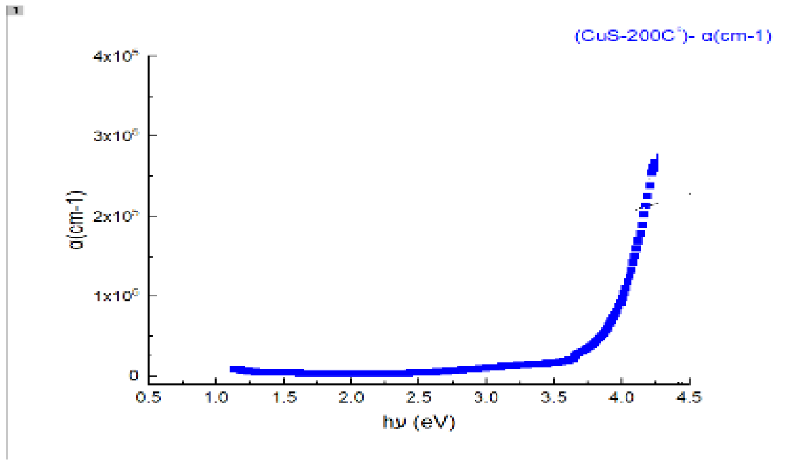


Fig. (4-b) The absorption coefficient of CuS

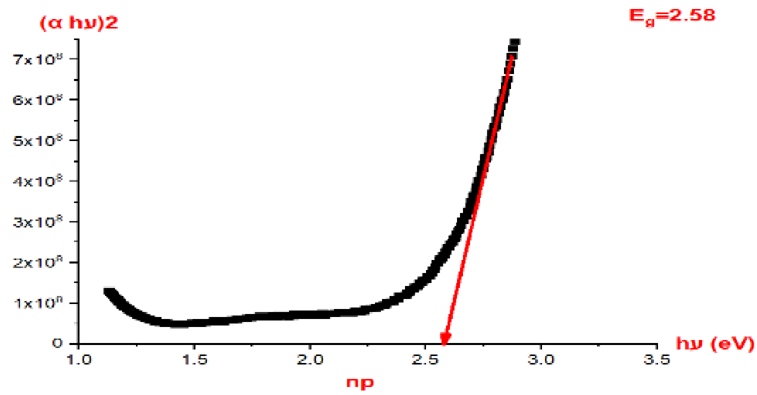


Fig. (5) Tauc plot of CuS

3-3 Electrical characteristics:

Fig. (6) depicts the relationship between conductivity and inverse temperature. As the temperature is increased from (313-453) K, the conductivity increases, demonstrating the films are semiconductors.

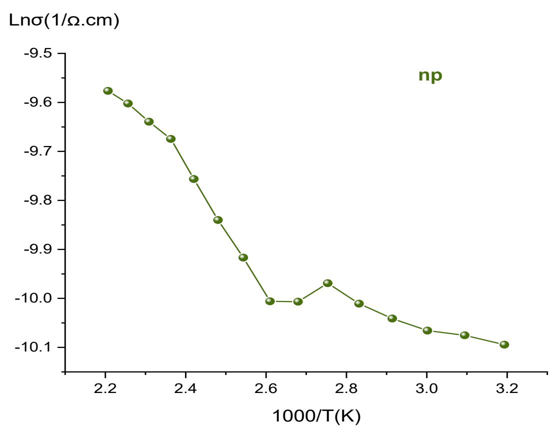


Fig.6 -Activation energy of CuS

As the temperature rises, the conductivity increases, and the activation energy drops. Good crystallization and large particle sizes may be to blame. In general, grain boundary scattering substantially impacts films' crystallinity and carrier charge's movement. In our case, the grain boundary scattering was reduced due to the growth of grains because of the charge carrier transport mechanism [18]. This electrical conductivity can be determined using the following relationship:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right)\ldots\ldots\ldots\ldots (3)$$

where E_a is the activation energy for conduction, $\sigma_\circ$ is a temperature-independent constant, K is the constant of Boltzmann's, and T is the absolute temperature. The values of conductivity and activation energy are shown in Table 2.

Fig. (6) shows the linear relationship between and 1000/T, which is used to calculate the activation energy (E_a) The change in the conduction mechanism is caused by the existence of two connected regions for the thin films CuS. The first zone is at a low temperature (313-363K), and the second is at a higher temperature (363-453K).[19]

3-3 (C-V) characteristics:

Capacitance variation has been studied as a function of the forward and reverse bias voltage in the range of (-1 V) to (1V) with a frequency equal to (10) kHz for the heterogeneous junction (n-p). The linear relationship between the voltage and the reciprocal of the capacitance square is shown in Figure 6, which revealed a straight-line relationship, which means that the junction was of the abrupt type. The intersection of a straight line with the voltage axis represents the value of V_{bi}. (C-V) measurement, as shown in Fig. (7)

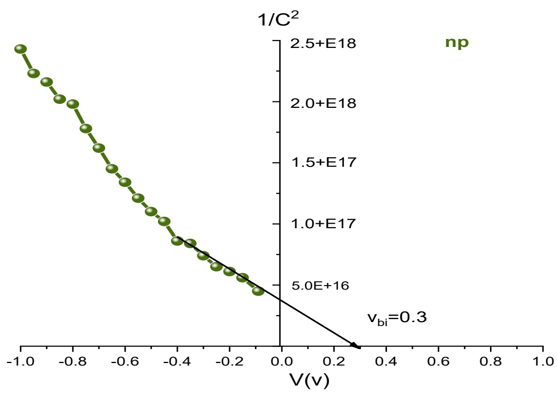


Fig. 7- Built-in voltage of CuS/Si

3-4 Energy Band diagram:

The energy beam diagram for CuS/Si heterojunction (pn) is drawn using the optical energy gap and DC measurement as shown in Fig. (8) At a heterojunction (asymmetric type), the connection between the p-type semiconductor and the n-type semiconductor when no external voltage is applied, the connection will cause the holes to diffuse from p-CuS to n-Si. Thus, the negative ions will remain diffused in CuS near the junction, causing the band to bend downward in CuS, while in n-Si, the band bends upward due to a decrease in valence band energy [14]. According to Anderson's model, the change in the conduction band is equal to The change in the valence band is equal to ΔE_v As shown in Fig. (8), All parameters to plot the energy band diagram are: ΔE_C **and** ΔE_v Which can be calculated from equations (1 and 2) [12].

$$\Delta E_C = \chi_1 - \chi_2 \ldots\ldots\ldots\ldots\ldots (1)$$

$$\Delta E_v = \Delta E_g - \Delta\chi \ldots\ldots\ldots\ldots (2)$$

Eg1 and Eg2 are the optical energy gaps for n-Si and p-CuS, respectively [14]. Experimentally, it is found that the two semiconductors have different energy gaps (Eg), different electron affinity values for n-Si and p-CuS, respectively. Table 2 shows the difference in the valence band, conductivity band, and optical energy gap of the (n-p).

Table (2) Difference in the valence band, connectivity band, electronic affinity, and optical energy gap for (pn)

sample	E_{a_1}	E_{a_2}	ΔE_v	ΔE_C	E_{g_1}	E_{g_2}	V_{bi}(eV)
pn	0.02346	0.08607	0.44	1.11	1.12	2.67	0.3

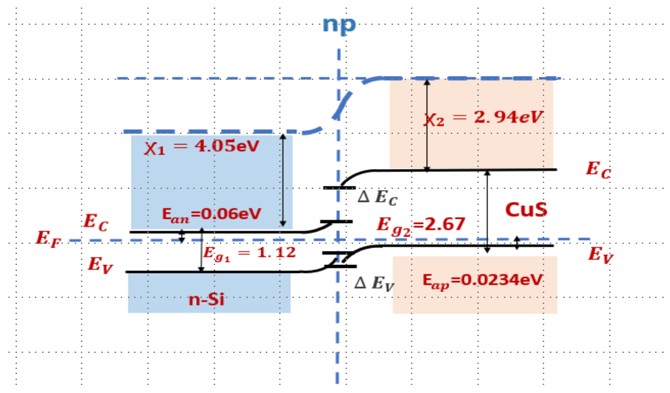


Fig. 8- Suggested band diagram of the p- CuS/ n-Si heterojunction

Conclusion:

p-CuS/n-Si heterojunction self-powered visible light photodetector (was efficient at 200 C^0substrate temperature. The pronounced layer's structural, morphological, and optical characteristics were thoroughly investigated; a nano-sized branchy dendrite -like structure and an optical band gap of 2.58 eV were attained. We have presented our energy band diagram model to illustrate the electron transition mechanism within the junction.

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