International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/140105

Photo Electrochemical Study on Brush Electrodeposited $CuGaS_2$ Thin Films

B. Kajamaideen[1,*], *A. Basker*[2] *and KR. Murali*[3]

[1] Department of Physics, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore-641 402, Tamilnadu, India
[2] Department of Chemistry, KIT-Kalaignarkarunanidhi Institute of Technology, Coimbatore-641 402, Tamilnadu, India
[3] ECMS Division, CSIR-CECRI, Karaikudi, 630 006, India

Received: 1 Sep. 2024, Revised: 12 Oct. 2024, Accepted: 12 Nov. 2024

Abstract: For the first time copper gallium sulphide ($CuGaS_2$) films were prepared using the brush plating method at various electrolyte temperatures between 30 and 80 degrees Celsius with a steady current density of 5.0mA cm^{-2} $CuGaS_2$ photo electrodes that were coated at 80 degrees Celsius and then post-heated at various temperatures with Intensity - 60 mW cm^{-2}. $CuGaS_2$ film electrode that was coated at a temperature of 80 degrees Celsius and post-heated at 525°C lead to variation in photocurrent with wavelength. $CuGaS_2$ films coated at temperatures ranging from 30°C to 80°C displays photocurrent - characteristic curve. $CuGaS_2$ photo electrode Mott Schottky graph with electrolyte temperature of 80°C and post-heat processing of 525°C.

Keywords: thin films, electronic material, and semiconductor.

---

1 Introduction

With a direct optical band gap between 2.4 and 2.5 eV, $CuGaS_2$ is a ternary compound with low toxicity. Because of this, CuGaS2 is expected to be employed as a Cd-free window layer for Cu(In1-xGax)Se_2-type solar cells or as a material that emits green light (Birkmire 2001, Jager-Waldau 2004).Metal-Organic Vapour-Phase Epitaxy (MOVPE) (Branch et al. 2005), Electron Beam Evaporation (Jeong & Park 2003), Modulated Flux Deposition (MFD) (Guillen & Herrero 2006), and Metal-Organic Chemical Vapour Deposition (MOCCVD) are four processes that can be used to deposit materials. MOCVD is just one of the few techniques that can be used to create CuGa (Chichibu et al 1995). $CuGaS_2$ was first deposited using the brush electroplating method. films in this work Brush plating are a technique that actually works the electroplating process with a portable device instead of a solution tank. This is a plating method in which a material is electrochemically coated on a wall while the work is cathodically connected to the power supply. An adjustable anode wire is linked to the plating after it has been applied with a brush, submerged in solution, and dried. The desired material is coated on the substrate surface via an electrochemical reaction that is powered by a direct current power supply. In order to achieve the best results while electroplating, stripping, activating, and other processes, contact between the anode and cathode is necessary. Currently, brush plating can be used to coat a wide variety of metals. The adaptability of brush plating is its significant advantage. Several processes can be relocated to various spots moved around a manufacturing facility. Brush plating is also adaptable due to the fact that the majority of electroplate types can be used on any substrate material that can be brushed by an electrode. When compared to tank plating, brush plating allows for larger current densities, which results in improved coating rates of as much as 0.01 mm/min Additionally, plate construction or repair is possible without the requirement for additional machining thanks to naturally perfect thickness control. Brush plated deposits require carefully controlled continuous movement of the anode relative to the cathode to produce high-quality deposits. Quality is affected by plating, though, by staying within a certain current density limit. Another sign of quality in electroplates is how they look. A burnt deposit, which is caused by excessive current density is typically represented as a gray in color or black colour deposit. In contrast, an enormous quantity of movement or inadequate current density results in a usually polished surface. Utilize a Philips X-ray diffractometer and Cu Ka radiation (k = 1:5,418 A °) to characterise the films for structural investigation. a Hitachi UV-VIS-NIR 3400 device. For the optical research, a Hitachi U 3400 UV-VIS-NIR spectrophotometer was employed. A JOEL 35 CFM scanning electron microscope was used to carry out the morphological tests. The band gap of $CuGaSe_2$ was found to be 1.66 eV, while for $CuGaS_2$ it rose up to 2.2 eV (Shafi et al. 2016). $CuGaS_2$ have a chalcopyrite tetragonal crystal structure (Karthikeyan & Vijaya 2023).

2 Experiential

Material and Methods

A Selectron Power Pack model 150 A - 40 V was used to carry out the brush electro deposition process. The conducting substrate with a tin oxide coating that is about 5.0 cm^2 in size were brush-electroplated. The anode

---

*Corresponding author E-mail: kajaphy@gmail.com

was a cotton wool-covered carbon rod stylus. The cotton fiber was kept in contact via a permeable sleeve. Prior to plating, cotton wool was soaked in the electrolyte and attached to the power source. As it made contact with the tin oxide substrate, the stylus was then moved uniformly. The current was identified when the pointer came into contact with the substrate.

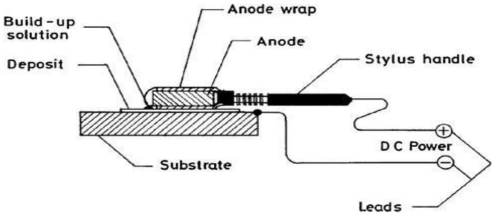

Fig. 1: Brush plating method schematic representation

This is because the $CuGaS_2$ thin film was formed as a result of the electrolyte ions that were trapped inside the cotton wool at the substrate being reduced more quickly. The bath included 5.0 mM of GaCl3, 2.0 mM of $CuCl_2$, and 1.0 mM of sodium seleno sulphate. The pH of the bath was maintained at 1.5 throughout the experiment. Each time, the power unit was programmed to run at 5.0 mA cm^{-2} current density. A temperature range of 30 to 80 degrees Celsius was observed for the electrolyte. The thin film needed to be coated in 20 minutes. The substrates used were 0.1 mm thick sheets of molybdenum and tin oxide coated glass. Utilizing the Mitutoyo surface profilometer, the thickness of the $CuGaS_2$ films is determined and fluctuated between 1.50 m and 2.40 m as the electrolyte temperature increased.

3 Results and Discussion

Because of an expansion in film thickness and light force, it is seen that the photocurrent ascends as the electrolyte temperature climbs. Figure 2 depicts how the photocurrent of $CuGaS_2$ films kept at various electrolyte temperatures changes with light. Photocurrent is improved as a result of the film's increasing crystalline structure as thickness increases. The rise in photocurrent is related to either a rise in pollutant centers that function as snares for minority transporters or an increase in the concentration of the majority transporters.

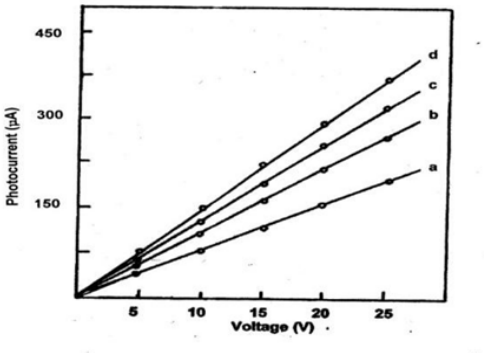

Fig. 2: Characteristics of photocurrent-intensity of $CuGaS_2$ films formed at various electrolyte temperatures.

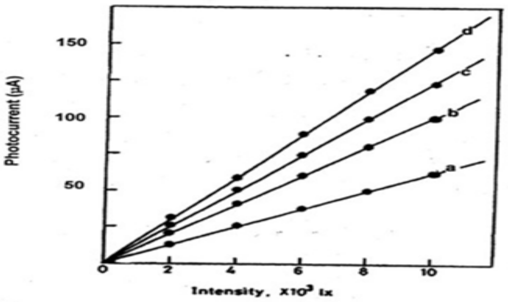

Fig. 3: Photocurrent and voltage properties at various temperatures.

Figure 4 represents the photocurrent spectra of $CuGaS_2$ layers formed at various electrolyte temperatures. Rose also saw a peak in the photocurrent spectra that is not far from the absorption edge (1955). The spectral response indicated at1.21 eV as the band gap for $CuGaS_2$ films. This is in good accord with the band gap value discovered from optical absorption measurements. The high absorption coefficient and surface location in the short wavelength region, where imperfection states have a shorter life span, are expected to be able to support the starved photocurrent.

Less photocurrent than the peak value is produced in the area of high wavelength absorption. It only partially absorbs the radiation Direct excitation of the carriers from the defect levels results in the spectra's tails, which go all the way to 1300 nm. In multiple researches, similar outcomes have been observed for films made with $CuInSe_2$ (Pal et al 1994, Fischer et al 2001).

The relationship between the rise in material conductivity in the presence of light and the increase in conductivity in the absence of light is known as photosensitivity.

Photosensitivity = $\Delta\sigma / \sigma = (I_L - I_d)/ I_d$

Where I_L and I_d, respectively, stand in for the current under light and darkness. It appears that some transitions that produce more free carriers actually lengthen the material's free life, enhancing its sensitivity to light.

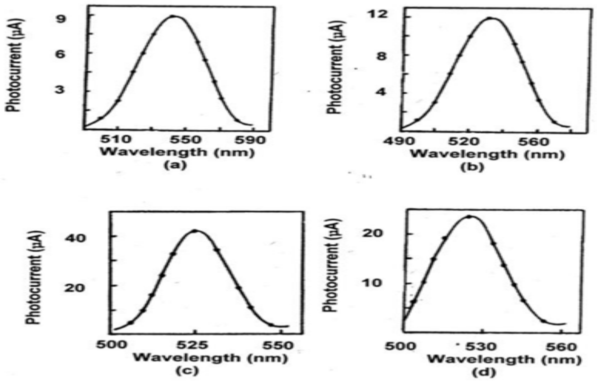

Fig. 4: Photocurrent spectra of $CuGaS_2$ layer generated at

different electrolyte temperatures, from (a) 30°C to (b) 50°C to (c) 70°C to (d) 80°C.

Figure 6 depicts light absorption of $CuGaS_2$ versus light intensity. The photosensitivity of thinner films is found to be mild, whereas that of thicker films is found to be higher. Thicker films are observed to have more photosensitivity than thinner films, which are thinner. Photosensitivity will rise in the presence of crystallographic flaws acting as trapping centres and fall in the presence of recombination centres.

Photoelectrochemical (PEC) cells were made using the films that had been formed on titanium substrates following heating at various temperatures.

The films were covered with polystyrene to prevent the redox electrolyte from coming into contact with the metal substrate areas.

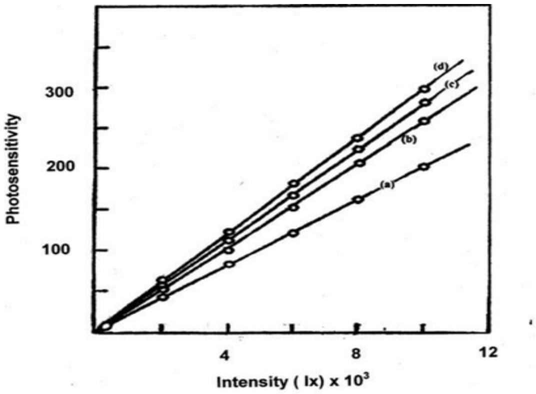

Fig. 5: illustrates the correlation between photosensitivity and the thickness of $CuGaS_2$ films produced at varied electrolyte temperatures. 30°, 50°, 70°, 80°, and 90° celcius.

These films make up the active electrode. The investigations on photo electrochemical cells employed a redox electrolyte composed of 1M NaOH, 1M Na_2S, and 1M S. The counter electrode used was graphite. The light source used for illumination was a 250 W ORIEL Tungsten halogen lamp. The PEC cell and the light source were separated by a water filter in order to filter out the IR region. Using a CEL suryamapi, the amount of illumination was measured. Those measurements are directly calibrated in $mWcm^{-2}$. The intensity of the light can be altered by adjusting the distance between the source and the cell. It was determined what voltage was produced across the load resistance and the resistance box and ammeter were connected in series to determine the cell's power output characteristics. A HIL digital multimeter was used to measure the output voltage, dark current, and photocurrent. For around 10 minutes in the dark, the $CuGaS_2$ photoelectrodes were submerged in the electrolyte to reach equilibrium. Measurements of voltage and dark current were made. After light source had lighted the cells, the resistance box setting was determined by measuring the current and voltage. The distinction between the illumination current and the dark current, as well as the illumination voltage and the dark voltage, were used to determine the photocurrent and photovoltage.

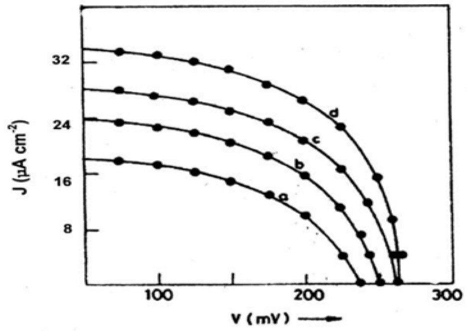

Fig. 6: depicts the $CuGaS_2$ load characteristics of films that were formed at various electrolyte temperatures, including 30°C, 50°C, 70°C, and 80°C.

Low photocurrent and photo voltage in PEC cells were the result of these coatings. The amount of light falling on the film was deposited and maintained at 60 mW cm^{-2} during various cycles. In films formed at an electrolyte temperature of 80°C, the highest photo output was noted. The films were post-heated in an argon atmosphere at different temperature after being coated at an electrolyte temperature of 80° to optimize the photooutput.

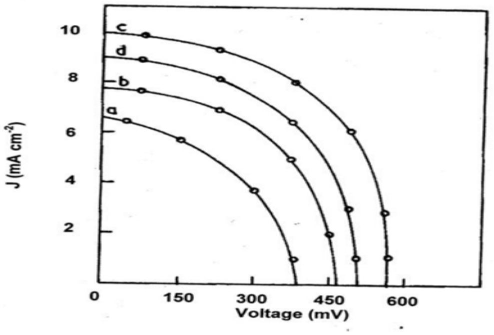

Fig. 7: demonstrate the post-heat-treated films' load properties.

$CuGaS_2$ set at 80°C electrolyte temperature and post-heated at various temperatures in an argon environment (a) 450°C (b) 475°C (c) 525°C (d) 550°C have variable load characteristics.

The figure demonstrates that for the electrodes heat-treated to 525°C, the PEC output values for short circuit current and open circuit voltage increased. Photo electrodes heat-treated above this temperature showed that the film's thickness reduces, and the stoichiometry barely changes, the open circuit voltage and short circuit current are decreased. The photovoltaic characteristics of a film coated at 80°C with an open circuit voltage and short circuit current of 0.56 V and 0.56 A, respectively, are shown in Table.1.

The photo output has increased since the previous report (Ueno et al 1990). The films produced at lower duty cycles after post-annealing in an argon atmosphere exhibit a remarkably low light output, as seen in Table 1.

Film output was found to be limited in lower duty cycles.

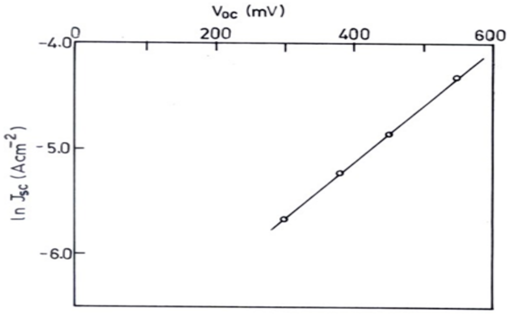

Fig. 8: shows the relationship between lnJsc and Voc for an electrode density of 10.0 mA cm^{-2} and a 60 mW cm^{-2} illumination.

Table 1: Photovoltaic parameters of CuGaS2 film deposited at different electrolyte temperature

Temperature treatment (°C)	Voc (V)	Jsc (mAcm^{-2})	ff	η (%)	R$_s$ (Ohm)	Rsh (k Ohm)
450	0.38	6.60	0.48	2.01	28	1.85
475	0.46	7.80	0.55	3.29	25	1.85
525	0.56	10.0	0.62	5.79	18	1.90
550	0.51	9.00	0.53	4.05	21	1.90
525 (After photoetch)	0.61	16.15	0.69	11.34	15	2.10

Figure.8 displays a straight line charting lnJsc versus Voc. We observed that both open circuit voltage and short circuit current rose when illumination intensity increased from 20 mW cm^{-2} to 100 mW cm^{-2}. The open circuit voltage became saturated at more than 80 mW cm^{-2} of light, which is common in photovoltaic and PEC cells. Jsc is discovered to rise linearly with illumination intensity.

The ideality factor (n), which was reported to be 2.1, was obtained by calculating the straight line's slope. A value of 9.1 x 10^{-8} A cm^{-2} is obtained by interpreting the line to the y-axis. The effect of photo etching on PEC efficiency was investigated by momentarily coupling the photo electrode and the graphite counter electrode under 100 mW cm^{-2} of HCl illumination for periods ranging from 0 to 100 seconds.

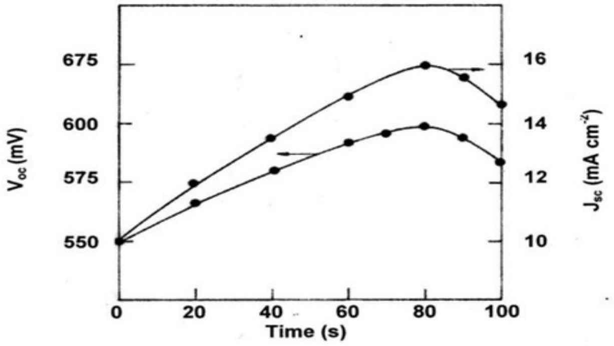

Fig. 9: Changes in V$_{oc}$ and J$_{SC}$ with photo etching time.

Voltage and current values fall after 80s photo etching, which is described by the reduction in thickness induced by photo etching. (Joo et al 1999).

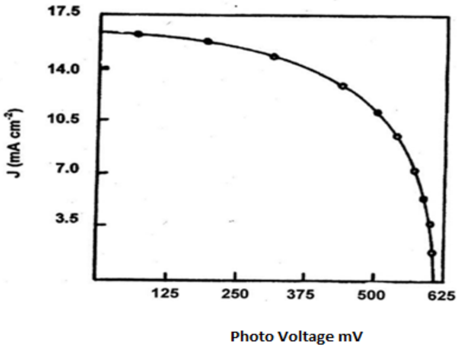

Fig. 10: $CuGaS_2$ load properties following an 80-second photo etching process at 525 °C in an inert environment. $CuGaS_2$ load properties during an 80-second photoetch in an inert environment at 525 degrees Celsius.10.34%, 0.69 fill factor, 16.15 mA cm-^{2} short circuit current, and 0.61 V voltage.

In figure 11, The Mott-Schottky plot's shape suggests that the film behaves as a p-type thin film coated at 80°C electrolyte temperature at 525°C. The plot's Vfb is 0.70V when extrapolated to the voltage axis. The slope of the graph results in a carrier density of about 2 x 1017cm^{-3}and it is equivalent to the current density found in hall device. A photo physics monochromator, 250 W tungsten halogen lamp, counter electrode, photo electrode and working electrode were used to study of the spectral response analyses of photo electrodes.

Figure 9 shows that the photovoltage and photocurrent increase until the 80s photoetch, at which point they begin to decrease.

Incidents of photo etching emerge in places where chemical etchants are ineffective. In order to achieve a 60 mWcm^{-2} intensity during photo etching, the short circuit current is enhanced from 10 mA cm^{-2} to 16.15 mA cm^{-2}, and the open circuit voltage is increased from 0.56 V to 0.61V.

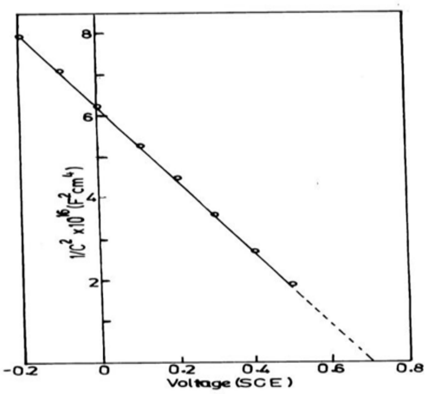

Fig. 11: Mott Schottky plots of $CuGaS_2$ coated at 80°C electrolyte temperature at 525°C.

The photocurrent was measured at wavelength ranging from 400m to 900m. By knowing this photo current value, the quantum efficiency of electrode is calculated with help of the formula (Huang et al 2004).

$$\Phi = \frac{1240 J_{sc}}{\lambda P_{in}}$$

where P_{in} is the input power of electrodes and J_{sc} is the photocurrent.

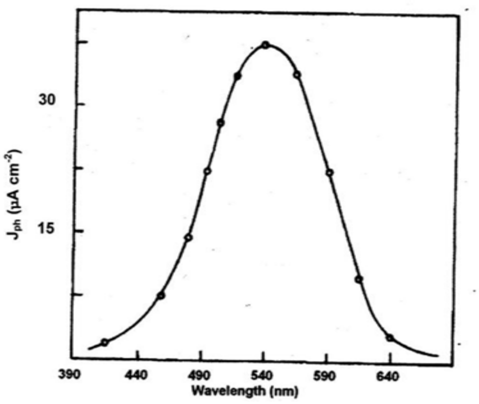

Fig. 12: Photocurrent variation with wavelength of $CuGaS_2$ thin film at post heat temperature.

4 Conclusions

Spectral response measurements revealed that $(J_{ph})_{max}$ occurs at a wavelength relating to the value of 2.29 eV. This number is quite close to the band gap identified by optical tests. Films coated at an electrolyte temperature of 80°C had the maximum photo output. The films coated a-22t 80°C were post heated to improve picture output in an inert environment for 15 minutes at temperatures varied from 450°C to 550°C. Mott Schottky graph illustrates V_{fb} values in the 0.70 V range. Based on the slope of the plots, ND is determined to be 2.0×10^{17} cm^{-3}. The films were of the p-type.

References

[1] Birkmire, RW 2001, ‘Compound olycrystalline solar cells: Recent progress and Y2K perspective’, Sol. Energy Mater. Sol. Cells, vol. 65, no. 1, pp. 17-28.

[2] Guillen, C & Herrero, J 2006, ‘$CuInS_2$ and $CuGaS_2$ thin films grown by modulated flux deposition with various Cu contents’, Phys. Status Solidi (A), vol. 203, no. 10, pp. 2438- 2443.

[3] Rose, A 1955, ‘Space-charge-limited currents in solids’, Phys. Rev, vol. 97, no. 6, pp. 1538- 1544.

[4] Pal, R, Chattopadhyay, KK, Chaudhuri, S & Pal, AK 1994, ‘Photoconductivity in CuInSe2 films’, Sol. Energy Mater. Sol. 24.

[5] Fischer, D, Dylla, T, Meyer, N, Beck, ME, Jager-Waldau, A & Lux-Steiner, MC 2001, ‘CVD of $CuGaSe_2$ for thin film solar cells employing two binary sources’, Thin Solid Films, vol. 387, no. 1, pp. 63-66.Cells, vol. 33, no. 2, pp. 241-251.

[6] Ueno, Y, Kojima, Y, Sugiura, T & Minoura, H 1990, ‘Electrodeposition of AgInSe2 films from a sulphate bath’, Thin solid films, vol. 189, no. 1, pp. 91-101.

[7] Joo, HY & Kim, HJ, Kim, SJ, & Kim, SY 1999, ‘Spectrophotometric analysis of aluminum nitride thin films’, J. Vac. Sci. and Technol. A, vol. 17, no. 3, pp. 862-870.

[8] Huang, CJ, Meen, TH, Lai, MY & Chen, WR 2004, ‘Formation of $CuInSe_2$ thin films on flexible substrates by electrodeposition (ED) technique’, Sol. Energy Mater. and Sol. Cells, vol. 82, no. 4, pp. 553-565.

[9] Shafi Ullah, Miguel Mollar & Bernabé Marí 2016 ‘Electrodeposition of $CuGaSe_2$ and $CuGaS_2$ thin films for photovoltaic applications, vol. 20, pp. 2251-2256.

[10] Karthikeyan Vijayan &S. P. Vijayachamundeeswari (2023) Effect of temperature and improving the optoelectrical attributes of copper gallium sulfide ($CuGaS_2$) thin films, vol.96, no.5, pp.350-360.