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INFRARED DETECTING BEHAVIOURS OF Cu_2NiSnS_4 PHOTODIODES

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Abstract

A photodetector in Al/p-Si/Cu_2NiSnS_4/Al form was fabricated with sol-gel method. The structural assessment of the photodetectors was investigated and Cu2NiSnS4 structures were formed in nanostructure in granular form. Current–time and current-voltage investigations illustrated that Cu_2NiSnS_4 photodiodes have infrared sensing properties. Photodetection properties such as linear dynamic rate, ideality factor, photosensitivity and photoresponse characteristics were assessed. Results also validate the infrared sensing properties of the diodes. The barrier height of the Cu_2NiSnS_4 diodes is calculated as 0.466 eV. Ideality factor of the diodes was found to be 5.16. Results indicate that our Cu_2NiSnS_4 photodetectors are suitable for infrared tracking device applications.

Keywords: Quaternary Functional Photodetectors; Infrared Detectors; Photodiodes; Photodetectors

Öz

Al/p-Si/Cu_2NiSnS_4/Al yapıdaki fotodedektörler sol-jel yöntemi kullanılarak üretilmiştir. Taramalı elektron mikroskobu (SEM) kullanılarak fotodedektörler yapısal olarak incelenmiştir. Mikroskopik incelemeler sonucunda Cu_2NiSnS_4 yapının nanoformda sentezlendiği ve nanoparçacıkların granüler yapıda bir arada bulunduğu gözlemlenmiştir. Akım – zaman ve akım - voltaj gafikleri Al/p-Si/Cu_2NiSnS_4/Al yapıda üretilmiş olan diyotlarımızın kızılötesini ışığı hisedebilme özellikleri gösterdiğini göstermiştir. Fotodedektör özelliklerini incelemede kullanılan lineer dinamik oran, idalite faktörü, fotohassasiyet, fototepki karasteriklikleri gibi karaktersistik özellikler çalışmamızda detaylıca incelenmiştir. İncelenen fotodiyot karakteristikleri de fotodiyotlarımızın kızılötesi dedektör özellikleri gösterdiğini doğrulamıştır. Al/p-Si/Cu_2NiSnS_4/Al yapıdaki diyotlarımıza ait bariyer yüksekliği 0.466 eV olarak hesaplanırken idealite faktörü ise 5.16 olarak bulunmuştur. Sonuçlar incelendiğinde Al/p-Si/Cu_2NiSnS_4/Al yapıda üretilmiş fotodiyotların infrared tarama cihazlarında kullanılmaya uygun olduğu anlaşılmaktadır.

Anahtar Kelimeler: Dört Bileşenli Fonksiyonel Fotodedektörler; Kızıl Ötesi Dedektörleri; Fotodiyotlar; Fotodedektörler

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1. INTRODUCTION

Photodiodes constitute the essential parts of photodetector and photosensor applications. Photodetectors and photodiodes were used in different types of technological implications. Therefore, scientists from different areas like physics, engineering, chemistry, materials engineering and science investigate the structural, electrical and optoelectronic properties of the photodiodes. Different materials can be used in the fabrication of photodetectors and photodiodes. Organic based molecules were often considered as fabrication materials, since they are easy to synthesize and abundant in the nature [1]–[3]. However, organic material based devices have some drawbacks such as instability, fragility and short lifetime [4], [5]. Therefore, different alternatives were applied. For example, organic material based photodiodes were often produced in composite forms or doped with other materials such as nanoparticles [1], [6]. It was evidenced by different papers that such a solution enhance mechanic, electric and optoelectronic properties of the photodiodes [7]–[9]. On the other hand, metallic thin film based photodiodes were found to be more reliable. Since, they are not easily affected by external factors, they are more durable, and they have astonishing electrical and optoelectronic properties. Hence, electric, electronic and magnetic properties of the metallic based diodes subject to an active research in the literature [10]–[14]. In addition, producing thin films in composite form and doping metallic thin films with other molecules help researchers to adjust the electrical properties of the metallic photodetectors [11], [15]–[19]. Thin films have relatively low energy band gap and good photoresponsive properties [20], [21]. Quaternary functional photodetectors have a special role [15] among the metallic based photodetectors. Quaternary functional photodetectors have a thin film layer which consist of four different material [22]. Quaternary functional photodetectors in different forms were reported in the literature. Cu_2NiSnS_4, Cu_2CoSnS_4 and Cu_2ZnSnS_4 structures are popular structures reported in the literature. Electrical properties of such structures were detailly investigated [23]–[26]. It was evidenced that such structures have strong potential to be used as infrared detectors [27], [28]. Previously HgCdTe structures were considered as infrared detectors [29]. However, HgCdTe structures have lattice mismatch problem [30]. The problem strongly affects the device quality mechanical properties of the infrared diodes. CdTe buffer layers were proposed to overcome such a drawback [30], [31]. However, CdTe buffer layers alter the electrical and optoelectronic properties of the HgCdTe structures. At this point, quaternary functional structures step forward.

In this work, we produced Al/p-Si/Cu_2NiSnS_4/Al diodes to assess their infrared sensing properties. Sol-gel method was used in the production of Cu_2NiSnS_4 active layer which was found to be in nanostructure form. Such method was cheap, reliable, and facile. I-V and I-t properties were assessed under infrared illumination. Photocharacterization of the photodiodes were performed. Photoresponse, photosensitivity, ideality factor, barrier height characteristics were also assessed under infrared illumination. It was concluded that photodiodes were reflects infrared sensing properties.

2. MATERIALS AND METHOD

Sol-gel technique was used in the production of infrared active Cu_2NiSnS_4 nanoparticles which were used in the core of the device. Before the production of Cu_2NiSnS_4 thin films. Cleaning procedures were applied to the Si wafers [32]. P-type Si substrate was used as the main platform of the device. Firstly, p-type Si wafers were rinsed with pure water and sonication procedure was applied for 5 mins in acetone. Wafer was rinsed and sonicated in pure H_2O. Si substrates were etched in HF:H_2O (1:10 ml) for 30 sec [32]. After the etching, Si substrates were rinsed in sonic bath. Al contact was applied to the one side of p-type Si substrate. Al/p-Si structure is heated at 570 ˚C. After annealing procedure Al/p-Si structure was rinsed. 2 m mol $CuCl_2$, 1m mol $SnCl_2$, 5 m mol CH_4N_2S (Thiourea) and 1m mol $NiCl_2$ were poured to 80ml DMF (Dimethylformamide). Mixture stirred at 500 rpm. Mixture was then poured in hydrothermal nanoparticle synthesis device where it was kept there for 24 h at 250 ˚C. To take the sediment from the result product, mixture was centrifuged. Drained sediment was dried and obtained nanopowders were used in the coating process. Cu_2NiSnS_4 nanoparticles were dissolved in chlorobenzene. Chlorobenzene dissolved mixture was dropwise placed on Al contacted Si substrate. Spin coating process was performed. As a result, fabrication of Al/p-Si/Cu_2NiSnS_4 structure was completed. Al/p-Si/Cu_2NiSnS_4 structure was heat treated to dry the excessive liquids. Finally, Al coating was performed and where Al/p-Si/ Cu_2NiSnS_4/Al quaternary functional photodiode fabrication was completed. FYTRONIX

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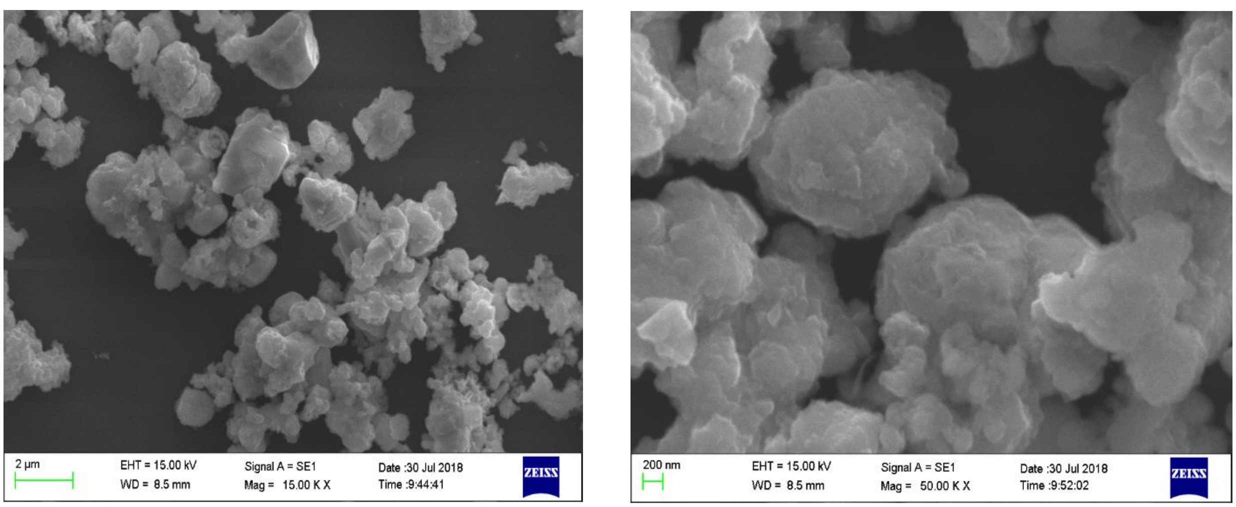
FY-INF1000 infrared characterization system was used in the device characterization. Karl Zeiss SEM was used in the microscopic investigations of the surface.

3. RESULT AND DISCUSSION

Figure 1 illustrates the SEM (Scanning Electron Microscopy) results of Cu_2NiSnS_4 quaternary functional photodiodes. Images obtained in 15 K (a) and 150 K (b) magnification; they were illustrated in Figure 1. Figure shows the nanostructures which form the active layer of Al/p-Si/Cu_2NiSnS_4/Al quaternary functional photodiodes. It was seen that active layer consists of Cu_2NiSnS_4 nanostructures which was in granulated shape where nanoparticles agglomerate and forms big lumps. Size of Cu_2NiSnS_4 nanoparticles were found to be between 200 nm – 500 nm. It was also understood that nanoparticles have narrow size distribution.



-a- -b-

Figure 1: SEM images of Cu_2NiSnS_4 obtained under 15K (a) and 50K (b) magnification.

To evaluate the electronic characteristics of Cu_2NiSnS_4 quaternary functional photodetectors, current-time (I – t) and current-voltage (I – V) behaviors were investigated. Various illumination intensities were used in the assessment of current-voltage characteristics. I-V behaviors of the Cu_2NiSnS_4 quaternary functional photodetectors were assessed between +3 V and -3 V. Only infrared illumination was used in the assessment. Current-voltage behaviors were given in Figure 2. Figure illustrates that Al/p-Si/Cu_2NiSnS_4/Al quaternary functional photodiodes respond to infrared light. Noticeable difference between dark measurement and measurements obtained under infrared illumination was seen. It was noticed that enhanced infrared illumination enhances the measured current in the backward bias region. Slight barrier voltage difference between dark measurement and infrared illumination measurement can be identified in the figure. Enhanced barrier voltage difference was seen for enhanced infrared illumination intensities.

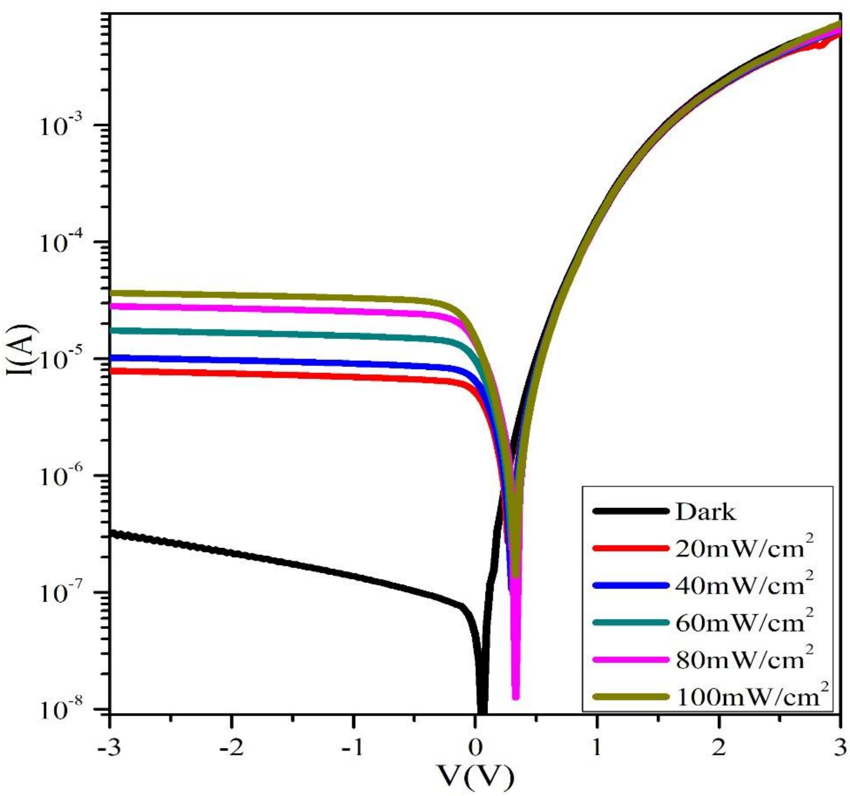


Figure 2: Current-voltage plot of Cu_2NiSnS_4 quaternary functional photodiodes obtained under infrared illumination.

Current-time behaviors of the Cu_2NiSnS_4 quaternary functional photodetectors were presented in Figure 3. Current-time characterization of the photodiodes were performed under 100 mW/cm^2 infrared illumination. Infrared light was applied for 5 sec intervals. Infrared illumination was kept on for 5 min and then turned off for 5 sec. At 100 mW/cm^2 infrared illumination intensity, maximum photocurrent was measured. The maximum photocurrent was found to be 3.1 x10^5 A. Shutting off the illumination resulted in a rapid cut off in the measured current. Repeated cycles

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give similar and successful results. It was seen that Cu_2NiSnS_4 quaternary functional photodetectors were susceptible to infrared light.

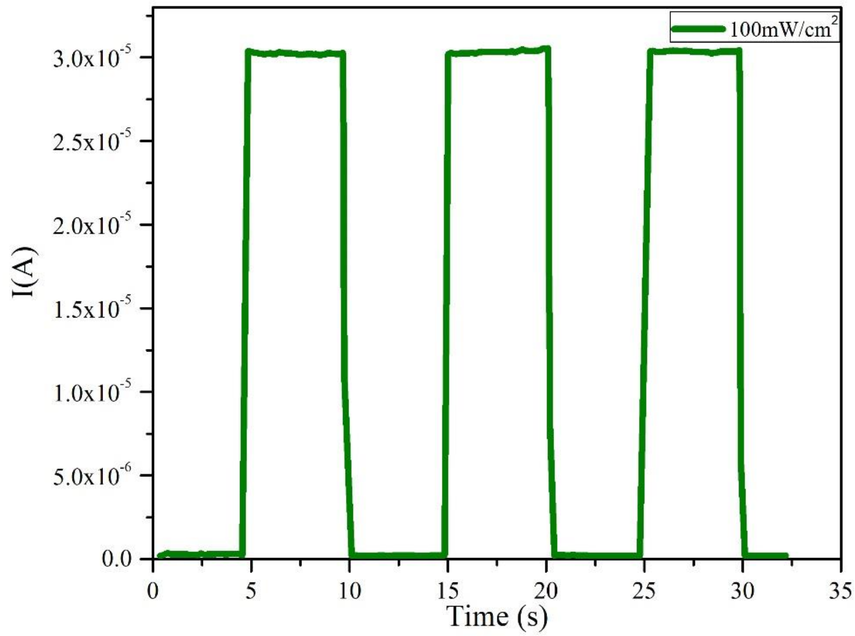

Figure 3: Current-time behaviors of Cu_2NiSnS_4 quaternary functional photodiodes.

Current-voltage and current-time characteristics was utilized to calculate the (n) ideality factor, (ϕ_b) barrier height, (R) photosensitivity and saturation constants. To calculate the photoelectric characteristics of the Cu_2NiSnS_4 quaternary functional photodetectors, thermionic emission theory was used [6], [33].

$$I = I_o\left[\exp\left(\frac{q(V-IR_s)}{nkT}\right)-1\right] \tag{1}$$

Formula above was used in the barrier height (ϕ_b) and ideality factor (n) calculation where n is ideality factor, T is absolute temperature, q is the charge of electron, k is Boltzman constant, I_o is backward bias current, R_s is serial resistance and V is applied voltage. I_o is calculated using Eq (2).

$$I_o = AA^{*}T^2\exp\left(-\frac{q\phi_b}{kT}\right) \tag{2}$$

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In Eq 2, A is the surface area of the diode, ϕ_b is the barrier height, A^* is the Richardson constant that is 32 A/cm^2K^2. The slope and the intercept of the forward bias In(I) vs. voltage (V) plot yield values for n and Φ_b, respectively. Table 1 represents the results exploited using thermionic emission theory. Ideality factor (n) was found to be 5.16. The expected value for the ideality factor is 1. However, there are many cases I the literature where ideality factor is greater than 1.

Barrier height of the Cu_2NiSnS_4 quaternary functional photodiodes were calculated as 0.466 eV which is within the range that were reported for the metallic thin film-based photodiodes in the literature. Barrier heights of Fe doped ZnO photodiodes were found to be between 0.45 eV and 0.51 eV [11]. Barrier height of Pt:carbon composite diodes were reported as 0.52 eV and barrier height for ZnO: carbon photodiodes were reported as 0.46 eV [1], [2].

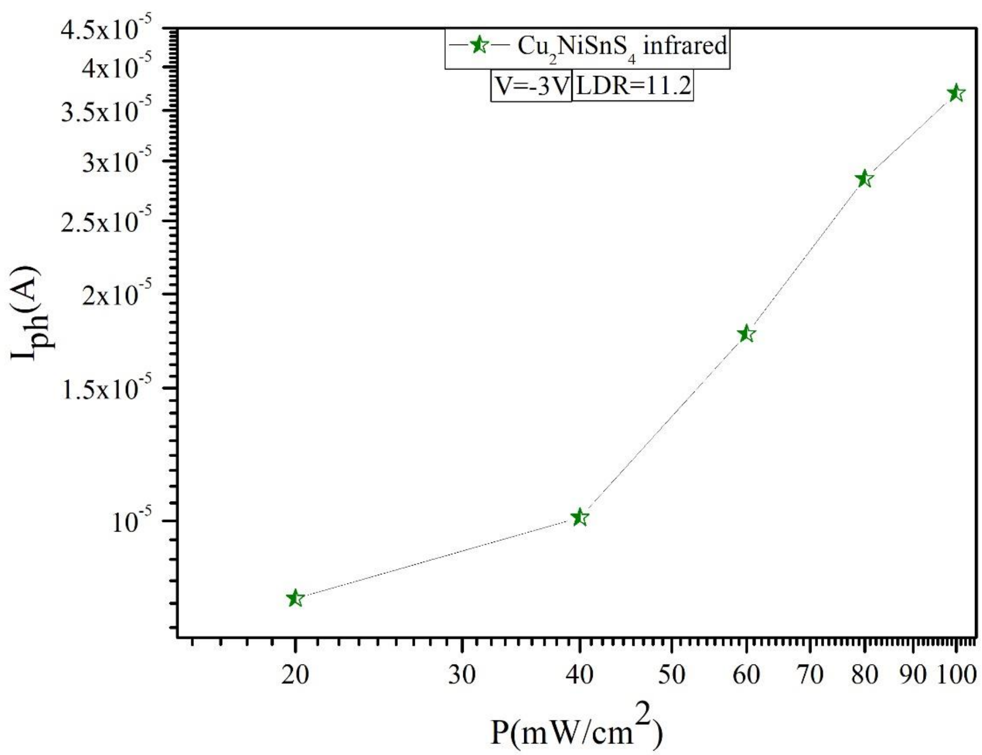

Figure 4: Photocurrent-Illumination intensity plot of Cu_2NiSnS_4 photodetectors.

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Table 1: barrier height (ϕ_b), ideality factor (n), photosensitivity (R) and saturation current (I_o) Cu_2NiSnS_4 photodiodes.

Photodiode	n	R(A/W)	ϕ_b(eV)	I_o(A)
IR Light	5.16	$4.90x10^{-5}$	0.466	$3.25x10^{-4}$

Photosensitivity of Cu_2NiSnS_4 quaternary functional photodetectors were assessed. In the calculation of the Cu_2NiSnS_4 quaternary functional photodetectors photocurrent is graphed as a function of illumination intensity. Photocurrent-illumination intensity characteristics was illustrated in Figure 4. Formula in Eq. 3 was used in the calculation

$$I_{PH} = KP^m \tag{3}$$

P represents the illumination and m is a constant in the Eq. 3.

Photocurrent-infrared illumination plot represents data obtained between $20mW/cm^2$ $100mW/cm^2$. Figure demonstrates that diodes respond to infrared light. Furthermore, enhanced photocurrent was seen for enhanced illumination intensity. $100mW/cm^2$ infrared illumination represents the highest photocurrent as $3.7.10^{-5}$ A. LDR(Linear Dynamic Rate) was evaluated utilizing the I_{Ph} – P slope. LDR of the Cu_2NiSnS_4 quaternary functional photodetectors were found to be 11.2 dB.

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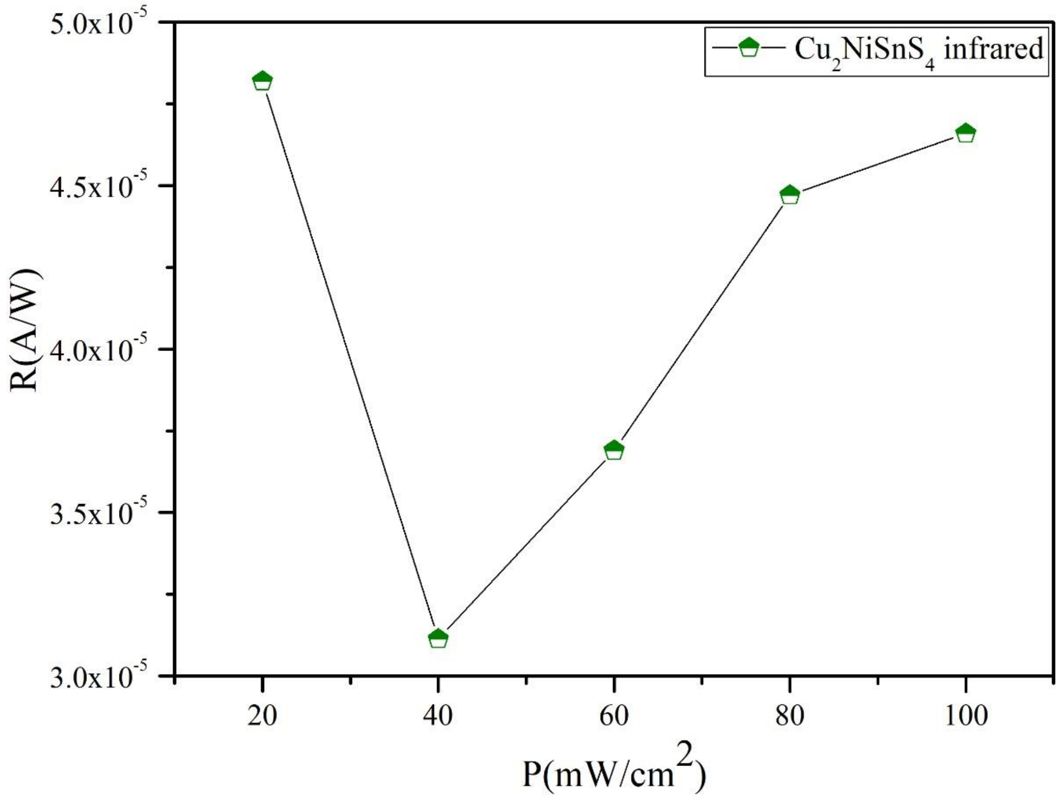

Figure 5: Photosensitivity-Illumination intensity plot of Cu_2NiSnS_4 photodetectors.

Photosensitivity (R) of Cu_2NiSnS_4 quaternary functional photodetectors were evaluated using the equation below

$$R = \frac{(I_p - I_d)}{PA} \tag{4}$$

where I_d, A, P, and I_p are dark current, surface area, illumination intensity and photocurrent, respectively.

Photosensitivity (R) of Cu_2NiSnS_4 photodetectors were demonstrated in Figure 5. 20 mW/cm^2 was found to be the highest photosensitivity which was 4.90.10^{-5} A/W. The lowest photosensitivity for Cu_2NiSnS_4 photodetectors was measured at 100mW/cm^2. Photosensitivity of the Cu_2NiSnS_4 photodetectors show diminishing trend with diminishing illumination.

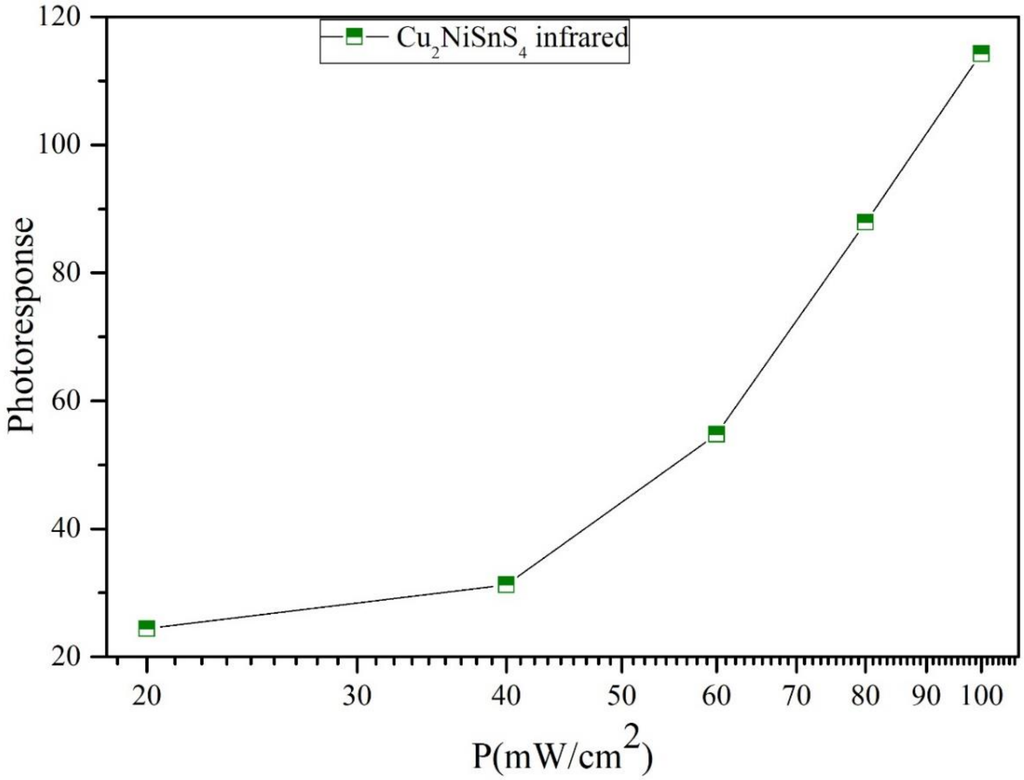

Figure 6: Photoresponse-Illumination plot of Cu_2NiSnS_4 quaternary functional photodetector.

Photoresponse behaviour of Cu_2NiSnS_4 photodetectors was presented in Figure 6. I-t characteristics was used in the assessment of photoresponse behaviours. Enhancing photoresponse characteristics was seen with augmenting infrared illumination. 100mW/cm^2 was found to be the value where the highest photoresponse was obtained. Photoresponse value was measured as $0.33.10^2$ for 100mW/cm^2 infrared illumination. Photoresponse behaviours illustrated that Cu_2NiSnS_4 quaternary functional photodetectors were responsive to infrared light and a good candidate for sensing implications such as infrared sensors, infrared tracking devices or photodiodes.

4. CONCLUSION

Cu_2NiSnS_4 nanoparticles were prepared using sol-gel method. Cu_2NiSnS_4 was spin coated to fabricate Cu_2NiSnS_4 photodiodes. Surface properties of the Cu_2NiSnS_4 quaternary functional photodetectors were evaluated using electron microscopy. Current-voltage and current-time

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behaviours of the Cu_2NiSnS_4 quaternary functional photodetectors revealed that diodes are responsive to infrared light. Ideality factor, saturation current, and barrier height characteristics were evaluated. We benefit from thermionic emission theory in our assessment and calculations. Results indicate that photosense, photoresponse characteristics of the Cu_2NiSnS_4 quaternary functional photodetectors have good infrared sensing properties. They have great potential to be used in infrared tracking device technologies.

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