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Infrared Sensing Properties of Quaternary Cu_2CoSnS_4 Photodetectors

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Quaternary functional semiconductor photodiodes were prepared in Al/p-Si/Cu_2CoSnS_4/Al structure. Sol-gel method was used in production process of photodiodes. SEM was used in the surface characterization of the photodiodes. Surface investigations revealed that photodiodes were formed in granulated structure. Infrared sensing properties of the photodiodes were assessed. Current – voltage (I – V) and current – time (I - t) properties indicate that photodiodes response to infrared light. Linear dynamic rate, barrier height, ideality factor, photoresponse, photosensitivity characteristics of the Si/Cu_2CoSnS_4/Al photodiodes were assessed using thermionic emission theory. Calculated barrier height was found to be 0.475 eV for the infrared illumination. Ideality factor of the Al/p-Si/Cu_2CoSnS_4/Al photodiodes were calculated as 3.97. Different photocurrent was obtained for different illumination intensities. Photosensitivity and photoresponse properties of the Al/p-Si/Cu_2CoSnS_4/Al photodiodes were assessed. Results indicate that photodiodes response to the infrared light and have sensing properties.

Keywords: Cu_2CoSnS_4 photodiodes; IR photodetectors; quaternary functional photodiodes.

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1. Introduction

Thin films are driving force of technological implications [1]. Different technological devices were built using thin films such as solar cells, photodiodes, transistors, microprocessors, etc [2]–[4]. Thin films are consisting of various materials such as carbon materials, nanoparticles, alloys and composite materials [5]–[8]. Each material has different properties that they can be used in a specified application. Moreover, it is possible to tune electrical, magnetic and optic properties of the thin films. For example, doping materials with different molecules alter the physical and chemical structure of the materials [9]–[11]. It was previously reported that doping metallic thin films with different materials increased electrical properties of the photodiodes [12], [13]. In addition, producing alloy and composite thin films in different composition helps researcher to tune the electrical properties of the thin films[14].

Depending on the purpose, different photodiodes and photodetectors were reported ranging from infrared detectors to gamma detectors [15]–[18]. Infrared detectors occupy important place among those, since infrared detectors can be used in various applications. For instance, infrared detectors have huge potential to be used in military industry since, infrared detectors can detect the infrared signals which can be used to assess the thermal state of the surface. Therefore, find applications in automotive, aeronautics, medical imaging, telecommunication industries [19], [20]. HgCdTe thin films are common thin films used in the infrared detector applications [21], [22]. However, such thin films have several drawbacks. Reports claim that HgCdTe thin films has lattice mismatch with the substrate that they were coated on [23]. Such a mismatch decreases the physical and electrical properties of the HgCdTe thin films. To overcome the problem, scientists propose buffer layers that CdTe buffer layer was applied between substrate and HgCdTe thin films [24], [25]. Such a buffer layer protects the HgCdTe thin films but reduce the electrical and optical properties of the HgCdTe thin films. Another material reported as infrared detector is GaSb thin films [26]. Such thin films were often used in medical applications. They find limited implication n avionics and military industry. At this point, producing a reliable and affordable photodetector susceptible to infrared light which may find implication in military and avionic industry is important. Since, decreasing the fabrication cost of the infrared detectors helps to reduce the production cost of devices used in this industry. Quaternary functional photodetectors may help to solve this problem. Quaternary functional photodetectors are reliable; electrical and optical properties of the quaternary functional detectors can be tuned. Cu_2CoSnS_4 and Cu_2NiSnS_4 are popular materials used in the quaternary functional photodetector fabrication[27], [28]. Different production methods were previously reported to produce such materials. Sol-gel method might be a promising method which can be used in the manufacturing of the Cu_2CoSnS_4 and Cu_2NiSnS_4 photodetectors since, sol-gel method provides good film thickness control and requires less complicated production procedure.

In this work, infrared sensing properties of the Cu_2CoSnS_4 photodiodes were investigated. Structural characteristics of the photodiodes were checked using scanning electron microscopy (SEM). Photoresponsive and photo sensing properties of the photodiodes were assessed under infrared (IR) light. Barrier hight (ϕ_b) and ideality factor (n) were checked calculated. Photoresponse and photo sensitive properties were determined and presented. Saturation current obtained under infrared light in different illumination intensities were obtained. Results indicate that Cu_2CoSnS_4 photodetectors are responsive to the infrared light. It was found out that Cu_2CoSnS_4 photodiodes have potential to be used as infrared detector.

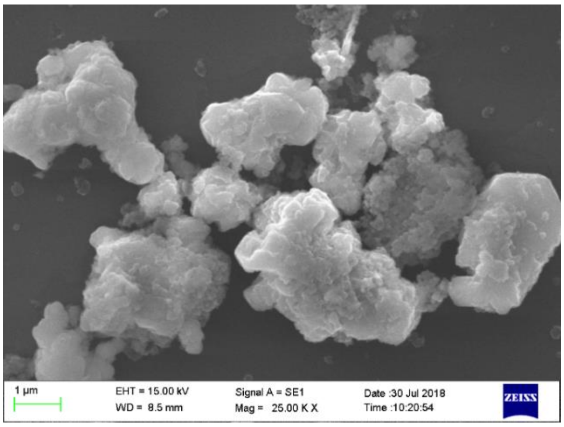
2. Experimental

Sol-gel technique was used to calculate the Cu_2CoSnS_4 solution. Before the application of the Cu_2CoSnS_4 solution cleaning procedure was applied on the substrate. p-type Si wafer was used as a substrate. p-type Si wafer were rinsed with deionized water and sonication procedure in acetone was applied for 5 minutes. Sonicated wafer was then rinsed and 5 more minute sonication process in ethyl alcohol was performed. Si wafers were etched in $HF:H_2O$ (1:10ml) for 30 secs. Etched wafers were rinsed with deionised water and sonicated for 5 mins in sonc bath. One side of the dried wafers were Al coated and annealed 570 ^{0}C. Si wafers in Al/Si structure were rinsed with deionised water. 2m mol $CuCl_2$, 1m mol $SnCl_2$, 5m mol CH_4N_2S (Thiourea) and 1m mol $CoCl_2$ were added to 80ml Dimethylformamide (DMF) and stirred at 500 rpm until dissolved. The solution was put in FYTRONIX FY 8000 hydrothermal synthesis device. Device was set to 250 ^{0}C for 24 hours. Sediment in of the result product was separated from the mixture using centrifuging. Sediment was dried for 4 hours that Cu_2CoSnS_4 nanopowders were obtained. Nanopowders were dissolved in chlorobenzene. Cu_2CoSnS_4 nanopowder solution was drop cast on Al/Si wafer and spin coating procedure was performed where Al/Si/Cu_2CoSnS_4 structures were obtained. Al/Si/ Cu_2CoSnS_4 were heated and to evaporate excessive liquids. Al/Si/Cu_2CoSnS_4 structures were coated with Al that Al/Si/Cu_2CoSnS_4/Al photodiodes were obtained. Karl Zeiss SEM was used in the surface characterization and FYTRONIX FY-INF1000 infrared solar simulator was used to assess the photoresponsive and photosensitive properties of the diodes.

3. Results and Discussion

Scanning electron microscopy (SEM) was used to assess the surface and physical properties of the diodes. Images obtained at 15K and 100K magnification was presented in Figure 1. It can be seen in the figure that Cu_2CoSnS_4 were formed in nanostructure form. Cu_2CoSnS_4 crystals were formed in granulated structure which were consisting of nanoparticles. The size of the nanoparticles was found to be less than 200 nm. Visual inspection of the SEM images revealed that nanoparticles have narrow size distribution.

To assess the electrical behaviours of the Cu_2CoSnS_4 photodiodes current – voltage(I – V) and current – time (I – t) behaviours were assessed in various illumination intensities. I – V characteristics were investigated between -3V and +3V. I – V characteristics of the photodiodes were investigated as a function of illumination intensity. Infrared light was used to investigate the effect of infrared light. Results belonging to I - V characteristics were presented in Figure 2. When the figure investigated, it was revealed that photodiodes respond to infrared light. In the backward bias zone, apparent difference between dark and infrared illumination was seen. It was also seen that increased infrared illumination intensities increase the measured current. Slight barrier voltage difference was obtained for the measurement conducted under infrared illumination and dark measurement. Increased barrier voltage was seen for the infrared illumination.



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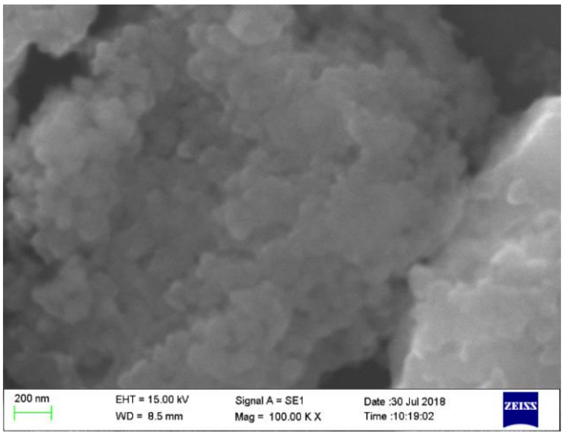

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Figure 1: *SEM images of Cu_2CoSnS_4 obtained at 15K(a) and 100K (b) magnification.*

Current – time (I – t) measurement of the Cu_2CoSnS_4 photodiodes were presented in Figure 3. Infrared light with 100mW/cm^2 illumination intensities was applied to Cu_2CoSnS_4 photodiodes for the 5 secs intervals. 5 secs infrared light with 100mW/cm^2 illumination intensities was applied to Cu_2CoSnS_4 photodiodes and then illumination was switched off. Measured current rapidly increased with the application of infrared illumination. Illumination was kept on for 5 secs. Then infrared illumination was switched off for 5 seconds. When the infrared light was on measured photocurrent stays stable at about 2.7x10^{-5} A. When the light was switched off measured current was dropped to the zero. The cycle was repeated successively where similar results were observed. It was concluded that Cu_2CoSnS_4 photodiodes are sensitive and responsive to the infrared light that they can be used as infrared detector.

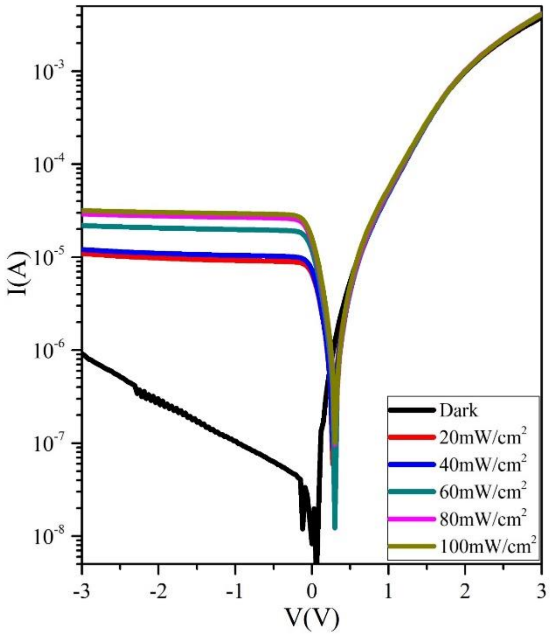

Figure 2: *I – V (current – voltage) characteristics of Cu_2CoSnS_4 photodiodes which was obtained under infrared illumination.*

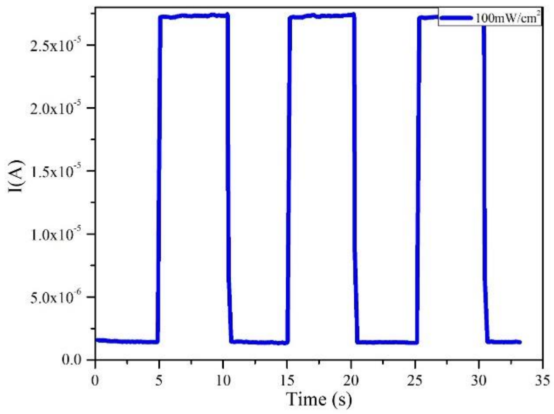

Figure 3: *I – t (current – time) characteristics of Cu_2CoSnS_4 photodiodes which was obtained under 100mW/cm^2 infrared illumination.*

Using the I – V and I – t data photoelectric properties such as barrier height (ϕ_b), ideality factor (n), saturation constant I_o, and photosensitivity (R) values were calculated. Thermionic emission theory was used in the assessment of the photoelectric properties of the Cu_2CoSnS_4 photodiodes. Following formula were used in the calculation of barrier height(ϕ_b) and ideality factor (n) [29], [30]:

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

where n ise ideality factor, q s the charge of electron, k is Boltzman constant, T is absolute temperature, I_o backward bias saturation current, V is applied voltage and R_s is serial resistance. I_o is calculated using Eq (4).

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

In Eq 4, A^* is the Richardson constant that is 32 A/cm^2K^2 for the p-type Si semiconductors, A is the area of the diode, and ϕ_b is the barrier height. The slope and the intercept of the forward bias In(I) vs. voltage (V) plot yield values for n and Φ_b, respectively. Results obtained from the thermionic emission theory was calculated in Table 1. *n* ideality factor was found to be slightly higher than the expected value that typical ideality factor was expected to be smaller regarding to thermionic emission theory. However, it is common for the metallic thin films to see the ideality factor greater than 1.

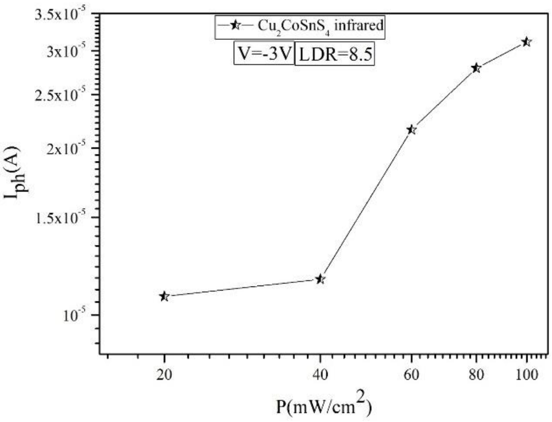

Figure 4: *Photocurrent – infrared illumination intensity graph of plot of Cu_2CoSnS_4 photodiodes.*

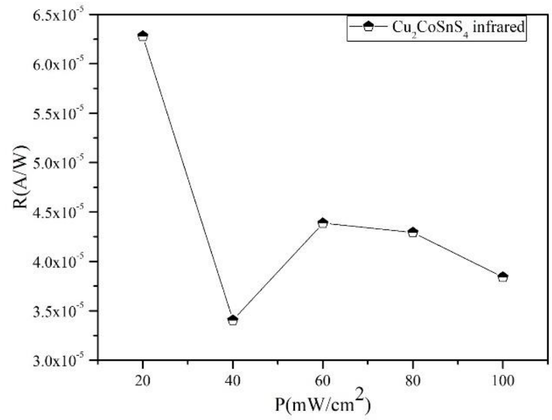

Figure 5: *Photosensitivity (R) – illumination power (P) behaviours of Cu_2CoSnS_4 photodiodes.*

Calculated barrier height of the Cu_2CoSnS_4 photodiodes were found to be coherent with the previous results reported for the metallic thin films based photodiodes. Previously, Coskun et al. was found the barrier height of the Fe doped ZnO photodiode between 0.45eV and 0.51 eV [3]. Similarly Aslan et al was calculated the barrier height of the ZnO doped amorphous carbon and Pt doped amorphous carbon photodiodes as 0.46 eV and 0.52eV, respectively [5], [10]. Results in the literature confirms that diodes are within the range with the results reported in the literature.

Table 1: Calculated ideality factor, barrier height, saturation current and photosensitivity of Cu_2CoSnS_4 photodiodes which was assessed using thermionic emission theory for the infrared light illumination.

Illumination Type	n	ϕ_b(eV)	I_o(A)	R(A/W)
IR Light	3.97	0.475	2.32×10^{-4}	6.2×10^{-5}

Photosensitivity of Cu_2CoSnS_4 photodiodes were characterized. To assess the photosensitivity of the Cu_2CoSnS_4 photodiodes photocurrent was plotted as a function of illumination intensity. Figure 4 illustrates photocurrent – illumination intensity graph. Following formula was used to assess the illumination intensity :

$$I_{PH} = KP^m \quad (3)$$

where m is a constant and P is the illumination intensity.

Photocurrent (I_{Ph}) – infrared illumination intensity (P) graph shows that diodes respond infrared light between 20mW/cm^2 and 100mW/cm^2. Moreover, increased photocurrent was obtained for increasing infrared illumination intensity. Maximum illumination obtained at 100mW/cm^2 which was found to be 3,12.10^{-5}A. Linear dynamic Range value (LDR) was calculated using the I_{Ph} – P slope. Linear dynamic range value of the diode was calculated as 8.5dB for the infrared illumination.

Photosensitivity (R) of the Cu_2CoSnS_4 photodiodes were assessed using the following equation [31], [32]

$$R = \frac{(I_p - I_d)}{PA} \quad (6)$$

where I_d, A, P, and I_p are dark current, area, illumination intensity and photocurrent, respectively. Photosensitivity graph as a function of function of infrared illumination was presented in Figure 5. The highest photosensitivity was measured for 20mW/cm^2 infrared illumination intensities as 6,2.10^{-5}A/W. The lowest photosensitivity value was measured at 100W/cm^2 infrared illumination intensity. Photosensitivity graph reflects decreasing behaviour for increasing infrared illumination.

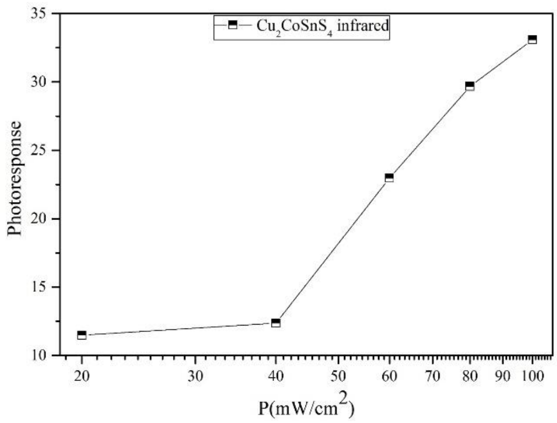

Figure 6: *Infrared light photoresponse characteristics of Cu_2CoSnS_4 photodiodes.*

Photoresponse characteristics of the Cu_2CoSnS_4 photodiodes was presented in Figure 6. Current – time characteristics was used in the calculation of Cu_2CoSnS_4 photodiodes. Increasing photoresponse trend was obtained for increasing infrared light illumination intensity. The highest photoresponse rate was obtained for 100 mW/cm^2 infrared illumination. Photoresponse rate was measured as 0,33.10^2 for the100 mW/cm^2 infrared illumination. It was understood that Cu_2CoSnS_4 photodiodes were suitable for infrared sensing applications such as infrared photodiodes and infrared tracking devices.

Conclusion

Cu_2CoSnS_4 photodiodes were produced and infrared sensing properties were assessed in this work. Sol-gel method was used in the production of the Cu_2CoSnS_4 nanoparticles. Spin coating method was used in the preparation of Cu_2CoSnS_4 photodiodes. SEM images confirmed that sol-gel technique was successfully applied. I - V and I - t assessments of the Cu_2CoSnS_4 photodiodes showed that photodiodes respond to the infrared light. Using thermionic emission theory, I - V and I – t graphs of the Cu_2CoSnS_4 photodiodes were assessed and ideality factor barrier height and saturation currents were calculated. It was seen that calculates performed for the Cu_2CoSnS_4 photodiodes are within the range of the results reported in the literature. Photo responsive and photo sensing properties of the diodes were investigated. It was seen that diodes are responsive to the infrared light. It was concluded that Cu_2CoSnS_4 photodiodes can be used as infrared tracking, infrared detector and infrared sensing applications.

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