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Cu_3BiS_3 Thinfilm Based metal-semiconductor-metal Near-infrared Photodetector

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Abstract: Semiconducting thin films of Cu_3BiS_3, with structure and composition corresponding to that of the mineral Wittichenite, have been fabricated on molybdenum-coated soda lime glass substrates by co-evaporation. The crystallinity and structure of Cu_3BiS_3 thin films are verified by X-ray diffraction and scanning electron microscopy. The chemical bonding configurations of Cu_3BiS_3 thin film were examined by x-ray photoelectron spectroscopy. The interdigitated electrode pattern was created, and photoconductive characteristics of Cu_3BiS_3 thin films have been studied in a metal–semiconductor–metal configuration.

***Index Terms*: Cu_3BiS, Coevaporation, photodetector, and sandwich**

I. INTRODUCTION

Near-infrared (NIR) photodetectors (PDs) offer a variety of possible uses, including optical communications, night vision, medical diagnostics,[1] and cognitive neuroscience research. The near-infrared (NIR) photodetector layer in thin film photodetector devices can comprise semiconductor thin films with a band gap of 0.9 - 1.7 eV. Cu (In, Ga) Se_2 (CIGS), $CuIn_{1-x}$ Al_xSe2 (CIAS), and CdTe are now the most technologically advanced semiconductors for thin-film photodetector applications. However, the availability of tellurium and indium may limit the generating capability of these devices to 4% of the current world electricity demand for CdTe and 1% for CIGS. [3] Therefore, it is necessary to develop novel semiconductors for use in thin-film photovoltaics and photodetectors if these devices are to play a substantial part in the long-term production of global energy. Many sulphide minerals are a prospective source of alternative materials to CIGS and CdTe, as some of them are anticipated to have good optical and electrical properties for photovoltaic applications.

Recently, it has been shown that Wittichenite (Cu3BiS3) thin films can be produced using a combination of chemical bath deposition and sputtering [4,5] and that the forbidden band gap of Cu3BiS3 thin films is approximately 1.4 eV [4], which is within the ideal range for solar energy conversion. Coevaporation produces thin films with excellent structural and optical qualities. [6,7] The optical and electrical properties of the obtained Cu_3BiS_3 thin films indicate that they satisfy the fundamental conditions for usage as absorbers in photodetector systems. Cu_3BiS_3 is also compatible with the goal of lowering material availability and toxicity issues. Bismuth is currently utilized as a substitute for lead in bullet solders and other materials when toxicity is problematic. Using bismuth-containing compounds instead of CIGS or CdTe would increase the energy production ceiling of thin film photovoltaic technology.

II. MATERIALS AND METHODS

The substrates were chemically cleaned and dipped in 5% HCl to remove the surface contamination. The Cu_3BiS_3 thin films were prepared by co-evaporation of the precursor species on a molybdenum-coated soda lime glass substrate, using a system constituted by an evaporation chamber connected to a vacuum system that allows working at pressures of about 10^{-6} Torr, two tungsten boats (used to evaporate Bi and Cu respectively), a quartz effusion cell to evaporate sulfur and a thickness monitor (INFICON SQC-310C) with a quartz crystal as a sensor, used to measure the evaporated elements flux. The substrate temperature was controlled with a programmable PID controller (TOHO TTM-P4). The chemical composition of the Cu_3BiS_3 films is controlled by controlling the substrate temperature and the evaporated mass of the precursor species.

X-ray diffraction (XRD) pattern was recorded on a Bruker D8 Advance X-ray powder diffractometer using graphite monochromatized Cu K_α (λ=1.54059 Å) radiation at 40KV and 40mA. Micro-Raman spectra were obtained at room temperature using a HORIBA Jobin-Yvon LabRAM HR 800 UV-Vis-NIR Raman microscope equipped with a 325 nm line of He-Cd laser as the excitation source and CCD detector. Composition and morphology of the thin films were characterized using scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) (FEI FESEM with EDX).

X-ray photoelectron spectroscopy measurements were carried out with an ESCA-3 Mark II Spectrometer (VG Scientific Ltd.) using Mg Kα radiation (1253.6 eV) as the excitation source. Binding energies were corrected for charging affects with reference to adventitious C_{1s} peak at 284.60eV and measured with a precision of ±0.2eV.

The optical characterization of Cu_3BiS_3 films was carried out by photoluminescence (PL) measurements using a closed cycle optical cryostat and Ar^+ laser of 514 nm excitation wavelength with a maximum input power of 30 mW. Additional characterization was carried out to measure the optical and electrical properties of the thin films. Transmission and reflection data (Perkin Elmer UV-VIS-NIR spectrophotometer, Lambda-90) was used to determine the optical band gap, band gap type, and optical absorption coefficient. A clean soda lime silicate glass substrate was used as the 100% transmission measurement standard. Reflection measurements were made at 10° from normal, and an aluminum mirror deposited on a soda lime silicate glass substrate was used as the 100% reflection standard.

The Hall measurements were conducted at room temperature under a 0.5 Tesla magnetic field. Samples of 5x5 mm^2 size were cut from the wafers, and aluminum metal dots were vacuum evaporated in the four corners to obtain electrical contacts in the Van der Pauw geometry. Then the circular contacts of diameter 400 μm were made on Cu_3BiS_3 and the Molybdenum surface by thermally depositing Al (thickness~300nm) metal and thermal annealing at 200ºC. Variable temperature *I-V* of the devices was measured in the air using a Keithley-236 source meter.

III. RESULTS AND DISCUSSIONS

The XRD spectra (Fig. 1) of the Cu_3BiS_3/Mo/SLG film stack indicate that the Cu_3BiS_3 film is a polycrystalline film with a preferred (131) orientation. Figures 2(a) and 2(b) depict the surface morphology of the Cu_3BiS_3 film deposited on the Mo layer using SEM. 500 nm is the thickness of the Cu_3BiS_3 film. The SEM images show that the Cu_3BiS_3 film has a smooth surface morphology, high grain size, and is continuous. As demonstrated later in the current-voltage (I-V) characterization, the Cu_3BiS_3 film was developed or particularly sulfurized to have ultra-large grain size in order to have fewer grain boundaries between electrodes and attain a lower leakage current.

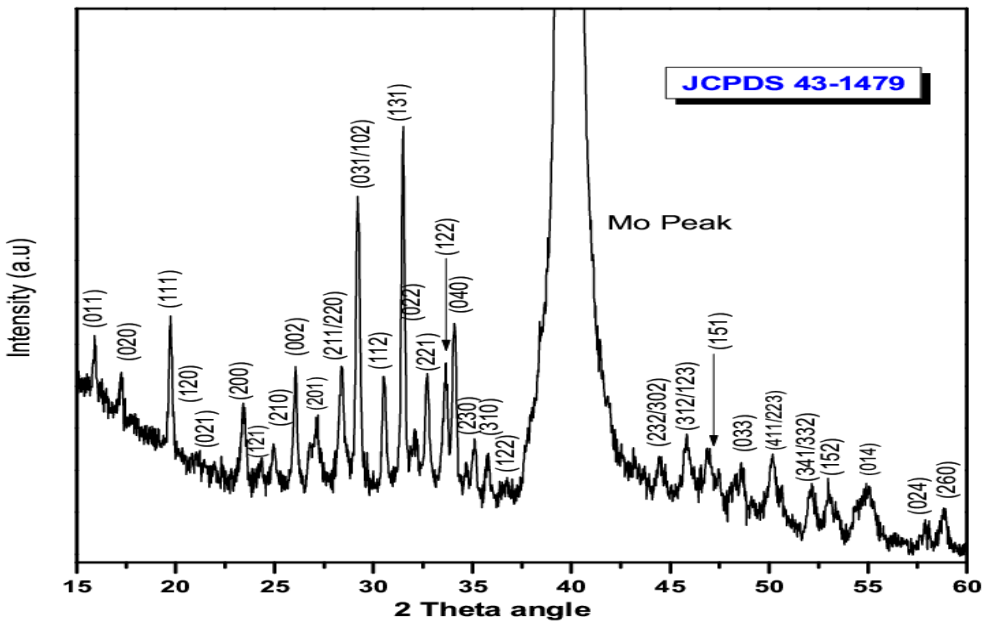

Fig. 1 X-Ray Diffraction Pattern of Cu_3BiS_3 thin film deposited on molybdenum-coated soda lime silicate glass.

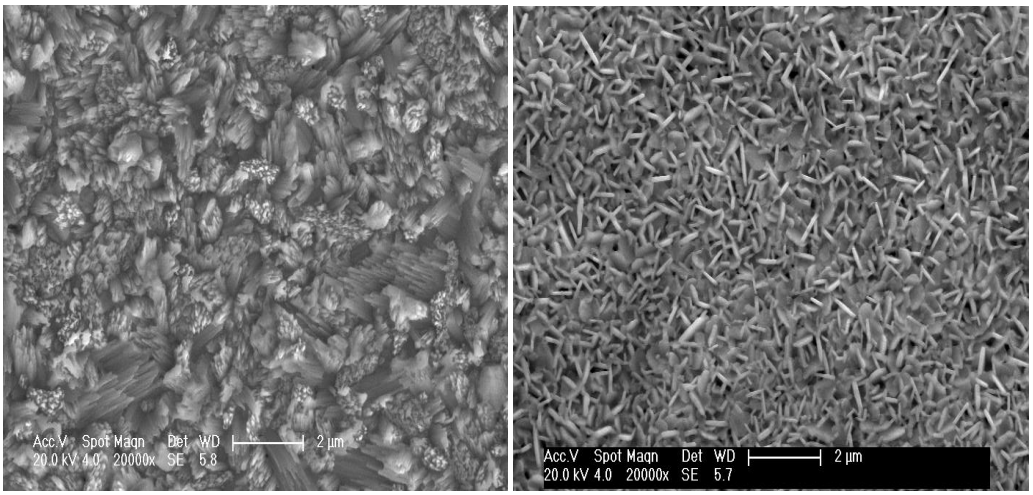

Fig. 2 Scanning Electron Micrographs of Cu_3BiS_3 thin film deposited on (a) Soda lime silicate glass and (b) Molybdenum coated soda lime silicate glass.

The low-temperature PL spectrum observed from the prepared Cu_3BiS_3 film is depicted in Figure 3. At 855 nm, the PL spectrum displays a prominent excitation-emission peak. The associated bandgap is 1.45 eV. Cu is a powerful oxidant that tends to migrate and accumulate at the film surface, where oxygen in the low vacuum selenization environment provides the driving force for the migration to achieve the lowest Gibbs free energy. The strong PL near-infrared excitation-emission peak suggests that the Cu_3BiS_3 film has excellent crystal quality, and Cu_3BiS_3-based PDs can be used for NIR detection. The Cu_3BiS_3/Mo/SLG MSM structure was utilized to assess the NIR detector performance following the deposition of the comb electrodes. The Schottky contact Al/ Cu_3BiS_3 has a measured Schottky barrier height of 0.69 eV.

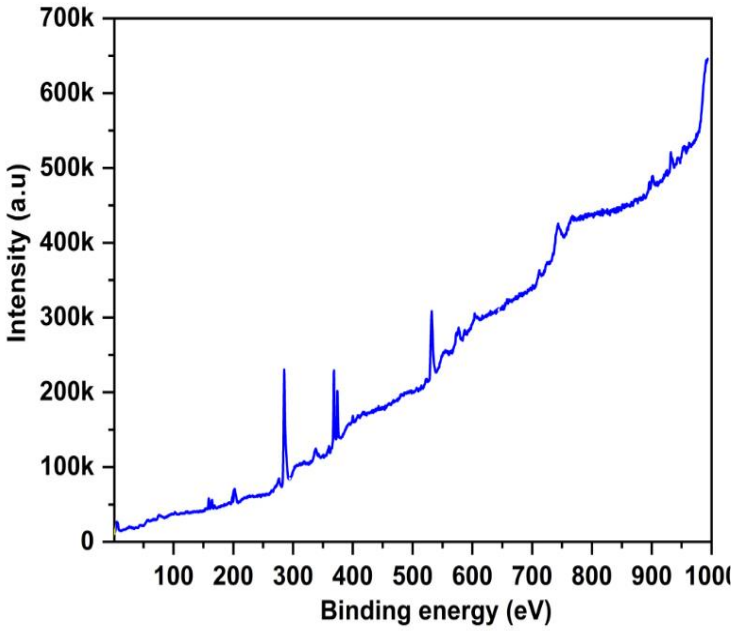

Fig. 3(a)

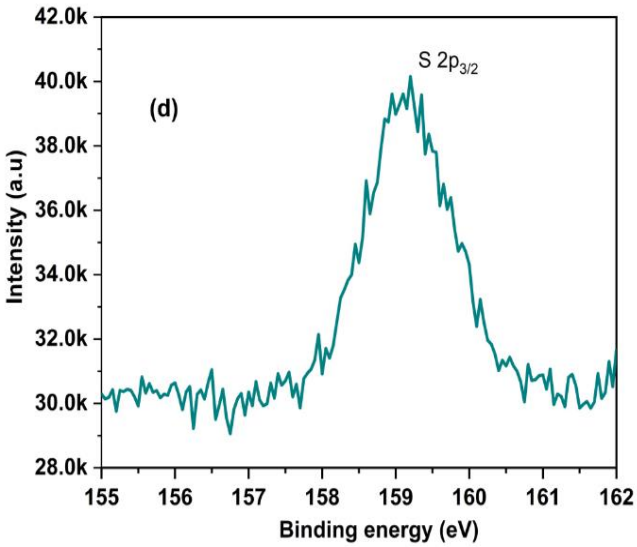

Fig. 3(b)

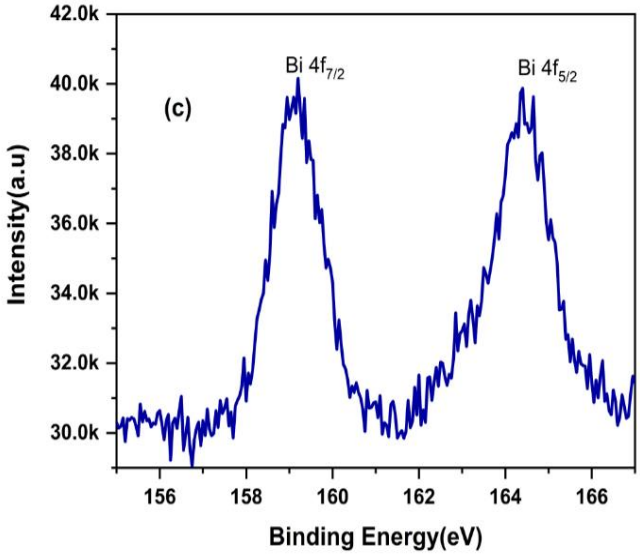

Fig. 3(c)

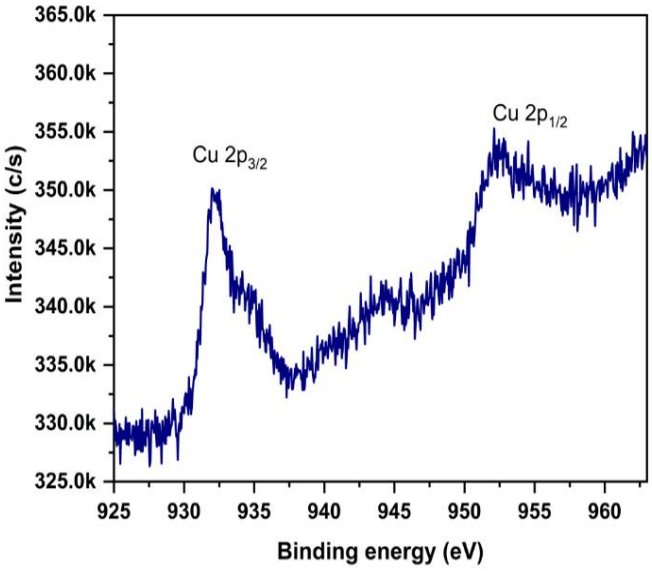

Fig. 3(d)

Fig. 3 (a) XPS survey spectrum of Cu_3BiS_3 thin film and (b), (c), (d) represents the X-ray photoelectron spectra of Cu 2p, Bi 4f and S 2p core levels of thin film respectively

Fig. 4a shows the *I-V* characteristics of the Cu_3BiS_3 PD with 10 μm electrode spacing at room temperature. With a 5V applied bias, the dark current of the PD is 2.36×10^{-6} A, whereas the photocurrent under NIR illumination is 1.69×10^{-3} A.

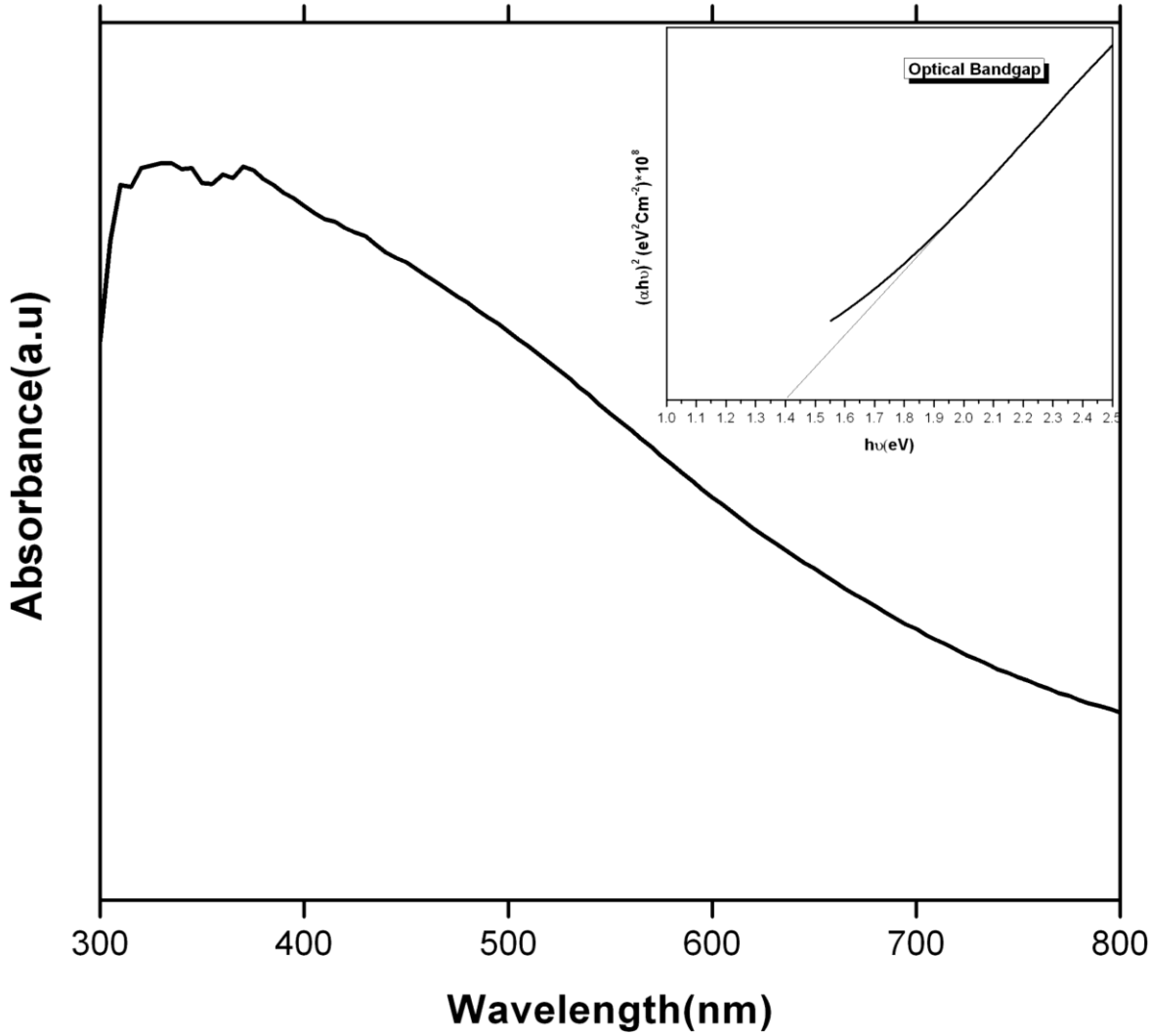

Fig. 4 Optical absorption spectrum of the Wittichenite (Cu_3BiS_3) thin film

The photocurrent amplification may have been limited by high recombination at the grain boundaries in the Cu_3BiS_3 film. Defects in grain boundaries, such as twins, dislocations, stacking faults, and Na (out-diffusion from SLG substrate), are located along this MSM structure's photocurrent paths. The increase in current upon illumination is more than four times of magnitude more significant than the dark current, and this is mainly attributed to grain boundaries between the electrodes and a shorter distance for carrier collection. The p-type Cu_3BiS_3/metal junction favors the injected or photo-generated electrons transportation because there is no energy barrier for the electrons to overcome.

Furthermore, the induced electric field near the metal caused by band bending helps the electron's acceleration which improves electron collection and minimizes recombination at the same time. As Fig. 2a shows, the Cu_3BiS_3 film surface is smooth, and its grain size can be as large as 1–2 μm so that the 5-μm-finger-spacing PD could have just a three-grain boundary between the electrodes. Fewer grain boundaries mean less photo-generated carriers' recombination, resulting in greater photocurrent magnification. The remarkable performance of the Cu_3BiS_3 PD is credited to (a) superior quantum efficiency; the Cu_3BiS_3-based material can be over 90% for wavelength from 500 nm to 850 nm; (b) favored photo-generated electrons transportation; (c) efficient collection; and (d) minimized recombination. Fig. 5 shows the spectral responses of the Cu_3BiS_3-based PD at 5 V bias. The responsivity of the 10-μm-spacing PD is 0.40 A/W, and the cut-off also occurs at 855 agrees with the PL analysis.

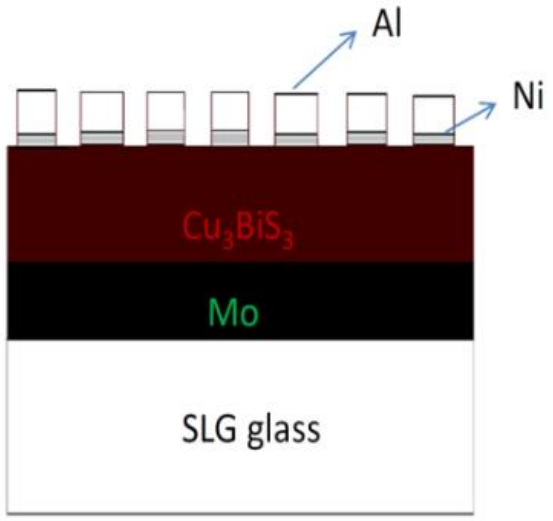

Fig. 5(a)

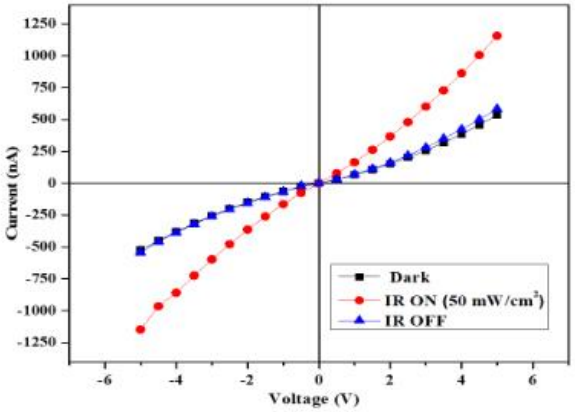

Fig. 5(b)

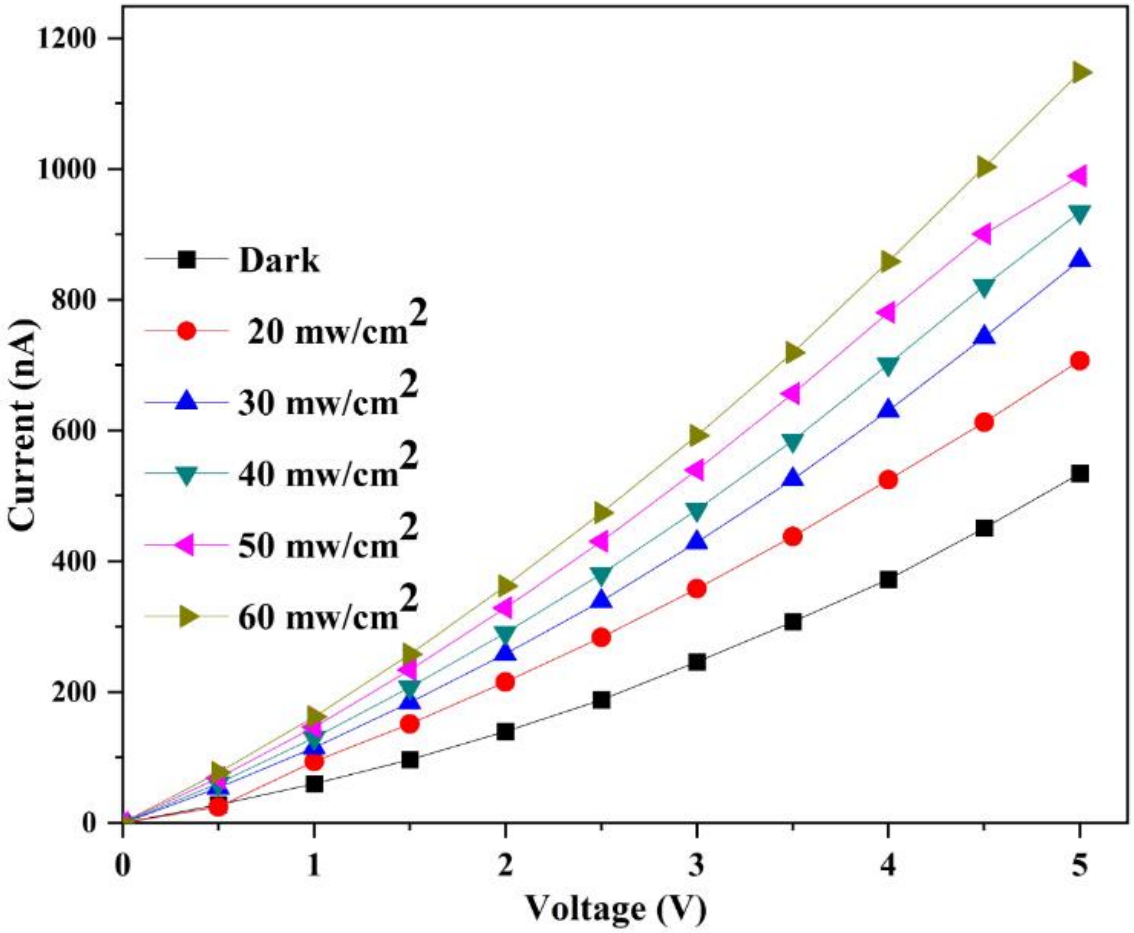

Fig. 5(c)

Fig. 5 (a) The device structure of the Infrared photodetector (b) The I-V characteristics of the device under dark and illumination at an optical intensity of 50 mW cm^{-2} (c) Dark and photocurrent response as a function of applied voltage at different illumination levels

IV. CONCLUSIONS

Using a unique approach based on the co-evaporation of the precursor materials in a two-step process, Cu_3BiS_3 thin films with characteristics suitable for use as photoconductive layers in near-infrared photodetectors were produced. It was discovered that, regardless of deposition conditions, only the orthorhombic Cu3BiS3 phase supports film growth. In addition, it was found that Cu_3BiS_3 films exhibit significant absorption coefficients (more than 10^4 cm^{-1}) and an energy band gap Eg of approximately 1.45 eV, indicating that this compound has favourable features for use as a photoconductive layer in near-infrared photodetectors. It has been established that Cu_3BiS_3 thin film can serve as the absorber layer of a near-infrared photodetector. With near-infrared illumination, the Cu_3BiS_3 photodetector is four times more sensitive regarding photocurrent. This material is, therefore, an excellent contender for near-IR photodetector applications.

IV. ACKNOWLEDGMENT

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V. References

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