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Rapid responsive Mg/$ZnSnP_2$/Sn photodetector for visible to near-infrared application

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ABSTRACT

A photodetector based on Mg/$ZnSnP_2$/Sn structure was fabricated on p-type silicon (100) to operate in the wavelength range of 450–850 nm. The observed current-voltage characteristics showed roll-over like features which was successfully modeled considering two Schottky junction diodes connected back to back. The device showed strong photo-response in both the forward and reverse bias configuration and the current-voltage curve shifted to the fourth quadrant under illumination. The barrier height and the ideality factor of the two Schottky diodes were evaluated using numerical simulation. The maximum values of responsivity, photosensitivity and detectivity were found to be 22.76 mA W^{-1}, 57.00 cm^2W^{-1} and 6.34 × 10^{10} cm $Hz^{1/2}$ W^{-1} in the forward bias and 3.48 mA W^{-1}, 48.22 cm^2 W^{-1} and 2.25 × 10^{10} cm $Hz^{1/2}$ W^{-1} in the reverse bias, respectively at illumination of wavelength 850 nm. The photodetector showed a fast response time of 47 μs and multiple recovery times of 725 μs, 1.2 ms and 1.3 ms respectively. The existence of traps within the $ZnSnP_2$ thin films was responsible for extending the time of recovery in comparison to time of response.

1. Introduction

Detection of optical signal starting from visible to near infrared (NIR) regime (450–900 nm) has numerous applications in the field of conventional imaging, night vision, medical diagnostics, telecommunication, robotics, environmental observation, neuroscience research etc [1–4]. Low bandgap semiconductor materials with constituent elements abundant in nature and non-toxic are highly desirable for NIR application in large scale. Many efforts have been made to successfully develop these materials, such as GaAs [5], CdS [6], HgCdTe alloy [7], and also complex epitaxial heterostructures [8] due to their unique light sensitive property in the particular region. However, relatively low abundance of elements such as Te and Ga and due to toxicity of Cd, Hg etc., high volume production of these devices with relatively low cost would be hindered. On the other hand, Si which is commercially used in photo detection in the said region is of indirect bandgap and its sensitivity is low compared to the devices made of direct band gap materials. In view of this, great attention is paid to develop suitable alternative materials with desired optical properties. Among these, $ZnSnP_2$, a ternary compound semiconductor belonging to II-IV-V_2 group has come into prominence recently which shows strong optical characteristics in the range of visible to NIR [9]. It exhibits a structural transformation from an ordered chalcopyrite to a disorder sphalerite structure at 720 °C [10]. The direct bandgap of $ZnSnP_2$ can be tailored from 1.71 eV to 0.75 eV by order to fully disorder transformation [10,11]. The control over cooling rates and temperature during its growth gives precise bandgap tuning [10]. $ZnSnP_2$ based thin films show high optical absorption, greater than 10^5 cm^{-1} above the fundamental absorption edge [9,12,13]. Considering these favorable features, $ZnSnP_2$ could be a good alternative material for the fabrication of photovoltaic devices and visible to NIR detectors. Moreover, this material is advantageous for being low toxic, earth abundant, inexpensive and free of hazardous metals (Hg, Pd and Cd). Recently, Al/ZnO:Al/ZnO/(Cd, Zn)S/$ZnSnP_2$/Cu based heterojunction solar cell with $ZnSnP_2$ absorbing layer has been fabricated which achieved a conversion efficiency of 3.44% [14]. However, no photodetector based on $ZnSnP_2$ thin films have been reported in literature till date.

In this work, we have reported a nonsymmetrical Mg/$ZnSnP_2$/Sn metal semiconductor metal (MSM) structure for photodetector application in the visible to NIR regime. The current voltage (I-V) characteristic of the structure is analyzed in dark and under illumination conditions with wavelength ranging from 450 to 900 nm. The observed I-V curves are fitted with standard current-voltage model suitable for the MSM devices to extract device parameters such as the barrier heights and ideality factors. The variation of detectivity (D), responsivity (R) and photosensitivity (S) of the grown photodetector is

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estimated with different illumination wavelengths in the range mentioned above and with different applied bias. The speed, stability of response and recovery of the device are also tested under a given bias.

2. Experimental

2.1. Material synthesis and characterization

Bulk $ZnSnP_2$ was first synthesized using a solvent technique [15], which was then used for deposition of thin films on silicon (Si) (100). Molten Sn was used as the solvent ($ZnSnP_2$:Sn = 1:3). The constituent elements (Zn, Sn and P) for the preparation of bulk ingot were sealed in a quartz ampoule in a vacuum of 10^{-3} mbar. The temperature profile and other controlling parameters for the growth process were reported elsewhere [9]. The ingot thus obtained was treated with 0.1 M HCl to collect pure $ZnSnP_2$ powder which was then used as a source material for thin film deposition on p-type Si (100) and glass substrates by thermal evaporation technique. During the thin film deposition, the substrate and chamber pressure were maintained at 300 °C and 10^{-6} mbar, respectively. The film deposition rate (1 nm/s) and the film thickness (~0.3 µm) were monitored by a quartz crystal monitor. Grazing incidence x-ray diffraction (GIXRD) technique at Cu K_α line (Rigaku Smart Lab) was employed to extract the information about crystallinity and microstructure of the film. Band gap of the films were determined by absorbance (A) spectra recorded at room temperature using Perkin Elmer Lambda-750 spectrophotometer. Magnesium (Mg) and Tin (Sn) were selected for the two metal contacts of the MSM structure which were also deposited by thermal evaporation. Measurements of room temperature I-V and temporal variation of the photocurrent at constant bias were performed using Keithley 4200 SCS and Agilent 54622A oscilloscope respectively. Spectral response of the device was measured using a 450 W Xenon lamp in conjunction with a monochromator (Gemini 180, Horiba Jovin Yvon). Time response of the devices were made using a chopper operating at a frequency of 250 Hz.

3. Results and discussion

The as-grown thin films on p-type Si (100) substrates were first characterized using GIXRD measurements which is shown in Fig. 1(a). Diffraction peaks related to (112), (200), (004), (303) and (316) planes of the $ZnSnP_2$ crystal structure were clearly observed, which indicates the polycrystalline nature of the grown film. Significant width of the diffraction peaks implies small crystallite size of the films which were calculated to be of ~7 nm using the Scherrer formula given as

$$\tau = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

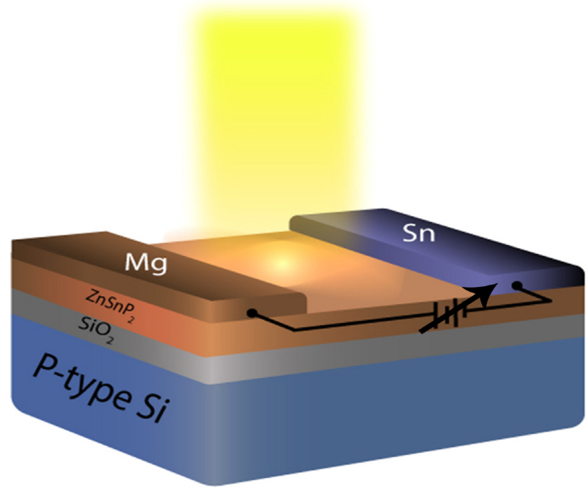

Fig. 2. A schematic representation of the fabricated photodetector.

where τ, K, λ, β and θ are mean size of the domain, the shape factor, wavelength of x-ray, full width at half maximum of the diffraction peaks and Bragg angle, respectively. Fig. 1(b) represents the optical absorption spectra in the form of $(\alpha h\nu)^2$ vs $h\nu$ plot for the film grown on glass, where α is the absorption coefficient of the films, h the Planck constant and ν is the frequency of light. The linear region of the graph was extrapolated to the $h\nu$ axis to obtain the bandgap of the film which was found to be ~1.46 eV at room temperature. The inset of Fig. 1(b) represents the variation of α with wavelength of light. The film showed threshold value of α corresponding to the incident wavelength of ~850 nm (1.46 eV) implying the deposited film was fairly dominated by chalcopyrite phases as predicted by VASP based hybrid density functional theory calculations [11]. A schematic representation of the fabricated device under forward bias is shown in Fig. 2. For the non-symmetrical MSM structure, a shadowed mask was used to illuminate only the semiconductor region of the device where light was allowed to incident normally during measurements. The I-V responses of the device in dark and under illumination at different wavelength (450–900 nm) are shown in the Fig. 3. The forward biased current varied depending upon the wavelength of illumination and being maximum at 850 nm, which corresponds to the optical band gap of the films as determined from optical absorption measurements. The forward bias current showed exponential increase at lower bias followed by a roll-over to linear regime at higher bias voltage of 0.59 V in dark. As wavelength of the incident light increased from 450 nm to 850nm, the corresponding roll-over voltage increased from 0.62 V to 0.69 V and then decreased thereafter to 0.6 V at 900 nm. Such behavior is usually

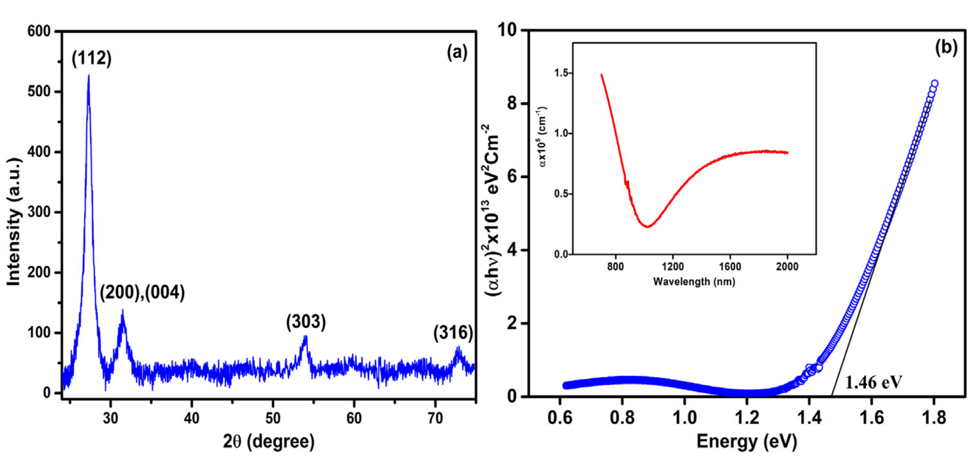

Fig. 1. (a). Grazing incidence x-ray diffraction of $ZnSnP_2$ on Si (b). Optical absorbance spectra of $ZnSnP_2$ grown on glass substrate.