Summary and Conclusions

In this thesis work, main attention is given for the fabrication of earth-abundant and environment-friendly $ZnSnP_2$ thin films using a simple and inexpensive deposition technique and studied their optoelectronic and related properties to find their suitability for the application of photovoltaic devices. All the key aspects of the work are given below.

The polycrystalline thin films of $ZnSnP_2$ are successfully deposited on various substrates like p-type Si (001), sapphire and glass using the electron beam evaporation technique. In this deposition process, $ZnSnP_2$ bulk material is used as an evaporent which is synthesized by the solution method. The selected area electron diffraction pattern and grazing incidence x-ray diffraction justify the formation of the polycrystalline nature of the grown structure ($Si/ZnSnP_2$). On the other hand, from fitting the x-ray reflectivity curve using Distorted Wave Born Approximation the electron density profile and the interface roughness are also investigated. High-resolution transmission microscopy operated in cross-section mode shows that film is not of uniform composition throughout the entire area. Crystallites are positioned little off-centered towards the surface of the film. The stoichiometry of the film is estimated from the energy dispersive x-ray study in the high-resolution transmission electron microscopy which is found to be 1:1:2 to an accuracy of ~± 10 %. The elemental mapping shows that in the film the $ZnSnP_2$ crystallites are surrounded by the amorphous compounds of Zn and P. The estimation of bandgap from the measured optical reflectance and transmittance spectra at room temperature is found to be 1.71eV. The absorption coefficient of the film is greater than 10^6 cm^{-1} above 1.6 eV of photon energy. The $ZnSnP_2$ films exhibit excess optical absorption and considerable band tailing in the low energy region of the spectrum which originates owing to the presence of various inter-band defect states. The low-temperature photoluminescence spectra of the thin film show non-symmetrical and consist of two wide and overlapped peaks at 1.529 eV and 1.643 eV, respectively at 15 K. The low energy peak is red-shifted with increasing temperature. A careful analysis using the dual-channel Arrhenius equation, the excitonic binding energies are found to be (10 meV and 56 meV) and (8 meV and 30 meV) for first and second peaks respectively. The peaks are originated due to the donor-acceptor pair related transitions. This claim is further confirmed from the intensity-dependent photoluminescence study. The energy position of the donor and acceptor levels are found to be 176 meV and 56 meV from the conduction and valance band, respectively. Antisite defects

(Sn_{Zn}-acceptor, Zn_{Sn}-donor) and vacancies (V_{Zn}) present in the $ZnSnP_2$ are suggested as native defects and mainly responsible for the light emission property.

In this Ph.D. work, we have reported a successful growth of non-symmetrical Mg/$ZnSnP_2$/Sn structure on p-type Si by thermal evaporation method for photodetector applications in visible to near-infrared region. The bandgap of the thermally evaporated $ZnSnP_2$ thin film is determined from optical absorption spectra which is found to be 1.46 eV. Faster deposition rate has resulted in lower bandgap due to the presence of partial cationic disorder. Grazing incidence x-ray diffraction measurement confirms the polycrystalline nature of the film with an average crystallite size of ~7 nm. The current-voltage characteristics of the device are investigated under dark and with illumination. The current has shown maximum enhancement under the illumination of wavelength 850 nm. We have used Lambert W function to fit the current-voltage curve assuming two diodes connected in a back-to-back configuration. Under the dark condition, the height of the barriers is found to be 0.89 eV and 0.71 eV for Mg and Sn contact, respectively which decreased to 0.73 eV and 0.57 eV under the illumination of wavelength 850 nm. The corresponding ideality factors are 3.0 and 2.9 under dark and 4.65 and 3.5 under illumination. Under illumination, during the separation process, the photogenerated minority carriers eventually recombined through the deep level trap states to make them empty resulting in an effective increase of the defect states. These increased vacant states are responsible for the effective lowering of barrier heights and the further increase of ideality factors. The photodetector shows responsivity, detectivity and photosensitivity of 22.76 mAW^{-1}, 57.00 cmW^{-1} and $6.34x10^{10}$ $cmHz^{1/2}W^{-1}$ in the forward bias and 3.48 mAW^{-1}, 48.22 cm^2W^{-1} and $2.25x10^{10}$ $cmHz^{1/2}W^{-1}$ respectively at 850 nm. The higher density of defect states makes these values lower in reverse bias. The rise time of the photodetector is found to be 47μs, which is considered to be quite fast compared to other devices. The device showed multiple characteristic decay times of 725 μs, 1.2 ms and 1.3 ms due to the presence of deep levels within $ZnSnP_2$.

We have demonstrated a successful fabrication of a simple asymmetrical coplanar Mg/$ZnSnP_2$/Sn high-performance metal-semiconductor-metal photodetector on a p-type Si by employing a less complicated and inexpensive growth process. At the time of deposition, the Sn contact is annealed to decrease the barrier height of that junction. The Mg/$ZnSnP_2$ and Sn/$ZnSnP_2$ junctions are characterized by variable illumination power and applied bias. Here, the two Schottky junctions Mg/$ZnSnP_2$ and Sn/$ZnSnP_2$ of the device are considered

independently. In the self-powered configuration, the value of the responsivity and detectivity are 0.2 AW^{-1} and $4.62x10^{12}$ Jones for the $Mg/ZnSnP_2$ and 0.03 AW^{-1} and $1.62x10^{11}$ Jones for the $Sn/ZnSnP_2$ junction, respectively. During biased mode of operation, these values become 4.7 AW^{-1} and $1.19x10^{12}$ Jones in case of $Mg/ZnSnP_2$ and 12.7 AW^{-1} and $4.78x10^{11}$ Jones for $Sn/ZnSnP_2$, respectively. For both the junctions, the power-dependent photocurrent showed a superlinear increment owing to the conversion of traps into the recombination centers which in turn increase the lifetime of electrons in the conduction band. The obtained values of the power exponents are 1.75 ± 0.19 and 1.42 ± 0.21 for the $Mg/ZnSnP_2$ and $Sn/ZnSnP_2$ junctions, respectively. The response and recovery speed of the PDs are also studied under variable bias and illumination power. Under an incident power of 0.34 mW, the rise and decay times for $Mg/ZnSnP_2$ and $Sn/ZnSnP_2$ are 200 μs, 2300 μs, and 390 μs, 240 μs, respectively at 2.5 V. Additionally, $Mg/ZnSnP_2$ junction has shown an unusual secondary decay channel which disappears during self-powered mode operation. This observation is correlated to the non-uniform distribution of defect states within the $ZnSnP_2$ thin film. The density of defect states is much higher near the $Mg/ZnSnP_2$ junction compare to the $Sn/ZnSnP_2$ junction which traps the photogenerated carriers. This mechanism is further confirmed from the frequency and illumination dependent capacitance measurements. On the other hand, we have also examined the broadband detection capability of both devices. Both the photodetectors are able to detect the photons in the UV-VIS-NIR portion of the electromagnetic spectra.