UNIVERSITY GRANTS COMMISSION

UGC Project No.F43-400/2014(SR)

PROJECT COMPLETION REPORT

Submitted to University Grant Commission

Project Title
Development, Synthesis and Characterization of ZnSnP₂ Chalcopyrite Thin Film for Photovoltaic Devices

Principal Investigator
Arabinda Nayak

Department of Physics
Presidency University, Kolkata- 700073
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

Annual/Final Report of the work done on the Major Research Project.
(Report to be submitted within 6 weeks after completion of each year)

1. Project report No.: Final Report
2. UGC Reference No.  F43-400/2014(SR) dated 03.09.2015
3. Period of report: from 18/12/2015 to 30/06/2018
4. Title of research project: Development synthesis and characterization of ZnSnP₂ chalcopyrite thin film for photovoltaic devices

5. (a) Name of the Principal Investigator: Arabinda Nayak
   (b) Deptt. : Department of Physics
   (c) University/College where work has progressed: Presidency University, Kolkata

6. Effective date of starting of the project: 18/12/2015

7. Grant approved and expenditure incurred during the period of the report:
   a. Total amount approved Rs. 11,91,000/-
   b. Total expenditure Rs. 10,02,851/-
   c. Report of the work done: (Please attach a separate sheet)

   i. Brief objective of the project
      • Growth of bulk material of ZnSnP₂ with varying cation disorder by solution growth (SG) method. The cation disorder is expected to produce variable band gap energy (1.66 eV – 1.20 eV) for ZnSnP₂. This is one of the main objectives of the proposed project.
      • Growth of thin films using PVD (Thermal & Cluster Beam) method at elevated temperatures on silicon, quartz and sapphire substrates.
      • Characterization of thin films using various analytical methods to evaluate structural (x-ray diffraction, TEM), electrical (resistivity - Hall Effect) and light absorption/emission (photoluminescence, optical absorption, reflectance etc) properties ZnSnP₂.
• N-type & p-type doping of ZnSnP₂ thin films and evaluating carrier concentration and resistivity at elevated temperatures.

• Fabrication and optimization of single/multi homo- junction high efficient solar cells using doped materials. For multi-junction devices a low resistance (n⁺/p⁺) tunnel junction to be made to isolate active regions.

• Accumulation and evaluation of experimental data for examining the suitability of the material/devices for their commercial applications in PV cells.

• Development of skilled man power (JRF) in the field photovoltaic research, one of the frontier areas of research in Physics.

ii. Work done so far and results achieved and publications, if any, resulting from the work
(Give details of the papers and names of the journals in which it has been published or accepted for publication)


iii. Has the progress been according to original plan of work and towards achieving the objective, if not, state reasons
Since the project was started approximately five months late (due to not receiving of funds), the studies related to the P and N type doping of ZnSnP₂, carrier transport properties, and formation of tunnel junction to increase the device performance (as mentioned in objective) were not able to be done. However, considering the recent research trends the application of ZnSnP₂ in the field of photo detection was also performed.

iv. Please indicate the difficulties, if any, experienced in implementing the project
ZnSnP₂ being a ternary material containing P, its growth was a challenge task. The reliable phase diagram for the growth of ZnSnP₂ is not available. Attempts had been
made to grow the bulk ZnSnP₂ material in an excess Sn solution (melt) considering the pseudo-binary phase diagram of Sn-ZnP₂ system.

v. **If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet.**

The effective duration of the project was 2 years 7 months. To complete fulfill the objectives another 6 months extension was expected.

vi. **If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission.**

Given in Annexure -IX.

vii. **Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any**

One person is appointed as a project fellow and enrolled in PhD.

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SIGNATURE OF THE PRINCIPAL INVESTIGATOR

(Seal) Arabinda Nayak, Ph. D
Professor of Physics
Presidency University, Kolkata

REGISTRAR/PRINCIPAL

(Seal) Registrar
Presidency University
Kolkata
PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE
FINAL REPORT OF THE WORK DONE ON THE PROJECT

1. Title of the Project
Development synthesis and characterization of ZnSnP$_2$ chalcopyrite thin film for photovoltaic devices

2. NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR
Arabinda Nayak, Professor, Department of Physics, Presidency University, Kolkata 700073

3. NAME AND ADDRESS OF THE INSTITUTION
Presidency University, Kolkata- 700073

4. UGC APPROVAL LETTER NO. AND DATE
F 43-400/2014 (SR)

5. DATE OF IMPLEMENTATION
18/12/2015

6. TENURE OF THE PROJECT
18/12/2015 to 30/06/2018

7. TOTAL GRANT ALLOCATED
Rs. 11,91,000/-

8. TOTAL GRANT RECEIVED
Rs. 10,18,238/-

9. FINAL EXPENDITURE
Rs. 10,02,851/-

10. TITLE OF THE PROJECT
Development synthesis and characterization of ZnSnP$_2$ chalcopyrite thin film for photovoltaic devices

11. OBJECTIVES OF THE PROJECT
- Growth of bulk material of ZnSnP$_2$ with varying cation disorder by solution growth (SG) method. The cation disorder is expected to produce variable band gap energy (1.66 eV - 1.20 eV) for ZnSnP$_2$. This is one of the main objectives of the proposed project.
- Growth of thin films using PVD (Thermal & Cluster Beam) method at elevated temperatures on silicon, quartz and sapphire substrates.
- Characterization of thin films using various analytical methods to evaluate structural (x-ray diffraction, TEM), electrical (resistivity - Hall Effect) and light absorption/emission (photoluminescence, optical absorption, reflectance etc) properties ZnSnP$_2$.
- N-type & p-type doping of ZnSnP$_2$ thin films and evaluating carrier concentration and resistivity at elevated temperatures.
Title of the Project
Development synthesis and characterization of ZnSnP₂ chalcopyrite thin film for photovoltaic devices

NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR
Arabinda Nayak, Professor, Department of Physics, Presidency University, Kolkata 700073

NAME AND ADDRESS OF THE INSTITUTION
Presidency University, Kolkata- 700073

UGC APPROVAL LETTER NO. AND DATE
F 43-400/2014 (SR)

DATE OF IMPLEMENTATION
18/12/2015

TENURE OF THE PROJECT
18/12/2015 to 30/06/2018

TOTAL GRANT ALLOCATED
Rs. 11,91,000/-

TOTAL GRANT RECEIVED
Rs. 10,18,238/-

FINAL EXPENDITURE
Rs. 9,77,147/-

TITLE OF THE PROJECT
Development synthesis and characterization of ZnSnP₂ chalcopyrite thin film for photovoltaic devices

OBJECTIVES OF THE PROJECT
- Growth of bulk material of ZnSnP₂ with varying cation disorder by solution growth (SG) method. The cation disorder is expected to produce variable band gap energy (1.66 eV – 1.20 eV) for ZnSnP₂. This is one of the main objectives of the proposed project.
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- Characterization of thin films using various analytical methods to evaluate structural (x-ray diffraction, TEM), electrical (resistivity - Hall Effect) and light absorption/emission (photoluminescence, optical absorption, reflectance etc) properties ZnSnP₂.
- N-type & p-type doping of ZnSnP₂ thin films and evaluating carrier concentration and resistivity at elevated temperatures.
• Fabrication and optimization of single/multi homo-junction high efficient solar cells using doped materials. For multi-junction devices a low resistance \((n^+/p^-)\) tunnel junction to be made to isolate active regions.
• Accumulation and evaluation of experimental data for examining the suitability of the material/devices for their commercial applications in PV cells.
• Development of skilled man power (JRF) in the field of photovoltaic research, one of the frontier areas of research in Physics.

12. WHETHER OBJECTIVES WERE ACHIEVED

The studies related to the P and N type doping of ZnSnP₂ and formation of tunnel junction to increase the device performance (as mentioned in objective) were not able to be completed due to late (approximately five months) starting of the project. Considering the recent research trends the application of ZnSnP₂ in the field of photo detection was also performed.

13. ACHIEVEMENTS FROM THE PROJECT

**Important achievements from work-1:**

The source material ZnSnP₂ for the deposition of thin films was grown by direct heating of the constituent elements (Zn, Sn, P) in an excess Sn solution (melt) considering the pseudo-binary phase diagram of Sn-ZnP₂ system at 750°C. Thin films of ZnSnP₂ had been successfully grown on P-type Si (100) by e-beam evaporation technique. A detailed x-ray reflectivity analysis of the films had been carried out. Distorted wave born approximation (DWBA) had been implemented to simulate the experimental result to find out the variation of electron density with depth of the film. Inter diffusion between ZnSnP₂ and native SiO₂ layers was observed in the electron density profile as obtained from the DWBA simulation.

**Important achievements from work -2:**

Thin films of ZnSnP₂ were successfully grown on p-type silicon (001), sapphire and glass substrate by e-beam evaporation method. The as-deposited films were characterized using scanning and high resolution transmission electron microscopes, reflectance and transmittance spectroscopy and photoluminescence measurement at low temperature. Polycrystalline nature of the films was verified by high resolution transmission electron microscopy. An optical band gap of 1.71 eV was estimated at room temperature. Two broad luminescence bands at 1.529 eV and at 1.634 eV were observed at 15 K. The light emission
characteristics of the ZnSnP₂ were explained in terms of donor-acceptor pair recombination mechanism. Tin-on-zinc sites and zinc vacancies/zinc-on-tin sites were considered as donor and acceptor due to presence of native defects in the films. A schematic band model based on the experimental finding was suggested to account for the DA pair recombination.

**Important achievements from work-3:**

A photodetector based on Mg/ZnSnP₂/Sn structure was fabricated on p-type silicon (100) to operate in the wavelength range of 450 nm to 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 mAW⁻¹, 57.00 cm²W⁻¹ and 6.34x10¹⁰ cmHz¹/²W⁻¹ in the forward bias and 3.48 mAW⁻¹, 48.22 cm²W⁻¹ and 2.25x10¹⁰ cmHz¹/²W⁻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 ZnSnP₂ thin films was responsible for extending the time of recovery in comparison to time of response.

**14. SUMMARY OF THE FINDINGS**

**Important outcome from work -1:**

We have successfully synthesized pure ZnSnP₂ from the constituent source materials and the thin film of the ZnSnP₂ on Si substrates. The structure of the grown layer was investigated with the help of grazing incidence x-ray diffraction (GIXRD) and x-ray reflectivity (XRR) technique. Distorted Wave Born Approximation formalism was employed to fit the experimental XRR data and the variation of electron density profile (EDP) with depth was obtained as a fitting parameter. EDP indicates the successful growth of ZnSnP₂ layer and existence of SiO₂ layer on crystalline silicon substrate. The interface roughness was found to be 2.5 Å and 1.2 Å for air-film and film-substrate interface respectively. There was interfacial diffusion between ZnSnP₂ and SiO₂ layers during growth of the thin film.
This work was published in

Important outcome from work -2:
Successful growth of polycrystalline ZnSnP₂ thin films on p-type Si (001), sapphire and glass substrates by e-beam evaporation technique is reported. Selected area electron diffraction pattern justifies the polycrystalline nature of the grown structure (Si/ZnSnP₂). Estimation of band gap from the measured optical reflectance and transmittance spectra at room temperature is found to be 1.71 eV. The absorption coefficient of the film is about > 10⁶ cm⁻¹ above 1.6 eV of photon energy. In low temperature PL measurement two broad emission peaks have been observed at 1.529 eV and 1.643 eV respectively. DA pair recombination model is considered to explain the luminescence spectra of the ZnSnP₂ films. Antisite defects (Sn₂⁺-acceptor, Zn₂⁻-donor) and vacancies (V₂⁻) present in the ZnSnP₂ are suggested as native defects and mainly responsible for the light emission property.

This work was published in

Important outcome from work -3:
In this work we have demonstrated a successful fabrication of non-symmetrical Mg/ZnSnP₂/Sn structure on p-type Si for photodetector application ranging from wavelength of 450 nm to 850 nm. The current-voltage curve is fitted using two diode connect back to back to extract device parameters like barriers height and ideality factors in presence of illumination and without illumination condition. Under the dark condition the barriers height were 0.89 eV and 0.71 eV for Mg and Sn contact, respectively which decreased to 0.73 eV and 0.57 eV under illumination of wavelength 850 nm. The corresponding ideality factors were 3.0 and 2.9 under dark and 4.65 and 3.5 under illumination. The photodetector shows responsivity, detectivity and photosensitivity of 22.76 mA/W⁻¹, 6.34x10¹⁰ cmHz¹/²W⁻¹ and 57.00 cmW⁻¹ in the forward bias and 3.48 mA/W⁻¹, 2.25x10¹⁰ cmHz¹/²W⁻¹ and 48.22 cm²W⁻¹ respectively at 850 nm. The rise time of the photodetector was found to be 47μs, which was considered to be quite fast compared to other
devices. The device showed multiple characteristic decay times due to the presence of defects within ZnSnP₂.

This work was published in


Important outcome from work -4:

In this work we have reported a successful growth of Mg/ZnSnP₂/Sn Schottky junction, ZnO/ZnSnP₂ and SnO/ZnSnP₂ based devices for photovoltage application. These devices offer conversion efficiency of 1.44x10⁻⁴ %, 6.75x10⁻⁴ % and 3.62x10⁻⁴ %, respectively. Formation of heterojunctions improved the device performance but the improvement was not so significant. Lattice mismatch of ZnO and SnO with ZnSnP₂ produces higher density of interface states which limits the device performance. Details of this work are mentioned in the project report.

This work was published in

This work is under communication for publication.

15. CONTRIBUTION TO THE SOCIETY

One JRF has been trained in the field of thin films growth, fabrication of photodetectors and PV cells using ZnSnP₂ material. Basic understanding of the physical processes involved and advancement of knowledge of the above fields are the scientific contributions to the society.

16. WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT

Yes, the Project Fellow, Mr. Sukhendu Mukherjee, was also enrolled as a Ph.D. student. He has worked on the topics and problems that have been studied under this project.

17. NO. OF PUBLICATIONS OUT OF THE PROJECT( PLEASE ATTACH)

No. of publications: 03
(Reprints of the Research Papers are attached with this report)