UNIVERSITY GRANTS COMMISSION
Major Research Project (MRP) 2013
APPLICATION FORM

Subject Applied

MRP ID : **MRP-MAJOR-MATE-2013-16190**
Research Project : Major
Broad Subject : Material Science
Areas of Specialization : Solar Energy Materials & Thin Film Solar Cell
Duration : 3 Year, View Declaration Certificate

Principal Investigator

Name : Dr. Arabinda Nayak, Male
Date of Birth : 25/08/1963
Category : GENERAL
Educational Qualification : M.Sc., Ph.D.
Designation : Associate Professor/Reader
Correspondence Address : Department of Physics Presidency University 86/1, College Street Kolkata - 700073. West Bengal
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Whether Principal Investigator is appointed on regular basis? :
Is Principal Investigator superannuated? : No

Experience Detail

Teaching Experience : 16
Research Experience : 16
Ph.D. Status :
Year of Award of Doctoral degree : 1993
Title of Thesis of Doctoral degree : Studies on Structural, Electrical and Optical Properties of Electron Beam Deposited Zn3P2-Cd3P2 Thin Films.

Publication Details with impact Factor(only for Science Subjects):

Papers Published : Accepted :23 Communicated :2
Books Published : Accepted :0 Communicated :0

1. Research Papers/Review Articles/Conference Proceedings (during last 5 years) *:

Title with page nos	Publication Type	Journal ISSN/ISBN No.	Refereed or Not	Sole/Co-Author

2. Research Publications-Books,Chapters,Edited work,Articles etc. (during last 5 years): *

Title of the Book(s)	Publication Type	Journal ISSN/ISBN No.	Refereed or Not	Sole/Co-Author	Publisher (city / country) & Year of Publication

View List of Paper[s]

Project Applied

Name of the Institute : Presidency University
Institute Address : 86/1, College Street, Kolkata - 700073 West Bengal
Department : Physics
University/College : University
Whether the college is located in rural/backward area : No

PRESIDENCY UNIVERSITY
KOLKATA

To certify that

a. The University/College/Institute is approved under Section 2(f) and 12(b) of the UGC Act and is fit to receive grants from the UGC

b. General physical facilities, such as furniture/ space etc., are available in the Department/ College.

c. I/we shall abide by the rules governing the scheme in case assistance is provided to me/us from the UGC for the above project

d. I/we shall complete the project within the stipulated period. If I/we fail to do so and if the UGC is not satisfied with the progress of the research project, the Commission may terminate the project immediately and ask for the refund of the amount received by me/us

e. The above Research Project is not funded by any other agency.

Name and Signature of Principal Investigator
(Dr. Arabinda Nayak)
Associate Professor of Physics
Presidency University, Kolkata

Signature of Co- Investigator

Registrar
(Signature with Seal)

Registrar
Presidency University
Kolkata-700 073

Forwarded

Professor & Head
Deptt. of Physics
Presidency University
Kolkata

Proposed Research work

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

Introduction : (Including Origin of the research problem..) :

During last few years, much research attention has been given for the design and development of low cost high efficient photovoltaic (PV) devices which find a wide range of application starting from supplying electricity in remote rural area to space. The most important challenges in PV research are lowering of the production cost of the devices and increasing efficiency using comparatively less complicated growth system, finding easily available new materials with desirable properties and producing homo-junction for minimizing recombination losses.

In recent years, solar cells are mainly fabricated by silicon, however, higher-performance and lower-cost solar cells are demanded for prevalence. Ternary chalcopyrite structured semiconducting compounds with the general valence type I-III-VI_2(I= Cu, Ag; III = Al, Ga, In & VI = S, Se or Te) have long been investigated due to their applications in optoelectronics, non-linear optics and as light absorber in solar cells [1, 2]. Recently, however, the relative expense and scarcity of In and Ga metals have motivated a drive for earth abundant materials suitable for mass-scale production [3]. In view of the above, recently effort has been given in the exploitation of I_2–II–IV–VI_4materials such as Cu_2ZnSnS_4 [4]. However, the conversion efficiency of its cell is about 6%. Therefore, it is necessary to investigate another group of solar cell materials for achieving high performance and low cost.

Though a potentially important solar cell material, comparatively little attention has been given on the growth and structure-property relationship of $ZnSnP_2$ (II-IV-V Chalcopyrite) in the form of thin semiconductor films. $ZnSnP_2$ is composed of relatively abundant elements and is found to crystallize in the chalcopyrite structure with an optical energy gap of (E_g) ≈ 1.68 eV at 300 K [5],which is close to the optimum band gap of 1.5 eV for a single junction PV cell. Therefore, $ZnSnP_2$ is promising to be a candidate material for high–performance solar cell. It is also interesting to note that $ZnSnP_2$ undergoes an order/disorder phase transition at 720°C from the chalcopyrite structure to a disorder sphalerite structure (E_g ≈ 1.22 to 1.38 eV) depending on growth temperature [5-7]. This suggests that the optical band gap of $ZnSnP_2$can be tailored by controlling atomic configuration. Usually the chalcopyrite structured material, such as $ZnSnP_2$, does not show any tetragonal distortion and hence the lattice constants for both the chalcopyrites and cubic sphalerite systems are expected to match perfectly. This opens up the possibility of fabricating a graded multi-junction solar cell using the order chalcopyrite as the top layer, with progressively more disordered layers underneath eliminating the problems of lattice mismatch [7, 8]. However, for achieving the above goal, the relationship between cation ordering and the physical properties of interest need to be studied and fully understood.

The recent Density Functional Theoretical (DFT) studies [8, 9] and contemporary literature survey gave us a strong realization that despite the great interest and potentialities for important technological applications of $ZnSnP_2$ (II-IV-V Chalcopyrite) in electronics industry, the material has not yet been exploited and studied extensively. The thin film data for this compound semiconductor is meager. The material, $ZnSnP_2$ (II-IV-V Chalcopyrite) has been selected for this project proposal because it meets several key criteria for PV devices: (i)The constituents are abundant for broad scale production. (ii) Tailoring of band gap around 1.5 eV is possible by suitably introducing order/disorder layered structure, thereby controlling some other important parameters such as carrier mobility; reverse saturation current etc. (iii) Homo-junction (p-n)could be made with minimizing lattice mismatching. A successful realization of an efficient stable, low cost thin film solar cell fabricated out of inexpensive and abundant materials would be beneficial not only to the PV industries but also to our society as a whole

Some preliminary work (M.Sc. projects)has been done in the Principal Investigator's laboratory at the department of Physics, Presidency University, Kolkata by the M.Sc. students. We have initiated the project for the first time in our country to investigate and assess the quality and properties of $ZnSnP_2$ thin films for their utilization in PV devices.

References:

1. E.Jaffe and A. A. Zunger, Phys. Rev. B27, 5176 (1983).
2. P.Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmannand M. Powalla, Prog. Photovoltaics 19, 894 (2011).
3. L.M.Peter, Philos. Trans. R. Soc. London, Ser.A369, 1840(2011).
4. A.Walsh, S. Chen, S.H. Wei and X.G. Gong, Adv. Energy Mater. 2, 400(2012).
5. P.St-Jean, G.A. Seryogin and S. Francoeur, Appl. Phys. Lett. 96, 231913 (2010)
6. J.L. Shay and J.H. Wemick, Ternary Chalcopyrite Semiconductors (Pergamon, Oxford,1975).
7. M.A.Ryan, M.W. Peterson, D.L. Williamson, J.S. Frey, G.E. Maciel and B.A.Parkinson, J. Mater. Res. 2, 528 (1987).
8. DavidO. Scanlon and Aron Walsh, Appl. Phys. Lett. 100, 251911(2012).
9. S.Sahin, Y.O. Ciftci, K. Colakoglu and N. Korozlu, J. Alloys. Compd. 529, 1(2012).
10. K. Nakatani, T. Minemura, K.Miyauchi, K. Fukabori, H. Nakanishi, M. Sugiyama and Sho Shirakata, Jp. J.Appl. Phys. 47, 5342 (2008).

Objectives :

We propose to synthesize and investigate the structure - property relationship for one of the very important but less-studied $ZnSnP_2$ (II-IV-V Chalcopyrite) semiconductor material with the final aim of designing and implementing an efficient and low-cost single/ multi-junction photovoltaic (PV) thin film device. $ZnSnP_2$, which is a semiconductor compound with chalcopyrite structure, has received a great deal of attention as a potentially interesting PV material which is composed of relatively abundant elements. The objectives in specific heads would be as following:

(a) 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.

(b) Growth of thin films using PVD (Thermal & Cluster Beam) method at elevated temperatures on silicon, quartz and sapphire substrates.

(c) Characterizationof thin films using various analytical methods to evaluate structural (x-raydiffraction, TEM), electrical (resistivity-Hall Effect) and lightabsorption/emission (photoluminescence, optical absorption, reflectance etc) properties$ZnSnP_2$.

(d) N-type& p-type doping of $ZnSnP_2$ thin films and evaluating carrierconcentration and resistivity at elevated temperatures.

(e) Fabricationand optimization of single/multi homo- junction high efficient solar cellsusing doped materials. For multi-junction devices a low resistance (n^+/p^+)tunnel junction to be made to isolate active regions.

(f) Accumulationand evaluation of experimental data for examining the suitability of thematerial/ devices for their commercial applications in PV cells.

(g) Developmentof skilled man power (JRF) in the field photovoltaic research, one of thefrontier areas of research in Physics.

Methodology :

For the successful execution ofthe proposed project and to reach the goal of outlined objective, the followingmethodology has been considered.

(a) Growthof $ZnSnP_2$ bulk materials from the constituent elements (Zn, Sn, P)bySG technique after due consultation of phase diagram. Disorder structure couldbe grown at higher temperatures (>720°C). Bulk n/p type material will beproduced with introducing proper impurities (Al/Cu) during growth. A vacuumsealed quartz ampoule will be used for the above growth processes.

(b) Knowledgeof phase diagram and kinetic barrier energies can be used as guidance for highquality film growth at elevated temperatures using Physicsl Vapour Depositionsystem. PVD is relatively simple, less expensive among the other deposition techniquesand suitable for synthesis $ZnSnP_2$ thin films. By successivelychanging the source materials the different layered structured will beproduced.

(c) Theas-grown bulk/thin films will be characterized/ realized with the help of X-raydiffraction analysis, X-ray photoelectron spectroscopy, Scanning & Transmissionelectron microscopy. These techniques will provide valuable information aboutthe microstructure, composition, crystallinity, grain size and strain producedin the films. UV-Vis spectroscopy will be used for band structure analysis. Onthe other hand, the defect and quality of the films will be studied usingphotoluminescence (PL) spectroscopy. The PL spectroscopy will be used to studythe free-to-bound transitions in $ZnSnP_2$. These results will be thefirst step towards realizing the novel function or optical device as a solarcell using $ZnSnP_2$.

(d) Oncehigh quality materials have been made, our focus will be given for thesynthesis of homo- junction solar cells. The details of its fabrication willdepend on our ability to dope top and bottom layers making both n & p type.If this is possible, p-n junction in a given layer can be a homojunction. Thisis a simple structure for minimizing recombination losses. Double/triplejunctions may be produced using relatively cation disordered phases(sphalerite).

(e) Wewill also focus significantly on synthesis of a *p-i-n*-heterostructure using the inorganic oxide (SnO_2or TiO_2) as n-type, CuSCN as p-type and very thin layer of $ZnSnP_2$as absorber. The main important attributes of such an extremely thinabsorber solar cell are effective charge carrier separation within theabsorber. The influence of $ZnSnP_2$ thickness and porosity of thestructure will be investigated by optical absorption and photocurrent densitymeasurement.

View Year wise plan of work

Year wise Plans

First year

1. Selection and recruitment of the Research Scholar (JRF) as per UGC guide lines.
2. Procurement of the starting chemicals (Zn, Sn, red P) and substrates. Optimization of the existing furnace for the growth of bulk $ZnSnP_2$.
3. Growth of bulk materials from constituents (Zn, Sn, red P)for thin film preparation below 700^0C for chalcopyrite structure. Growth of bulk material above 720^0C for sphalerite structure. XRD characterization of bulk materials and realization.
4. Optimization of the growth parameters (rate of heating, substrate temperature, vapour pressure during growth etc.) for thin film growth.
5. Growth of few thin films of $ZnSnP_2$ on various substrates at different substrate temperatures (Room temperature to 400^0C) using chalcopyrite and sphalerite bulk materials. Microstructural characterization of as-grown $ZnSnP_2$ films using XRD, HRTEM.
6. Observation of the nature of crystallinity and cation disorder in the film.

Second year

1. Determination of the composition of the films by XPS studies. Change of growth parameters if the desire result is not achieved.
2. Thermal annealing of as-deposited $ZnSnP_2$ films.
3. Optical characterization (T & R spectra) and determination of the as-deposited and annealed films.
4. Study of variation of optical band gap and optical absorption spectra with (i) substrate temperature (T_S), (ii) annealing temperature for a fixed T_S and (iii) cation disorder. The later part should be looked more carefully.
5. Photoluminescence (PL) investigation of all the above films (4 K – 300 K). The PL spectroscopy will be used to study the free-to-bound transitions in $ZnSnP_2$. These results will be the first step towards a solar cell using $ZnSnP_2$.
6. Doping of $ZnSnP_2$ films and their electrical characterization. Determination of carrier concentration and resistivity using standard Hall effect set up.

Third year

1. Once high quality material is produced, we will focus to synthesis a homo- junction solar cell using $ZnSnP_2$ for particular structure whose band is around 1.5 eV. The details of its fabrication will depend on our ability to dope top and bottom layers making both n & p type. If this is possible, p-n junction in a given layer can be a homojunction. This is a simple structure for minimizing recombination losses.

2. Making of double/triple junctions cells using relatively cation disordered phases (sphalerite).

3. Synthesis of a *p-i-n*-heterostructure using the inorganic oxide (SnO_2 or TiO_2) as n-type, CuSCN as p-type and very thin layer of $ZnSnP_2$ as absorber. The main important attributes of such an extremely thin absorber solar cell are effective charge carrier separation within the absorber.

4. The influence of $ZnSnP_2$ thickness and porosity of the above structure will be investigated by optical absorption and photocurrent density measurement.

5. Evaluation and finding the suitability of $ZnSnP_2$ thin films as solar cell materials.

Details of Collaboration, if needed :

For the successful execution of the proposed project, we highly need a collaboration with the nearby Institute.

Name & Designation of of the collaborator:

Dr. Satyaban Bhunia,
Reader
Surface Physics Division
Saha Institute of Nuclear Physics (SINP)
1/AF, Bidhannagar, Kolkata 700 064
Email: satyaban.bhunia@saha.ac.in

Photoluminescence studies and solar cell device characterization will be done at SINP, Kolkata.

Financial Assistance

Research Personnel : Project Fellow (Net/Get/Slet/@ Rs: 16000/-p.m + HRA)
Hiring Services : 0
Field Work and Travel : 0
Chemicals and Glassware : 60000
Contigency (including special needs) : 220000
Honorium to retired teacher : 0
Books and Journals : 20000
Equipment if needed : Yes

Please specify name and approx. cost along with the quotation :

Tubular graded zone heating furnace for bulk material synthesis (700 - 900^{0}C).
Approximate Cost: Rs. 80000/=

Total : 380000

Whether the teacher has received support for the research project from the UGC from any other agency? : No

Details of the Project/scheme completed or ongoing with the P.I :

ResearchProject (Completed):

Development of Tetragonal Ge-nanocrystals byIonized Cluster Beam Deposition Technique: A New Light Emitting Materials forFuture Optoelectronic.

Sponsoring Authority: DST, Govt. of India. (D.D. No. SR/S2/CMP-53/2003).Amount:24 Lakh. Duration: 11/10/2006 to 10/10/2009.

ResearchProject (On Going):

Polymer-InorganicHybrid Nanocomposites - Preparation, Characterization and their Potential asNanodielectrics.

Sponsoring Authority: CSIR, NewDelhi. (Sanction no: CSIR-01(2342)/09/EMR-II).

Amount: 13.68 Lakh. Duration: from 01.11.2009 to 31.10.2013. (In collaboration withDepartment of Chemistry).

Institutional and Departmental facilities available for the proposed work :

(1) High Vacuum Chamber for PVD system
(2) Spectro Radiometer: UV-Vis-NIR withDriving Software & Accessories (Analytical Special Devices)
(3) PanAnalytical X'PERT PRO MPD 3060 X-RayDiffraction Unit
(4) FTIR Spectrophotometer (Perkin ElmerMade)
(5) HIOKILCR High Tester (Model: 3532 50)

Other Infrastructural facilities :

(1) Electricity & water
(2) Networking:

we have a campus-wide LAN Connection through twoISPs: NKN (1 Gbps connectivity) and TCL (14 Mbps connectivity). It connects alldepartments including laboratories. The Physics department is covered bywireless routers, accessible in all areas, including offices and laboratories.

(3) Library

Any other information which the investigator may like to give in support of this proposal which may be helpful in evaluating :

During last few years bothPrincipal Investigator and Collaborator at SINP, Kolkata are actively working on the developmentof similar materials like nanocrystalline ZnO, Diamond-Like Carbon film,Zinc/Cadmium Phosphide films and metal oxide-polymer nanocomposite systems. Itis expected that the proposed project will be executed successfully.

DECLARATION

Publication of Dr. Arabinda Nayak during last 5 years

1. S.R. Halder, A. Nayak, T.K. Chini, S.K. Roy, N. Yamamoto and S. Bhunia, Vapor condensation growth and evaluation mechanism of ZnO nanorod flower structures. Phys. Stat. Sol. (a),Vol. 207, 364 (2009). (Impact Factor: 1.316).
2. S.R. Halder, A. Nayak, T.K. Chini and S. Bhunia, Strong temperature and substrate effect on ZnO nanorod flower structures in modified chemical vapor condensation growth. Current Appl. Phy., Vol. 10, 942 (2010). (Impact Factor: 1.821).
3. I. Haldar, A. Kundu, M. Biswas and A. Nayak, Preparation and evaluation of a poly (N-vinylcarbazole) – Fe_3O_4 (PNVC-Fe_3O_4) nanocomposite. Matter.Chem & Phys., Vol. 128, 256 (2011). (Impact Factor: 2.234).
4. I. Haldar, M. Biswas and A. Nayak, Microstructure, dielectric response and electrical properties of polypyrrole modified poly (N-vinylcarbazole) – Fe_3O_4 (PNVC - Fe_3O_4) nanocomposites. Synthetic Metals, Vol. 161, P. 1400 – 1407 (2011). (Impact Factor: 1.829).
5. I. Haldar, M. Biswas and A. Nayak, Preparation and evaluation of microstructure, dielectric and conductivity (ac/dc) characteristics of a polyaniline/ poly N-vinylcarbazole/ Fe_3O_4 nanocomposites. J. Polym. Res., Vol. 19, 9951:1-9 (2012) (Impact Factor: 1.733).
6. I. Haldar, M. Biswas and A. Nayak and S. Sinha Ray, Morphological, dielectric and electrical conductivity characteristics of clay-containing nanohybrids of poly (N-vinylcarbazole) and polypyrrole. J. Nanosci. Nanotech., Vol. 12, 784 (2012). (Impact Factor: 1.563).
7. A. Nayak and S. Bhunia, Microstructure and dielectric functions of Ge nanocrystals embedded between amorphous Al_2O_3 films: study of confinement and disorder. J. Expt. Nanosci., Published on line. doi:10.1080/17458080.2012.669852 (2012). (Impact Factor: 1.004).
8. I. Haldar, M. Biswas and A. Nayak and S. Sinha Ray, Dielectric Properties of Polyaniline-Montmorillonite Clay Hybrids. J. Nanosci. Nanotech., Vol. 13 (1-6), 1824 (2013). (Impact Factor: 1.563).