



**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

Final Report of the Work Done on the Major Research Project

1. Title of the Project **Deposition of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})$ thin films by a novel Spray-CVD method and fabrication of efficient solar cells**
2. Name of the principal investigator **Prof. (Dr.) Pramod Shankarrao Patil**

Address **Office:
Thin Film Materials Laboratory,
Department of Physics, Shivaji
University, Kolhapur-416004,
Maharashtra, India.**

**Residential:
"Ashirwad", 584E/13, Sunita Vihar,
Rajendra Nagar, Kolhapur-416 004,
Maharashtra, India.**
3. Name and address of the institution **Shivaji University, Vidyanagar,
Kolhapur- 416 004. Maharashtra, INDIA.**
4. UGC approval letter No. and date **F. No. – 43-517/2014(SR) Nov 2015**
5. Date of implementation **01.07.2015**
6. Tenure of the project **01.07.2015 to 30.06.2018**
7. Total grant allocated **Rs. 13,46,382/-**
8. Total grant received **Rs. 12,61,244/-**

9. Final expenditure **Rs. 12,27,419/-**
10. Title of the project **Deposition of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})$ thin films by a novel Spray-CVD method and fabrication of efficient solar cells**

11. Objectives of the project

- ✓ Fabrication of an automated spray-CVD method
- ✓ Optimization of preparative parameters, $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio and deposition strategy to obtain high quality CZTSSe precursor films on molybdenum substrates, followed by sulfo-selenization
- ✓ Detailed characterization of these films and determination of desired composition and physic-chemical and opto-electronic properties
- ✓ Deposition of other constituent layers like CdS (buffer layer), i-ZnO and n-ZnO layers, metallic fingers and their optimization
- ✓ Investigations on photovoltaic properties using I.P.C.E., I.M.P.S./I.M.V.S., J-V plots, etc. and estimation of photon conversion efficiency.

12. Whether objectives were achieved: Yes

- ✓ Design and fabrication of Novel Spray-CVD instrument with new design of spray nozzle is completed.
- ✓ We have fabricated the low-cost Syringe pump to control the rate of flow of solution.
- ✓ For the deposition of CZTS thin films, deposition parameters such as reactor zone temperature has been studied and optimized.
- ✓ The role of chalcogen ratio on the band gap by varying chalcogen ratio has been studied and optimized.
- ✓ All prepared thin film samples are characterized by XRD, Raman Spectroscopy, XRF, UV-VIS and PCE performance.
- ✓ The solid-state device is fabricated using following configuration

Glass/Mo/CZTSSe/CdS/i-ZnO/n-ZnO/Al-Ni

- ✓ The highest PCE is found to be 0.4 for the thin film sulfo-selenized at 540 °C having band gap 1.3 eV
- ✓ The low efficiency of 0.4 is due to presence of defect levels, carbon impurities arises from non-aqueous solvent.

13. Achievements from the project

- ✓ A novel deposition method is developed for the synthesis of thin semiconducting films
- ✓ The transparent conducting oxides deposited by Spray CVD instrument, Which shows excellent characteristic towards conductivity and transparency.
- ✓ The researchers and PG students take benefits of these equipment's for annealing synthesized samples in inert gas atmosphere and synthesis of carbon nanostructures.
- ✓ One Ph.D. student and above 5 master student projects are successfully completed in supervision of PI within the project tenure.
- ✓ 6 International papers have been published in peer reviewed journals.
- ✓ 2 papers are submitted to international journals
- ✓ One Indian patent manuscript is under preparation on spray-CVD instrument

14. Summary of the findings

Key findings in this project includes the fabrication of novel Spray-CVD instrument, to control the pattern and zone of ejection of the coating material solution, new design of spray nozzle is fabricated. A microprocessor-controlled syringe pump is manufactured to deliver constant flow of spraying solution.

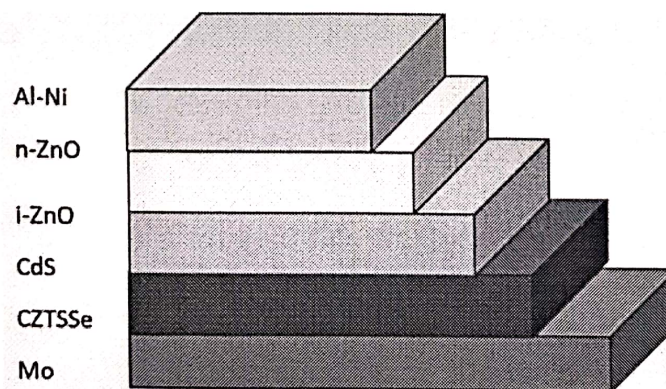
The aim of the present project concerns with the synthesis of CZTS thin films with suitable optical and electrical properties by using simple and low-cost Spray-CVD method for their application in solar cells. Different deposition parameters have been optimized such as the reactor zone temperature. The hot reactor zone temperature is optimized by characterizing the obtained films by XRD, Raman, FE-SEM and UV –Vis

spectroscopy. Effect of hot reactor zone temperature on the properties of CZTS films has been investigated. The XRD patterns of CZTS thin films deposited at different hot reactor zone temperature reveal that the films are polycrystalline and exhibit kesterite crystal structure. It is found that as the hot reactor zone temperature increases, the intensity of (112) plane increases. The formation of CZTS phase is confirmed by Raman analysis. FE- SEM micrographs shows the densely packed grains with increase in grain size with temperature. Band gap energy for CZTS film deposited at 400 °C is found to be 1.4 eV. Here, the bandgap tailoring from 1.7eV to 1.40 eV with the reactor zone temperature for CZTS thin films is observed which can be useful in devising photovoltaic cells. The best PCE performance of 0.10 is obtained for sample CZTS 400.

The influence of different chalcogenides concentration on properties of CZTSSe thin films prepared by Spray CVD has been investigated. The structural, morphological, compositional, optical study and J-V performance are carried out. XRD analysis shows that As the concentration of selenium is increased the peak positions of the (112) plane shifted towards a lower diffraction angle. Phase purity of the films are further confirmed using Raman analysis. FE-SEM micrographs shows, increase in grain size with compact morphology. The bandgap tailoring from 1.47 eV to 1.18 eV with the increase in selenium concentration for CZTSSe thin films is observed. From all the above studies, CZTS_{0.6}Se_{0.4} thin film sulfo-selenized at 520 °C shows higher efficiency i.e. 0.40% than rest of the samples.

The solid-state device was fabricated using following configuration

Glass/Mo/CZTSSe/CdS/i-ZnO/n-ZnO/Al-Ni



15. Contribution to the society

Engaging the public with research helps to empower people, broadens attitudes and ensures that the work of universities and research institutes is relevant to society and wider social concerns. By starting an ongoing discussion between the research community and the public, society can benefit more fully from the outputs of research. The knowledge generated by this project will contribute to the international research effort to develop low-cost solar cells. The broad scope of the research will also help facilitate the transfer of ideas between researchers of India and world. By demonstrating new deposition technique i.e Spray-CVD for the fascinating nanomaterials family of materials should generate considerable interest within both the academic and public spheres.

16. Whether any Ph.D. enrolled Yes

17. No. of publications out of the 6 Published and 2 Submitted
project

List of Publications

1. Sr. no.	Title of the paper	Authors	Name of journal	Volume	Page No	Year
2.	TiO ₂ /PbS/ZnS heterostructure for panchromatic quantum dot sensitized solar cells synthesized by wet chemical route	T.S.Bhat, S.S.Mali, A.D.Sheikh, S.D.Korade, K.K.Pawar, C.K.Hong, J.H.Kim, P.S.Patil	Optical Materials	73	781-792	2017
3.	Structural and electrochemical analysis of chemically synthesized microcubic architected lead selenide thin films	T. S. Bhat, A. V. Shinde, R. S. Devan, A. M. Teli, Y. R. Ma, J. H. Kim, P. S. Patil	Applied Physics A	34	124	2018
4.	ZnS passivated PbSe sensitized TiO ₂ nanorod arrays to suppress photocorrosion in photoelectrochemical solar cells	T.S.Bhat, S.S.Mali, A.D.Sheikh, N.L.Tarwal, S.D.Korade, C.K.Hong, J.H.Kim, P.S.Patil	Materials today Communications	16	186-193	2018
5.	Photoelectrochemical performance of dye and semiconductor sensitization on 1-D hollow hexagonal ZnO rods: A comparative study	S. S. Patil, N L. Tarwal, H. M. Yadav, S. D. Korade, T. S. Bhat, A. M. Teli, M. M. Karanjkar, J. H. Kim, P. S. Patil	Journal of Solid-State Electrochemistry	22	3015–3024	2018
6.	Facile green synthesis of In ₂ O ₃ bricks and its NO ₂ gas sensing properties	K.K. Pawar, V.L. Patil, N. L. Tarwal, N.S. Harale, J. H. Kim, P. S. Patil	Journal of Materials Science: Materials in Electronics	29	14508–14518	2018
7.	Highly reliable multilevel resistive switching in a nanoparticulated In ₂ O ₃ thin-film memristive device	K.K. Pawar, D.V.Desai, S.M. Bodake, H.S. Patil, S.M. More, A.S. Nimbalkar, S.S Mali, C.K. Hong, S. Kim,	Journal of Physics D: Applied Physics	52	175306	2019

		P.S. Patil, T.D. Dongale				
8.	Synthesis and characterization of CZTS thin films by modified spray CVD method: Influence of reactor zone temperature	S. D. Korade, V. C. Karade, M. P. Surywanshi, T. S. Bhat, S. B. Sadale, M. Boshta, J. H. Kim, P. S. Patil	Journal of Materials Science: Materials in Electronics (Submitted)			
9.	The role of chalcogens ratio on photovoltaic performance of spray CVD deposited CZTSSe thin films	S. D. Korade, M. P. Surywanshi, S. B. Sadale, M. Boshta, J. H. Kim, P. S. Patil	Optik, (submitted)			
10.	Deposition of CZTSSe absorber layer by novel spray CVD method.	S. D. Korade, S. B. Sadale, G. R. Shinde and P. S. Patil	Indian patent Under preparation			

(PRINCIPAL INVESTIGATOR)

Professor,
Department of Physics,
Shivaji University,
Kolhapur.

(REGISTRAR)

Registrar
Shivaji University, Kolhapur



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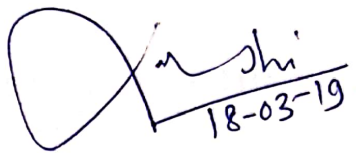
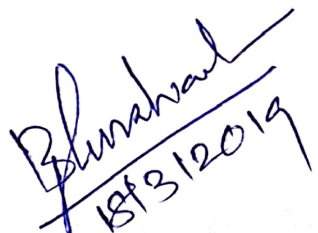
Final Report Assessment / Evaluation Certificate

It is certified that the final report of Major Research Project entitled, "Deposition of $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})$ thin films by a novel Spray-CVD method and fabrication of efficient solar cells" by Prof. Pramod S. Patil, Department of Physics has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee: -

Quality of the work done under the UGC Project is very good and well in depth and has been implemented systematically. special efforts were taken to fabricate indigenous and novel spray-CVD technique. This resulted into good number of publications. It is planned to file patent.

Name & Signatures of Experts with Date: -

	Name of Expert	University/College	Signature
1	Prof. S. S. Suryavanshi	School of Physical Sciences, Solapur University, Solapur.	 18-03-19
2	Prof. B. J. Lokhande	School of Physical Sciences, Solapur University, Solapur.	 18/3/2019

It is certified that the final report has been uploaded on UGC-MRP portal on

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It is also certified that final report, Executive summary of the report, Research documents, monograph academic papers provided under Major Research Project have been posted on the website of the University.


Registrar

 **Registrar**
Shivaji University, Kolhapur