UNIVERSITY GRANTS COMMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI – 110 002

Title of the Project	:	**Development of FTO / N - Implanted TiO_2 Window Layer for Large Area Stacked Cu (In Ga) S_2 / Mo / Glass - Based Thin Film Solar Cells**
Name and Address of the Principal Investigator	:	**Dr. C. Ravi Dhas** **Assistant Professor & Head** **PG & Research Department of Physics** **Bishop Heber College (Autonomous)** **Tiruchirappalli - 620017** **Tamil Nadu, India.**
UGC Approval Letter No. and Date	:	**F.No: 42 – 903 / 2013 (SR)** **Dated: 25.03.2013**
Tenure of the Project	:	**From 01.04.2013 to 31.03.2017**
Total Grant Allocated	:	**Rs. 11,25,800/-**

OBJECTIVES OF THE PROJECT

- Fabrication of p- type $CuInGaS_2$ (CIGS) thin films using magnetron sputtering technique and evaluation of its structural, electrical and optical properties.
- Preparation of TiO_2 thin films and implantation with nitrogen ions for effective transport of radiation and thus to serve as an effective window layer of the proposed device.

- Fabrication of the device structure **FTO/ N-TiO_2 / CIGS /Mo** for tapping solar energy and effective conversion to green energy with ample conversion efficiency.
- Endowing suggestions to researchers for improving the device in near future.

SUMMARY AND FINDINGS

For the accomplishment of the objectives of the project, FTO/N-TiO_2/$CuInGaS_2$ (CIGS)/Mo – based thin solar cell was successfully fabricated. Each layer has been deposited and characterized using X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectrometer, energy dispersive X-ray spectroscopy, Raman spectroscopy, photoluminescence and optical studies. Finally, the FTO/N-TiO_2/CIGS/Mo solar cell device was fabricated and the photocurrent conversion efficiency was estimated.

Initially, CIGS thin films has been successfully deposited by DC reactive magnetron sputtering at different sputtering powers by employing CIG ternary alloy target and H_2S gas. From the experimental results, CIGS thin film deposited at 90 W showed tetragonal structure with better crystallinity and larger grain formation as evidenced by both XRD and SEM. This film has high optical absorbance in the visible region with the optical band gap of 1.3 eV, suitable for tapping energy from the solar spectrum. Two different conduction mechanisms were observed in the low and high temperature region from Arrhenius plots.

Optimization of preparative parameters (molarity and substrate temperature) for the deposition of TiO_2 films using nebulizer spray pyrolysis is discussed in detail. Titanium tetrachloride was chosen as precursor and a mixture of water and ethanol was used as solvent. XRD pattern revealed the presence of anatase phase TiO_2 with tetragonal structure. Substrate temperature of 350 °C and 0.5 M was found to be the optimized deposition conditions for the preparation of high quality TiO_2 films.

Nitrogen ion implantation on deposited TiO_2 films were carried out at room temperature for different ion fluences such as 1 x 10^{15} and 1 x 10^{16} ions/cm^2. The structural and optical properties of ion implanted films were studied. The XRD patterns revealed the transformation of crystalline to amorphous nature on nitrogen ion implantation into TiO_2 lattice. Scanning electron microscope observation revealed that the TiO_2 thin film implanted to a fluence of 1 x 10^{16} ions/cm^2 exhibited uniform and densely packed agglomerated particles. EDS results confirm the presence of nitrogen in N-ion implanted TiO_2 thin films. The band gap values estimated from the optical measurements are found to be shifted from 3.2 to 2.9 eV which shows that the band gap can be tailored upon nitrogen incorporation. From the photoluminescence emission spectra, it was observed that the increase in nitrogen dosage decreases the band-to-band recombination and creates a greater number of oxygen defects in TiO_2 lattice which is responsible for the reduction of optical band gap. The optical studies revealed the obtained films could be more suitable for optoelectronic device applications.

Finally, the device fabrication was carried out by adopting the following procedure: TiO_2 thin film was deposited over the FTO substrate at

350 °C by nebulizer spray technique. Nitrogen ion was incorporated for 60 keV (1 x 10^{16} ions/cm^2) into the optimized TiO_2 thin film by ion implantation technique. CIGS thin films were prepared by DC magnetron reactive sputtering for different sputtering powers (70, 90 and 110 W) onto a FTO/N-TiO_2 films. Thin molybdenum and aluminium layers were coated using DC sputtering that serve as electrical contacts. At last, the fabricated solar cells were tested using the Solar Simulator under AM 1.5 condition and 100 mW/cm^2 illumination. The fabricated FTO/ N-TiO_2 / CIGS /Mo solar cell device yielded maximum power conversion efficiency (η) of 0.13 % and short circuit current density of (J_{sc}) 2.26 mA/cm^2.

ESTABLISHED ATTAINMENTS

- Successful fabrication of single phase $CuInGaS_2$ (CIGS) thin films by DC reactive magnetron sputtering at different sputtering powers by employing CIG ternary alloy target and H_2S gas at room temperature.
- Introduction of a new cost-effective nebulizer spray pyrolysis technique for the formation of Nanocrystalline anatase TiO_2 thin films with interconnected nano-wire like morphology for different molarities and substrate temperatures.
- Dissemination of new technique for modifying the properties of the optimized TiO_2 thin films by Nitrogen ion implantation. Spherical morphology with better luminescence behavior was observed in films implanted with nitrogen ions to a fluence of 1 x 10^{16} ions/cm^2.

- Conquering fabrication of layer structured FTO/ N-TiO_2 /CIGS /Mo solar cell device with photocurrent conversion efficiency (η) of 0.13% and short circuit current density (J_{sc}) of 2.26 mA/cm^2.

CONTRIBUTIONS TO THE SOCIETY

- Among the available solar photovoltaic technology with costly silicon wafers panels, fabricated cost-effective $CuInGaS_2$ (CIGS) thin films can be used widely in heterojunction solar cell devices as an absorber layer.
- Our recently established finding of using $CuInGaS_2$ as a counter electrode in dye-sensitized solar cells by replacing platinum electrodes can be utilized for photon to current conversion efficiency (η) of 4.32 %.
- Replacement of highly toxic CdS layer with eco-friendly N-TiO_2 thin film in the established device is a boon to environment protection.
- Evidenced high luminescence emmision in N-TiO_2 thin films suggest the use of the layer in fabrication of photo-diode and photosensor applications.
- Established FTO/ N-TiO_2 /CIGS /Mo solar cell device has moderate efficiency, however beneficial to mankind.

FUTURE PROSPECTS

- Conversion efficiency of the CIGS based solar cell devices can be further enhanced by annealing in N_2 atmosphere.
- Optimization and inclusion of appropriate narrow band gap buffer layer between CIGS and N-TiO_2 layers to improve passivation of defects and thereby efficiency can be improved.
- Application of CIGS p-type absorber layer in photodiodes and photoconductors needs further investigations.

CONTRIBUTED PUBLICATIONS TO THE SCIENCE COMMUNITY

1. **C. Ravi Dhas,** A. Jennifer Christy, R. Venkatesh, D. David Kirubakaran, R. Sivakumar, K. Ravichandran, A. Moses Ezhil Raj, C. Sanjeeviraja, "*Effect of sputtering power on properties and photovoltaic performance of CIGS thin film solar cells*"
   Materials Research Innovations, 21, 2017, 286-293.

   Impact Factor: 0.830
2. **C. Ravidhas,** B. Anitha, A. Moses Ezhil Raj, K. Ravichandran, T.C. Sabari Girisun, K. Mahalakshmi, K. Saravanakumar, C. Sanjeeviraja, *"Effect of nitrogen doped titanium dioxide (N-TiO_2) thin films by jet nebulizer spray technique suitable for photoconductive study"*
   Journal of Materials Science: Materials in Electronics, 26, 2015, 3573-3582.

   Impact Factor: 2.019
3. **C. Ravi Dhas**, A. Jennifer Christy, R.Venkatesh, K.S. Anuratha, K.Ravichandran, A. Moses Ezhil Raj, B. Subramanian, Subhendu K. Panda "*Nebulizer spray deposited $CuInGaS_2$ thin films, a viable candidate for counter electrode in dye-sensitized solar cells"*
   Solar Energy, 157, 2017, 58 – 70.

   Impact Factor: 4.018

4. **C. Ravi Dhas**, A. Jennifer Christy, R.Venkatesh, Subhendu K. Panda, B. Subramanian, K.Ravichandran, P. Sudhagar, A. Moses Ezhil Raj *"Solvent volume dependent physical properties and electrocatalytic ability of nebulizer spray deposited $CuInGaS_2$ counter electrode for dye – sensitized solar cells"*
   Thin Solid Films, 653, 2018, 73-81.

   Impact Factor: 1.879

5. **C. Ravi Dhas,** A. Jennifer Christy, R.Venkatesh, Subhendu K. Panda, B. Subramanian, K.Ravichandran, P. Sudhagar, A. Moses Ezhil Raj "*Solvent volume-driven $CuInAlS_2$ nanoflake counter electrode for effective electrocatalytic tri-iodide reduction in dye-sensitized solar cells*"
   Journal of Solid State Electrochemistry, 22, 2018, 2485-2497.

   Impact Factor: 2.316

6. **C. Ravi Dhas**, A. Jennifer Christy, R.Venkatesh, Esther Santhoshi Monica. S,Subhendu K. Panda, B. Subramanian, K.Ravichandran, P. Sudhagar, A. Moses Ezhil Raj *"Low – cost and eco – friendly nebulizer spray coated $CuInAlS_2$ counter electrode for dye sensitized solar cells"*
   Physica B: Condensed Matter, 537, 2018, 23-32.

   Impact Factor: 1.386

7. **C. Ravi Dhas**, A. Jennifer Christy, R.Venkatesh, Esther Santhoshi Monica. S, Subhendu K. Panda, B. Subramanian, K.Ravichandran, P. Sudhagar, A. Moses Ezhil Raj *"Facile preparation of hierarchical nanostructured $CuInS_2$ counter electrodes for dye-sensitized solar cells*"
   Materials Research Express, 4, 2017, 12500

   Impact Factor: 1.068

8. **C. Ravi Dhas**, A. Jennifer Christy, R. Venkatesh, B. Anitha, A. Juliat Josephine, D. David Kirubakaran, D. Arivukarasan, P. Sudhagar, A. Moses Ezhil Raj and C. Sanjeeviraja "*$CuInS_2$ Layer Deposition Through Nebulizer Spray Technique for Solar Cell Fabrication*"
   Recent Trends in Materials Science and Applications, Springer Proceedings in Physics, 189, 2017, 451 – 464.
   ISBN: 978-3-319-44889-3

9. B. Anitha, **C. Ravidhas,** R. Venkatesh, A. Moses Ezhil Raj, K. Ravichandran, B. Subramanian, C. Sanjeeviraja *"Self assembled sulfur induced interconnected nanostructure TiO_2 electrode for visible light photoresponse and photocatalytic application"*
   Physica E, 91, 2017, 148–160.

   Impact Factor: 2.221

10. **C. Ravidhas**, B. Anitha, R. Venkatesh, S. Esther Santhoshi Monica, D. Gopalakrishna, A. Moses Ezhil Raj, K. Ravichandran *"Role of fluorine doping on luminescence centers and enhanced photocatalytic performance of nebulizer sprayed TiO_2 films under visible light"*
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    Impact Factor: 2.686

11. **C.Ravidhas**, B.Anitha, D.Arivukarasan, R.Venkatesh, A.Jennifer Christy, K.Jothivenkatachalam, A.Nithya, A.Moses Ezhil Raj, K. Ravichandran, C. Sanjeeviraja *"Tunable morphology with selective faceted growth of visible light active TiO_2 thin films by facile hydrothermal method: Structural, optical and photocatalytic properties"*
    Journal of Materials Science: Materials in Electronics, 27, 2016, 5020-5032.

    Impact Factor: 2.019