DYE SENSITIZED SOLAR CELLS BASED ON POROUS (NANO) MATERIALS

The present work on the “Dye sensitized solar cells based on porous (nano) materials” was carried out in Thiagarajar College, Teppakulam, Madurai, affiliated to Madurai Kamaraj University, Madurai, India, during the period 2013-2020 towards the doctoral degree in Physics. The thesis is broadly divided into six chapters. The salient features of each chapter are given briefly below. The author has published some of these investigations in various international journals and conferences (Appendix I).

CHAPTER – I

Introduction

In this chapter a brief account of renewable energy sources, particularly solar energy for the development of a globally sustainable society. There is an immediate and urgent need for high efficiency solar cells which are cost effective per unit area to meet the scarcity of power and an alternate source of energy. Here, a brief introduction about the operational principle of Dye Sensitized Solar Cell (DSSC), advantages of DSSC over PN junction solar cells and the measurement to be done for characterization of DSSC. Also Porous materials and their usefulness and applications are discussed then a brief review of porous silicon (PSi) is also given. A brief account of usefulness and technologically importance of synthetic dye, so given as these are mainly useful for optoelectronic device fabrication particularly for solar cell applications. The background and the motivation of the thesis are also discussed at the end of this chapter.

In the present scenario works are going on in this area for the past two decades. But after the advent of nano materials, this has taken a new turn. The efficiency depends on the amount of solar radiation falls on the surface area of the material and if this surface is made larger, then the solar voltage will be enhanced much [1]. In this context, the physics of nano materials comes as handy, as the surface to volume ratio of the nano materials is very large, and then much of advantage can be tapped from these materials. Hence, here it is proposed to construct high efficiency solar cells from porous and nano materials.

The crystalline silicon is an important and dominant material over several years due to its well-known properties and established infrastructure for photovoltaic manufacturing. It is the basic material for the production of solar cell and about 90% of fabricated solar modules are made of crystalline silicon. The solar cells prepared by using bulk and porous silicon had shown an efficiency range of 8 to 18% which is very low. However, high efficiencies on silicon have been achieved on monocrystalline (bulk) cells using expensive, high-quality silicon wafers. And these bulk crystalline silicon devices are approaching the theoretical limiting efficiency of 29% [2]. Many works are available on gold and silver coated porous silicon. But the solar cells prepared by these techniques have limited efficiency.

In solar cells normally the silicon acts as both the source of photoelectrons, as well as providing the electric field to separate the charges and create a current. The key parameters that determine the efficiency of light harvesting is large surface area of the materials used. Here porous semiconductors will be used to design solar cells as these porous semiconductors have larger surface compared to bulk materials. Now a day much attention is being paid to dye sensitized solar cell (DSSC) due to its advantage over conventional solar cells such as low cost, simple fabrication process, high energy conversion efficiency and large scale production.

One of the main requirements of the photoanode in solar cells is to harvest more amount of light and hence it will be more appropriate to use materials with high porosity. Using porous silicon [3] in solar cells with its textured nature of surface can traps light and reduces the reflectance losses, tune of band gap for optimum sunlight absorption, and conversion into direct band gap semiconductor with large quantum efficiency [4].

Hence, here attempts were be made to fabricate solar cells using dye sensitized porous semiconductors. This has an enhanced efficiency due to more capture of radiation because of increased surface area and activation of increased electron conversion because of dye. In the bulk dye-sensitized solar cell, the photoelectrons are provided from a separate photosensitive dye. The porous semiconductors (like silicon, ZnSe, GaAs and CdS) due to variation in bandgap and size of the particle could be used along with dyes to artificially list the electron conversion to enhance the efficiency. The typical dye sensitizers such as Chloroaluminum Phthalocyanine (ClAlPc), Blackdye- N719 (N7) and Eosin-Y (Ey) will be used here.

Motivation and the reason for choosing Porous Silicon substrate, Nano filler (ZnSe, GaAs and CdS) and dye sensitizers Such as ClAlPc, N7 and EY for investigations are discussed in this chapter.

CHAPTER – II

Synthesis, Characterization and Optimization of Porous silicon (PS) substrate for DSSCs

The discovery of strong visible photoluminescence (PL) at room temperature from electrochemically etched porous silicon has resulted in a great deal of attention because of the potential applications in Si-based optoelectronics.

This chapter deals with preparation and optimization of porous silicon substrate for DSSC fabrication. Porous silicon (PS), a nanostructured material has the advantages such as broaden band gap, wide absorption spectrum and high optical transmission range from 700 - 1000 nm [5]. The pores present allow the penetration of chemical and biological substances, liquids, cells, molecules to change the optical behavior of the original system. Hence PS has been given considerable attention for solar cell and sensor applications [6]. Samples used in this study are boron doped crystalline silicon (c-Si) wafers (thickness 517 μm and resistivity 0.2- 0.5 Ω cm) grown by Czochralski (CZ) method in (100). The porous samples were prepared by electrochemical anodic dissolution of doped silicon (p-Si) in 48% hydrofluoric acid, H_2O and ethanol with platinum electrode as cathode. The electrolyte was prepared by mixing HF (48%), H_2O and ethanol in 1:1:2 ratios. The porous layers on the surface of these samples (p- type c-Si) were prepared at a current density of 30 mA/cm^2 for etching periods of 10, 20, 40 and 60 minutes.

The particle size of the porous silicon (PS) was calculated by XRD measurement using Scherrer's approximation and the sizes are in the range of 12 to 61 nm. The peak intensity of the sample increases with etching time. Porosities of the PS were calculated by measuring mass loss and are in the range of 52 – 78 %. Then the samples were optimized to find the maximum absorption with respect to current density and etching time using PL and UV-DRS techniques. PL spectra of PS showed blue shift in band gap than that of the bulk silicon (1.1eV). The band gap of PS is slightly blue shifted with increase in etching time. Then samples were sensitized with typical dye sensitizers such as Chloroaluminum Phthalocyanine. Again the above said characterizations were done on these samples. The dependence of absorption and emission intensities on these samples indicate that ClAlPc/PS prepared at current density of 30mA/cm^2 for etching time of 60 min indicate that it is good absorber of radiations and can be used for solar cell application. The prepared ClAlPc/PS photoanodes with different porosities were used to fabricate DSSCs with platinum as counter electrode and iodide as liquid electrolyte. I-V characterization was done using Keithely source meter under illumination of 80 mW cm^{-2}. The maximum conversion efficiency of 2.84% was obtained for the DSSC based on ClAlPc/PS.

CHAPTER – III

Synthesis, Characterization and Optimization of ZnSe/PS substrate for DSSCs

This chapter is dedicated to preparation and optimization of porous silicon with Zinc Selenide (ZnSe) nanofillers substrate for DSSC fabrication.

ZnSe is one of the group II-VI semiconductors and it has a direct band gap of 2.7 eV. This makes it suitable for a variety of optoelectronic applications in the wavelength range 0.38-0.55μm including light emitting diodes (LEDS), ultraviolet (UV) detectors and lasers. Its large band gap makes it suitable for use as a window layer of solar cells [7]. ZnSe is used as a material for production of optical elements (windows, lenses, prisms) for infrared (IR) range including passive laser optic elements. It also has a superior optical transmission in the wavelength range of 0.5-2.0 μm. There are several advantages associated with ZnSe heterojunction based devices over silicon (Si) homojunctions or Aluminium Gallium Arsenide (AlGaAs) heterojunction based devices. The first advantage is that above the band gap (>2.7eV), high energy photons are absorbed by the ZnSe n-type layer before they can reach and damage the pn junction. The second is that the junction can be placed deeper within the device away from lifetime killing surface states thus increasing efficiency, because large band gap ZnSe layer is transparent to most of the sun's light spectrum. This reduces the series resistance of the window [8].

The porous layers on the surface of these samples (p-type c-Si) were prepared at a current density of 30 mA/cm^2 for etching periods of 10, 20, 40 and 60 minutes. The ZnSe was coated on the PS by using doctor blade techniques. The structural characterization of ZnSe/porous silicon (PS) was done by XRD and SEM measurement. From the XRD pattern, the characteristic peaks at 26.872° (0 0 2), 29.156° (2 2 2) and 32.367° (1 0 1) confirms the formation of ZnSe (JCPDF Card No: 89-2940) and the intensity of the peak corresponding to the plane (0 0 2) decreases with increase in etching time. The particle sizes were calculated using Scherrer's approximation and are in the range of 10 to 50 nm. The morphological variation of the sample were analysed using SEM. The bandgap of the sample and optimization for maximum absorption and minimum in accordance with variation of current density and etching time were done using PL and UV technique. UV-Vis absorbance spectra of sample has two peaks located in the range of 220-240 nm and 350 - 370 nm, with absorbance 20- 50 and 15 - 45 respectively (in arbitrary unit). The absorbance value for ClAlPc/ZnSe/PS was higher than that of as prepared ClAlPc/PS, due to the presence of nanofillers. From the PL spectra of ClAlPc/ZnSe/PS, it is clearly noted that the blue shift in bandgap occurs compared to the ZnSe/PS. In all the samples, the band gap of PS is slightly blue shifted with increase in etching time. From this observation it is understood that the bandgap of the material can be tuned by adding appropriate nanofillers and varying the etching time during anodization process. The prepared ClAlPc/ZnSe/PS photoanodes with different porosities were used to fabricate DSSCs with platinum as counter electrode and iodide as liquid electrolyte. I-V characterization was done using Keithely source meter under illumination of 80 mW cm^{-2}. The maximum conversion efficiency of 4.61% was obtained for the DSSC based on ClAlPc/ZnSe/PS.

CHAPTER – IV

Synthesis, Characterization and Optimization of GaAs/PS substrate for DSSCs

The chapter, presents the preparation and optimization of porous silicon with Gallium Arsenide (GaAs) nanofillers substrate for DSSC fabrication. Direct band gap materials prove that the use of an optimum configuration leads to a highly functional single- or multiple junction solar cells. The interest in GaAs solar cells has become more popular in the recent years due to its band gap (1.42 eV) close to the standard spectrum and also the GaAs solar cell has greater electron saturation velocity and higher electron mobility compared with silicon solar cells [9]. In this chapter, preparation of DSSC with PS substrate with GaAs nanofillers is presented. Then GaAs/PS samples were sensitized with typical dye sensitizers such as Chloroaluminum Phthalocyanine.

The structure of the prepared samples were analyzed by XRD techniques and the crystalline size of the particles are calculated using Debye Scherrer's approximation. The characteristic peaks at 27.58° (1 1 2) and 53.98° (2 2 2) confirms the formation of GaAs and the intensity of the peak corresponding to the plane (1 1 2) decreases with increase in etching time. And also the characteristic peaks at 45.58° (2 2 0) and 73.09° (3 3 1) confirms the absorption of ClAlPc dye on the surface. The characteristic peak at 66.28° (4 0 0) depict porous nature of the silicon (80-0018). The optical properties of the samples were studied using PL and UV-Vis measurements. The DSSCs were fabricated using the ClAlPc/GaAs/PS photoanode with different porosities with platinum as counter electrode and iodide as liquid electrolyte. The DSSCs fabricated using ClAlPc/GaAs/PS prepared at current density of 30mA/cm^2 with etching time of 60 min shown maximum conversion efficiency of 3.39%.

CHAPTER – V

Synthesis, Characterization and Optimization of CdS/PS substrate for DSSCs

It deals with the preparation and optimization of porous silicon with Cadmium Sulphide (CdS) nanofillers substrate for DSSC fabrication. The efficiency of a cell also depends upon the anchoring of the dye on the mesoporous semiconductor. CdS (2.42eV) is a wide band gap semiconductors from II-VI group which may be an attractive candidate for application in solar cell due to its high absorption co-efficient and considerable energy conversion efficiency [10].

The CdS colloidal solution was prepared by mixing CdS powder with acetic acid and hydrochloric acid. The prepared CdS/PS substrate was sensitized with Chloroaluminum phthalocyanine dye. Characterization XRD reveals the formation of porous nature of silicon and represented by the peak 69.29° (4 0 0). The characteristic peaks at 26.58°(0 0 2), 43.86° (1 1 0) and 51.88° (1 1 2) confirms the formation of CdS nanofillers and the intensity of the peak corresponding to the plane decreases with increase in etching time. The reflection peaks are indexed to hexagonal CdS with lattice constants of α = 4.141 Å and c = 6.718 Å, which are in good agreement with the literature (JCPDS card no. 41-1049). The bandgap of the samples were calculated using PL technique. There is an occurrence of red shift from as prepared PS sample and the PL emission intensity decreases with increases in etching time due to the presence of nanofillers into the sample. The nanofillers was incorporated into the porous structure, which can absorb more amount of light which falls on its surface. As the bandgap range of 1.69 to 1.82 eV is required for preparation of solar cells, the sample ClAlPc/CdS/PS prepared at current density of $30mA/cm^2$ with etching time of 60 min can be used to fabricate DSSCs. I-V characterization was done using Keithely source meter under illumination of 80 mW cm^{-2}. The maximum conversion efficiency of the DSSC prepared using ClAlPc/CdS/PS photoanode with platinum as counter electrode and iodide as liquid electrolyte has shown conversion efficiency of 5.82%.

CHAPTER – VI

Comparative study on the efficiency of DSSCs based on various substrates and dye sensitizers

The comparative study of the efficiency of the DSSC prepared by various photoanodes like PS, ZnSe, GaAs and CdS and the photoanodes sensitized with various dyes such as ClAlPc, Blackdye and Eosin-Y are given.

Nanostructured porous silicon (PS) sample were prepared at a current density of 30 mA/cm^2 for etching period 60 minute. Cadmium sulfide (CdS), Gallium Arsenide (GaAs) and Zinc Selenide (ZnSe) nanomaterials are used as nanofillerson PS samples. Then the photoanodes were prepared by sensitizing the surfaces of these nanofillers/PS samples with various dyes such as chloroaluminium phthalocyanine (ClAlPc), N7 and Eosin – Y (EY). The bandgap of the samples were calculated from Photoluminescence (PL) measurements and are in the range of 1.9 - 2.0 eV. The photocurrent and photovoltage of the cells were measured using Keithely source meter. The maximum conversion efficiency of 5.82% observed for ClAlPc/CdS/PS based DSSC.

CHAPTER – VII

Summary

The seventh chapter summarizes all the results obtained in our work. It includes the discussion of structural and optical properties of prepared substrates like PS, ZnSe/PS, GaAs/PS and CdS/PS and optimization of these substrate with ClAlPc dye sensitizer for the fabrication of DSSCs. The comparative study on the DSSCs using various dye sensitizer such as ClAlPc, N7 and EY are discussed. The efficiency of the fabricated DSSCs are calculated and are discussed.

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Appendix – I

Publications in International Journals

1. K. Gangadevi, K. Ramachandran, R. Srinivasan, " Optical studies on ClAlPc (dye) decorated porous silicon for solar cell application" International Journal of Scientific & Engineering Research, 5(3), 178-180, 2014.
2. K. Gangadevi, K. Ramachandran, and R. Srinivasan, "Dye Sensitized Solar cell based on porous silicon and ClAlPc dye" AIP Conference Proceedings. 1665, 060028 (1-3), 2015.
3. K. Gangadevi, K. Ramachandran, and R. Srinivasan, "Preparation and characterization of porous silicon photoelectrode for dye sensitized solar cells" Nanosystems: Physics, Chemistry, Mathematics, 7 (4), 629–632, 2016.
4. K. Gangadevi, and R. Srinivasan, "Effect of etching time of PS on the efficiency of ClAlPc/PS DSSC", IJCSET, 3(1), 23-26, 2017.
5. S. Manickam Christopher, K. Gangadevi, K. Ramachandran, and R. Srinivasan, "A study on the effect of silver nanofillers in porous silicon" AIP Conference Proceedings 1591, 1455-1457, 2014.

Papers presented in National/ International conferences

1. Dye sensitized solar cell based on porous silicon and ClAlPc dye, **K. Gangadevi**, R. Srinivasan and K.Ramachandren 59th DAE Solid State Physics Symposium during Dec. 16-20, 2014 at VIT University, Vellore, Tamilnadu.
2. Optical studies on the effect of ClAlPc(dye) in porous silicon for Solar cell application, **K. Gangadevi** , R. Srinivasan and K.Ramachandren, International Conference on Recent advances in Physics for interdisciplinary developments on 23, 24 Jan, 2014.
3. Synthesis and Characterization of ClAlPc Sensitized Nanostructured Porous Silicon for DSSC, **K. Gangadevi**, R. Srinivasan and K. Ramachandren International Conference on Nano Science & Engineering Application 2014, 26th - 28th June,2014 at Jawaharlal Nehru Technological University Hyderabad.
4. Studies on Optical and Electrical properties of ClAlPc sensitized nanostructured porous silicon for DSSC, **K. Gangadevi** , R. Srinivasan and K. Ramachandren, 5^{th} International Conference on Perspectives in Vibrational Spectroscopy during 8-12^{th} July 2014, Centre for Molecular and Biophysics Research, Department of Physics, Mar Ivanios College, Thiruvananthapuram, Kerala.
5. Synthesis, optical and electrical properties of Beta - Carotene dye sensitized TiO_2 solar cell, K.Renukadevi, **K. Gangadevi**, R. Srinivasan and K. Ramachandren International Conference on Perspectives in Vibrational Spectroscopy during 8-12^{th} July 2014, Centre for Molecular and Biophysics Research, Department of Physics, Mar Ivanios College, Thiruvananthapuram, Kerala.
6. Studies on optical and photovoltaic properties of ClAlPc on porous silicon DSSC, **K. Gangadevi**, and R. Srinivasan National Seminar on Recent Trends in Crystal Growth and Nano Materials (NSCGNM2014), 7^{th} -9^{th} August 2014, Department of Physics, National College(Autonomous), Tiruchirappalli.
7. Preparation And Characterization Of Porous Silicon Photoelectrode For Dye Sensitized Solar Cells, **K. Gangadevi**, and R. Srinivasan International Conference on Nanomaterials And Nanotechnology (Nano -15), K.S. Rangasamy College of Technology, Tiruchengode, Tamilnadu.

8. Effect of etching time of PS on the efficiency of ClAlPc/PS DSSC, **K. Gangadevi**, and R. Srinivasan, International Seminar on Nanoscience and Technology, (ISNST-2016), Mother Teresa Women's University, Kodaikanal, September 20, 2016.
9. Study of ClAlPc/CdS dye sensitized solar cells, **K. Gangadevi**, and R. Srinivasan, 1st International Conference on Nanoscience and Nanotechnology, (ICNAN'16), VIT University, Vellore, October 19-21, 2016.
10. Effect of dye sensitizer on Nanostructured CdS/PS Based DSSCs, **K. Gangadevi**, and R. Srinivasan, International Conference on Functional Materials (ICFM), Thiagarajar College, Madurai, 7-8, September 2017.
11. The study on effect of dye sensitizer on nanostructured ZnSe/PS based DSSCs, **K. Gangadevi**, and R. Srinivasan International conference on Advanced Functional Materials for Energy, Environment and Biomedical Applications (AFMEEB - 2017) at Madurai Kamaraj University, Madurai December 11 - 12, 2017.
12. The study on effect of dye sensitizer on nanostructured GaAs/PS based DSSCs, **K. Gangadevi** , and R. Srinivasan, MRSI National Symposium on Advances in Functional and Exotic Materials at SRM Hotel and the Symposium is jointly organized by MRSI Trichy Chapter and the Centre for High Pressure Research, Bharathidasan University, Tiruchirappalli, 14 -16th February 2018.
13. A study on effect of etching time on the efficiency of ZnSe/PS based DSSCs, **K. Gangadevi**, and R. Srinivasan, National Conference on Recent Advanced Materials (NCRAM -2018), Thiruvalluvar University College of Arts & Science (TVUCAS) Campus, Thennangur, 23-24, Februrary 2018.
14. A study on effect of etching time on the efficiency of CdS/PS based DSSCs, **K. Gangadevi**, and R. Srinivasan, International conference on Momentous role of Nanomaterials in Renewable Energy Devices (ICMNRE-2018), Alagappa University, Karaikudi, 1-2, March 2018.
15. The study on effect of porosity on the efficiency of nanostructured N7/GaAs/PS based DSSCs, **K. Gangadevi**, B. Booma and R. Srinivasan International

conference on Momentous role of Nanomaterials in Renewable Energy Devices (ICMNRE-2018), Alagappa University, Karaikudi, 1-2, March 2018.

16. A study on effect of porosity on the efficiency of nanostructured EY/GaAs/PS based DSSCs, **K.Gangadevi** , and R. Srinivasan, Proceedings of the International Conference on Advanced Nanomaterials for Energy, Environment and Healthcare applications 2018 (ANEH-2018), at KSR College of Arts & Science for Women , Thiruchengode on 31st August & 1st September 2018.
17. Comparative Study on the efficiency of Dye sensitized solar cells based on various natural dyes, K.Renukadevi, **K.Gangadevi**, and R. Srinivasan Proceedings of the International Conference on Advanced Nanomaterials for Energy, Environment and Healthcare applications 2018 (ANEH-2018), at KSR College of Arts & Science for Women , Thiruchengode on 31st August & 1st September 2018.
18. The Study on Effect of porosity on efficiency of nanostructured EY/GaAs/PS based DSSCs, **K. Gangadevi,** B.Booma, and R. Srinivasan International Conference on Exploring Nanostructures for Enhanced Power Conversion Efficiency of Solar Cells (ICENES'19), at The Gandhigram rural University, Gandhigram on 7-8, January, 2019.
19. Optimization of ZnSe/Porous silicon photoanode using Eosin-Y dye sensitizer for DSSC fabrication, **K. Gangadevi** , and R. Srinivasan 64th DAE Solid State Physics Symposium at Indian Institute of Technolgy, Jodhpur, Rajasthan, Dec. 18-22, 2019.
20. A study on effect of dye sensitizers on the efficiency of ZnSe/PS based DSSCs, **K. Gangadevi** , and R. Srinivasan One day International Conference on Recent Advanced Materials (ICRAM - 2020), on Tiruvalluvar University College Arts & Science , Thennangur, Vandavasi.
21. A comparative study on efficiency of Rhodamine/ PS based DSSCs prepared, A. Sowmiya, **K. Gangadevi** , and R. Srinivasan One day International Conference on Recent Advanced Materials (ICRAM - 2020), on Tiruvalluvar University College Arts & Science , Thennangur, Vandavasi.

Seminars/Workshops Attended

1. UGC sponsored National Seminar on Current Trends in Crystal growth and Solar Energy, Sri Meenakshi Government College for Women, Madurai, 22nd January 2013.

2. Silver Jubilee Celebration- International Conference on Advanced Materials, Processing and Devices (AMPD – 2013), School of Chemistry, Madurai Kamaraj University, 15 – 16 July, 2013.

3. UGC – SAP, DST- FIST and DST PURSE sponsored International workshop on advanced materials, Alagappa University, Karaikudi, March 20 -21, 2014.

4. Seminar on Advanced Technologies and Innovations in Energy and Environment (ENERGY FEST'14), School of Energy, Madurai Kamaraj University, 28th March, 2014.

5. INUP Hands on training workshop on Nanofabrication Technologies**,** Centre for Nanoscience and Engineering, Indian Institute of Science and Technology, Bangalore, August 19 – 28, 2014.

6. UGC sponsored National Seminar on Nanomaterials: Synthesis, Characterization and Applications, G. Venkataswamy Naidu College, Kovilpatti, 6 – 7 August, 2015.

7. One day National Seminar on Recent Trends in Energy Technologies, The American College, Madurai, 14th August 2015.