ADSORPTION OF LEAD ANTIMONY SULPHIDE QUANTUM DOTS ON THE ZnO NANOSTRUCTURED PHOTOELECTRODE, FOR SOLAR CELL APPLICATIONS.

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ABSTRACT: *In our work, lead antimony sulphide ($Pb_5Sb_8S_{17}$) quantum dots are successfully adsorbed on the ZnO photoelectrode by successive ionic-layer adsorption and reaction (SILAR) method. Post annealing converts the PbS and Sb_2S_3 into $Pb_5Sb_8S_{17}$.Absoption increases with increasing SILAR cycles up to four cycles and further decreases in the near infrared (NIR) region. It has lowest band gap value (1.6eV) at fourth SILAR cycle that is very close to the optimum band gap of solar spectrum. $Pb_5Sb_8S_{17}$ quantum dots are characterized by X-ray diffraction (XRD), UV–visible absorption and energy-dispersive x-ray spectroscopy (EDX). We use titanium tetrachloride ($TiCl_4$) pre-treatment for avoiding recombination possibilities and direct contact between electrolyte and fluoride doped tin oxide (FTO) glass, to improve the solar cell efficiency.*

Keywords: Zinc oxide Nanorods, Lead antimony sulphide, Quantum dot, hydrothermal method, successive ionic-layer adsorption and reaction (SILAR) method

1.1 INTRODUCTION

In the third generation of solar cell, Dye sensitized solar cells (DSSCs) are auspicious candidate as a renewable photovoltaic sources. In these cells organic dye is used to absorb light from sun. Ruthenium complexes organic dyes most commonly are used, which have large absorption in visible range about 300 to 700nm but it has weak absorption in the infrared spectrum. This leads to search for materials which absorb infrared range as well as visible range for improving the solar cells performance. Semiconductor sensitizers are promising broad-band solar absorbers, which also show absorption in the infrared region. Liquid-junction semiconductor-sensitized solar cells and extremely thin absorber (ETA) solar cells are two types of Semiconductor sensitized solar cells. These sensitizers have some advantages over organic dyes such as: tunable absorption bands due to the quantum-size effect, by a single incident photon it shows multi-electron− hole pair generation and it has high extinction coefficient. [1]

Many semiconductors, such as CdSe, Ag_2S, PbS, SnS and Sb_2S_3 are used as sensitizers in the semiconductor synthesized solar cell (SSCs)[2-5]. All these semiconductors belong to the binary group because it has two materials. In comparison with binary, ternary semiconductor SSCs such as $AgBiS_2$, $CuInS_2$, $SnSb_2S_4$, $AgSbS_2$ and $Pb_5Sb_8S_{17}$ are less discovered because of the involvement of three elements and they are difficult to grow. [6]

$Pb_5Sb_8S_{17}$ is a significant ternary semiconducting material, belongs to IV−V−VI group of semiconductors. It is synthesised from Sb_2S_3 and PbS binary semiconducting materials on the broad band materials such as TiO2, ZnO etc. It is a low cost, available abundantly, non-hazardous semiconducting material. It has band gap of 1.53 eV that match to optimal spectra (1.39eV) and large absorption coefficient $\alpha=1\times10^5$ cm^{-1}. All these features give that $Pb_5Sb_8S_{17}$ is a potential candidate for solar cell applications. [7]

In the recent work $Pb_5Sb_8S_{17}$ quantum dots are formed on the TiO_2 nanoparticles by successive ionic layer adsorption and reaction (SILAR) method. TiO_2 nanoparticles provide path to flow the electron. The photovoltaic performance is explored as a function of SILAR cycles, illumination intensity and passivation treatment.[8]

In present work, successive ionic layer adsorption and reaction (SILAR) process is used to synthesis $Pb_5Sb_8S_{17}$ quantum dots on a ZnO nanorods photoelectrode. ZnO is used as electron acceptor; its electron transfer mobility is thousand times greater than that of the TiO_2. As ZnO nanoparticles randomly formed on the substrate surface, in the electron transfer random walk appear, decreases carrier collection that's why we use ZnO nanorodes for providing direct pathway to the electron from the quantum dots to the collector [9]. The conversion efficiency of the 1dimentional structures is higher than that of the nanoparticles [10]. $TiCl_4$ pre-treatment is used as a blocking layer to minimize the recombination promises and for avoiding contact between the FTO and electrolyte [11]. It is observed that $TiCl_4$ pre-treatment modified surface of FTO glass; used as substrate, increase the performance of the devices [12].

2 EXPERIMENTATION

All the chemicals are purchased from Sigma Aldrich and all are in pure form.

2.1 Growth of ZnO nanorodes by hydrothermal method

In this work, FTO glass is used as a substrate which is ultrasonically cleaned in acetone, deioned water and ethanol. Then substrate is dipped for 30 min at a temperature 70 ºC in 40mM concentration of TiCl4 solution. After that, it is cool down to room temperature. Next step is the growth of seed layer. A Thin seed layer is deposited onto the surface of the substrate by using 2000 rpm per 30 seconds. 10mM zinc nitrate hexahydrate [Zn $(NO_3)_2.6H_2O$] aqueous solution is poured on the substrate by using dropper. When the spin coated FTO glass becomes dry, it is placed into furnace. Here it is soaked at 450 °C for half hour. Then it is cool down to room temperature. This process made a smaller particle seed layer appear on FTO glass. To grow ZnO nanorodes, prepared seed layer FTO glass is subsequently put in an auto-clave filled with an equimolar (35mM) aqueous solution of Zn $(Oac)_2$ $.2H_2O$ and HMTA. The reaction is carried out in an oven at 80 ºC for 5 hours. Finally substrate is washed with DI water and dried by nitrogen gas.

2.2 Deposition of Pb-Sb-S quantum dots on ZnO nanorods

PbSbS quantum dots are synthesised on ZnO nanorodes photoelectrode by using two-stage SILAR method. ZnO electrode is first dipped at room temperature, in 50mM aqueous Pb (NO3) solution for 30 sec, washed with deionised water and then dried by heating in air at 65 ºC. The electrode is then dipped into 0.1 M Na_2S methanol solution at room temperature for 30 sec, rinsed with methanol, and dried by heating in air. This process prepared one PbS SILAR cycle, producing PbS quantum dots on the ZnO electrode. To increase the amount of PbS material, the SILAR cycles are repeated n times before starting the second-stage SILAR process. To prepare Sb-S layer, the PbS coated ZnO electrode is dipped into 0.1 M $SbCl_3$ ethanol solution at room temperature for 15 sec, washed with ethanol, and dried by heating in air. The electrode is then immersed into 0.1 M Na_2S methanol solution at room temperature for 30 sec, washed with methanol, and dried by heating in air. Now Sb−S SILAR cycle is completed. The number of Sb−S SILAR cycles equal to that of PbS SILAR cycle. The double layered PbS/Sb−S structure is transferred to the Pb−Sb−S phase by heating at 350 ºC in nitrogen (N_2) gas for 1h. Samples are label by S1, S2, S3, S4, S5, S6, S7 respectively in the order according to which SILAR cycles are varied from 1-7. The schematic diagram of Pb-Sb-S coated ZnO photoelectrode is shown in the figure 1.

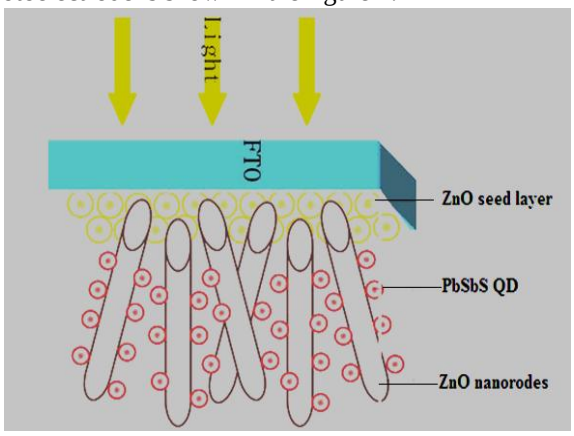

Fig. 1: A schematic diagram of photoelectrode.

3 CHARACTERIZATIONS

Optical absorption spectra are measure using a Genesys 10S UV-VIS spectrophotometer. X-ray diffraction is performed by using aX'ert Data Collector XPERT-PRO diffractometer. Energy-dispersive x-ray spectroscopy is accomplished by EDAX Apollo 40 SDD.

4 RESULTS AND DISCUSSION

4.1 UV-Visible analysis

Absorbance spectra are taken at room temperature in air to obtain information of the optical properties of the Pb−Sb−S-coated ZnO photoelectrode with several SILAR cycles that is shown in Fig.2. The figure shows that absorption increases with increasing number of SILAR cycles in infrared region which indicates the increase of amount of Pb-Sb-S quantum dots grown on the ZnO nanorodes. Absorption increases up to 4 SILAR cycles and by further increasing SILAR cycles absorption decreases gradually. The absorption band is characteristic of the high-level excitonic excitation absorption of a semiconductor, clearly showing the successful deposition of Pb-Sb-S QDs on the ZnO surface. The peak at ~350 nm is due to the ZnO nanorodes absorption edge. The maximum absorption is shown at S4 that indicates the maximum number of quantum dots is present. However, when SILAR cycles exceed 4, the adsorbed Pb-Sb -S increase along the thickness direction, the aggregation of Pb-Sb-S QDs and bad coverage of the ZnO nanorodes surface, the gap between ZnO nanorods decrease due to this absorption decreases by further increasing SILAR cycles.

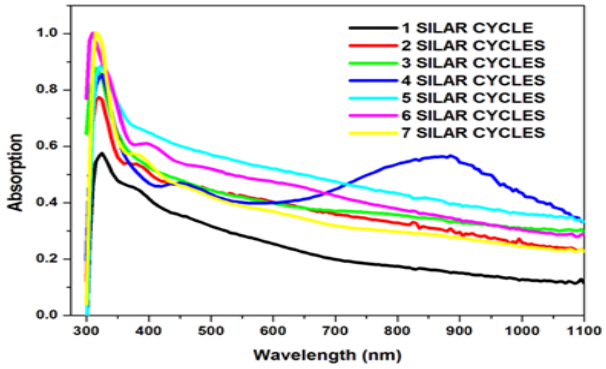

Fig. 2a: Absorption spectra of Pb−Sb−S nanoparticles with various SILAR cycles.

The band gap can be deduced from a plot of $(\alpha h\nu)^2$ versus photon energy (hν). From figure 2b it is clear that the value of band gap is decreased from 1.97eV to 1.62eV for samples S1 to S4. This decrease in the band gap is because of the increase in the size of the quantum dot. The sample S_4 has band gap of ~1.6 eV, which is very close to 1.53 eV of bulk $Pb_5Sb_8S_{17}$ [13,14]. It is also observed that the value of band gap is increased from 1.72eV to 1.90eV for samples S_5 to S_7.This increase in the band gap is due to the decrease in the size of the quantum dot. The absorption coefficient α is calculated in the fundamental absorption region from the absorbance data. Using Lambert law, [15,16]:

a = 2.303(A/d)…… (i)

Where "A" is Optical absorbance and "d" is the film thickness.

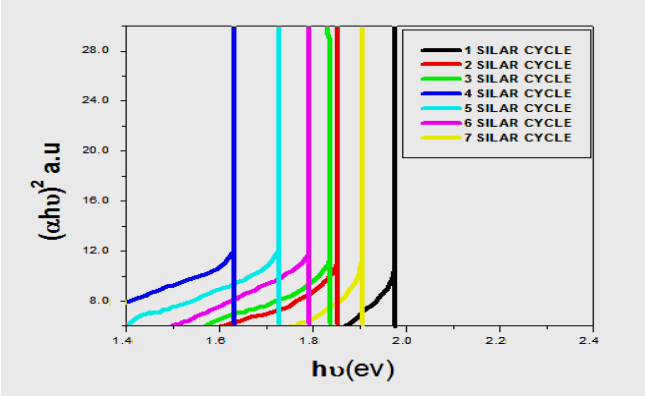

Fig.2b: Band gap graph of Pb−Sb−S nanoparticles with several SILAR cycles.

4.2 XRD Analysis

The XRD pattern of ZnO photoelectrode, which coated with Pb−Sb−S is shown in figure 3.1. The given spectrum is showing the pattern of coated photoelectrode without annealing and with annealing at 350°C. The peaks of ZnO are exhibited by Δ. The FTO/ZnO spectra (a) is shown by (002) plane, which demonstrating the high degree of c-axis alignment of developed ZnO nanorods that have hexagonal structure. The spectrum (b) is exhibited the peaks of PbS and Sb_2S_3 according to literature and have the cubic and orthorhombic structure respectively. After annealing, the prepared sample is matched the $Pb_5Sb_8S_{17}$ phase, which has orthorhombic structure. The annealed sample has lowest amount of peaks of PbS and Sb_2S_3 but has maximum number of peaks of $Pb_5Sb_8S_{17}$ that is indicated the successful growth of $Pb_5Sb_8S_{17}$ phase. The annealed sample has some other peaks such as the peak at 31.7° and 37.7° that do not match with $Pb_5Sb_8S_{17}$phase so, the annealed sample has multiphase orientation.

4.3 EDX Analysis

Figure 4 show the pattern of EDX (energy-dispersive x-ray spectroscopy) of Pb−Sb−S coated ZnO nanorods with 3 SILAR cycles. The SEM image is shown in the box beside with EDX pattern. By taking the Comparison of SEM image with the EDX pattern, it is proven the existence of $Pb_5Sb_8S_{17}$ quantum dots on the surface of ZnO. It is confirming the successful growth of $Pb_5Sb_8S_{17}$ quantum dots on the surface of ZnO photoelectrode.

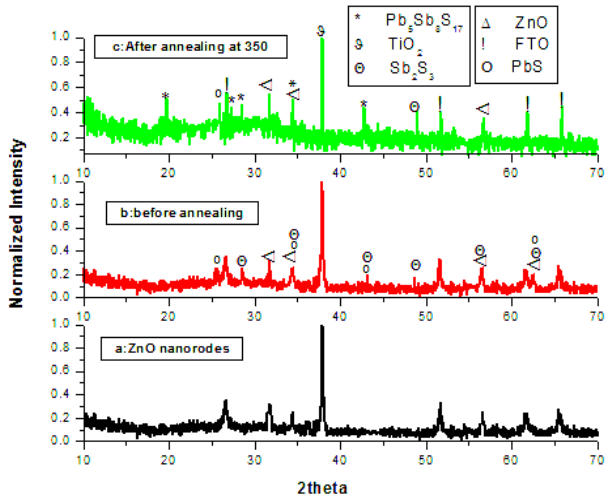

Fig.3: XRD patterns of photoelectrode: (a) ZnO nanorodes (b) Pb−Sb−S-coated ZnO before annealing, and(c) after annealing at 350◦C.

CONCLUSION

$Pb_5Sb_8S_{17}$ quantum dots are successfully adsorbed on the surface of ZnO nanorods photoelectrode. The energy band gap value of quantum dots is too low and it shows absorption in the Near IR region. There is the inverse relation between the band gap value and the SILAR cycles. From 1 to 4 SILAR cycles the energy band gap value is decreased. By

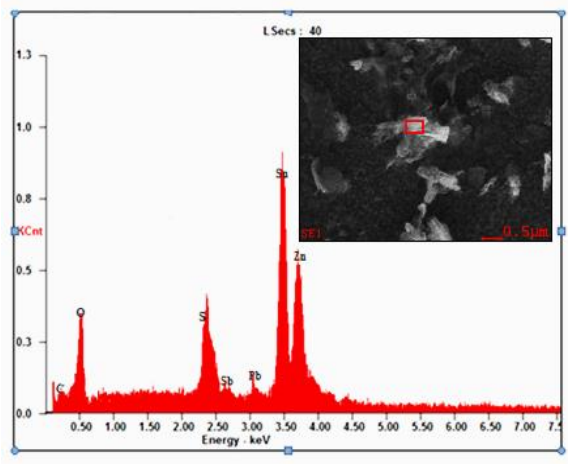

Fig.4 SEM image and EDX pattern of Pb−Sb−S-coated ZnO photoelectrode with 3 SILAR cycles

further increasing the SILAR cycles the relation between the SILAR cycles and band gap value is become direct. The $TiCl_4$ pre-treatment is used to decrease the recombination promises and for avoiding contact between the FTO and electrolyte.

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