Improvement in the CIGS Solar Cell Parameters by Using Plasmonic (Au) Nanoparticle

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Abstract Surface Plasmon from the metal nanoparticles is responsible for the light scattering which make them striking for light trapping in photovoltaic applications. Chemical synthesis of colloidal nanoparticles is one of the low-temperature; low-cost, easily scalable technique can produces the highest monodispersion nanostructure. Similarly, electrodeposition from non-aqueous bath allows depositing layer at higher bath temperature which may be helpful to enhance the crystallinity and particle size. In this study we demonstrate a active SPR effect with gold (Au) nanoparticles onto the Cu(In,Ga)Se₂ (CIGS) active semiconductor layer. The CIGS layers is fabricated onto the fluorine doped tin oxide (FTO) coated glass substrates by electrodeposition technique from non-aqueous electrolyte. The Au nanoparticles are deposited onto the CIGS layer with dip coating for different durations. The optical, morphological, electrical and optoelectronic properties of gold nanoparticle implanted in the CIGS thin film were studied and demonstrated the improvement in the solar cell parameters.

Keywords Light trapping, Plasmonic, Thin-film solar cell, CIGS

1. Introduction

Plasmonic photovoltaic has found to be an attractive approach in the recent research area. It is based on the scattering and light trapping from metallic nanoparticles (NPs) deposited on top of the thin-film solar cells (TFSC) to improve the power conversion efficiency. The surface plasmon resonance (SPR) in metal nanoparticles is mainly responsible to increase light absorption by light trapping in TFSC. Different size and shape of NPs have different SPR. The 19 % enhancement in photocurrent is reported by Pillai et al. [2] with Ag nanoparticles coated on Silicon solar cell. Temple et al. [3] also reported the effects of silver (Ag) NPs layers to the front surface of p-n junction Si solar cells. Polycrystalline CuInGaSe₂ (CIGS) have emerged as a leading material in thin film solar cell technology due to their applicability as absorber materials for highly efficient ~21.7% [4]. Vacuum or solution based techniques can be used for the deposition of the chalcopyrite layer. CIGS can be deposited using vacuum deposition techniques like sputtering [5], co-evaporation [6], flash evaporation [7], molecular beam epitaxy [8], pulsed laser deposition [9] and stacking elemental layers [10], which are reasonably expensive due to the capital investment and the use of highly pure source materials. Highly crystalline with controlled stoichiometric binary, ternary and quaternary semiconductor

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thin films can be prepared by vacuum techniques, however the technical issues such as deposition over large area, slow deposition rate, are unresolved. A non-vacuum technique such as, spray paralysis [11], chemical bath deposition (CBD) [12], sol-gel and electrodeposition (ED) [13-16] have also been used successfully for the preparation of CIGS thin films. The most intensely studied cost effective method is the electrochemical route. CIS/CIGS layers are electrodeposited from aqueous electrolyte have several issues such as the formation of low crystalline films and deposition of secondary phases, which may directly affect on the short circuit current (J_{SC}) of the device. This can be controlled in some extent with post-annealing treatment. The high temperature annealing impacts on the device junction (CdS/CIGS), which ultimately influences the open circuit voltage (V_{OC}) . To defeat these issues non-aqueous solvents can be used. Non-aqueous bath allow depositing layers at higher bath temperature which may be helpful to enhance the crystallinity and particle size. In this article we have studied the optical and optoelectronic (light trapping) morphological, electrical properties of gold nanoparticle implanted in the CIGS thin film, and also demonstrated the improvement in the solar cell parameters after Au NPs incorporation.

2. Experimental Details

2.1. Gold Nanoparticle Synthesis

Hydrogen tetrachloroaurate(III) trihydrate (HAuCI₄3H₂O) was used as a Au source and trisodium citrate dehydrate $(Na₃C₆H₅O₇ 2H₂O)$, sodium borohydride $(NaBH₄)$ and

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Ascorbic acid were used as reducing agent. Cetyltrimethylammonium bromide (CTAB) was employed as a capping agent to control the particle size. The gold nanoparticles of \sim 10 nm size were synthesized.

2.2. Electrodeposition of CIGS thin Films

The CIGS thin films were potentiostatically electrodeposited from non-aqueous (ethylene glycol) bath at temperature 130 °C. Using Biologic potentiostat/galvanostat model SP150. CIGS layers have been electrodeposited at -1 V versus Ag/AgCl reference electrode which was obtained by cyclic voltammetry experiments.

A conventional three-electrode geometry with Ag/AgCl as reference, FTO as working and graphite as counter electrode were used. $CuCl₂$, InCl₃, GaCl₃ and SeCl₄ purchased from Sigma- Aldrich of purity at least 99.9% were used as received. LiCl was used as supporting chemical compound to control the ionic conductivity of bath. Deposition potentials, versus Ag/AgCl reference optimized by CV measurement were chosen to electrodeposit CIGS thin films. The temperature of bath was maintained at 130 °C during CV measurements and growth of thin films without agitation. The properties of prepared CIGS thin films and Au NPs were individually characterized by using various characterization techniques. The optical properties were studied by using JASCO UV-Vis-NIR spectrophotometer. Current density-voltage (J-V) measurement was performed using Biologic Potentiostat attached with probe station and necessary software. Transmission electron microscopy (TEM) images were recorded using TECNAI G^2 20U-Twin microscope with operating voltage 200 kV. The film morphology was examined using JEOL JSM-6360A field emission scanning electron microscopy (FESEM) at accelerating voltage 20 kV and probe current 1 nA.

2.3. Device Fabrication

CdS/CIGS samples were etched in Br-methanol and NaCN solution to remove the unwanted secondary phases of Cu and Se. The nanoparticles were deposited on the prepared CIGS thin film by dip coating for different dipping time. Finally, a circular Au metal contact of area 3 mm diameter were made by vacuum thermal evaporator. The optoelectronic properties of superstate FTO/CdS/CuInGaSe₂ /Au NPs/metal structure device were measured under illumination with power intensity 100 mW/cm² at room temperature \sim 25 °C.

3. Results and Discussion

The prepared nanoparticles show the SPR at 527 nm which are of size 10 nm -20 nm as shown in figure 1. The as-prepared (without any post-heat treatment) CIGS films were used to study the effect of Au NPs on solar cell parameters.

Figure 1. TEM image of Au NPs, inset shows the absorption spectra of respective Au NPs

Figure 2 depicts the optical absorption spectra of CIGS thin films dipped in Au NPs solution for different duration. The enhancement in the absorption in visible region upon incorporation of Au nanoparticles in the CIGS thin film for different duration is obtained.

Figure 2. Optical absorption spectra for the CIGS thin films dip coated with Au NPs for different duration

The deposition of Au nanoparticles on CIGS thin film, morphological study was carried out by using FESEM. Figure 3 shows the FESEM image of CIGS thin film dipped in Au NPs for 300 sec. The Au nanoparticles are found to be spread uniformly on the CIGS thin film.

Figure 3. SEM image for the CIGS thin films dip coated with Au NPs

We have also studied the J–V characteristics of CIGS thin films with and without Au NPs as shown in the figure 4A) and B), respectively. All sample shows the rectifying behavior, furthermore enhancement in the current density was observed with increasing the dose of Au NPs in the CIGS thin film.

Figure 4. Current –voltage measurements of FTO/CdS/CIGS/Metal (A) and FTO/CdS/CIGS/Au NPs/Metal (B)

Superstrate configuration FTO/CdS/CIGS/Au NPs was used to study the solar cell parameters. The solar cell prepared for different dose of Au NPs with CIGS Figure 5 shows graph for the variation in solar cell parameters, V_{OC} , J_{SC} , FF and n . All parameters show the linear enhancement with increasing the dose of Au NPs. The strong influence of Au NPs is observed on the J_{SC} which could be due to the scattering of light in the CIGS. The percentage enhancement in the short circuit current (J_{SC}) is calculated by the following relation,

Percentage enhancement photocurrent

$$
= \frac{J_{\rm SC}(\text{With Au NPs}) - J_{\rm SC}(\text{Without Au NPs})}{J_{\rm SC}(\text{Without Au NPs})} \times 100\% \quad (1)
$$

Upon addition of Au NPs in the CIGS layer the short circuit current was increased by 54% and 130% for the samples dipped in Au NPs for 90 sec and 390 sec, respectively. The increase in current is proposed due to the scattering of the incident light within the material which is responsible to generate the more electron-hole pair.

Figure 5. Variation of solar cell parameters for FTO/CdS/CIGS/Au NPs structure at different duration

4. Conclusions

The distribution of Au nanoparticles onto the CIGS layer is well analyzed under FESEM. The systematic improvement in optical properties has been observed for nanocomposite layers. For CIGS/Au layers, the optical properties like absorbance have been increased in visible region with increasing the dose time of Au NPs. The SPR from the Au NPs effects on absorption of CIGS/Au layer, which contributed to improve the performance of the solar cell. The enhancement in the short circuit current 54% and 130% was measured for the dipping of CIGS in Au NPs for 90 and 390 sec, respectively.

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