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Energy Procedia 10 (2011) 38 – 42

Energy

Procedia

European Materials Research Society Conference
Symp. Advanced Inorganic Materials and Concepts for Photovoltaics

Application of PLD to the production of plasmonic structures containing Ag nanoparticles based on chalcopyrite solar cells

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Abstract

The effect of a single layer of Ag nanoparticles (NPs) embedded in amorphous Al₂O₃ grown on Cu(In,Ga)Se₂ (CIGSe) thin film solar cells is analyzed. CIGSe thin films with Cu/(In+Ga)= 0.62-0.81 atomic ratios are used as absorber layers. Ag NPs with mean diameters ≈2 nm and Surface Plasmon Resonance close to 400 nm were deposited by pulsed laser deposition (PLD) on top of the solar cell. An efficiency of 15.9 % is achieved for hybrid Ag NPs-CIGSe solar cells, close to that obtained by the best reference cell without the metallic NPs. These results suggest that PLD is a valid approach to produce plasmonic PV solar cells.

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Selection and/or peer-review under responsibility of Organizers of European Materials Research Society (EMRS) Conference: Symposium on Advanced Inorganic Materials and Concepts for Photovoltaics.

Keywords: Plasmonic photovoltaics; Ag nanoparticles; CIGSe, Pulsed laser deposition.

1. Introduction

The need of reducing the costs and improving the efficiency of photovoltaic (PV) device technology to make it competitive against non-renewable energy sources has boosted the research on new materials and designs for solar cells. A way to increase the cell efficiency is by excitation of surface plasmon resonances (SPR) in structures containing noble metal NPs placed at nanometric distances of the active layer. There are different plasmonic effects that have been proposed to increase the performance of solar cells depending on the size and configuration of metal NPs[1]. In particular, for NPs having sizes in the 5-20

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nm range it has been proposed that the extremely large enhancement of electromagnetic (EM) field amplitude observed in the vicinity of metal NPs under resonant excitation conditions, may be able of transferring energy to the active layer of the solar cell leading to the creation of electron-hole pairs [1,2,3].

In this case, the control of the size and shape of the NPs, as well as the characteristics of the surrounding medium becomes essential to improve the efficiency of the cells[1]. Among the different methods considered to produce noble metal NPs [4], PLD has been seldom used in the case of plasmonic PV applications [5]; even though it offers an extraordinary control over the size, and distribution of NPs in metal-dielectric nanocomposites [6]. Furthermore, it is a room temperature process that allows producing the metal NPs and the dielectric layer that it embeds them in a single step. However, the presence of high energy ions in the PLD deposition process may damage the surface of the growing film. Thus, in the present work we have explored the applicability of the technique to produce PV structures starting from the same fabrication concept we have used in the past in the case of nonlinear optical applications [6].

2. Experimental

Hybrid Ag:NPs-CIGSe solar cells were produced by depositing Ag NPs on top of a CIGSe solar cell by PLD. Figure 1 shows the structure of a cell. Initially, 2.3 μm -CIGSe thin films were grown on Mo coated float glass substrates using a multi-stage co-evaporation process [7]. CIGSe thin films with Cu/(In+Ga) ratios of 0.62 and 0.81 and Ga/(In+Ga) ratios of 0.20 and 0.22, respectively were used as absorber layers. Apart from the Cu(In,Ga)Se₂ phase, the Cu poorer thin film is also characterized by the presence of a vacancy compound, Cu(In,Ga)₃Se₅ [7]. Device completion was realised by deposition of a chemical bath deposited CdS buffer layer (50 nm thick) and a rf-sputtered ZnO/ZnO:Al bilayer (130 nm/250 nm thick). Then a single layer of Ag NPs embedded in amorphous Al₂O₃ (10 nm thick) was grown by PLD in vacuum (10⁻⁶ mbar) at room temperature. The structure was completed by evaporating Ni/Al front contact on top of the Ag:Al₂O₃ nanocomposite layer to facilitate current collection. The total area of the device is of 0.5 cm².

The Ag:Al₂O₃ nanocomposite layer was grown using an ArF excimer laser beam ($\lambda=193$ nm, $\tau=20$ ns, Energy density ≈ 3 J cm⁻²) that was alternatively focused on the surface of high purity Al₂O₃ and Ag targets. The laser repetition rate was 20 Hz and 5 Hz respectively. PLD allows controlling the amount of metal deposited and thus, the NP size through the number of laser pulses on the metallic target. At room temperature, PLD allows producing quasi-spherical NPs for low metal contents that evolve to ellipsoids when the metal content is increased due to coalescence. In the present work we have restricted ourselves to metal contents that guarantee the deposition of spherical Ag NPs according to previous calibrations [6].

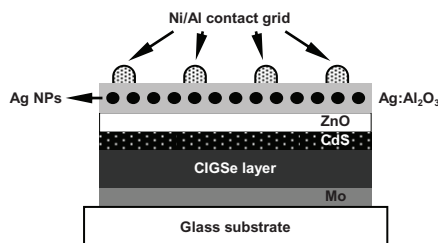


Figure 1. Structure of hybrid Ag NPs-CIGSe solar cell.

Reference Ag:Al₂O₃ nanocomposite samples containing a single layer of Ag NPs were deposited on soda-lime glass substrates to characterize the optical absorption spectra of the NPs in the range 350-800 nm. A bare glass was used to rule out any contribution from the substrate. Finally, hybrid and reference

CIGSe solar cells were characterised by measuring the external quantum efficiency (EQE) and the current-density–voltage (j -V) curve under simulated AM 1.5 illumination at 25 °C. The reference solar cells are those coming from the same deposition processes without Ag NPs.

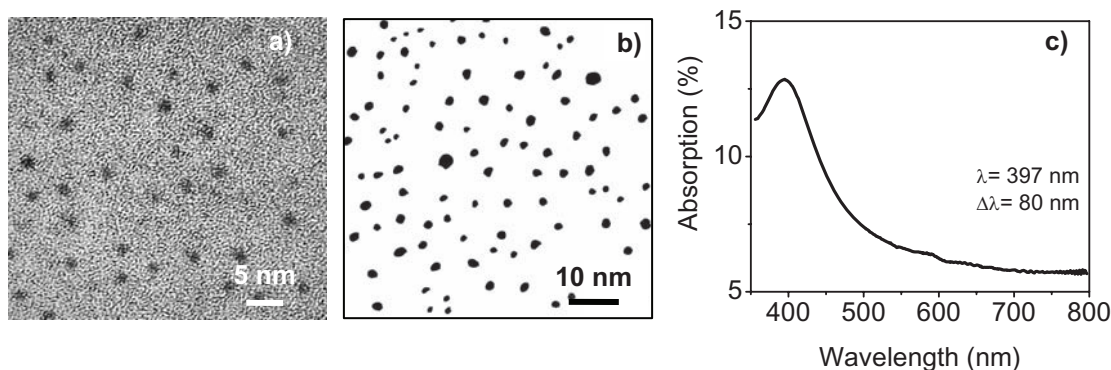


Figure 2. (a) Plan view HREM image and (b) the corresponding binary image of reference Ag:Al₂O₃ nanocomposite samples. (c) Absorption spectra of a reference Ag:Al₂O₃ nanocomposite sample containing a single layer of Ag NPs.

3. Results and discussion

3.1. Morphology and optical properties of reference Ag:Al₂O₃ nanocomposite layers.

Figure 2a shows a plan view high resolution electron microscopy (HREM) image of a single layer Ag:Al₂O₃ nanocomposite sample produced in an earlier work under similar experimental conditions [6,8]. The NPs (dark areas) present a circular shape and are randomly distributed in the plane. In order to investigate their in-plane shape and size distribution, this image was digitized following the procedure described elsewhere and the result obtained is shown in Figure 2b [8]. The main morphological parameters obtained from this analysis are summarized in Table 1.

Table 1. Morphological parameters obtained from HREM of a Ag:Al₂O₃ nanocomposite reference sample.

Ag content (at. cm ⁻²)	$\approx 1.0 \times 10^{15}$
Areal density %	5.2 ± 0.5
In plane Average diameter (nm)	2.0 ± 0.5
Average height (nm)	2.0 ± 0.5
In-plane surface to surface mean separation (nm)	4.6 ± 0.5
No. of NPs per cm ²	$2.3 \pm 0.2 \times 10^{12}$

Figure 2c shows the optical absorption spectra of a Ag:Al₂O₃ nanocomposite reference sample. The spectra shows an absorption band related to the Surface Plasmon Resonance (SPR) of Ag NPs, that peaks at 397 nm and it has a FWHM of $\Delta\lambda \approx 80 \text{ nm}$. This result optically confirms the small size and narrow size distribution of the produced Ag NPs. Plasmonic solar cells containing NPs with comparable size ($\varnothing \sim 4 \text{ nm}$) have been prepared from colloidal solutions [9]. However, in that case the SPR peak shifted from 412 nm (NPs in solution) to 465 nm when producing the layer of Ag NPs, while in our case the peak at 397 nm corresponds to the Ag:Al₂O₃ nanocomposite, which suggests that EM interparticle coupling, observed in the case of larger NPs, is absent in the present case.

3.2. Characterization of hybrid and reference CIGSe solar cells.

In each case the corresponding reference solar cells have been characterized to determine the effect of the Ag:Al₂O₃ nanocomposite layer on the performance of the cells. Figure 3 shows (a) the current density-voltage curves and (b) external quantum efficiency measurements of the best hybrid and reference solar cells in the case of the absorber with Cu/(In+Ga)=0.81 and Ga/(In+Ga)= 0.22. Table 2 displays the photovoltaic (PV) parameters of the best cells investigated with different compositions. The lower efficiency of the cells with lower Cu content is related to the significant presence of the vacancy compound [7]. The deposition of the metallic NPS does not lead to an enhanced device performance in all the cases independent of the Cu content. A lower spectral response is observed for $\lambda > 750$ nm (Figure 3b), which results in a lower short circuit current I_{sc} . But, why is not a higher photocurrent obtained after the deposition of the Ag:Al₂O₃ nanocomposite layer?

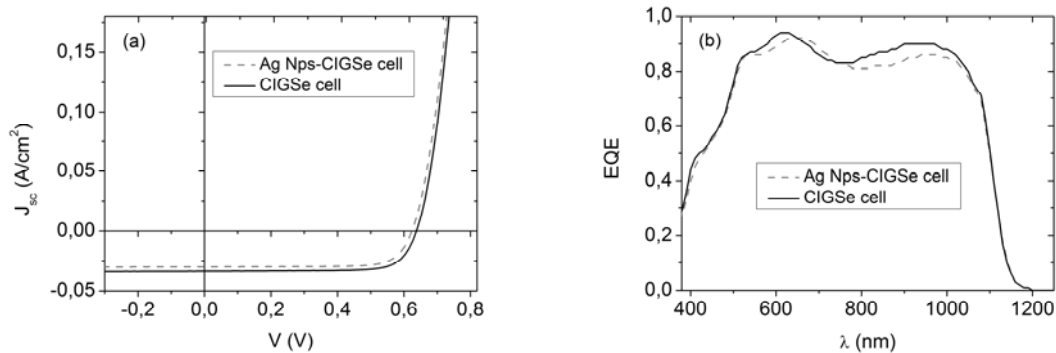


Figure 3. (a) J-V characteristics and (b) EQE measurements of hybrid Ag NPs-CIGSe and reference CIGSe solar cells with Cu/(In+Ga)=0.81.

Table 2. Performance of hybrid Ag NPs-CIGSe and reference CIGSe solar cells. J_{sc} was calculated from EQE measurements.

	Cu/(In+Ga)	V_{oc} (mV)	J_{sc} (mA cm ⁻²) ^{aa}	FF (%)	Efficiency (%)
Ag NPs-CIGSe	0.81	624	33.1	76.9	15.9
Reference CIGSe	0.81	637	34.0	76.4	16.5
Ag NPs-CIGSe	0.62	593	32.0	70.0	13.3
Reference CIGSe	0.62	595	32.9	73.9	14.5

aa: active area

PLD is characterized by the presence of a significant fraction of ions with large kinetic energies (KE). In particular in the case of laser ablation of Ag and Al₂O₃ at ≈ 3 Jcm⁻², it has been observed that $\sim 40\%$ of the ions detected in the case of Ag have KE larger than 200 eV, whereas and this percentage increases up to $\sim 60\%$ in the case of Al ions [10]. These ions may damage the surface of the layer acting as substrate through implantation or sputtering, thus damaging the material and therefore, affecting significantly the device performance. However, the results presented here suggest that these processes are not relevant in the present case, although no enhancement of EQE or the J_{sc} is observed in any of the hybrid cells. As it is shown in Fig.2, the produced Ag NPs are considerably small ($\varnothing \sim 2$ nm) and they are well separated. Thus, no enhancement due to light scattering processes should be expected [1], and only near field effects could lead to the enhancement of the cell performances. Near EM fields associated to Surface Plasmons in

metal NPs exponentially decrease with the distance to become negligible for distances longer than 5-10 nm in the case of very small NPs such as the ones considered here. Thus, as a consequence we should not expect an improvement of the photocurrent of the solar cell under the present configuration. An optimization of the NPs size and position within the solar cell structure is necessary [11], which is under investigation.

4. Conclusions

We have demonstrated that PLD can be easily combined with the production process of chalcopyrite thin film solar cells without damaging their performance significantly. However, the experimental results suggest the necessity of a new configuration of the solar cell to enhance the plasmonic absorption and the device efficiency. This can be achieved by placing the NPs closer to the active layer and simultaneously producing larger Ag NPs which can be easily achieved by PLD.

Acknowledgements

The authors acknowledge the financial support of Spanish Ministry of Science and Innovation (Project MAT2009-14282-C02-01). G. B. acknowledges a CSIC–JAE predoctoral grant partially supported by the European Social Fund. The authors would also like to thank T. Münchenberg, J. Schniebs, R. Schwieger, C. Kelch, M. Kirsch and M. Galvan for technical support.

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