

PEDOT:PSS for hybrid solar cells with β - and γ - Ga₂O₃ nanoparticles

Marina García-Carrión¹, Julio Ramírez-Castellanos², Emilio Nogales¹, Bianchi Méndez¹, Chang Chuan You³, Smagul Karazhanov³, and E. S. Marstein³.

¹Department of Physics of Materials, Faculty of Physical Sciences, University Complutense Madrid, 28040 Madrid, Spain.

²Department of Inorganic Chemistry, Faculty of Chemical Sciences, University Complutense Madrid, 28040 Madrid, Spain.

³Department for Solar Energy, Institute for Energy Technology, PO BOX 40, 2027, Kjeller, Norway.

Abstract

Herein, hybrid composite layers made of nanocrystalline β -Ga₂O₃ or γ -Ga₂O₃ within PEDOT:PSS have been studied in order to be incorporated into hybrid solar cells. Structural, morphological, optical and electrical characterization has been carried out with X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), PL excitation (PLE), cathodoluminescence (CL) and Raman spectroscopy. The effect that the β - and γ - nanocrystals phases induce on key performance parameters, such as the minority carrier lifetime and sheet resistance, of the hybrid system will be discussed.

Keywords

Gallium oxide, nanoparticles, PEDOT:PSS, hybrid solar cell, luminescence,

Introduction

One of the ways of reducing the cost of the fabrication of solar cells in recent years is by using organic materials. Among them, poly(3,4-ethylenedioxythiophene):-polystyrene (PEDOT:PSS) is a conducting polymer that has been studied for the new generation of solar cells [1–8]. Besides, the research on this polymer has recently been

incremented by its functionalization with nanocrystalline transparent conductive oxides (TCO) with the aim to improve their stability and electrical behavior [9, 10].

In the present work, we study the effect of added nanoparticles (NPs) in the PEDOT:PSS of the top electrode on a hybrid solar cell. To this purpose, Ga₂O₃ NPs of beta and gamma phases have been synthesized by chemical routes and characterized from the structural and luminescence point of view. NPs have been incorporated into the PEDOT:PSS and the final product has been deposited on a silicon wafer. The results of the measured optical and electrical parameters of the fabricated hybrid systems are discussed.

Experimental method

β -Ga₂O₃ and γ -Ga₂O₃ NPs were prepared dissolving gallium nitrate hydrate (Ga(NO₃)₃·xH₂O) in distilled water. Ammonium hydroxide solution was slowly added into that solution to obtain a basic pH (pH~8). The resultant precipitate was filtered and dried in air. The obtained powder was calcined in air at 250 °C to produce γ -Ga₂O₃ phase, or at 750 °C to obtain β -Ga₂O₃ phase [9–14].

The functionalization of the PEDOT:PSS with the oxide NPs has been achieved following three different routes. The first one (method A) has been done by mixing 2 ml of PEDOT:PSS solution, 5 % wt. of dimethyl sulfoxide (DMSO) and 0.1% wt. of surfactant (Triton x-100). This solution was stirred and filtered with a PES membrane (0.45 μ m porosity). β -Ga₂O₃ NPs were added to a 1 % wt. concentration, stirred and sonicated. The second method (B) was based on a solution of PEDOT:PSS stirred with 0.1 % wt. of surfactant, and a second solution of DMSO and β - or γ -Ga₂O₃ NPs in a weight ratio 5:1. The latter solution was added into the former one to a concentration of 5 % wt. Finally, the last method (C) consists of PEDOT:PSS with 5 % wt. DMSO, filtered with a PES membrane (0.45 μ m porosity), to which 0.1 % wt. surfactant and 1 % wt. of the γ -Ga₂O₃ NPs were added, stirred and sonicated. The samples with better results were β -Ga₂O₃ NPs by method A (sample β -A), β -Ga₂O₃ NPs by method B

(sample β -B), γ -Ga₂O₃ NPs by method C (sample γ -C) and γ -Ga₂O₃ NPs by method B (sample γ -B). A reference sample with PEDOT:PSS with DMSO and Triton mixed with by method C, but without NPs, has been used for the sake of comparison.

X-ray diffraction has been done by using PANalytical X'Pert MPD (CuK α irradiation, $\lambda=1.5404$ Å) and Raman spectroscopy in a Horiba Jobin Yvon LabRAM HR800 confocal microscope. The luminescence properties have been assessed by cathodoluminescence (CL) in a Hitachi S2500 scanning electron microscope (SEM) and a Hamamatsu PMA-11 CCD camera. Photoluminescence (PL) and PL excitation (PLE) were performed using a monochromatic light beam in an Edinburgh Instruments FLS1000 spectrometer system equipped with a 450 W Xe lamp. All luminescence spectra were acquired at room temperature.

Photoconductance decay was characterized by quasi steady-state photoconductance (QSSPC) using a LIS-R1 PL imaging setup from BT Imaging with an excitation wavelength of 808 nm and a constant illumination intensity of $4.2 \times 10^{-2} \text{ W cm}^{-2}$. [15–17] Finally, I-V curves were obtained with a [Keithley 4200 Semiconductor characterization system](#).

Results and discussion

Fig 1 shows the XRD patterns of β -Ga₂O₃ (**a**) and γ -Ga₂O₃ (**b**) synthesized NPs. Cubic structure (ICDS Collection code: 236276) is assigned to γ -Ga₂O₃ NPs and monoclinic (ICDS Collection code: 83645) to β -Ga₂O₃ NPs. Average sizes around 30 nm for the β -Ga₂O₃ NPs and 10 nm for the γ -Ga₂O₃ NPs are estimated through Scherrer formula. Raman spectra from the two phases, **Fig 1 c-d**, confirm assignment of the phases to the corresponding NPs [11,18].

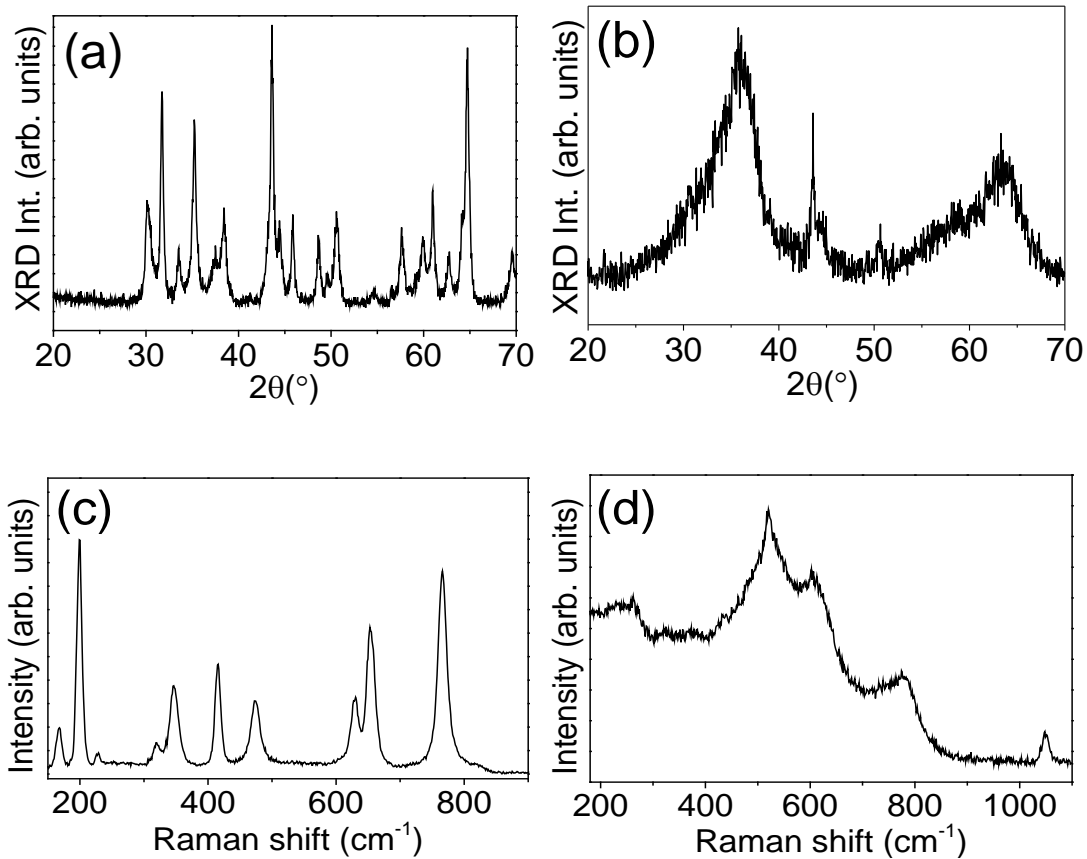


FIG 1 XRD pattern of (a) β - Ga_2O_3 NPs and (b) γ - Ga_2O_3 NPs. (c)-(d) Corresponding Raman spectra of β - and γ - Ga_2O_3 NPs respectively.

Fig 2a shows room temperature PL (black), CL (red) and PLE (blue) spectra of β - Ga_2O_3 NPs. CL spectrum is dominated by a broad blue band centered at 2.9 eV (428nm), while PL emission exciting with $\lambda_{\text{exc}} = 254$ nm (4.9 eV) shows a band with similar properties, but slightly red-shifted, being centered at 2.7 eV (457 nm). This strong β - Ga_2O_3 blue emission is well known and attributed to native point defects [13, 14]. The shift between the position of the peaks obtained by CL and PL is usually related to the different excitation conditions in each of the techniques. Finally, PLE spectrum from these β - Ga_2O_3 NPs with $\lambda_{\text{em}} = 454$ nm (2.7 eV) detection wavelength yields a bandgap value $E_{\text{g}\beta} = 4.9$ eV, the expected value for β - Ga_2O_3 . In the case of γ - Ga_2O_3 NPs, the dominant bands in CL and PL spectra are centered at 2.8 eV (443 nm) (**Fig 2b**, red and black lines, respectively). Besides, a less intense UV band centered at 4.7 eV (264 nm) is also observed in the CL spectrum. PLE spectrum (**Fig 2b**, blue)

from the gamma NPs shows the bandgap, $E_{gr} = 4.7$ eV, in good agreement with the value reported in the literature [9–14]. Hence, the above mentioned CL 4.7 eV band coincides with the bandgap and can be assigned to interband transitions. It is very interesting that the interband luminescence emission can be obtained in gamma gallium oxide, as it is not observed in the beta phase and it has not been obtained before from the gamma, to the best of our knowledge.

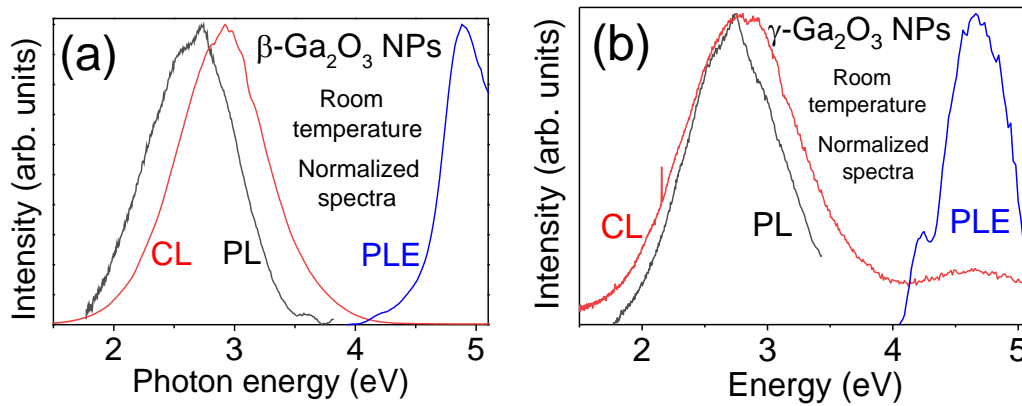


FIG 2 CL (red), PL (black) and PLE (blue) spectra from (a) β - Ga_2O_3 and (b) γ - Ga_2O_3 . Excitation wavelengths for the PL spectra were 254 nm (4.9 eV), 262 nm (4.7 eV) for β - and γ - phases, respectively. Emission wavelengths for PLE spectra were 454 nm (2.7 eV) and 452 nm (2.7 eV) for β - and γ - phases, respectively.

Functionalization of the PEDOT:PSS with the synthesized NPs has been studied. The hybrid mixtures were deposited on a n-type Float Zone (FZ) Silicon wafer by spin coating to form a thin layer. A thermal treatment was conducted to remove any remaining water [2,5,7,8]. In order to study the effective charge carrier lifetime values of the nanocomposite coated Si wafer, we measured the photoconductance decay by quasi steady-state photoconductance (QSSPC). **Figs 3 a-d** display the PL decay maps of samples β -A, β -B, γ -C and γ -B, respectively. Homogeneity of the spin-coating and carrier lifetime values are assessed from these maps. Lifetime values are summarized in **Table 1**, along with the sheet resistance (R_{sheet}) obtained by the 4-point-probe method. γ -C sample presents the higher carrier lifetime, 335 μs , slightly higher than

that of the reference sample. β -A and β -B show the lower sheet resistance among the hybrid structures, but still higher than that of the reference. All the samples present a similar absorption in the visible range to that of the reference sample (not shown).

Table 1. Summary of the most relevant results of PEDOT:PSS with Ga_2O_3 NPs.

SAMPLE	R_{sheet} ($\text{K}\Omega/\text{sq}$)	τ (μs)
β -A	$1,15 \pm 0,10$	288
β -B	$1,13 \pm 0,10$	301
γ -C	$5,15 \pm 0,10$	335
γ -B	$3,17 \pm 0,10$	309
PEDOT-REFERENCE	$0,75 \pm 0,10$	310

I-V curves in dark conditions are shown for samples β -A, β -B (**Fig. 3e**) and γ -C, γ -B (**Fig. 3f**), showing a Schottky-contact behaviour, as expected [1–8]. The current is increased in a 7-8 % in the hybrid layers, in comparison with the reference one. A schematic of the system, including Ag contacts, is shown in **Fig 3 g**.

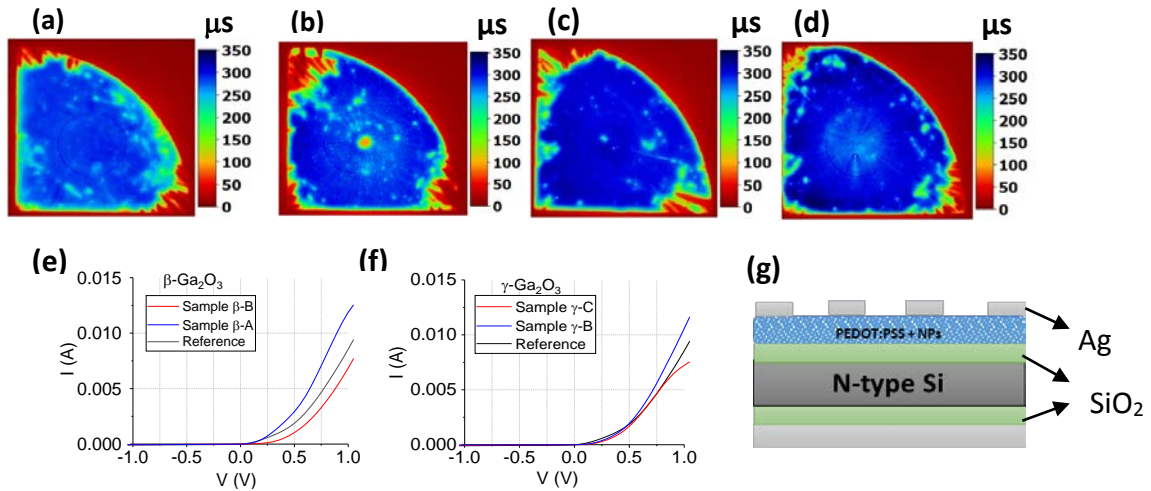


FIG 3 PL images of samples (a) β -A (b) β -B (c) γ -C (d) γ -B. I-V curves of composites with NPs and reference PEDOT:PSS with Ag contacts (e) β - Ga_2O_3 (f) γ - Ga_2O_3 . (g) Contact montage scheme.

Conclusion

PEDOT:PSS has been functionalized with β -Ga₂O₃ and γ -Ga₂O₃ NPs. Characterization of the crystal structure and room temperature luminescence properties of these NPs has been carried out. Nanocrystals present pure phases with average diameters around 10 nm for γ -Ga₂O₃ and 30 nm for β -Ga₂O₃. Broad blue luminescence bands centered around 2.7 eV are observed for the two phases and the bandgaps obtained from PLE are 4.9 eV for beta and 4.7 eV for gamma phases. Besides, a CL band at 4.7 eV is obtained in the γ -Ga₂O₃ NPs, assigned to interband transitions. Improvement of the carrier lifetime of PEDOT:PSS with γ -Ga₂O₃ NPs has been achieved as compared with the unmixed polymer.

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