Solar Energy Materials & Solar Cells ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Size dependent light absorption modulation and enhanced carrier transport in germanium quantum dots devices

S. Cosentino [a,*], E.G. Barbagiovanni [a], I. Crupi [a], M. Miritello [a], G. Nicotra [b], C. Spinella [b], D. Pacifici [c], S. Mirabella [a], A. Terrasi [a]

[a] MATIS IMM-CNR and Dipartimento di Fisica e Astronomia, Università di Catania, via S. Sofia 64, 95123 Catania, Italy
[b] IMM-CNR, VII strada 5, 95121 Catania, Italy
[c] School of Engineering, Brown University, Providence, RI 02912, USA

ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form
5 September 2014
Accepted 8 September 2014

Keywords:
Germanium
Quantum dots
Quantum confinement
Light absorption
Photovoltaics

ABSTRACT

Quantum confinement in closely packed arrays of Ge quantum dots (QDs) was studied for energy applications. In this work, we report an efficient tuning mechanism of the light harvesting and detection of Ge QDs. Thin films of SiGeO alloys, produced by rf-magnetron sputtering, were annealed at 600 °C in N_2 to induce precipitation of small amorphous Ge QDs into the oxide matrix. Varying the Ge content, the QD size was tailored between 2 and 4 nm, as measured by high resolution transmission electron microscopy. X-ray photoelectron spectroscopy (XPS) measurements indicate the formation of pure SiO_2, as well as the presence of a sub-stoichiometric Ge oxide shell at the QD interface. Light absorption spectroscopy shows a clear size-dependent shift of the QD optical bandgap (E_g), between 1.4 and 2.1 eV, and was modeled using the standard effective mass approximation (EMA) or a spatially dependent effective mass approximation (SPDEM) model. The reported quantum confinement effect was exploited to enhance light harvesting capability in Ge QDs-based devices. Metal–insulator–semiconductor devices with Ge QDs in the insulating layer exhibit a significant photo-response under reverse bias. Whereby, we demonstrate a large photoconductive gain (up to 1500%) that is tunable with QD size and is based on a preferential trapping of photo-generated holes by QDs, which enhances the charge carrier collection. Our results provide a new route for the application of Ge QDs in light harvesting devices and solar cells.

1. Introduction

Quantum confinement (QC) in nanostructures (NS) affects many properties relevant to light harvesting, such as the optical bandgap, luminescence efficiency and oscillator strength [1–3]. In particular, group IV quantum dots (QDs) attracted significant attention regarding their possible use in photovoltaic applications [4–6]. The size-dependent bandgap, E_g, in a confined system was advocated to potentially increase the fraction of absorbed light from the solar spectrum in multi-junction QD-based solar cells [7]. Considering the terrestrial solar spectrum (AM1.5G, 1000 W m^{-2}), the optimal band-gap of the top cell required to maximize energy conversion efficiency is 1.7–1.8 eV for a tandem solar cell combined with a crystalline Si (c-Si) bottom cell [8]. Recently, Hu et al. studied the miniband formation in closely packed Si QD superlattices embedded in SiO_2 or SiC matrices [9]. The predicted conversion efficiency was 50.3% for an intermediate band solar cell architecture. In this regard, the light harvesting potentiality of silicon rich oxide has been deeply investigated in the past. For example, Perez-Wurfl et al. reported on doped Si QD diodes fabricated by sputtering on quartz substrates that showed an open circuit voltage of 0.492 V upon illumination [10]. Very recently, Guha et al. reported on multi-junction solar cells incorporating nanocrystalline Si with an efficiency as high as 16.3% [11]. However, to date, all the reported experiments on similar types of cell demonstrated a reduced open circuit voltage (V_{oc}) and a lower short circuit current (I_{sc}) with respect to single-junction Si solar cells, due to photocarriers recombination [8,12,13].

While a lot of research has been carried out on Si NS for solar cell applications, on the other hand, Ge NS have been often underrated because of their lower abundance, higher cost and the poor quality of the Ge oxide. However, Ge demonstrates more potential than Si at the nanoscale. Compared to Si, Ge nanostructures have a larger exciton Bohr radius (~24 nm in Ge compared to ~5 nm in Si [14,15]), a lower synthesis temperature and a larger optical absorption efficiency, making them a valuable candidate for future

* Corresponding author. Tel.: +39 0953785289.
E-mail address: Salvatore.cosentino@ct.infn.it (S. Cosentino).

http://dx.doi.org/10.1016/j.solmat.2014.09.012
0927-0248/

optoelectronics applications and new generation photovoltaics [16–18]. Ge NS have been successfully used in the development of optical modulators [2], Vis-IR photodetectors [17] and solar cells [18–20]. Recently, we reported on the light absorption of Ge QDs synthesized in SiO_2 and Si_3N_4 matrices by plasma-enhanced chemical vapor deposition. We found that the optical bandgap can be effectively tuned with QD size in agreement with effective mass theory predictions and can be used as active layer in low-bias operable photodetectors [21]. Moreover, also the QD–QD distance plays an important role in the light absorption process, being more effective for densely packed multilayers of QDs [22]. Recently, *p-i-n* solar cells with the intrinsic layer containing multilayers of Ge QDs embedded in Si demonstrated an increased conversion efficiency for wavelengths $\lambda > 1400$ nm [18,19]. In addition, with proper control of the optical and electronic properties of QD-based solar cells, one can effectively boost the photo-conversion performance beyond the actual limit of conventional solar cells [20]. For example, enhanced photon capture and photo-conversion was demonstrated in *p-i-n* solar cells employing two-dimensional photonic nanocrystals coupled with Ge QDs [20].

Despite these recent developments, some concerns still remain regarding the multi-step fabrication processes of QD-based solar cells, which may not be compatible with large-scale production in terms of time and costs. Moreover, the optical and carrier conduction properties of thin films with Ge QDs may not depend on size only. Other concomitant effects can play a strong role, such as: defects at the QD interface, shape and QD crystallinity, as well as stoichiometry of the hosting matrix. For this reason, a detailed investigation into the light absorption and photo-carrier extraction process in films containing Ge NS is important to understand both the fundamental physics and also for performance optimization in light harvesting Ge NS devices.

In this work, we report a detailed investigation of the synthesis and light absorption process in closely packed Ge QDs in SiO_2. We provide insight into the role of QD size and chemical arrangement at the QD interface as fundamental parameters for the optical bandgap tuning and light conversion capability. Finally, we demonstrate a large electrical photoresponse in Ge QDs based devices, due to a preferential trapping mechanism for photo-generated holes in Ge QDs. These results clearly demonstrate the great potential of Ge QDs in high-efficiency and Si-compatible light detectors and their potential application for future low-cost solar cells.

2. Experimental details

Ge-rich silicon oxide thin films (hereafter denoted: SiGeO) were deposited by rf-magnetron co-sputtering of SiO_2 and Ge targets (5×10^{-3} mbar Ar atmosphere, nominal deposition temperature 400 °C) on fused silica or *n*-type (40–120 Ω cm resistivity) Si substrates. Different Ge concentrations were obtained by varying the power of the Ge target from 30 to 60 W, while the power of the SiO_2 target was kept constant at 500 W. As deposited films underwent thermal annealing at 600 °C for 1 h in N_2 atmosphere to induce phase separation in the SiGeO alloy and the precipitation of the excess of Ge into quantum dots. Rutherford backscattering spectrometry (RBS, 2.0 MeV He^+ beam in random configuration, 165° backscattering angle) was performed to measure the elemental composition of the films, as reported in Table 1. The presence and size distribution of Ge QDs, as well as the film thicknesses, were evaluated by cross sectional transmission electron microscopy (TEM) analysis, using a JEOL 2010F TEM microscope at 200 kV operating in a conventional dark field mode. We recognized the QDs by automatic particle identification software or manually by locating their boundaries, as described in Refs. [21,23].

Table 1
Ge target power, film thickness, composition and Ge atomic content of SiGeO alloys deposited on quartz and annealed at 600 °C in N_2.

Power at the Ge target (W)	Thickness (nm)	at% Si	at% Ge	at% O	% Ge excess	Ge content, D (at/cm^2)
30	210	27	8	65	2.5	1.15×10^{17}
40	300	24.5	11.5	64	4	1.77×10^{17}
50	250	24	15	61	9	3.0×10^{17}
60	290	22.5	18.5	59	11.5	3.4×10^{17}

The chemical states of Ge and Si in the SiGeO films were identified by means of X-ray photoelectron spectroscopy (XPS) using a VG CLAM4 MCD analyzer system. The Al Kα emission line (1486.6 eV) was used as photon source. A pass energy of 23.4 eV was used for all scans, giving an overall resolution of 1.1 eV, while the acquisition was performed at a fixed angle of about 70° from the surface. The Si^{2p}, Ge^{3d} and O^{2s} peaks were measured and the corresponding binding energies were calibrated using the C^{1s} peak, due to surface contamination.

Normal transmittance (T) and the 20° reflectance (R) spectra in 200–2000 nm wavelength range were acquired using a Varian Cary 500 double-beam scanning UV/visible/NIR spectrophotometer (approximately 1 nm resolution). The absorption coefficient spectra (α) were calculated by combining T and R spectra of Ge QDs thin films, as described in Ref. [24].

Ge QDs embedded in SiGeO films were used to fabricate prototypical light harvesting devices. A metal–insulator–semiconductor (MIS) configuration was obtained by sputtering nominal 100 nm thick In_2O_3:ZnO (IZO) contacts (circular shape, 0.5 cm^2 area) upon SiGeO films grown on *n*-type Si substrate. Current vs. voltage measurements were performed in dark and under monochromatic illumination, between 400 and 1100 nm, with a Keithley 4200 semiconductor characterization system. The radiation source consists of a 250 W tungsten–halogen lamp coupled with a SP-2150 monochromator and a fiber bundle (consisting of 19 individual optical fibers) to focus the light at different wavelengths on a Karl Suss probe station. The energy of the monochromatic radiation, having a power from ~3 to 10 μW, was monitored by an Ophir Nova II optometer.

3. Results and discussion

3.1. Structural characterization

Table 1 summarizes the values of thickness (from TEM) and the atomic composition (from RBS) of SiGeO films annealed at 600 °C. All the films have a similar thickness d of 200–300 nm. The atomic content, D, of Ge increases with the sputtering power from 1.15×10^{17} to 3.4×10^{17} at/cm^2. From a closer evaluation of the atomic composition of the SiGeO alloys, one can estimate that the excess of Ge (with respect to eventually formed GeO_2) is considerably low for low Ge target power. In this case, most of the Ge atoms are expected to bond with excess O atoms in the film. For higher sputtering powers, a larger fraction of excess Ge atoms can participate to Ge QD nucleation.

Thermal annealing of the SiGeO alloys induces nucleation and growth of small Ge precipitates. The TEM images in Fig. 1 reveal the presence of closely packed amorphous Ge QDs, visible as bright spots. Their size linearly increases from about 2 to 4 nm with increasing Ge concentration from 8% to 18.5%, as shown in Fig. 2. Moreover, we can estimate the mean QD concentration by considering the atomic Ge content (D) measured by RBS and the QD mean size ($2r$) extracted from the TEM analysis. We assume that after annealing all the excess of Ge in the alloy (with respect

Please cite this article as: S. Cosentino, et al., Size dependent light absorption modulation and enhanced carrier transport in germanium quantum dots devices, Solar Energy Materials and Solar Cells (2014), http://dx.doi.org/10.1016/j.solmat.2014.09.012