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Formation of thin-film-like Ge quantum dots array in thermally oxidizing SiGe pillar technique for energy harvest/conversion applications

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1. Introduction

Semiconductor quantum dot (QD) structures have been subjected energetic researches and marked with dramatic progress not only on growing and placing QD but also demonstrating their unprecedented tunability and never before seen applications to science and technology. Taking advantages of quantum confinement effect, Coulomb blockade effect and strong charge coupling, QDs have successfully improved the efficiency and expanded the functionality of sensing, computation, memory, and information technologies. Consequently employing QDs into photovoltaic (PV) and thermoelectric (TE) devices is a nature extension for boosting the efficiency of energy saving and even energy harvest or conversion technologies.

Experimental works have demonstrated the effectiveness and the feasibility of QD solar cells [1, 2] and QD TE devices [3, 4]. However, many of these materials are not practical for large-scale commerical use because they are fabricated by atomic layer deposition or fortuitous nanofabrication processes, making them slow and expensive to fabricate and being not producible in large quantity. Leaping over the proof-of-principle level, we are approaching the stage of realizing optimal designed and dense QD structures in forms of sheets or three-dimensional (3D) array using bulk Si integrated-circuit compatible process.

The challenge for realizing high efficiency 'rainbow' QD solar cells is how to create a solar cell out of differently sized QDs in arrangement, so that each one acts on a specific wavelength of the electromagnetic spectrum based on size-quantization effect, thus harvesting most of the power light carries. While the difficulty of fabricating TE materials with high figure of merit is how to produce thin-film-like dense and thermodynamically stable QD arrays for sufficient heat dissipation and power generation.

We have reported that size-controllable Ge QD sheets or nanowire matrices could be formed by thermally oxidizing SiGe structures, and the position, number and density of Ge QDs are determined by the terminal points where the oxidation process stops and Ge content in SiGe [5, 6]. In this paper, we propose a simple method, thermally oxidizing vertical SiGe pillar matrix, for generating dense and size-tunable Ge QD array in a self-organized manner. The knowledge gained from this 3D QD array system is readily transferable for fabricating QD photovoltaic and TE devices.

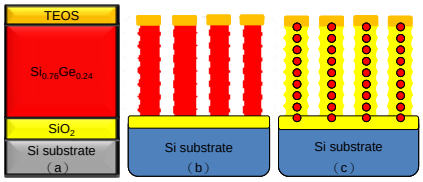

Fig. 1 Schematic process flow for forming 3D Ge QDs array. (a) as-grown SiO_2/poly-SiGe/SiO_2/Si-substrate, (b) abacus pillar matrix definition, and (a) Ge QDs arrays formed by thermally oxidizing poly-SiGe pillar.

2. Experimental and Results

The fabrication of thin-film-like Ge QD 3D arrays started from depositing a 50 nm SiO_2 and then a $Si_{1-x}Ge_x$ thin film (500~1000 nm) with uniform or grading Ge composition on top of a Si substrate. Then pillar matrices were defined using lithography and a peculiar cycling plasma etching. Notably abacus-like pillars were generated by 9 cycles plasma process, in which each cycle consists of alternative SF_6/O_2 plasma (130 sccm/13 sccm, 5 sec) and C_4F_8 plasma (85 sccm, 6 sec). SF_6 plasma is employed for isotropic etching poly-SiGe and the subsequent C_4F_8 plasma is used for passivating the pillar sidewall, thus each cycle plasma process produces one bead in the pillar. In turn the bead's size and number, respectively, in a pillar is determined by the competition between SF_6 etching and C_4F_8 passivation within a cycle and the cycle numbers. After thermally oxidizing poly-SiGe abacus pillars, Ge QDs will reside in the center of each bead and line-up to each other vertically and horizontally. The schematic process flow for forming 3D Ge QDs array is sketched in Fig. 1. Forming Ge QDs in either uniform or grading size distribution is attainable by modulating the Ge composition, the pillar diameter, abacus etching and oxidation conditions. The properties of Ge QDs such as size, density, and optical

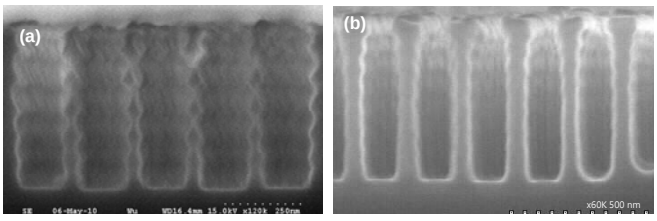

Fig. 2 SEM images of (a) poly-Si and (b) poly-$Si_{0.76}Ge_{0.24}$ abacus pillars formed by SF_6/C_4F_8 plasma alternatively.

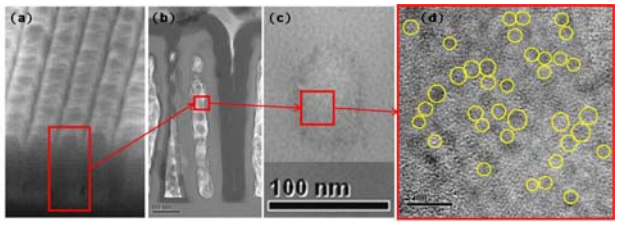

Fig. 3 (a) SEM and (b) TEM images of oxidized poly-SiGe pillar, (c) and (d) enlarged TEM images of abacus beads including Ge QDs wherein.

band gap energy, respectively, are characterized by transmission electron microscopy (TEM) and cathodoluminescence (CL).

Figure 2 shows the scanning electron microscopic (SEM) images of poly-Si and poly-$Si_{0.76}Ge_{0.24}$ abacus pillars formed by an alternative SF_6/O_2 and C_4F_8 plasma etching process. Six tiny beads in a width of 30 nm and a height of 75 nm were generated in one poly-Si abacus pillar. While the abacus bead becomes rounded in shape and smaller in height (~55 nm) in the poly-SiGe pillar because the faster SF_6 plasma etching rate in poly-Ge than in poly-Si, thus resulting in a slightly insufficient sidewall passivation in the pillar sidewall. This also leads to creating more beads (9 beads by 9 cycles of plasma etching) using a pillar in a fixed cycling plasma process.

Figure 3(a) and (b) shows the cross-sectional SEM and TEM images of oxidized poly-SiGe pillar matrix. Figure 3(c) illustrates that a Ge cluster instead of a Ge QD was generated within each bead in the poly-SiGe pillars after thermally oxidizing them at 900 ^oC for 12 min in H_2/O_2 ambient. This probably originates from limited oxidation time and thus insufficient thermal energy provided for Ge atom agglomeration into an equilibrium state. Similar observation has been reported [7, 8] and we expect a prolonged thermal oxidation process will transfer Ge clusters into single-crystalline Ge QDs. The enlarged TEM image in Fig. 3(d) clearly shows that there are tiny Ge nanocrystals randomly distributed within a single Ge cluster in a dot size of 1-2 nm and an effective spatial density of 1.8×10^{13} cm^{-2}, which indicates that such small nanocrystals are in large quantity and sufficient for solar cells and TE applications. Furthermore, Ge nanocrystals have clear lattice fringes with a lattice spacing of 3.2 Å corresponding to Ge {111} planes in the diamond structure.

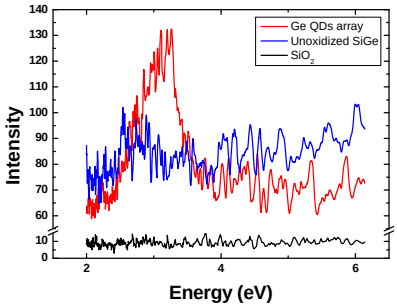

Fig. 4 Room-temperature CL spectra of Ge QDs, poly-SiGe pillar matrix and a bulk SiO_2 film.

Figure 4 shows the CL spectrum of Ge QDs measured at room temperature in the wavelength range of 200-800 nm with a monochromator resolution of 0.3 nm. The CL spectra of poly-SiGe pillars and a SiO_2 film were also plotted for clarifying origin of photoemission. A visible photoemission at 3.3 eV is observed from Ge nanocrystals in the abacus pillars, while no emission signals were discernable in poly-SiGe pillars and a bulk 500 nm SiO_2 film. For reference, our previous work has also reported a systematic blue-shift in the emission peak from 2.5, 2.8 to 3.1 eV as Ge QDs size decreases from 9 nm, 6 nm, to 3 nm. The aforementioned CL results indicate the photoemissive origin predominantly originates from Ge QDs system and the quantum-size effect induced tunable bandgap is a plausible mechanism.

It is noted that small nanocrystals in Fig. 3(d) are closely packed in large quantity, which is beneficial to improve the efficiency of PV and TE devices. This also enables strong electron coupling and intermediate band formation between nanocrystals, so that excitons will have a longer lifetime, facilitating the collection and transport of 'hot carriers' to generate electricity at high voltage and making multiple excitons generation possible from the absorption of a single photon [1, 2]. To realize ideal 'rainbow' solar cells, one common strategy is incorporating closely packed QD in different size into device structure. Large QDs in the top layer absorb photons of relatively long wavelengths, including infrared and some of the visible light. Photons of lower wavelengths pass through the upmost layer into a second and a third ones, which is designed to mainly absorb visible light. Tiny QDs at the bottom layer capture the high-energy photons penetrating the top layers and transform them into electrical power. Optimization of the etching, poly-SiGe deposition and thermal oxidation process conditions would be carried out for producing dense Ge QD arrays with grading size distribution, so that the photovoltaic efficiency could be maximized.

Acknowledgements

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