DIELECTRIC COATED SI OR GE QDS FOR IMPROVEMENT OF SOLAR CELLS

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Introduction

Since Becquerel observed the first photovoltaic effect in 1839, harvesting solar energy has been a scientific and commercial goal.[1] Silicon solar cells are the most widely used solar cells today. However, with their current efficiencies (27%) nearing the theoretical maximum efficiency (31%), researchers are looking for more efficient, less expensive solar cells.

Green and coworkers have proposed an all-silicon tandem cell using an existing silicon solar cell as the bottom layer and silicon quantum dots (QDs) in a silica (SiO_2) matrix as the top layer with a theoretical maximum efficiency of 63%.[2] This idea is very interesting in terms of mass-production, as it incorporates nontoxic and inexpensive materials. If an all-silicon tandem cell is to be produced, the entire process could take place in the same facility because there would be no concern for external contaminants for the silicon wafers instead of having to build a second facility to make the second layer. Green et al. have been trying to produce this by altering the original silicon wafer itself with chemical etching, laser ablation, or co-sputtering silicon and quartz to produce silicon quantum dots within a silicon dioxide matrix, but they have little to no control over the size or spacing of the quantum dots using these techniques.[2]

The research presented here is based on trying to produce an all-silicon tandem cell by synthesizing silicon quantum dots, coating them with silica using a liquid phase deposition (LPD) method, and then arraying the silica coated quantum dots on a silicon wafer (see Figure 1). The quantum dots must be in a silica matrix to produce a quantum well, which facilitates electron-hole separation. The quantum dots cannot be farther than 10 nm from each other to facilitate good electron flow throughout the array.

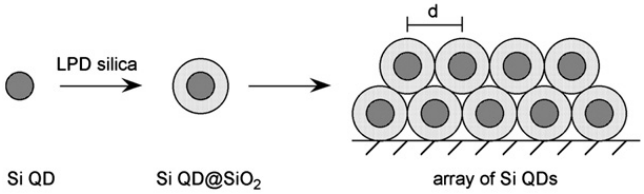

Figure 1. Schematic of the overall goal for this project. (Reprinted with permission from Oliva, B. L.; Barron, A. R. *Mat. Sci. Semicon, Proc.* **2012**, *15*, 713-721. Copyright 2012 Elsevier.)[3]

Experimental

Quantum Dot Synthesis. Both silicon and germanium QDs were synthesized with a "bottom-up" method.[3,4] Because the quantum dots are very oxygen sensitive, the synthesis was completed in a glove box under an argon atmosphere. The QDs were required to be hydrophilic in order to coat them with silica, so an additional step to make these particles hydrophilic was done to cover them with allylamine.[3,4]

Silica Coating. The QDs were coated with silica using two different liquid phase deposition (LPD) methods.[3,5] One method used H_2SiF_6 as the silicon precursor, and the other method was a modified Stöber reaction with TEOS as the silicon precursor. Both methods use low temperatures (25-30°C) to produce the silica coating on the quantum dots.[3,5]

Array of Silica Coated QDs. Once the coated QDs were made, these particles were suspended in water, ethanol, or a mixture of water and ethanol to determine which solvent produced the best film. A quartz slide was submerged vertically in a suspension of the particles, and the solution was allowed to evaporate to produce the array.[3]

Characterization. TEM were performed with a JEOL 2010 transmission electron microscope with a CCD camera. HRTEM was performed on a JEOL 2100 field emission gun TEM with a CCD camera. AFM was performed on a Digital Image Nanoscope IIIA in tapping mode. XPS was performed on a PHI Quantera X-ray photoelectron spectrometer. SEM was performed with an FEI Quanta 400 ESEM FEG scanning electron microscope equipped with an EDAX energy dispersive spectroscope. Photoconductivity of the films was tested with white light and UV light (254 nm) in a circuit that included a voltmeter, a 0.1 Ω resistor, a 9 V battery, and the solar cell on a breadboard.[3,5]

Results and Discussion

The quantum dots were synthesized according to the procedures in literature.[3,4] The quantum dots were then immediately coated with silica. Due to imaging issues, Ge QDs were used for analysis instead of Si QDs to determine if and where the QDs were in the silica particle because silicon inside of silica is difficult to observe. Figure 2 shows a HRTEM image of a Ge QD within a silica particle. Most of the silica particles had multiple QDs within it, which is better for intra quantum dot distances. Figure 3 is the XPS data from these particles, which also shows both silicon (in the form of SiO_2) and germanium (in the form of Ge and GeO_2). The silica coated QDs were originally synthesized using hexafluorosilicic acid as a silicon precursor.[3] This reaction was easy to control in terms of size and shape of the particle with a surfactant (DTAB); however, this reaction produces a toxic byproduct of HF, and Ostwald ripening is observed over time. Because of these drawbacks, another method of coating the QDs with silica was investigated. The traditional Stöber method produces 300 nm silica particles, which is not ideal for this project. However, a modified Stöber method using L-lysine as a bulkier base has been proven to produce 12-20 nm silica nanoparticles.[5] This method produced particles that had <10 nm between each QD in 68% of the sample. Due to the size of the particle, the intra QD distances, and the non-toxicity of the reaction, this method is the preferred method used to coat the QDs with silica.

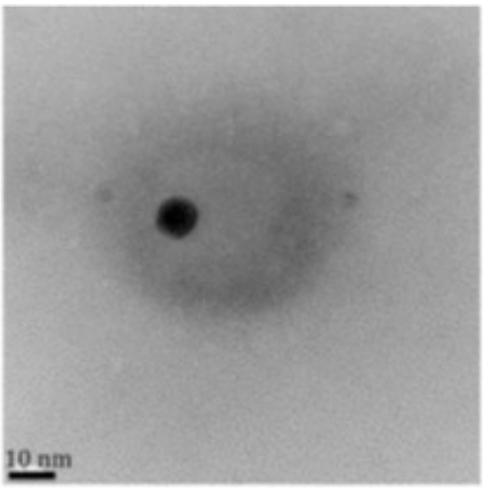

Figure 2. HRTEM image of Ge@SiO_2 nanoparticle. (Reprinted with permission from Oliva, B. L.; Barron, A. R. *Mat. Sci. Semicon, Proc.* **2012**, *15*, 713-721. Copyright 2012 Elsevier.)[3]

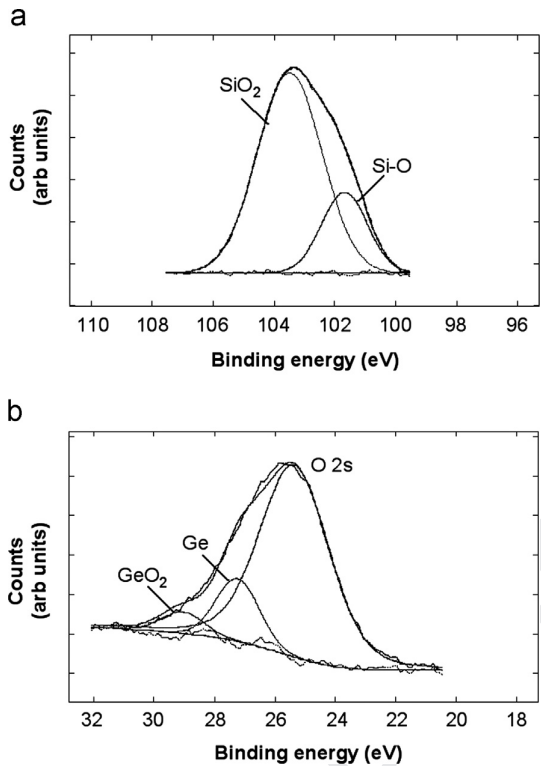

Figure 3. High resolution XPS data of (a) Si 2p and (b) Ge 3d. (Reprinted with permission from Oliva, B. L.; Barron, A. R. *Mat. Sci. Semicon, Proc.* **2012**, *15*, 713-721. Copyright 2012 Elsevier.)[3]

Once the silica coated QDs were successfully synthesized, they were deposited on quartz slides as a thin film using a vertical evaporation technique. Solvents including water, ethanol, and a 3:1 ratio of water:ethanol were tested to determine which would yield more closely packed arrays.[3] The ethanol suspension produced a very sparse deposition of particles on the slide because it evaporated too quickly to allow the particles to arrange themselves on the surface. The water/ethanol mixture was a little bit better in terms of covering the surface of the slide, but the film was not uniform in any direction.[3] Figure 4 shows SEM images of silica coated silicon quantum dot particles deposited from a water-only suspension. These particles were made much larger (150 nm) so the SEM could image the individual particles. From afar (Figure 4a), the film looks very uniform. However, up close (Figure 4b) the film is not quite a close-packed array although it is very near to being so.[3]

The films were then tested for photoconductivity. The particles were deposited on ITO coated quartz slides, and silver paste was used as front and back contacts. White light and 254 nm UV light were both used to test the photoconductivity of the cells.[3] Both Si@SiO_2 and Ge@SiO_2 films were made. With white light, only the Ge QD film showed areas of photoconductivity equivalent to a 2 mA photocurrent.[3] With UV light, both cells produced a greater photoconductivity. The Si QD film showed a change in potential equivalent to a 4 mA photocurrent. The Ge QD film showed a change in potential equivalent to a 7 mA photocurrent.[3] Although the photoconductivity of the cells was variable across the sample surface, these are positive results suggesting that the cells, with further improvement and optimization, could be completely photoconductive.

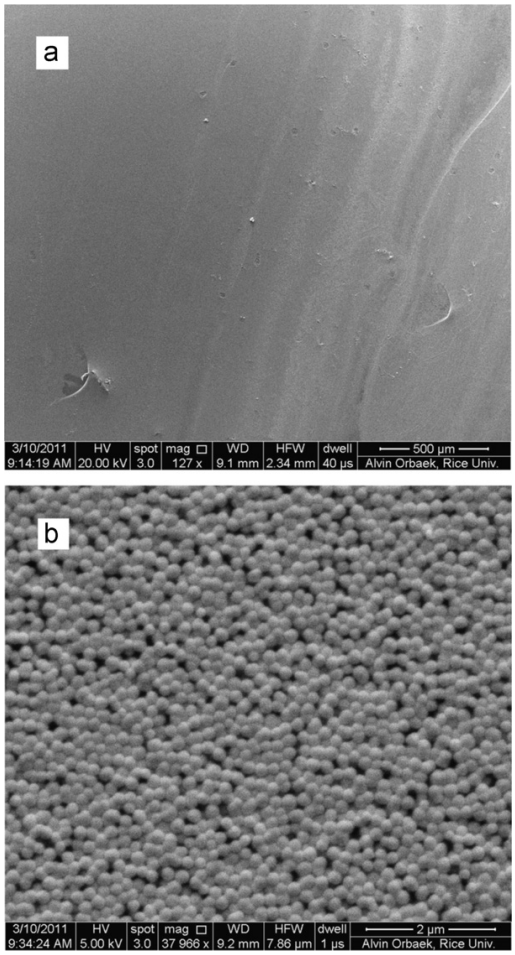

Figure 4. SEM images of Si@SiO_2 films formed from H_2O suspension. (Reprinted with permission from Oliva, B. L.; Barron, A. R. *Mat. Sci. Semicon, Proc.* **2012**, *15*, 713-721. Copyright 2012 Elsevier.)[3]

Conclusions

Si QDs and Ge QDs were successfully synthesized and coated with silica using LPD methods to create Si@SiO_2 and Ge@SiO_2 nanoparticles. The silica thickness could be controlled depending on the LPD method used. A thin film of these particles was made using a vertical evaporation drying technique. Although, the film produced was not a true uniform array, the intra quantum dot distance was small enough (<10 nm) throughout most of the particles, which is important for electron transfer.

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