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# Imbedding germanium quantum dots in silica by a modified Stöber method



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### ABSTRACT

Monodispersed silica nanoparticles 20 nm in diameter were synthesized with germanium quantum dots (QDs) as seeds using a modified Stöber process. The resulting structures comprise of germanium QD core within a silica sphere (Ge@SiO<sub>2</sub>). Films of the Ge@SiO<sub>2</sub> Stöber particles result in an average QD<sup>…</sup>QD distance of 9.6 nm, which is less than the maximum distance required for good electron transfer (10 nm). Thus, this method represents an efficient alternative to the previously reported liquid phase deposition (LPD) of silica on Ge QDs where many silica particles contained more than one QD, resulting in a wide range of QD<sup>…</sup>QD distances.

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### 1. Introduction

Solar energy represents a potential alternative clean energy generation source. Unfortunately, it is presently unable to compete with traditional hydrocarbon combustion in terms of cost per kW/hour. If solar is to compete (in the absence of government subsidies) it must either have a lower cost or higher efficiencies than those currently available. Efforts are ongoing to create low cost solar cells [1–4]. On the other hand one method of improving solar cell efficiency is through the creation of tandem solar cells, which have multiple p-n junctions allowing the absorption of many wavelengths of light [5,6]. The majority of tandem cell designs are based upon III-V semiconductor cells [7]; however, Green and co-workers proposed a unique approach to the inclusion of a tandem layer into first generation silicon solar technology [8–10], by the inclusion of an

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array of semiconductor quantum dots coated within an insulating material. The major drawback with this structure is that fabrication on a large scale is difficult, in particular the control over the QD size and the QD<sup>...</sup>QD distance [8–10]. In seeking an alternative approach, we have recently proposed that if a suitable silicon or germanium QD were coated with a uniform coating of silica (i.e., Si@SiO<sub>2</sub> or Ge@SiO<sub>2</sub>), then arraying the resulting spheres would result in a QD<sup>...</sup>QD distance defined by the coating thickness (Fig. 1) [11].

Our initial attempts involved the coating of hydrophilic Si or Ge QDs with silica using liquid phase deposition (LPD). Unfortunately, while some silica particles were prepared with a single QD inside (e.g., Ge@SiO<sub>2</sub>), others showed evidence for multiple QDs per silica sphere, i.e.,  $Ge_x@SiO_2$  [6]. Furthermore, while films of both Si@SiO<sub>2</sub> and Ge@SiO<sub>2</sub> showed good photocurrent indicating a sufficient number of QD<sup>...</sup>QD distances were within the 10 nm required for electron transfer to be possible [8–10], transmission electron microscopy (TEM) analysis suggested that these were not a majority. A second issue involved the hydrofluoric acid waste produced during the

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Fig. 1. Schematic representation of a bottom-up approach to Ge QD arrays.

LPD process using hexafluorosilicic acid as the silica precursor [12]. What is needed is a method that can reproducibly produce solely individual Si or Ge QDs within single silica particles of a suitable diameter such that thin films will maximize the fraction of QD<sup>...</sup>QD distances that are within the 10 nm limit.

In 1968, Werner Stöber published a method of creating spherical, mono-dispersed silica nanoparticles ranging in size from 50 nm to  $2 \mu m$  [13]. Although mono-dispersed particles are produced using this original method, they cannot be synthesized with small enough diameters for our present application. However, Yokoi et al. have reported that by catalyzing the hydrolysis reaction used to make the silica particles with a bulkier organic base such as L-lysine, mono-dispersed silica nanoparticles as small as 12 nm have been reported [14,15]. Based upon this result, we propose that germanium QDs can be coated with a thin layer of silica by using the modified Stöber method with a bulky base and using the germanium quantum dots as seeds. The results of this study are reported herein.

### 2. Experimental

### 2.1. Materials and methods

Tetraoctylammonium bromide (98%), lithium aluminum hydride (1.0 M in tetrahydrofuran), chloroplatinic acid hydrate (99.9%), allylamine (99+%), and L-lysine (97%) were obtained from Aldrich Chemical Company. Germanium tetrachloride (99.99%) was obtained from Acros Organics. Tetraethoxysilane (TEOS) (99.999+%) was obtained from Alfa Aesar. Ethanol (200 proof) was obtained from Decon Laboratories. Toluene (99.98%) was obtained from EMD, and was distilled under argon prior to use. Methanol ( $\geq$  99.8%) was dried by refluxing over Drierite (CaSO<sub>4</sub>) then distilled over dried 4A molecular sieves, and hexanes ( $\geq$  98.5%, mixture of isomers) were obtained from Sigma Aldrich. Unless noted, the chemicals were used without further purification.

UV–visible absorption spectroscopy was performed with an Agilent 8453 spectroscope. X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantera X-ray photoelectron spectroscope. Silicon wafers cleaned with RCA-I and RCA-II treatments were used as the substrate for film growth [16]. High resolution TEM was conducted using a Jeol 2100 field emission gun transmission electron microscope (200 kV) using CCD camera capture. Hydrophilic germanium quantum dots capped with amines were synthesized using a previously reported procedure [11]. The quantum dots were analyzed with UV–visible spectroscopy using a 1 cm quartz cuvette to verify presence of the quantum dots. Solutions were pale yellow in color and showed an absorption at 260 nm. All reactions were carried out in air unless otherwise noted.

The photoconductivity of the Ge@SiO<sub>2</sub> thin films was tested with white light. Indium tin oxide (ITO) coated glass plates  $(75 \times 25 \times 1 \text{ mm}^3, 8-12 \Omega/\text{sq} \text{ surface resistivity})$  purchased from Sigma Aldrich, were used as the substrate for films of Ge@SiO<sub>2</sub>. The thin film was painted with conductive graphite on part of the plate that was not coated with the film and on spots that were coated to make contacts to complete the circuit [11].

### 2.2. Coating of germanium quantum dots by the unmodified Stöber method

The reaction was carried out in a 100 mL round bottomed flask. Methanol (35.0 mL), Ge QD solution (4.0 mL in DI H<sub>2</sub>O), and ammonium hydroxide (4.0 mL, 32%) were added to the flask and stirred with a magnetic stir bar for 10 min at room temperature. To this was added TEOS (7.0 mL, 31 mmol) drop wise over the course of approximately 5 min. After addition of half of the TEOS, the reaction turned a translucent white. Upon addition of all of the TEOS, the reaction was an opaque white. The reaction was stirred overnight. The particles were washed by centrifugation 3 times each with EtOH and deionized (DI) water. The washed pellet remained opaque white. They were then stored in DI water.

## 2.3. Coating of germanium quantum dots by the modified Stöber method with *L*-lysine

The reactions were all conducted in a 1.5 mL microcentrifuge tubes at room temperature. In a typical reaction hexanes (0.06 mL), L-lysine (1.0 mg, 6.8 mmol), and the quantum dot solution (1.05 mL in DI water) were mixed in the microcentrifuge tube at room temperature for 10 min, followed by a dropwise addition of 0.09 mL TEOS. As an alternative the concentration of QDs was reduced by 50% by the use of 0.52 mL of the quantum dot solution while the total volume of the reaction was maintained by the addition of 0.52 mL DI water. A control reaction was run using hexanes (0.06 mL), L-lysine (1.0 mg, 6.8 mmol), and DI water (1.05 mL) with TEOS (0.09 mL, 0.40 mmol). For all reactions stirring was then followed by a period of 24 h without stirring. The reaction containing the quantum dots

**Table 1**Summary of experiments.

QD solution (mL)	TEOS (mL)	MeOH (mL)	Hexanes (mL)	NH₄OH (mL)	L-lysine (mg)	DI H <sub>2</sub> O (mL)	Time stirred (h)
4.0	7.0	35.0		4.0			12
1.05	0.09		0.06		1.0		12
0.51	0.09		0.06		1.0	0.51	24
1.05	0.09		0.06		1.0		24
	0.09		0.06		1.0	1.05	24



Fig. 2. High resolution TEM image of a typical Ge QD particles.



Fig. 3. UV-visible spectrum of synthesized Ge-QDs.

became cloudy white, and the control remained clear. The reactions were then centrifuged for 10 min. Only the reaction with the quantum dots had any visible sediment, which was a pale yellow. The supernatant liquid was clear, indicating that there was a low to zero concentration of Ge QDs in the liquid. The sediment was washed 6 times with EtOH and 3 times with DI water, and was then stored in DI water. It was a cloudy, very pale yellow. The experiment was also repeated following the same procedure as listed above with the exception that the reactions were only allowed to stir for 12 h prior to sitting for 24 h. A summary of the various reactions is given in Table 1.

### 3. Results and discussion

While the original design of a tandem cell layer by Green and co-workers used Si QDs within a silica matrix due to the method of manufacture [8–10], Ge QDs are ideal for



**Fig. 4.** TEM image of non-uniform Ge QD-SiO<sub>2</sub> composite particles showing the location of the Ge QDs on the surface of the Stöber particles.



Fig. 5. TEM image of  $SiO_2$  particles prepared by the same methodology as used for those shown in Fig. 4.

laboratory experiments because they can be easily produced with inexpensive, clean materials, and their quantum confinement is relatively large (11.5 nm), thus making their production easier than quantum dots with smaller Bohr radii [17]. They also are distinguishable from silica in transmission electron microscope (TEM) images, unlike silicon quantum dots [11]. A representative TEM image of the Ge QDs prepared herein is shown in Fig. 2, while the UV–visible spectrum is shown in Fig. 3.

The particles produced using the unmodified Stöber method were analyzed by TEM. A representative example is shown in Fig. 4, showing that while the reaction produced spherical nanoparticles incorporating the Ge QDs, they appear to be coating the outside of the SiO<sub>2</sub>



Fig. 6. High resolution (a) Si 2p and (b) Ge 3d X-ray photoelectron spectra of  $Ge@SiO_2$  nanoparticles.

particle rather than incorporated within the nanoparticle as intended (i.e., compare Fig. 4 with the ideal structure shown schematically in Fig. 1). Furthermore, these particles are not mono-dispersed, unlike the typical Stöber particles (Fig. 5). This result suggests that the QDs did not seed the formation of the silica nanoparticles. Since these do not meet our requirements, no further analysis of these particles was conducted.

In the case of the Ge QDs coated by the modified Stöber method in the presence of L-lysine, the as prepared samples were analyzed with XPS. The high resolution Si 2p and Ge 3d spectra (Fig. 6a and b, respectively) confirmed the presence of Si–O bonding environment (102 eV), SiO<sub>2</sub> (104 eV), elemental Ge (27.5 eV), and oxidized germanium, GeO<sub>2</sub> (29 eV) [11,18]. The presence of germanium peaks is evidence that the particles were either adhered to the surface or imbedded within the silica. If they had not bonded with (or become imbedded within) the silica particles, they would not be present post washing in the XPS analysis due to their hydrophilic nature.

TEM analysis confirms that the QDs are actually coated with, not just on the surface of, the silica (Fig. 7a and b). However, we note that not all the particles are ideal core shell (c.f., Fig. 1) and some show the presence of a single Ge QD at the edge of a SiO<sub>2</sub> particle. However, the important observation is that the Ge QDs are uniformly dispersed throughout the film rather than aggregated on the surface of SiO<sub>2</sub> particles as seen in Fig. 4. From the TEM images it is possible to determine the nearest neighbor QD QD distances within the films. The distribution for the Ge@SiO<sub>2</sub> particles produced with stirring for 12 and 24 h is shown in Fig. 8a and b, respectively. From this data an average distance of 9.0 nm and 10.3 nm is calculated, showing the ability to control the QD distance through reaction time. As may be expected with increased reaction time, and increased particle size, the standard deviation of the QD QD distance also increases from 2.6 nm to 3.4 nm. Irrespective of reaction time, however, the majority of the QDs are close enough to neighbors to allow electron transport [8-10]. It is also important that the particles have a small size distribution so that they will



Fig. 7. Representative TEM images of Ge@SiO<sub>2</sub> prepared with (a) 12 h and (b) 24 h reactions.



Fig. 8. Distance between adjacent Ge QDs for films deposited of Ge@SiO2 particles prepared with (a) 12 h and (b) 24 h reactions times.



Fig. 9. Particle sizes of the SiO<sub>2</sub> Stöber particles Ge@SiO<sub>2</sub> particles prepared with (a) 12 h and (b) 24 h reactions times.

array with minimal defects. In this regard, the particles are spherical and mono-dispersed. It is interesting to note, however, that with longer reaction times the average particle size for the silica is smaller (see Fig. 9). This suggests that with increased reaction times aging of the silica particles occurs.

The differences between the particles formed by the modified Stöber method in the presence of L-lysine (Fig. 7) and those produced when using the unmodified Stöber process (Fig. 4) indicate that the particles are forming by different growth mechanisms. It is commonly thought that Stöber particles begin through a nucleation process [19]. In the case of the less bulky base, ammonia, the nucleation is less hindered, perhaps not allowing the quantum dots to act as seeds. When using L-lysine, the germanium quantum dots were able to act as seeds, possibly due to the nucleation process being more hindered.

Photoconductivity testing was performed on  $Ge@SiO_2$ films from samples prepared for 24 h. These thin films were grown from aqueous suspension on ITO glass instead of quartz [11]. UV–visible absorbance measurements compared to ITO glass confirmed the presence of the appropriate film. The photoconductivity of the solar cell was tested with white light. As may be expected from the simple test set-up and potential variability of the packing of the particles, the results were only obtained on certain areas of the cell. With white light, the Ge@SiO<sub>2</sub> cell showed areas of photoconductivity as measured by a 6.3 mV change in potential, which equals 6.3 mA of photo-current. This is significantly higher (2 mA) than our previous results for Ge@SiO<sub>2</sub> films prepared using the LPD method, which is consistent with closer (and more consistent) spacing of the Ge QDs (see Fig. 8).

### 4. Conclusions

Germanium QDs were successfully coated with a thin layer of silica using a modified Stöber process with L-lysine. The unmodified process was unsuccessful, indicating that the bulkier base made it possible for the quantum dots to seed the synthesis of the particles. In comparison with our previously reported LPD method, the modified Stöber process produces a more uniform material in which each QD acts as a seed to a silica particle. Most importantly, in thin films of the Ge@SiO<sub>2</sub> particles the majority of nearest neighbor QD<sup>…</sup>QD distances are within the 10 nm limit required for photoconductivity. Finally, the use of the modified Stöber process eliminates the necessity of dealing with the HF waste from the LPD method.

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