Quantum confinement of volume plasmons and interband transitions in germanium nanocrystals

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(Received 2 October 2012; published 17 December 2012)

The plasmonic properties of individual quantum-sized Ge nanocrystals (NCs) were observed and systematically analyzed by aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). For this purpose, Ge NCs embedded in an SiO₂ matrix with controllable size, density, and structure were fabricated using magnetron sputtering. The size dependence of the Ge plasmon energies in the size range of 5–9 nm is shown to be well depicted by the so-called medium quantum confinement (QC) model, with an effective mass of $0.57m_0$ (contrary to expectations of a stronger quantum effect). In the very low-loss region of the EEL spectra, an apparent blue shift of the E_2 interband transition peak up to 2 eV and a strong reduction in the oscillator strength were measured for the NCs in the size range of 4–6 nm. It indicates for this smaller size range a transition to a QC regime where the band structure and the density of states are modified dramatically. These trends are explained by a combination of low-loss and core-loss EELS results, which show that the Ge NCs are surrounded uniformly by nearly stoichiometric SiO₂. This local chemistry is shown to provide an infinite potential barrier and to confine electrons and holes in the spherically shaped Ge NCs. In addition to pure QC effects in the Ge NCs, the SiO₂ matrix thus plays an important role in the strength of the observed QC and interband transitions.

DOI: [10.1103/PhysRevB.86.245316](https://doi.org/10.1103/PhysRevB.86.245316)

PACS number(s): 73.22.-f, 73.21.La, 73.63.Bd

I. INTRODUCTION

Ge and Si nanocrystals (NCs) embedded in dielectric matrices such as SiO₂ have attracted a great deal of attention due to their tailorable electronic and optical properties for a wide range of optoelectronic and solar cell applications.¹ It is well demonstrated that the electronic structure of the valence band and the conduction band are strongly modified in these NCs.^{2,3} For example, by engineering the sizes and morphologies of Si and Ge nanostructures, a widening of effective band gaps and an efficient interband absorption over a certain spectrum range can be obtained.⁴ Therefore, in order to tailor these systems for optoelectronic applications, it is extremely important to understand how their properties evolve as a function of NC size and structure.

If the “particle in a box” model is applied to the aforementioned systems, one would expect the band gap to increase and the characteristic transition energies, such as excitons, to move to higher energies due to the quantum confinement (QC) effects in the confined directions.⁵ The consequences of these effects have been studied extensively by a variety of techniques, including theoretical calculations,^{3,5,6} a combination of low-loss and core-loss STEM-EELS,^{7–9} and x-ray absorption spectroscopy (XAS).¹⁰ More complicated quantum behaviors of different interband transitions away from the Brillouin zone center of Ge atomic-like discrete structures, which cannot be described completely by the “particle in a box” model, have also been studied through optical absorption, Raman scattering, and ellipsometry.^{11,12} Although these optical methods are commonly used to characterize the optoelectronic properties of such systems, the quantitative information they collectively yield is difficult to interpret due to several factors contributing to the uncertainty of experimental results: size dispersion of NCs, different shapes, density, and interface structures of NCs as well as electron, photon, and phonon transfer between NCs.

Consequently, there have been many apparently conflicting reports on these systems. For instance, Tognini *et al.*¹¹ reported absorption spectra from Ge NCs showing a blue shift of the E_2 transition, which occurs near the X point of the Brillouin zone, and a weakening of the E_1 transition, which is along the Λ direction, with decreasing Ge NC size. By contrast, Heath *et al.*¹² studied extinction spectra from Ge NCs and suggested that E_1 and E_2 remain unaffected by QC. Finally, Melnikov and Chelikowsky¹³ calculated absorption spectra of Ge NCs using *ab initio* calculations and showed that both E_1 and E_2 energies are expected to blue shift owing to QC. The discrepancies between the reported experimental results and theoretical calculations demand further investigation in order to predict more accurately the quantum behaviors of these transitions.

One of the most important factors for consideration, when studying QC effects experimentally, is the spread in NC sizes in the samples, which can lead to uncertainties in exciton line positions and widths.¹⁰ Among the variety of available experimental techniques, aberration corrected STEM-EELS is particularly suited to probing the local electronic structure and elemental distribution inside the individual NCs and their surrounding matrices thanks to its key advantage of very high combined spatial and energy resolutions.¹⁴ The low-loss part of the EELS spectrum provides inherent information about plasmon densities and band structures of semiconducting and insulating materials.¹⁵ In addition, the energy-loss near edge structure (ELNES) in core-loss EELS reflects the local density of empty states above the Fermi level, which provides information about the chemistry and bonding of the material under investigation.¹⁶ In the present paper we combine experimental low-loss and core-loss STEM-EELS to study a number of phenomena related to QC in individual Ge NCs embedded in an SiO₂ matrix. The observed phenomena include an apparent blue shift in plasmon energies and an enhancement

of Ge interband transitions with decreasing NC size. In order to facilitate the interpretation of the experimental results, theoretical simulations have also been carried out for similar confined nanostructures to predict possible behaviors of the excitations in the low-loss EELS and thus provide a clearer physical understanding. In addition to the quantum size effects, chemical states and electronic properties of the SiO_2 matrix as well as effects due to changes in the Ge crystal structure are also investigated and discussed.

II. EXPERIMENT

A four-layer structure thin film composed of an SiO_2 buffer layer followed by two SiGeO middle layers with different Ge contents and a capping SiO_2 layer was deposited on a (100)-oriented single-crystal Si substrate by radio frequency (rf) magnetron sputtering in Ar atmosphere. These layers will be hereafter named as layers 1, 2, 3, and 4 for simplicity. Prior to sputtering, the chamber was evacuated to 5×10^{-7} mbar. During the film deposition the Ar pressure in the chamber was kept at 1×10^{-3} mbar. Layers 2 and 3 of SiGeO were obtained by co-sputtering and deposition from SiO_2 and Ge targets without any intentional substrate heating. The different Ge content between these layers was achieved by adjusting the sputtering rate for the Ge target, while the sputtering rate for the SiO_2 target was kept constant. With the purpose of forming Ge NCs in the oxide matrix, the sample was subsequently annealed at 800°C for 1 h in a sealed SiO_2 glass tube evacuated to a vacuum of better than 1×10^{-2} mbar. High-resolution transmission electron microscopy (HRTEM) observations were performed at 200 keV primary beam energy with a JEOL 2010F microscope. The STEM-EELS experiments were performed at 60 keV in a C_s -corrected Nion UltraSTEM¹⁷ equipped with a Gatan Enfina spectrometer. The cold field electron emitter of this instrument has a native energy spread of 0.35 eV, as determined from the full width at half maximum of the zero-loss peak in typical operating conditions. The EELS experiments were carried out with a probe size of 1.1 Å, the collection semiangle was 4 mrad for the low-loss data sets and 32 mrad for the core-loss data sets. The probe convergence semiangle was 30 mrad. Both 2D-EELS spectrum imaging and distributed-dose “SMART EELS”¹⁸ line-scan techniques were employed. The latter was used in order to mitigate the effects of radiation damage and contamination by distributing the electron dose received by individual NCs. Postmortem images were systematically acquired in order to check for possible specimen drift during the data collection and to assess specimen beam damage.

III. RESULTS AND DISCUSSION

A. Structural and chemical characterization

HRTEM imaging and electron diffraction confirmed the formation of Ge NCs in both layers 2 and 3. As shown in Fig. 1, layer 2 has a higher density and bigger grain size of Ge NCs (5–10 nm) than layer 3 (2–5 nm). For both layers, the NCs are nearly spherical in shape and uniformly distributed in the bulk of these layers. The results of quantitative energy dispersive x-ray spectroscopy analysis showed that the concentration of elemental Ge in layers 2 and 3 are 40% and 12%, respectively.

FIG. 1. HRTEM image of the three layers: layer 2 has a higher density and bigger grain size of Ge NCs (5–10 nm) than layer 3 (3–5 nm). The inset shows clear lattice fringes of a Ge NC in layer 2.

Some of the NCs, which precipitated densely in layer 2, are interconnected and/or formed twinning defects, while all of the NCs in layer 3 are well separated and defect-free. In addition, for layer 3 the lattice fringes inside the NCs and the interfaces between them and the matrix were not resolved in the HRTEM images as clearly as those in layer 2. Especially the particles with sizes ~ 2 nm in layer 3 were found to be amorphous, which is in good agreement with XAS results reported by Araujo *et al.*¹⁹ on Ge NCs implanted in an SiO_2 matrix, and molecular-dynamics results for Ge NCs embedded in an amorphous matrix reported by Bording and Taftø.²⁰

It is well known that the optical properties of Si and Ge NCs are strongly affected by the structural and chemical properties of their surfaces since NCs have a high surface to volume ratio.²¹ The interface between a NC and its surrounding matrix can play a crucial role in the optoelectronic properties of the NCs.^{22,23} By analyzing the Si $L_{2,3}$ edge from the core-loss EELS line scans across the surrounding matrix to the NC core, useful information about the local bonding, defect, and chemical state at the site where the atom is being excited can be obtained. Figure 2(a) shows the HAADF STEM survey image of a Ge particle in layer 2 where the trace of a core-loss EELS line scan taken across the particle is marked from A to D. Figure 2(b) shows background-subtracted, averaged EELS spectra of the Si $L_{2,3}$ edge (each spectrum in this figure is an average of 20 adjacent spectra) from the four probe positions indicated in Fig. 2(a). The spectra correspond to the areas marked A to D in Fig. 2(a). Compared to the Si $L_{2,3}$ edge of stoichiometric SiO_2 reported by Erni *et al.*,¹⁶ the four spectra show similar peak energies and ELNES. It is expected that the suboxides (Si^{1+} , Si^{2+} , and Si^{3+}) should show a broad intensity band in front of the Si $L_{2,3}$ edge.^{16,24–26} As seen in Fig. 2(b), no extra intensity in the pre-edge region is observed. The only difference is found in the intensities of the edges, which are as expected higher in the matrix than in the NC core. Therefore the Ge NCs appear to be surrounded uniformly by nearly stoichiometric SiO_2 , and if there is any chemical modification in the matrix [e.g., O deficiency, coexistence of $(\text{SiO}_2)_x(\text{GeO}_2)_y$...], the concentration of any secondary phases must be too low to be detected at the Si $L_{2,3}$ edges.

FIG. 2. (Color online) (a) HAADF STEM survey image of a Ge particle in layer 2 where the trace of core-loss EELS line scans taken across the particle is marked from A to D. (b) Background-subtracted, averaged EELS spectra of the Si $L_{2,3}$ edge from the four probe positions indicated in (a). The spectra correspond to the areas marked A to D in (a), respectively.

A similar behavior was observed for the averaged core-loss EELS line scans across the film structure from layer 1 to 3, at both Si $L_{2,3}$ and O K edges. The intensities of these edges are highest in layer 1 of pure SiO_2 and lowest in layer 2 where Ge NCs precipitated densely. The fact that the similar shape and sharp features of the Si $L_{2,3}$ edge can be observed in the three layers indicates that the suboxide content is negligible and the chemical structure of the matrix, which is stoichiometric SiO_2 , is independent of the Ge content in layers 2 and 3. This information is essential for deconvoluting the contribution of the matrix in the low-loss EELS data that will be discussed in the following section of this paper.

B. Experimental and calculated low-loss EELS

The controllable sizes, spatial distributions, and structures of Ge NCs in layers 2 and 3 allow us to study the size-dependent volume plasmon and interband transition energies of individual NCs in a large range of sizes with different crystal densities and structures under the same experimental conditions. Due to the radiation damage sensitivity of the Ge- SiO_2 system and

in order to improve the signal to noise ratio, the distributed-dose SMART EELS acquisition technique was employed for low-loss EELS. The typical setting of SMART acquisitions is shown in Fig. 3(a), where the HAADF image is marked with the trace of the line scan taken across a Ge NC in layer 2, while the dose is distributed by displacing the probe along the other direction at each point in the line scan, as indicated. Figure 3(b) shows zero-loss peak subtracted (using a power-law function), averaged plasmon EELS spectra from the line scan in Fig. 3(a). Each spectrum in Fig. 3(b) is an average of 20 adjacent spectra (of a line scan containing a total of 150 spectra). The spectra correspond to the areas marked A to C in Fig. 3(a), respectively. Moving from the matrix to the NC core, the plasmon peak shifts to lower energy. The plasmon response of this heterostructure is expected to contain contributions from both the Ge NCs and the surrounding SiO_2 matrix. Therefore, a deconvolution of these broad plasmon peaks is needed in order to identify the individual constituents.⁹ By using the Voigt functional-form fitting method, different component peaks are resolved for spectrum B taken at the NC core as shown in Fig. 3(c). The two main components under the plasmon peak were assigned to the volume plasmons of the Ge NC and SiO_2 matrix respectively. The position of the SiO_2 matrix plasmon was verified independently by acquisition of low-loss EEL spectra from the matrix immediately surrounding each studied NC. The plasmon energy of the matrix was found to be in the range of 23–24 eV. This is in agreement with the core-loss EELS results, which showed that the matrix composition is uniform and is nearly stoichiometric SiO_2 . The remaining components correspond to the broad $M_{4,5}$ ionization edge of Ge NCs at around 29 eV²⁷ and a broad peak with maximum around 6 eV. This peak, seen only in spectra acquired in layer 2 (Fig. 3) and layer 3 (not shown), could have several origins, including interband transitions from Ge NCs, retardation effects, such as Čerenkov radiation and guided light modes, or interface plasmon excitation between Ge NCs and the SiO_2 matrix.

In order to determine the origin of the low-loss peak at 6 eV we performed low-loss EELS calculations for a simplified sandwich structure of $\text{SiO}_2/\text{Ge}/\text{SiO}_2$ as well as for amorphous SiO_2 and Ge of varying thickness, for conditions that reflect

FIG. 3. (Color online) (a) Typical setting of EELS SMART acquisitions for the low-loss line scan, where the HAADF image is marked with the trace of the line scan taken across the Ge NC. (b) Zero-loss peak subtracted, averaged plasmon EELS spectra from the line scan in (a). The spectra correspond to the areas marked A to C in (a), respectively. (c) Different component peaks are resolved for spectrum C taken at the NC core by using the Voigt functional-form fitting method.

FIG. 4. (Color online) Calculated low-loss EELS spectra at 60 kV for four systems: 75 nm of SiO₂, 75 nm of Ge, 5 nm of Ge, and (35 nm SiO₂ / 5 nm Ge / 35 nm SiO₂). For the last three systems, the interband transition ~ 2.5 and 5 eV is well described.

the experimental setup. In these simulations, we use the Ge and SiO₂ bulk dielectric functions,²⁸ and apply the dispersion bracket formalism of Bolton and Chen^{29,30} which allows for calculating surface/interface and bulk plasmons as well as (relativistic) radiation losses. QC effects are not included as they would require corresponding dielectric data.^{31,32} The calculations show that the very low-loss regions (0–10 eV) of the EELS spectra from the Ge and SiO₂/Ge/SiO₂ systems are dominated by interband transitions at ~ 2.5 and 4.8 eV originating from the thin Ge layers (Fig. 4). These features, which are present in the calculated spectra of a pure Ge slab of thickness 75 and 5 nm, respectively (green and dark blue curves), as well as in the spectrum of the sandwich structure of a 5 nm thick Ge slab embedded in 70 nm amorphous SiO₂ (red curve), closely resemble the E_1 (2.3 eV) and E_2 (4.4 eV) transitions reported in bulk Ge.^{33,34} No interface plasmons between SiO₂ and Ge thin layers were predicted by the simulation, implying that there is no strong coupling of the dielectric functions. The fact that the features and intensities of the peak around 6 eV observed experimentally in our spectra do not vary as the beam moves from the particle core to the matrix/particle interface further confirms that these features are not likely related to the interface plasmons. Hence, the experimental data can be interpreted in terms of a superposition of a spectrum that is due to the SiO₂ matrix and another part that is due to the Ge NCs. Moreover, there are no significant peaks present in the calculated spectra that are due to retardation effects such as Čerenkov losses or losses due to the excitation of guided light modes. Indeed, the absence of significant radiation losses can be expected at a primary electron energy of 60 keV. Yet, what cannot be completely ruled out is that residual radiation damage leads to the creation of electronically active defects in SiO₂ that could contribute to the absorption in the sub-10 eV energy range.^{35–37} However, as the spectrum recorded from amorphous SiO₂ does not show significant intensity in the sub-10 eV range, the overall effect of residual radiation damage must be small. Therefore, the

experimental spectra reflect the actual dielectric characteristics of the material (the interband transitions from Ge NCs) rather than the interaction with the matrix or electron beam. It is therefore concluded that the peak observed at 6 eV peak more likely corresponds to the E_2 interband transition, blue shifted with respect to its bulk value.

C. Quantum confinement of E_2 interband transition

The E_1 transitions (~ 2.3 eV) were not observed in our experimental low-loss EELS spectra, possibly due to the weakening of these transitions with the NC size reduction due to a transfer of oscillator strength from E_1 to E_2 transition¹¹ and the potential overlap with the tail of the zero-loss peaks. Furthermore, Guerra *et al.*³⁸ reported density functional theory (DFT) calculations on the absorption spectra of Si NCs embedded in SiO₂ matrix and suggested that the absorption at low energy (< 4 eV) is strongly damped due to the screening induced by polarization effects at the NC interfaces. Therefore, it can be expected that the E_1 transition features tend to vanish in the presence of local field effects at the NC interfaces.

As discussed above, the 6 eV peak can be assigned to the E_2 interband transition, which is one of the most dominant absorption peaks in the visible region reported in the literature.^{11,33,34,39} Figure 5(b) shows the evolution of the E_2 peak position with NC size, as determined by the zero crossing of the first derivative of the low-loss spectrum^{11,33,39} [Fig. 5(a)]. The E_2 peaks show a very strong size dependence in the size range of ~ 4 –6 nm. Radiation damage in the very small NCs does not permit a more detailed study of the behavior of this transition in the size range lower than ~ 4 nm. When the NC size decreases from 6 to 4 nm, a dramatic blue shift of the E_2 peak by ~ 2 eV is observed, in addition to a depression of its features. A similar behavior of this transition in optical extinction spectra was reported by Hayashi *et al.*³⁴ for sputtered Ge NCs embedded in SiO₂ thin films, who suggested that for small Ge NCs (~ 2.7 to 4.2 nm) the whole band structure and the density of states are altered dramatically.

FIG. 5. (Color online) (a) First derivative of E_2 transition peaks of Ge NCs with different sizes. The zero crossing of the curves determines the shift of E_2 peaks. (b) The blue shift of E_2 transitions with decreased NC size.

Compared to the shift of the E_2 transition obtained by *ab initio* calculations of the absorption spectra for hydrogenated Ge NCs reported by Melnikov *et al.*,¹³ our data show a higher shift. This might be attributable to the propensity of local density approximation calculations to underestimate the energy of the E_2 transition.¹³ A smaller shift is also found for the optical absorption data measured from Ge NCs confined in $\text{Al}_2\text{O}_3/\text{Ge}$ multilayer structures by Bottani *et al.*,³⁹ or from Ge NCs embedded in SiO_2 by Hayashi *et al.*,³⁴ albeit with the same trend of size dependence. This can be expected since optical absorption data are acquired with a broader beam over an average of NC size distributions, while our EELS data are obtained directly from individual NCs by using a very small probe size (~ 1.1 Å). The impact of using different dielectric matrices and growth methods on the observed quantum size effects is also very important in the interactions between NCs and matrices, interface structures, induced stress, and local field effects.^{6,38,40,41} As shown by DFT calculations on the absorption spectra of Si NCs embedded in SiO_2 matrix by Guerra *et al.*,³⁸ local field effects cause a blue shift of the main absorption peak (~ 5.5 eV), in particular for small NCs, which show a sensitivity to their surrounding environment related to perturbations of the absorption resonance conditions. Therefore, we suggest that the higher blue shift of the E_2 transition observed in our experiments as compared to other reported data^{13,39} can be attributed to the contribution of local field effects at the interfaces between Ge NCs and the SiO_2 matrix. Crucially, this enhancement of interband absorption with the reduction of Ge NC sizes and the variations of this absorption with the crystal quality suggest a practical way of tuning the efficiency of interband absorptions over certain spectral ranges.

D. Quantum confinement of volume plasmon energy

Depending on the Bohr radius (a_B) and the NC diameter (d), three regimes of QC can be defined by the effective-mass approximation (EMA):^{5,6} weak, medium, and strong confinement (for more details, refer to Refs. 5 and 6). For Ge, a_B is ~ 24 nm, which means that for the size range of Ge NCs in this work (~ 2 –10 nm) the strong confinement regime would be expected. Moreover, the blue shift of the plasmon energies E_P with decreasing particle diameter is attributed to the quantum size effect of the band gap that affects the plasmon energy through the oscillator strength as described by Mitome *et al.*⁴² Experimental EELS data of Si NCs and Ge nanowires have revealed trends of $E_P \propto 1/d^2$ and $E_P \propto 1/d^{1.2}$, respectively.^{8,9,42} Under the same experimental conditions, Si and Ge NCs with similar structure and geometry embedded in a dielectric matrix can be expected to follow the same trend of $E_P \propto 1/d^2$. The size dependence of plasmon energies for Ge NCs (Fig. 6) is plotted against theoretically predicted trends in three different regimes: strong, medium, and weak confinement. The theoretical QC curves follow the $E_P \propto 1/\mu d^2$ relation, where μ is the effective mass of the electron-hole pair in each of these three QC regimes.^{5,42} Overlaying our experimental data points with the theoretical curves, it appears that the strong regime predicted for the NC sizes considered here overestimates the QC effects observed experimentally. The experimental data show instead

FIG. 6. (Color online) NC size dependence of the Ge volume plasmon energy. The dotted-dashed, dotted, and dashed curves show the theoretically predicted $E_P \propto 1/d^2$ relationship in three different regimes: strong, medium, and weak, respectively. The inset shows the data fitting for NCs > 4 nm.

that most of the NCs in layer 2 (> 4 nm) follow closely the medium confinement curve and are best fitted by the equation $E_P = 31.58/d^2 + 15.87$ (see the inset in Fig. 6), which gives an estimated effective mass $\mu = 0.57m_0$, where m_0 is the electron rest mass, consistent indeed with a medium confinement model. By contrast, the NCs in layer 3 (< 4 nm) appear to follow the weak confinement curve, although fewer data points are available. The error bars indicate the accuracy in determining the plasmon shift, which was verified statistically from experiments and the instrument resolution.

While neither case appears to follow the initial theoretical expectation of strong confinement behavior, the observed medium confinement trend for the Ge NCs > 4 nm is in fact in good agreement with the experimental EELS results reported by Mitome *et al.*⁴² for freestanding Si NCs. They also agree with the effective mass theoretical models calculated by Barbagiovanni *et al.*⁶ for Si and Ge NCs embedded in an SiO_2 matrix. The latter were further confirmed by photoluminescence⁴³ and XAS¹⁰ data.

It is of interest to compare the strength of QC effects in the valence band of Ge NCs and of a similar system consisting of Si NCs, as observed through the blue shift of plasmon energies. We recently reported a strong QC in Si NCs embedded in a silicon nitride matrix,⁹ far stronger than the present Ge NCs embedded in an SiO_2 matrix. While this may appear to contradict earlier theoretical calculations⁴⁴ and experimental XAS results¹⁰ (which showed stronger QC effects in Ge than in Si), we believe it illustrates the pivotal role of the matrix used when fabricating these devices.⁴⁵ As suggested by Barbagiovanni *et al.*,⁶ the SiN_x matrix acts as a finite potential barrier, allowing for tunneling of carriers; hence, quantum dots in SiN_x can be described quite accurately by a strong confinement model. By contrast, SiO_2 acts as an infinite potential barrier⁶ and the confinement strength in this system can be expected to be lower. More importantly, recent DFT calculations have shown that in addition to QC effects in small NCs, the matrix must be taken into account when evaluating the resultant energy levels.⁴⁶ With

increasing polarity of the bonds between the NCs and the matrix, there is an increasing dominance of the interface strain over the QC effects. Therefore, we suggest that in the system of NCs embedded in a polar SiO₂ matrix, the QC can be drastically reduced as it competes against interface effects.

A combination of factors is likely to contribute to the observed downward shift in volume plasmon energies for the NCs < 4 nm, from medium to weak confinement. First, it has been reported both experimentally and theoretically that interface states could play an important role in NCs smaller than a critical size (~ 3 nm), whereas the larger crystals simply follow the usual QC model.^{46–48} Second, there are reports of lattice instability, which could cause a structural transition from a diamond-type structure to an amorphous phase in very small crystallites (<3 nm).⁴⁹ As mentioned earlier, the particles with sizes ~ 2 nm observed in layer 3 were found to be amorphous. Bording and Taftø have used molecular-dynamics simulations to predict a critical size of 2 nm for Ge NCs, below which the entire crystal will to some degree be deformed or eventually be assimilated in the amorphous phase.²⁰ This transition would very likely change the physical properties related to the electronic band structure. Calculation of Ge band structure modifications caused by phase transitions (using plasmon energy shifts as an indicator) could further confirm this hypothesis. Finally, the higher density and smaller distance between the NCs > 4 nm in layer 2 could cause stronger coupling effects than in the more sparsely populated layer 3. This could in turn enhance the optical absorption cross sections and the stronger plasmon coupling between NCs could give rise to the stronger confinement trend in layer 2. This suggestion still remains explorative: further experimental and theoretical studies would be required to reach a more certain conclusion.

E. Comment on the band gap of the SiO₂ matrix

Besides pure NC size effects, the chemistry of the matrix can play an important role in the observed quantum size effects in term of potential barrier height. In order to ascertain the presence of any change in the SiO₂ matrix band gap (compared to pure SiO₂) we compared low-loss EEL spectra from layers 1 and 2 [Fig. 7(a)]. Figure 7(b) shows the corresponding zero-loss peak subtracted plasmon peaks, extracted from the SMART line scan at positions A and B [Fig. 7(a)] and averaged over 20 adjacent data points to improve the signal-to-noise ratio. Spectrum A from layer 1 shows a sharp peak at 24 eV corresponding to the plasmon energy of pure SiO₂, while spectrum B from layer 2 shows an asymmetric plasmon peak which is skewed toward the lower energy side, implying a contribution from both Ge and SiO₂ signals. The deconvolution of spectrum B revealed component peaks at 23 and 17 eV corresponding to the plasmon energies of SiO₂ and Ge NCs, respectively. In addition to the distinct plasmon peaks, the very low-loss energy regions from 4 to 11 eV in spectra A and B exhibit significant differences in features and intensities. The visible band gap signal of the stoichiometric SiO₂ in spectrum A is estimated to be at 9.5 eV (from the intersection of a straight line originating from the background level with a linear fit to the onset of the low-loss signal spectrum), while

FIG. 7. (Color online) (a) HAADF-STEM image of layers 1 and 2 with different probe positions labeled from which corresponding averaged low-loss EELS SMART line scans were acquired. (b) Plasmon peaks extracted from the SMART line scan at different positions indicated in (a). The inset shows visible band gap signal of the stoichiometric SiO₂ in spectrum A which is estimated to be at 9.5 eV, while it becomes hardly to recognized in spectrum B. The arrow points out position of the exciton peak observed in both spectra A and B.

it is no longer visible in spectrum B. This can be attributed to the overlap with the E_2 interband transition at ~ 6 eV in front of the band gap onset in spectrum B. Therefore, it is impossible to conclude directly if there is a real change in the SiO₂ band gap energy from layer 1 to layers 2 and 3 or whether this is caused by the contribution of Ge NCs to the low-loss spectra. On the other hand, any change of the characteristic exciton peak around 11 eV¹⁶ just at the band gap signal observed in all of our low-loss EELS spectra might be used as an indirect evidence of a band gap change of SiO₂. The exciton peaks measured in layers 1, 2, and 3 are 11.0, 10.8, and 10.9 ± 0.3 eV respectively. These values compare well with literature data for crystalline SiO₂, which indicate an exciton peak at 10.8 eV.⁵⁰ Thus, if there is a band gap variation of the SiO₂ matrix, it is too small to be detected within our experimental error. This is consistent with the core-loss EELS results, which show that the features and peak energies of the Si $L_{2,3}$ absorption edges of layers 2 and 3 do not change compared to that of the stoichiometric SiO₂ in layer 1.

IV. CONCLUSION

Our studies have shown clear evidence of QC effects on the volume plasmons and interband transitions of individual Ge NCs embedded in an SiO₂ matrix. We have explained some of the discrepancies between earlier theoretical and experimental works on the behavior of the E_2 transition, by demonstrating a blue shift of ~ 2 eV when the NC size decreases from 6 to 4 nm. The theoretical medium confinement curve reproduces well the overall size dependence of plasmon energies, although it appears to overestimate the QC for NCs smaller than 4 nm, which are better described by a weak confinement model. This double regime, as well as the overall weaker confinement effects (a stronger confinement was expected from initial theoretical considerations) can be interpreted as the result of structure reconstruction and enhanced interface effects in the very small NCs. The influence of the SiO₂ matrix on the optical response of the NCs was also investigated. The nearly stoichiometric SiO₂ matrix is found to provide not only an

infinite potential barrier to confine electrons and holes in the spherical shape Ge NCs but also an increasing polarity of the bonds at the interfaces between the NCs and the matrix compared to the SiN_x matrix. These factors are very important to determine the strength of the observed QC and the enhanced interband transitions.

ACKNOWLEDGMENTS

The authors would like to thank the University of Oslo for financial support. The SuperSTEM Laboratory is funded by the UK Engineering and Physical Sciences Research Council (EPSRC).

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