Electronic structure and chemical environment of silicon nanoclusters embedded in a silicon dioxide matrix

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Using photon-in-photon-out soft x-ray spectroscopy, the electronic structure of silicon nanoclusters embedded in an electrically insulating SiO2 host matrix is investigated as a function of nanocluster size. We find the nanoclusters to be of a core-shell structure with a crystalline Si core and a thin transition layer of a suboxide. Effects of electronic quantum confinement are detected in the Si cores. We find that the influence of confined excitonic states manifests itself predominantly in the unoccupied electronic states. © 2006 American Institute of Physics. [DOI: 10.1063/1.2193810]

Often, nanomaterials have to be embedded in a matrix in order to be suitable for technological applications, for example, in order to achieve stability under ambient conditions or in order to interface to other components of an integrated device. In the past, Si nanoparticles were produced in a silicon dioxide matrix by ion implantation, sputtering of Si rich oxides, reactive evaporation of Si rich oxides, and high temperature annealing of SiO/SiO2 superlattices. While the optical properties of such structures are accessible by optical spectroscopy in the visible or infrared spectral range, the underlying electronic structure is difficult to probe directly. The electrically isolating glass matrix hampers efforts to perform transport measurements, tunneling spectroscopy, or photoelectron spectroscopy. We report on a direct and nondestructive investigation of the electronic structure of Si nanoclusters in a SiO2 matrix by photon-in-photon-out soft x-ray spectroscopy.

Si nanocluster/nanocrystal arrays in SiO2 with a narrow size distribution have been prepared by growth of a SiO/SiO2 superlattice with subsequent annealing, as reported by some of us earlier. Annealed samples initially consisting of 45 periods of SiO(d)/SiO2(5 nm), d = 5, 4, 3, 2 nm, on a quartz substrate have been investigated. Soft x-ray spectroscopy has been carried out at BESSY. The electronic density of states (DOS) with s or d symmetry locally at the excited atoms is measured by soft x-ray emission spectroscopy (SXE) for the occupied states and by soft x-ray absorption spectroscopy (SXA) for the unoccupied states. The incident photon energy resolution was set to 50 meV. As the Si 2p3/2 and Si 2p1/2 binding energies increase by 1 eV for each silicon-oxygen bond formed as compared to bulk silicon, this energy resolution allows us to selectively excite pure silicon or different oxides. The fact that we can obtain local information and excite with chemically sensitivity allows us to analyze the electronic structure in the Si nanoclusters separately from the suboxides and the SiO2 matrix. SXE is detected in a Rowland spectrometer with an energy resolution of 300 meV. We measure the SXA spectrum with 50 meV resolution via the partial fluorescence yield (PFY) detected in the Rowland spectrometer. This mode of operation is tedious but absolutely crucial in this material system due to the possibility to discriminate against diffuse, elastic scattering of the incident beam. Without this suppression, the energy dependence of the reflectivity dominates the fluorescence yield.

Si nanoclusters are formed upon annealing of the SiO/SiO2 superlattices. As we will show below, the spectroscopic evidence in this work indicates that the core of the particles consists of crystalline Si. Nevertheless, on the length scale of a few interatomic distances a transition between the Si core and the surrounding SiO2 has to occur, and we can expect local configurations corresponding to suboxides to be present. We denote such configurations as Si–SiOx–y, with x describing the first nearest neighbor silicon and oxygen occupancy for a given, fourfold coordinated Si atom. Over this transition layer with possibly varying x, the electronic structure will vary. The thickness and composition of this transition layer thus determine the effective potential well confining electrons and holes in the nanoclusters, which is of basic importance for the resulting optoelectronic properties.

Series of SXE spectra as a function of incident photon energy were recorded for all samples; in Fig. 1 we present data for the sample with an initial SiO layer of 4 nm thickness. With an excitation energy of 100.0 eV the 2p3/2 core level of crystalline Si can be exited. The SXE spectrum resembles the spectrum for crystalline Si (dashed line). The deviation between the SXE spectrum for the nanoclusters and crystalline silicon in the region around 96 eV emission energy can to some extent be explained by momentum conservation effects which emphasize specific parts in the Brillouin zone. Such effects can be expected to be reduced when the electronic wave functions are confined to regions of a few nanometers in size. On the other hand, the spectrum of the nanoclusters is distinctly different from the one for amorphous silicon, where the peaks at 89.5 and 91.5 eV emission energies merge to one structure due to the lack of long range order. These findings demonstrate that from the viewpoint of the resulting electronic structure, the core of the nanoclusters is not amorphous, but has a high degree of crystallinity. This result is in agreement with high resolution transmission electron microscopy images.
At an incident photon energy of 100.6 eV the Si $2p_{1/2}$ level can be excited in addition to $2p_{3/2}$. With further increase in the primary energy, Si atoms with oxygen neighbors will be excited. The SXE spectra then are a superposition of the valence band emission from all Si atoms with a $2p$ binding energy below the excitation energy. The spectra with excitation energies 100.6 and 101 eV are virtually identical, indicating that suboxides with stoichiometry Si–Si$_x$O$_{1-x}$ are not present. A slight change of the emission spectrum can be observed when raising the excitation energy to 102 eV. Spectra excited at 103 and 104 eV are significantly different from the low energy excited spectra. They cannot be described by a superposition of the spectrum excited at 101 eV and the SiO$_2$ spectrum, which is obtained for excitation energies $\approx$108 eV, when Si in the stoichiometric SiO$_2$ matrix is excited. This spectral shape suggests the presence of small amounts of suboxides with a stoichiometry Si–Si$_x$O$_{1-x}$, $x \approx 2$. We observe this general behavior for the all samples with different Si nanocluster sizes.

We estimate the amount of suboxide around the Si core by evaluating their respective contributions to the SXE spectra on the basis of their different spectral shapes. We make the approximation that the Si L fluorescence efficiency of the oxides and of pure Si is proportional to the number of silicon atoms per unit volume in these materials. The results of this procedure are listed in Fig. 1. Assuming that the final structure has a total diameter equal to the initial thickness of SiO layer, we obtain the sizes of Si cores and suboxide layers for the samples, as summarized in Table I. They are in agreement with the results published earlier reporting a decreasing size distribution for decreasing size.$^{5,6,10}$ The absolute suboxide thickness is in agreement with imaging results on virtually identical samples$^{14}$ and on silicon nanocrystals grown by similar thermodynamic principles as our samples but not from layered precursors.$^{15}$

We now focus on the details of the electronic structure within the Si core of the nanoclusters as a function of nanocluster size. Results on annealed samples with 5, 4, 3, and 2 nm initial SiO layers for 100.5 eV incident photon energy are presented in Fig. 2(a). As only $2p$ core levels of Si atoms without oxygen neighbors are excited the spectra reflect the occupied $s/d$-DOS of the Si nanocluster core. The $s/d$-DOS observed for the nanoclusters of all sizes indicate the presence of crystalline Si, with its characteristic three-peak structure. The detailed shape of the spectra differs from the SXE spectrum of the crystalline Si wafer and changes with the particle size. The peak around 95 eV emission energy is more “steplike” in the Si nanoclusters as compared to the “peaklike” shape in bulk crystalline Si. Similar changes in the SXE spectral shape have been observed for nanoporous silicon in the past, where they could be attributed to changes in the $s/d$-DOS due to quantum confinement.$^{16,17}$ We note the existence of an inelastic feature on the low energy side of the elastically scattered x rays, which also exists in pure quartz. This feature makes a quantitative determination of the energy of valence band maximum in the nanoclusters difficult. Nevertheless it is clear from the spectra that the position of the valence band maximum moves to the lower energies with decreasing particle size, as expected in a quantum confinement model. We estimate the maximum shift, seen in the 2 nm sample, to be 0.5±0.1 eV relative to bulk silicon, while the shift in the 3, 4, and 5 nm nanocluster samples amounts to 0.3±0.1 eV. These findings are in good agreement with the diameter dependence obtained for passivated silicon nanocrystals on a germanium surface.$^{18}$

The PFY-SXA spectra as a function of particle size are presented in Fig. 2(b). Geometric fluorescence yield saturation effects$^{19}$ influence the spectral shape to some extent but are kept constant, so that spectra of different samples can be directly compared. In spite of the limited signal to noise ratio in the nanocluster spectra, some conclusions can be drawn. The Si $2p_{3/2}$-$2p_{1/2}$ spin orbit splitting of 0.6 eV which is clearly visible in bulk crystalline silicon (edge inflection points at 99.8 and 100.4 eV) can still be observed in the Si nanocluster samples down to the smallest size. This indicates

![FIG. 1.](image1) (Color online) Series of SXE spectra as a function of incident photon energy recorded for the sample with an initial SiO layer of 4 nm thickness. The intense elastic peaks are clipped for clarity. For 100.0 eV excitation energy the SXE spectrum for a bulk Si has been added for comparison (dashed line). The inset displays schematically how the as grown Si/SiO$_2$ multilayer structure (top) is converted into Si nanoclusters embedded in a SiO$_2$ matrix upon annealing (bottom), as described in detail in Ref. 5. The Si–Si$_4$ contribution to the total emission spectrum is listed on the right.

![FIG. 2.](image2) (Color online) (a) SXE spectra excited at 100.5 eV and (b) PFY-SXA spectra are presented as a function of nanocluster size: 5 nm (red), 4 nm (blue), 3 nm (orange), and 2 nm (green) are the initial thicknesses of the SiO layer. A spectrum of bulk crystalline Si (black) has been superimposed for comparison. Vertical lines mark the VB and CB edges of the bulk crystalline Si. Elastic peaks in SXE spectra are clipped for clarity.

### TABLE I. Size dependent compositional and geometric parameters of the silicon nanocrystals as determined from the SXE spectra.

<table>
<thead>
<tr>
<th>L$_{\text{SiO}}$ (nm)</th>
<th>Si-core contribution (%)</th>
<th>Suboxide content (%)</th>
<th>$D_{\text{Si-core}} \pm 20%$ (nm)</th>
<th>Suboxide thickness $\pm 20%$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>77</td>
<td>37</td>
<td>4.0</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>79</td>
<td>35</td>
<td>3.2</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>77</td>
<td>37</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
<td>30</td>
<td>1.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>
that inhomogeneous broadening, e.g., due to particle size variation, is small. The most obvious change in the PFY-SXA spectra is a shallower onset in the nanocluster samples. Again, this behavior is identical to porous silicon and silicon nanoclusters on surfaces. In contrast to the case of porous silicon, we cannot detect a quantum confinement shift of the conduction band minimum with decreasing nanocluster size. In a simple quantum confinement model based on the effective masses of the bands in crystalline silicon and using experimental findings for porous silicon and deposited nanocrystals, one would expect about one-third of the total increase in band gap to be due to a conduction band shift. An effect of this magnitude should be clearly detectable by our PFY-SXA measurements. In contrast, we observe the onset of the absorption edge for the 3 and 2 nm samples at about 90 and 140 meV lower photon energies as compared to the bulk silicon crystal, respectively. In combination with the effects in the valence band, this still amounts to an increase of the total band gap by 0.36±0.1 eV over the value for crystalline bulk silicon for these samples. This is in agreement with a shift of the photoluminescence peak positions of 0.35 eV when going from 5 nm to 2 nm particles in our samples. The fact that this shift is almost entirely due to a change in the occupied electronic states within the Si core is surprising and incompatible with a simple quantum confinement model based on the bulk Si band structure. We rule out that the possible presence of strain in the clusters is responsible for this effect, as the conduction band edge in 0.4% biaxial strained Si on SiGe is shifted to higher energies by 40 meV (not shown).

In the following, we discuss if excitonic effects can explain our observations. The existence of core excitons is in line with the population of valence excitonic states upon optical pumping. Interaction between the electron excited into the conduction band and the core hole will lower the total energy of the electronic system. For hydrogen passivated Si quantum dots in vacuum, excitons were found to be confined by the quantum dot dimension for diameter $D < 4$ nm. For Si, the associated energy reduction due to Coulomb interaction in the excitonic state can be parametrized as $E_C = 1/D^2$ 454 (meV/nm) when the dielectric constant $\varepsilon = 11.4$ of bulk Si is used. A smaller effective dielectric constant in nanoclusters will lead to a correspondingly larger energy contribution. An additional energy correction is obtained upon inclusion of the image contribution to the exciton binding energy and the dielectric constant for SiO$_2$ in the theory, as listed in Table II. Apparently, the interplay of the band structure and size of our Si nanoclusters is such that excitonic and quantum confinement contributions are of similar size and can thus approximately cancel each other with respect to the position of the conduction band minimum, as predicted earlier for free, hydrogen passivated clusters. Details of the concept of the dielectric constant and its magnitude in nanosized structures are still a matter of recent theoretical debates and the immobility of the core hole is not taken into account in the current model. Interestingly, the x-ray absorption edges of nonembedded nanostructures such as porous silicon and hydrogen passivated nanoclusters show a stronger size dependent shift to higher energies as observed here, while the changes in the occupied states are in agreement, suggesting a possible influence of the nanocrystal to matrix interface on the exciton properties in the silicon core.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
$D_{\text{Si}}$ (nm) & CBM shift & $1/3$ QC & $E_{\text{exc}}$ & $E_{\text{exc}}$ & $E_{\text{exc}}$ \\
\hline
 & & & $\varepsilon_{\text{bulk}}$ & $\varepsilon_{\text{nan}}(D)$ & $\varepsilon(SiO_2)$ \\
\hline
4.0 & 0 & 0.10 & -0.11 & -0.14 & -0.19 \\
3.2 & 0 & 0.15 & -0.14 & -0.18 & -0.24 \\
2.4 & -0.09 & 0.38 & -0.19 & -0.27 & -0.34 \\
1.6 & -0.14 & 0.60 & -0.28 & -0.48 & -0.62 \\
\hline
\end{tabular}
\caption{Comparison of the experimental shift of the absorption edge (a) with the theoretical calculations: quantum confinement prediction in effective mass approximation assuming infinite barriers and no excitonic contribution (b); exciton contribution, without (Ref. 21) (c) and with (Ref. 22) (d) size dependent dielectric constant within the nanocrystal; exciton contribution including the image contribution to the exciton binding energy and $\varepsilon(SiO_2) = 3.9$ (e) (Ref. 25). The excitonic contributions have to be subtracted from column (b) for comparison with the experimental result in (a). All energies are in eV.}
\end{table}