Strong quantum-confinement effects in the conduction band of germanium nanocrystals

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Quantum-confinement effects in the conduction band of deposited germanium nanocrystals are measured to be greater than in similar-sized silicon nanocrystals. The germanium particles are condensed out of the gas phase and their electronic properties are determined with x-ray absorption spectroscopy. The conduction band edge shifts range from 0.2 eV for 2.7 nm particles up to 1.1 eV for 1.2 nm particles. © 2004 American Institute of Physics. [DOI: 10.1063/1.1751616]

Over the last decade nanometer-sized structures have attracted tremendous interest due to their size-dependent properties.1 Germanium nanocrystals embedded in SiO 2 matrices have drawn significant attention since their blue luminescence was first reported.2 However, the source of the luminescence has been questioned in recent calculations, which suggest that germanium and silicon nanoparticles should exhibit a similar band gap due to structural changes in the Ge conduction band.3

It is known that the electronic structure of germanium nanocrystals upon size reduction. Various calculations suggest strong confinement in Ge and thus a critical particle size, below which the band gap of germanium becomes larger than that of silicon.4-7 These predictions have been questioned in recent calculations, which suggest that germanium and silicon nanoparticles should exhibit a similar band gap due to structural changes in the Ge conduction band.8

Little is known about the electronic structure of germanium nanocrystals upon size reduction. Various calculations suggest strong confinement in Ge and thus a critical particle size, below which the band gap of germanium becomes larger than that of silicon. These predictions have been questioned in recent calculations, which suggest that germanium and silicon nanoparticles should exhibit a similar band gap due to structural changes in the Ge conduction band.8

To date, no experimental investigations exist which can unambiguously identify quantum-size effects at the conduction band edge of germanium nanocrystals. Moreover, the theoretical approaches to this matter are contradictory. The present experiments focus on probing the size-dependent electronic structure of germanium nanocrystals with synchrotron radiation based x-ray absorption (XAS). This technique has been previously shown to be very powerful to study the conduction band of reduced-dimensional structures.9 It allows the independent investigation of the conduction band edges, not possible with optical spectroscopy techniques. Consequently it is possible to unambiguously identify the origin of changes in the electronic structure, and to answer the questions concerning the extent of quantum confinement in germanium nanocrystals and its comparison to silicon.

The germanium nanoparticles are condensed out of the gas-phase and subsequently deposited in situ at the synchrotron facility.10 Their average size can be tuned from 1 to 5 nm and they exhibit a narrow size-distribution of 20% full width at half maximum (FWHM) as determined by atomic force microscopy.11 As substrates, HF-etch cleaned silicon wafers are used for the XAS measurements. The produced films consist of randomly scattered, individual, and nontouching particles. Structural analysis of nanoparticles reveals the bulk-like cubic (diamond) crystal structure.10

The electronic structure of the deposited nanocrystals is probed with XAS at the high resolution and high flux undulator beamline 8.0 of the Advanced Light Source at the Lawrence Berkeley National Laboratory.11 In XAS a Ge 2p core electron is excited into the empty states of the conduction band. The conduction band minimum has both, s- and p-like contributions12 and hence the excitation of a p electron into the bottom of the conduction band (CB) is dipole allowed. If the conduction band minimum of the clusters shifts to higher energies by $\Delta E_{\text{CB}}$ due to confinement effects in the nanoclusters, the absorption threshold will also shift by $\Delta E_{\text{CB}}$ to higher energies. The experimental resolution of the absorption measurements at the Ge L edge (around 1219 eV) is approximately 0.3 eV,11 small enough to permit observation of small CB shifts in our clusters. It should be noted that this resolution describes the experimental, i.e., gaussian broadening of the spectra. Peak positions can be fit and compared with higher accuracy. In Fig. 1 the XAS data of a Ge bulk crystal reference and three nanocrystal samples with decreasing average sizes are shown. The absorption edge is blueshifted with decreasing particle size, consistent with the predictions of the quantum-confinement model. The nanocrystal edges are slightly broadened with respect to the bulk and their density-of-states features are washed out. This effect was observed in earlier experiments on Si nanocrystals, where it had been attributed to the particle size distribution.9 Each individual cluster size contributes with its distinct quantum shift to the overall absorption edge, resulting in an edge broadening. None of the reported fingerprints for oxide...
FIG. 1. X-ray absorption spectra of a Ge bulk crystal and three nanocrystal samples. The XAS edges of the nanoparticles are blueshifted with respect to the bulk edge. The arrows indicate the inflection point of each absorption edge.

In Fig. 2 the data points from the XAS experiments for the Ge conduction band shifts are summarized. For comparison previously published silicon data points are added to the graph. In case of Ge the conduction band shifts range from $0.2 \pm 0.1$ eV for $2.7 \pm 0.3$ nm particles up to $1.1 \pm 0.2$ eV for $1.2 \pm 0.4$ nm particles. The error bars in $x$ indicate the FWHM of the particle size distributions. The larger error bars for the 1.2, 1.6, and 1.8 nm XAS data are due to a wider FWHM of the size distribution for these samples which were condensed in an Ar buffer. The error bars in $y$ indicate the uncertainty in determining the edge shift. The Si conduction band shifts range from $0.1 \pm 0.1$ eV for $2.8 \pm 0.3$ nm particles up to $0.4 \pm 0.1$ eV for $1.1 \pm 0.2$ nm particles. The observed shift of the Ge conduction band edge is larger than the shift of the Si conduction band edge over the complete range of investigated particle sizes. Additionally the quantum confinement effects in Ge are increasingly stronger than in Si. The difference between the Ge and Si conduction band edge shifts grows from $0.1$ eV for $2.7$ nm particles up to $0.7$ eV for $1.2$ nm particles.

In a previous optical study on chemically prepared germanium and silicon nanocrystals, stronger quantum confinement for specific optical transitions from the upper split-off conduction band to the valence band at $\Gamma$ in germanium with respect to silicon nanocrystals were observed. However, no conclusions could be drawn about the extent of quantum confinement at the band edges. In other studies about the optical properties of germanium nanocrystals embedded in a SiO$_2$ matrix ambiguous results were obtained. It was later concluded that the optical properties of these systems were dominated by interface and defect states. In the present study, relying on synchrotron radiation based spectroscopy techniques, the conduction band edges are investigated independently and the whole particle electronic structure is probed. Thus, we were able to conclusively show that germanium exhibits stronger quantum confinement at the conduction band edge than silicon.

From a theoretical point of view there is an ongoing and vibrant discussion about quantum confinement in germanium nanocrystals. Two independent empirical tight binding calculations, which have been able to describe silicon systems well, are in good agreement with the obtained experimental results on germanium. They both predict stronger quantum confinement effects in Ge compared to Si. However, these calculations are tailored to describe the optical properties of nanocrystals involving valence excitons. Therefore, they are not able to predict the behavior of the conduction band edge for decreasing particle sizes. In contrast to these tight binding calculations, another theoretical approach utilizing the empirical pseudopotential method predicts that the band gap of germanium and silicon should be similar upon size reduction. The predicted similarities in the electronic structure of Si and Ge are explained with size-dependent structural changes in the conduction band of germanium: the conduction band minimum is found to move from the $L$ point to the $X$ point for reduced particle sizes and thus the germanium conduction band minimum becomes silicon-like for small sizes. In our experiments we always find stronger quantum confinement effects for germanium compared to silicon upon size reduction (Fig. 2) what is in contrast to these EPM calculations. The conduction band minimum of germanium shifts from $0.2$ eV for $2.7$ nm particles up to $1.1$ eV for $1.2$ nm particles (Fig. 2), compared to $0.1$ up to $0.4$ eV for similar particle sizes in the case of silicon. However, the experimental data allows only statements about the absolute conduction band shift and none about the possible existence of the $L$-to-$X$ crossover in Ge.

In this context it should also be mentioned that both the cubic and tetragonal phase have been suggested for Ge nanoparticles. The creation of either phase has been explained with the employed synthesis routes. The presently investigated samples have been shown with electron diffraction to be in the cubic phase for particles above $3$ nm and for smaller sizes no indications for phase transitions, monitored by Ge 3$d$ core level photoemission, have been found.

On a final note an estimate for the overall band gap behavior shall be done. It has been reported experimentally...
and theoretically\textsuperscript{16} that the band gap in semiconductor nanocrystals opens with a fixed ratio of the valence to the conduction band edge shift $\Delta E_{\text{VBM}}: \Delta E_{\text{CBM}}$. This ratio was determined experimentally for Si nanocrystals to $\Delta E_{\text{VBM}}: \Delta E_{\text{CBM}}^{\text{Si}} = 2$ and for Ge theoretically to be $\Delta E_{\text{VBM}}: \Delta E_{\text{CBM}}^{\text{Ge}} \approx 1$. The overall nanocrystal band gap can be extrapolated from this ratio and the well-known bulk band gap according to $E_{\text{gap}}^{\text{NC}} = E_{\text{gap}}^{\text{bulk}} + \Delta E_{\text{CBM}} + R \Delta E_{\text{CBM}}$ with $R = 2$ for Si and $R = 1$ for Ge. Using the quantum shift data from Fig. 2 for 1.2 nm particles a nanoparticle gap of 2.4 eV results for Si and a gap of 3.0 eV results for Ge. This estimate shows that the band gap of Ge may become larger than that of Si upon size reduction what is expected to have a significant impact on the importance of Ge as a material for reduced-dimensional structures.

In conclusion strong quantum confinement effects in the conduction band of deposited germanium nanocrystals have been observed. With respect to the bulk value the conduction band edge of germanium has been determined to shift from 0.2 eV for 2.7 nm particles up to 1.1 eV for 1.2 nm particles. In the range of investigated particle sizes the quantum size effects of Ge nanocrystals are always stronger compared to Si particles of similar size. These results reveal that germanium nanocrystals exhibit a high tunability of their electronic properties making them a promising material for potential optoelectronic applications.

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