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Quantum Confinement in Germanium Quantum Dots Observed by Electron Energy-Loss Spectroscopy

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Germanium quantum dots (Ge QDs) embedded in dielectric matrices such as silicon dioxide, 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 QDs [2]. In order to tailor these systems for optoelectronic applications, it is extremely important to understand how their properties evolve as a function of QD size and structure. Motivation for our work are recent advances in aberration-corrected Scanning Transmission Electron Microscopy (STEM) and Electron Energy Loss Spectroscopy (EELS) that allow the investigation of electronic structures and chemistry of materials with sub-angstrom spatial resolution. We present direct observation of quantum confinement (QC) effects in the electronic structure of size-controlled Ge QDs in a silicon dioxide thin film matrix [3]. The film was grown by magnetron sputtering and subsequently annealed in vacuum condition at 800 ^{o}C. The size, density and structure of the precipitated Ge QDs were controlled by varying Ge content in different layers of the film (Fig 1).

For the first time, we present changes in volume plasmon and interband transition energies of individual Ge QDs to their size and structure. Changes in the band gap structure of the QDs arising from QC can be observed by shifts to higher energies (blue-shift) of volume plasmon and interband transition energies with decreasing QD size. The shifts in the plasmon energies (Figure 2a) and the E_2 interband transition (Figure 2b), acquired within individual QDs, are showing a direct correlation to their size and structures (Figure 1). We show that the volume plasmon energy E_p (eV) is related to the size d (nm) of Ge QDs by $E_p = 15.87 + 31.58/d^2$ (see the inset in Figure 2a), which gives an estimated effective mass $\mu = 0.57m_0$, where m_0 is the electron rest mass, consistent with the so-called medium confinement model. 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 QDs in the size range of 4–6 nm. This indicates that for this small size range there is a transition to a QC regime where the band structure and the density of states are modified dramatically. We also highlight the important role of structure reconstruction and enhanced interface effects between the very small Ge QDs and the matrix, which is a likely cause of discrepancies between several publications presenting theoretical calculations and experimental works. Crucially, the observed variation of Ge band structure via engineering the QD size, structure and the matrix composition suggests a practical way of tuning the efficiency of optoelectronic devices.

References

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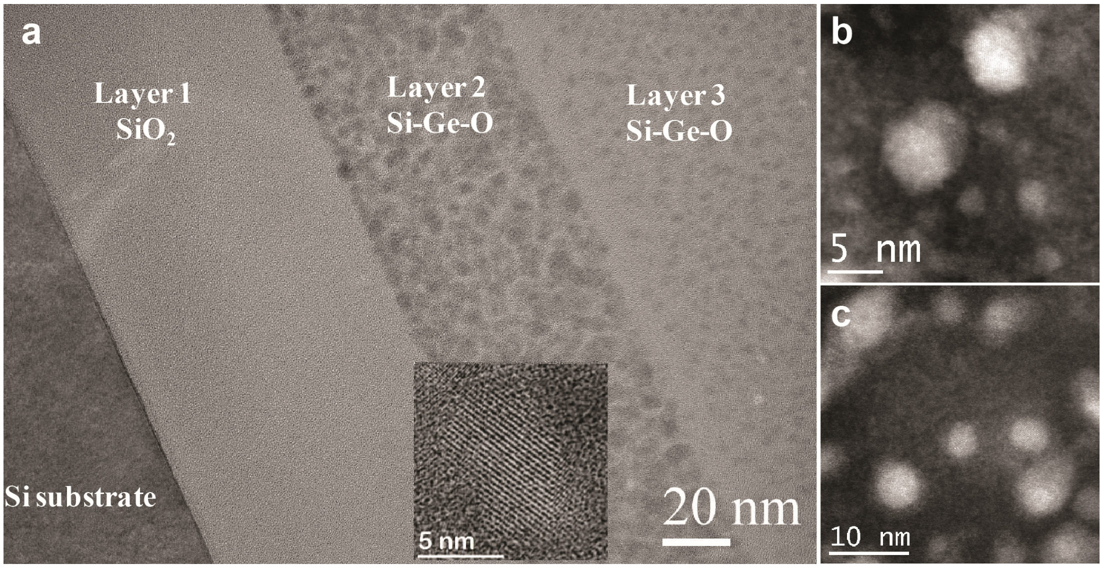

Figure 1. (a) Cross-sectional high-resolution transmission electron microscope image showing the sample structure: layer 2 has a higher density and bigger grain size of Ge QDs (5–10 nm) than layer 3 (3–5 nm). The inset shows clear lattice fringes of a Ge QD in layer 2. (b) and (c) High-angle annular dark-field (HAADF) STEM images of Ge QDs in layer 2 and 3, respectively.

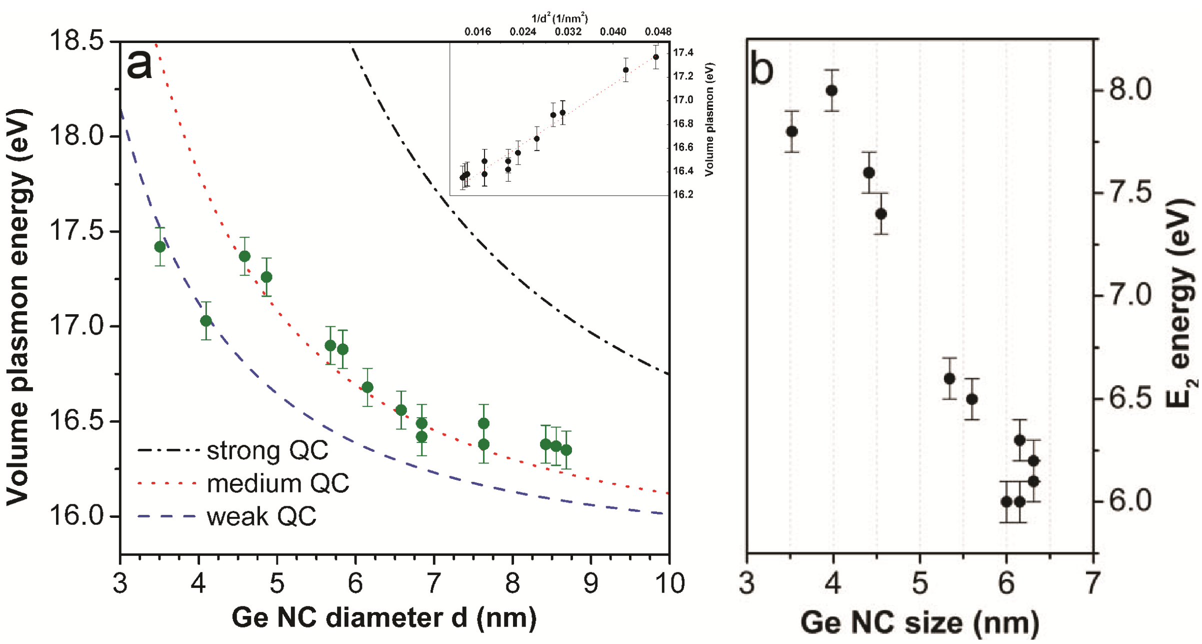

Figure 2. (a) QD size dependence of the Ge volume plasmon energy, extracted from low loss EELS spectra acquired at the cores of individual Ge QDs. The dotted-dashed, dotted, and dashed curves show the theoretically predicted $E_P \propto 1/d^2$ relationship in three different regimes: strong, medium, and weak quantum confinement, respectively. The inset shows the data fitting for QDs with diameters > 4 nm. (b) The blue shift of E_2 transitions with decreased QD size.