Size-suppressed dielectrics of Ge nanocrystals: skin-deep quantum entrapment

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Although the dielectric behavior of nanostructured semiconductors has been intensively investigated, the physics behind observations remains disputed with possible mechanisms such as quantum confinement and dangling bond polarization. Here we show that theoretical reproduction of the measured dielectric suppression of Ge nanocrystals asserts that the dielectric suppression originates from the shorter and stronger bonds at the skin-deep surface, the associated local densification and quantum entrapment of energy. Coordination-imperfection induced local quantum entrapment perturbs the Hamiltonian that determines the band gap and hence, the process of electron polarization consequently.

Introduction

Recently, much limelight has been given to germanium nanostructures (nc-Ge) due to its unique properties which are promising for applications in optoelectronic devices as well as memory devices. By miniaturizing the three dimensions of Ge to nc-Ge, properties of nc-Ge that vary from bulk Ge can be unleashed. For applications such as memory devices, nc-Ge is usually embedded in the gate oxide as a charge storage node, but the inclusion is expected to affect the gate capacitance. Thus, a basic understanding of nc-Ge’s dielectric properties is critical for designing devices of desired performance; for instance, the nc-Ge size dependency is correlated with the properties of resistance and capacitance, photoluminescence, and band gap. However, the mechanism for dielectric properties has not yet been well understood despite the developed models such as quantum confinement, nearly free electrons and single-oscillator. Wang and Zunger proposed that the changes to the dielectric function of the material are due to the surface of the quantum dot, not the overall size of the dot. Delerue et al. had earlier thought that dielectric suppression is due to the band gap opening induced by the confinement, but later it was found to be due to the breaking of surface polarizable bonds, which supports the earlier findings of Wang and Zunger. This mechanism has been shown to be consistent for Si nanostructures, polycrystalline materials and nanopowders.

In this work, the size dependency of dielectric constant ($\varepsilon_r$) and dielectric susceptibility ($\chi$) of the self-assembled nc-Ge were examined from the perspective of the bond order–length–strength (BOLS) correlation. The BOLS correlation indicates that the broken bonds at skin-depth cause local bond contraction, bond strength gain, densification and quantum entrapment of charge and energy, and hence, modulate the local atomic cohesive energy, the binding energy density, the Hamiltonian of the entire specimen and their relevant properties.

Theory and modeling

Numerically, the BOLS correlation is expressed as:

$$\frac{d\varepsilon}{db} = C_{\varepsilon} = 2\left[1 + 2\exp\left(\frac{(12 - z_i)/8z_i}{2}\right)\right]$$ (bond contraction)

$$\frac{E_{\varepsilon}}{E_{b}} = C_{\varepsilon}^{m}$$ (bond strengthening)

The bond energy is written as $E$ and the bond length as $d$, while the subscripts $z$ and $b$ denote an atom with $z$ neighbors and in the bulk as a standard, respectively. The subscript $i$ denotes an atom in the $i$th atomic layer, which may be counted up to three from the outermost atomic layer to the centre of the solid as reduction in coordination number (CN) is expected for $i \leq 3$. The bond contraction coefficient ($C_{\varepsilon}$) varies only with the effective CN ($z_i$) of the atom of concern regardless of the nature of the bond. The bond nature indicator $m = 5.38$ has been optimized for Ge nanostructures. For a diamond-structure spherical particle, $z_1 = 4(1 - 0.75/K)$, $z_2 = z_1 + 2$ and $z_3 = 12$, where $K$ denotes the number of Ge atoms lined along the shortest length in the dimension (diameter of a Ge atom is 0.2732 nm).

The dielectric constant ($\varepsilon_r$) and dielectric susceptibility ($\chi$) describe the response of the electron polarization to an external electric field, with a relation of $\chi = \varepsilon_r - 1$. The size-induced relative change of the dielectric susceptibility can be expressed as:
where $\Delta_H$ represents Hamiltonian perturbation caused by CN imperfection, $B$ is the electron–phonon (e–p) coupling coefficient, $\Delta_{e-p}$ represents the e–p coupling in the surface skin and $\Delta_d$ represents bond length change. $\gamma_i$ represents the surface-to-volume ratio, while $C_{zi}$ represents the coefficient for bond contraction, as discussed in eqn (1). Both the $\gamma_i$ and $C_{zi}$ play an important role in determining the unique properties of a nanometric structure.

The surface-to-volume ratio ($\gamma_i$) is dependent on the shape and size of the nanostructure, and can be expressed as $\gamma_i = \tau C_{zi}/K$, where $\tau$ represents the dimensionality of the nanostructure. For ideal cases, $\tau =$ 1, 2, and 3 for a thin film, a rod and a spherical dot, respectively. However, for the self-assembled nc-Ge which was dome-shaped as discussed in previous work, $\tau$ is 3.2, larger than an ideal spherical dot.\(^a\) The performance of the surface atoms becomes more dominant with reduced nanostructure size, causing a larger $\gamma_i$.

**Experimental methods**

We began the experiment by synthesizing the nc-Ge. Firstly, the $p$-type (100) Si substrate was cleaned using a standard RCA process and then put into the furnace for 1 hour of dry oxidation at 950 °C for the growth of a 3 nm SiO\(_2\) layer. Using the electron beam evaporation method, a very thin Ge layer (2, 2.5, 3, 4, 5 and 6 nm) was deposited on the SiO\(_2\) layer, with a deposition rate of 0.07 nm s\(^{-1}\) and a base pressure of 5 \times 10\(^{-6}\) mbar. For the formation of nc-Ge, the samples underwent a rapid thermal annealing (RTA) at 450 °C for 50 seconds under nitrogen ambient. The nc-Ge formed were observed using an atomic force microscope (AFM), as shown in the inset of Fig. 1.

A metal–insulator–semiconductor (MIS) structure is required for the capacitance–voltage ($C$–$V$) measurement. Thus, the next step was the deposition of a 25 nm SiO\(_2\) capping layer through the plasma-enhanced chemical vapor deposition (PECVD) method on the samples. Finally, a 200 nm thick aluminum (Al) layer was deposited on the top of the SiO\(_2\) capping layer to form a gate electrode, while another 200 nm aluminum layer was deposited on the backside of the Si wafer (after removing the native oxide) to form the ohmic contact. The diameter of the circular gate electrode is 150 μm. A MIS control sample with 28 nm SiO\(_2\) insulator layer was also prepared. The MIS structure for the $C$–$V$ measurement is as shown in the inset of Fig. 1. The $C$–$V$ measurements were conducted with frequency at 1 MHz in a dark environment at room temperature, using a Keithley 4200 semiconductor characterization system.

The capacitance per unit area of the MIS, based on the inset of Fig. 1, can be modeled as\(^{28}\)

$$\frac{1}{(C/A)} = \left[\left(\frac{\varepsilon_{SiO_2} - \varepsilon_i}{d_1}\right)^{-1} + \left(\frac{\varepsilon_{SiO_2} - \varepsilon_i}{d_2}\right)^{-1} + \left(\frac{\varepsilon_{SiO_2} - \varepsilon_i}{d_3}\right)^{-1}\right]^{-1}$$

where $A$ is the area of the gate electrode, $\varepsilon_i$ is the permittivity of free space ($\approx 8.85 \times 10^{-14}$ F cm\(^{-1}\)), $\varepsilon_{SiO_2}$ is the dielectric constant of SiO\(_2\) (=3.9), $\varepsilon_i$ is the effective dielectric constant of the nanocrystal layer, while $d_1$, $d_2$ and $d_3$ are the thickness of SiO\(_2\) layer just on top of the Si substrate (=3 nm), nanocrystal layer, and SiO\(_2\) capping layer, respectively. The thickness of $d_3$ depends on $d_1$ (=25 $-$ $d_2$) nm, and at the same time, $d_2$ depends on the size of the nc-Ge. Based on the atomic force microscopy characterization, the average sizes of the nc-Ge obtained after the RTA of 2, 2.5, 3, 4, 5 and 6 nm Ge film deposition are 3.0, 5.2, 6.1, 7.5, 8.7 and 9.8 nm, respectively.

**Results and discussion**

The inclusion of the nc-Ge in the SiO\(_2\) layer leads to an increase in the capacitance under the accumulation conditions, compared to the SiO\(_2\) layer without nc-Ge. Fig. 1 shows an example of a typical $C$–$V$ measurement for this experiment (the nc-Ge size is 6.1 nm in this case). The reason for the increase in the capacitance is mainly because the effective dielectric constant of the SiO\(_2\) layer embedded with nc-Ge is no longer the same as that of a pure SiO\(_2\) layer (3.9). The increase in the capacitance also indicates that the dielectric constant of the nc-Ge ($\varepsilon_{nc-Ge}$) is larger than the dielectric constant of SiO\(_2\) ($\varepsilon_{SiO_2}$). The effective dielectric constant for the nc-Ge layer can be modeled using the Bruggeman effective medium approximation:\(^{26}\)

$$\frac{\varepsilon_{nc-Ge} - \varepsilon_i}{\varepsilon_{nc-Ge} + 2\varepsilon_i} f = (f - 1) \frac{\varepsilon_{SiO_2} - \varepsilon_i}{\varepsilon_{SiO_2} + 2\varepsilon_i}$$

where $f$ is the volume fraction of nc-Ge in the nc-Ge layer, which was obtained from the AFM as 0.859, 0.652, 0.558, 0.536, 0.512 and 0.508 for the nc-Ge sizes of 3.0, 5.2, 6.1, 7.5, 8.7 and 9.8 nm, respectively. $\varepsilon_{nc-Ge}$ is the parameter that we are interested in and yet to be determined. By using eqn (3) and (4), we were able to calculate the MIS capacitance as a function of $\varepsilon_{nc-Ge}$. Fig. 2 demonstrates the capacitance as a function of $\varepsilon_{nc-Ge}$ for the 6.1 nm sized nc-Ge. From Fig. 1, the capacitance at the accumulation region was obtained at 21.78 pF for pure SiO\(_2\) and 24.70 pF for SiO\(_2\) embedded with nc-Ge. With the capacitance of 24.70 pF...
for SiO2 embedded with nc-Ge, we obtained the $\varepsilon_{nc-Ge}$ from Fig. 2 for the 6.1 nm sized nc-Ge as 14.06. The methodology to extract the $\varepsilon_{nc-Ge}$ and accuracy of the obtained $\varepsilon_{nc-Ge}$ result was proven because the dielectric constant of SiO2 obtained from Fig. 2 with the capacitance of 21.78 pF for pure SiO2 was 3.9 (which is the well-established value for pure SiO2). This method was applied to other sizes of nc-Ge to obtain their $\varepsilon_{nc-Ge}$ as well. The dielectric susceptibility of nc-Ge can then be calculated using the relation of $\chi = \varepsilon_t - 1$ (note that the bulk Ge dielectric susceptibility is 15 as the dielectric constant of bulk Ge is 16).

The $\varepsilon_{nc-Ge}$ was calculated as $11.91, 13.72, 14.06, 15.37, 15.62$ and $15.78$ for nc-Ge sizes of $3.0, 5.2, 6.1, 7.5, 8.7$ and $9.8$ nm, respectively. A significant quantum size effect can be observed as the $\varepsilon_{nc-Ge}$ decreases with the reduction in nc-Ge size. From the $\varepsilon_{nc-Ge}$ values, the relative change of dielectric susceptibility was calculated and matched to BOLS prediction in eqn (2), which gave $B = 2.1$, as shown in Fig. 3. A good match to the BOLS calculation confirmed that the dielectric properties of nc-Ge are influenced by the contribution of e–p coupling, quantum trapping and broken-bond induced local strain at the surface of skin depth, while the core interior bonds remain the same as in the bulk.\textsuperscript{21,24} The determination of the values of $m$ and $B$ allows us to discriminate the effect of crystal binding and the effect of e–p coupling.\textsuperscript{24} Therefore, for the nc-Ge studied here, as $m$ is larger than $B$, this implicated that the contribution from Hamiltonian perturbation, caused by the bonds deficiency of undercoordinated atoms in the crystal skin, has a stronger influence compared to the effect of e–p coupling.

**Conclusion**

In summary, the dielectric properties of self-assembled nc-Ge can be determined from the $C–V$ measurement with the help of Bruggeman effective medium approximation. The dielectric constant of all the different sizes of nc-Ge was found to be lower than that of the bulk Ge, suggesting a strong quantum size effect. The dielectric suppression of nc-Ge matched BOLS prediction, thus implicating the size dependency of nc-Ge on their dielectric properties, was contributed by the bond order deficiency at the surface of skin-depth.

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**References**

9. The band gap of self-assembled dome-shaped Ge nanocrystals was described with bond order-length-strength correlation and found to be shape and size dependent. The dimensionality was calculated to be 3.2 and band gap expansion increases when Ge nanocrystals size decreases. The bond nature indicator was optimized as 5.38.
16. The relative change of the dielectric susceptibility of nc-Ge as a function of the number of Ge atoms (K).

![Fig. 2](image1.png)

Fig. 2 Capacitance as a function of $\varepsilon_{nc-Ge}$ for the 6.1 nm sized nc-Ge, calculated based on eqn (3) and (4). The $\varepsilon_{nc-Ge}$ of the 6.1 nm sized nc-Ge was obtained through the intercept of the measured capacitance with the calculated value.

![Fig. 3](image2.png)

Fig. 3 The relative change of the dielectric susceptibility of nc-Ge as a function of the number of Ge atoms (K).