Influence of GeSi interfacial layer on Ge–Ge optical phonon mode in SiO$_2$ films embedded with Ge nanocrystals

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The Ge–Ge optical phonon peak at 300 cm$^{-1}$ acquired from amorphous SiO$_2$ films embedded with Ge nanocrystals by Raman scattering is sensitive to the Si content. When the Si concentration is high, a thin GeSi interfacial layer forms around the Ge nanocrystals. A tensile stress is produced to partially offset the compressive stress imposed by the SiO$_2$ matrix on the Ge nanocrystals, consequently downshifting the frequency of the optical phonon and increasing its linewidth. Theoretical calculation based on phonon confinement and compressive effects discloses that the interfacial layer plays a crucial role in the optical phonon behavior.


Raman scattering studies on Ge nanocrystals (NCs) embedded in SiO$_2$ matrix are of scientific interest$^{1–4}$ Owing to the complex surface structure of Ge NC, the Raman peak from the Ge–Ge optical phonon at about 300 cm$^{-1}$ is frequently fixed at the same position and there is no obvious size dependence. This is largely different from the case of Si NCs. The size-independent behavior is mainly ascribed to the compressive stress induced by the matrix,$^{5,6}$ which compensates the downshift caused by phonon confinement. However, the effect of compressive stress is still unclear so far because heat treatment not only increases the NC size but also changes the NC surface stress.$^{8,9}$ This makes it difficult to understand the respective role of these two factors in the peak shift. Although some studies on the Ge–Ge optical phonon property under hydrostatic pressure were reported,$^{10–14}$ how the interface composition affects the Raman shift is still under demand.

In this work, we prepare Ge-NC-embedded SiO$_2$ films with different Si concentrations and experimentally demonstrate that the frequency of the Ge–Ge optical mode is very sensitive to the GeSi concentration at the interface between the NC and matrix. Spectral analysis and calculation reveal that the Ge–Ge optical phonon frequency and full width at half maximum (FWHM) depend on both phonon confinement effect and compressive stress caused by the GeSi interface and SiO$_2$ matrix. This work improves our understanding of the Ge–Ge optical phonon characteristics in the Ge-NC-embedded structures.

The samples were prepared by radio-frequency magnetron cosputtering using instrumental conditions similar to those reported earlier.$^{15}$ The ∼3-μm-thick SiO$_2$/SiO$_2$:Ge:Si/SiO$_2$ samples were produced on cleaned Si (100) substrates in argon. The Ge and Si chips were placed on a large silica target and then cosputtered using 1 Pa Ar gas at 140 W power and room temperature. The areas of the Ge and Si chips on the silica target were $P_{\text{Ge}}=4\%$ and $P_{\text{Si}}=0\%, 2\%, 3\%, \text{and } 6\%$, respectively. Four sets of samples were deposited and then annealed at temperature between 850 and 1050 °C in a N$_2$ ambient for 30 min. The sample morphologies were inspected by high-resolution transmission electron microscopy (HR-TEM, JEOL-2010) and the Raman spectra were acquired on a T64000 triple Raman system in the backscattering geometry using the 514.5 nm line of an Ar-ion laser as the excitation source.

Figure 1 depicts the TEM image of a typical cosputtered product after annealing at $T_a=950$ °C and discloses that NCs with a mean size of 5.1 nm are embedded in an amorphous matrix.$^{15}$ The inset shows the HR-TEM image of a representative NC which is almost spherical and has lattice fringes corresponding to the {111} plane of Ge. Since Si–O bonds are more stable than Ge–O ones, under high $T_a$, Ge ions decomposed from Ge–O bonds will more easily segregate into the Ge NCs. For samples annealed at different $T_a$, our TEM results indicate that the NCs have mean sizes of 3.5–8.5 nm. The lattice image of the Ge NC reveals that the interface is sharp and there is no apparent composition deficiency between the NC and surrounding amorphous matrix.$^{16}$

FIG. 1. Representative TEM image obtained from the Ge-NC-embedded amorphous SiO$_2$ film fabricated with $P_{\text{Ge}}=2\%$, $P_{\text{Ge}}=4\%$, and $T_a=950$ °C. The inset shows the HR-TEM image of a typical Ge NC.
This indicates that the interfacial layer has a density between those of Ge and SiO$_2$ (Ref. 16) and is most likely composed of binary GeSi or ternary GeSiO as reported previously.\textsuperscript{15}

Figure 2 shows the Raman spectra of the three samples with different $P_{Si}=6\%$, 3\%, and 0\%, $P_{Ge}=4\%$, and $T_a=950$ °C. The sharp peak at 521 cm$^{-1}$ originates from the Si substrate. For the $P_{Si}=6\%$ sample, the three peaks at $P_1=291$ cm$^{-1}$ (Ge–Ge vibration), $P_2=409$ cm$^{-1}$ (Ge–Si vibration), and $P_3=481$ cm$^{-1}$ (Si–Si vibration) imply that the formed products are GeSi alloy NCs.\textsuperscript{15,16} No noticeable $P_2$ and $P_3$ peaks are observed from the other samples, indicating that the formed NCs are composed of Ge. In the $P_{Si}=5\%$ sample, a similar situation occurs except that the $P_1$ peak downshifts to 298.1 cm$^{-1}$. This result indicates that the Si concentration impacts the formation of different kinds of NCs. The $P_1$ optical phonon peak of the GeSi alloy NC sample is at 292.7 cm$^{-1}$. It exhibits a larger downshift than the $P_1$ peaks at 299.2 and 303.1 cm$^{-1}$ observed from the other two Ge NC samples. Since the GeSi alloy NCs are in good contact with the SiO$_2$ matrix,\textsuperscript{16} it can be inferred that the downshift in the Ge–Ge optical mode observed from the Ge-NC-embedded SiO$_2$ film with a larger Si concentration should also be due to the formation of a thin GeSi interfacial layer, otherwise the optical mode position will not change with increasing $P_{Si}$.\textsuperscript{7} We have also further examined the Raman spectra of the 400–430 cm$^{-1}$ Ge–Si vibration mode and found that the mode actually has very weak intensity.\textsuperscript{7,17} Since our infrared absorption spectra also indicate that the matrix is quite similar to that of amorphous Si dioxide\textsuperscript{15} and the HR-TEM images verify that the embedded NCs are Ge, the GeSi layer associated with the Ge–Si vibration should occur at the interface of the Ge NCs.

To determine the dependence of the $P_1$ peak on $T_a$, Raman spectra acquired from the sample with $P_{Si}=3\%$ are presented in Fig. 3(a). The three asymmetrical Raman spectra can be Lorentzian divided into two peaks, one at around 280 cm$^{-1}$ ($\omega_1$) and the other at 300 cm$^{-1}$ ($\omega_2$). With increasing $T_a$, the relative intensity of the broad $\omega_1$ peak diminishes and its FWHM decreases as well. Meanwhile, its position blueshifts. The behavior of the $\omega_1$ peak has been ascribed to crystallization of the GeSi component during high-temperature annealing.\textsuperscript{17} In our samples, it is believed to arise from the improved ordering of the Si–Ge bonds on the Ge NC surfaces. The Ge–Ge optical phonon frequency ($\omega_2$) is independent of the NC size, but its FWHM diminishes slightly with increasing $T_a$. Figure 3(b) displays the Raman spectra of the four samples with $P_{Si}=0\%$, 2\%, 3\%, and 6\%, and $T_a=950$ °C. It can be observed that with increasing Si concentration, the Raman peaks (red lines) show distinct different positions. The Ge–Ge optical mode observed from the $P_{Si}=0$ sample is at 303.1 cm$^{-1}$ and has a FWHM of 7.4 cm$^{-1}$. By adding more Si, a thin GeSi interface forms to partially offset the compressive stress on the Ge NC imposed by the matrix. As a result, the upshift in the Ge–Ge phonon mode begins to decrease. When $P_{Si}$ is increased to 6\%, the peak position downshifts to 292.7 cm$^{-1}$ and the FWHM increases to 18.7 cm$^{-1}$. Compared to the case in Fig. 3(a), it can be inferred that the interfacial GeSi component directly affects the frequency and FWHM of the Ge–Ge optical phonon. Hence, the frequency shift and FWHM increase observed from the Ge–Ge optical phonon appear to originate from the synergetic stress induced by the GeSi interfacial layer and SiO$_2$ matrix in conjunction with the phonon confinement effect.

To further study the role of the GeSi interface, we first calculate the Raman spectra caused by phonon confinement on a spherical Ge NC, as shown in Fig. 3(b) (black lines).\textsuperscript{7,18,19} In our calculation, a 5.1 nm Ge NC size from the sample with $P_{Si}=2\%$ at $T_a=950$ °C is used.\textsuperscript{15} According to our above analysis, the Si content mainly affects the interfacial composition. Thus, the size of 5.1 nm can be used generally for other samples. In fact, our x-ray diffraction (XRD) results also give similar NC sizes. The shift $\Delta \omega$ of the optical phonon mode induced by the compressive stress exerted on the Ge NC can be expressed as\textsuperscript{7,15}

\begin{equation}
\Delta \omega = \frac{1}{2 \omega_0} (P + 2Q) \times e_{trr},
\end{equation}

where $e_{trr}$ is defined as the strain related with $(a-a_{Ge})/a_{Ge}$. $a$ and $a_{Ge}$ are the strained and unstrained lattice constants, respectively, $P=-1.3 \omega_0^2$, $Q=-1.65 \omega_0^2$, and $\omega_0=300.5$ cm$^{-1}$ is the frequency of Ge crystalline peak. The strain-induced FWHM is calculated using the following equation:\textsuperscript{13}

\[ \text{FWHM} = 2 \omega_0 \sqrt{e_{trr}}. \]
TABLE I. Calculated frequency $\omega_c$, FWHM $\Gamma_c$, frequency shift $\Delta \omega$, and FWHM change $\Delta \Gamma$ of the Ge–Ge optical phonon mode induced by the interface stress and quantum confinement effect. The last columns show the experimental and calculated mode frequency $\omega$ and FWHM $\Gamma$ for comparison.

<table>
<thead>
<tr>
<th>Si content</th>
<th>Strain (%)</th>
<th>$\Delta \omega$ (cm$^{-1}$)</th>
<th>$\Delta \Gamma$ (cm$^{-1}$)</th>
<th>$\omega_c$ (cm$^{-1}$)</th>
<th>$\Gamma_c$ (cm$^{-1}$)</th>
<th>Expt</th>
<th>Theor</th>
<th>Expt</th>
<th>Theor</th>
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<tr>
<td>$P_{Si}=0%$</td>
<td>1.8</td>
<td>12.4</td>
<td>1.2</td>
<td>290.6</td>
<td>8.3</td>
<td>303.1</td>
<td>303.0</td>
<td>7.4</td>
<td>7.1</td>
</tr>
<tr>
<td>$P_{Si}=2%$</td>
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<td>10.9</td>
<td>1.1</td>
<td>290.6</td>
<td>8.3</td>
<td>301.6</td>
<td>301.5</td>
<td>7.5</td>
<td>7.2</td>
</tr>
<tr>
<td>$P_{Si}=3%$</td>
<td>1.4</td>
<td>8.7</td>
<td>0.9</td>
<td>290.6</td>
<td>8.3</td>
<td>299.2</td>
<td>299.3</td>
<td>7.8</td>
<td>7.4</td>
</tr>
<tr>
<td>$P_{Si}=6%$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>$\ldots$</td>
<td>292.7</td>
<td>$\ldots$</td>
<td>18.7</td>
<td>$\ldots$</td>
</tr>
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$\Delta \Gamma \sim \delta (\Delta \omega) = \frac{1}{2\omega_b} \left[ -p \frac{2C_{12}}{C_{11}} \delta (e_{rr}) + 2q \delta (e_{rr}) \right], \quad (2)$

where $\delta (e_{rr})$ are the variation in $e_{rr}$, $C_{12}$ (482.5 kbar) and $C_{11}$ (1288 kbar) are components of the fourth rank elastic tensor, and $p \approx -4.7 \times 10^{27} \text{s}^{-2}$ and $q \approx -6.167 \times 10^{27} \text{s}^{-2}$ are the deformation potentials.$^{13,20}$

The XRD results provide information about the compressive strain on the Ge NCs.$^{21}$ The diffraction angle of the (220) peak shifts from $2\theta = 44.50^\circ$ (the corresponding lattice spacing $a_0 = 0.2034$ nm for Ge single crystal) to $45.32^\circ$ ($a = 0.1999$ nm for the sample with $P_{Si} = 0\%$). The high potential barrier provided by the GeSi interface layer reduces the interaction between the NC internal atoms, leading to the lattice dilation to $a = 0.2002$ nm ($2\theta = 45.23^\circ$ for the sample with $P = 2\%$) and $a = 0.2007$ nm ($2\theta = 45.13^\circ$ for the sample with $P_{Si} = 3\%$). We can then calculate the Ge NC optical phonon frequencies and FWHMs and the results are listed in Table I. It can be seen that the introduction of a thin GeSi interface leads to compressive strain gradually decreasing from 1.8% to 1.4%. This is because Ge (bulk modulus $K_1 = 750.17$ kbar) is easier to compress than Si ($K_2 = 978.87$ kbar).$^{22,23}$ Both of them have to shrink together to form Ge–Si bonds at the interface under pressure. So the SiO$_2$ ($K_2 = 361$ kbar) matrix experiences more tensile stress near the SiO$_2$/GeSi interface than the SiO$_2$/Ge interface.$^{22,23}$

The existence of the GeSi interfacial structure nonuniformly distributed around the Ge NCs effectively modifies the surrounding stress field. Consequently, high Si concentration releases the interface stress thereby reducing the stress effect and leading to the frequency shift caused by the stress being unable to compensate for the downshift caused by phonon confinement. The process is equivalent to decreasing the stacked matrix effect of the SiO$_2$ matrix on the Ge NC surface, as is the case for the GeSi-NC-embedded SiO$_2$ matrix.

In summary, Raman spectra acquired from Ge-NC-embedded SiO$_2$ films reveal that as the Si concentration increases, a thin GeSi interfacial layer forms around the Ge NCs. Consequently, the frequency of the Ge–Ge optical mode downshifts and its linewidth increases. The phenomenon can be attributed to the release of compressive stress originally exerted on the Ge NC by the SiO$_2$ matrix due to the emergence of the GeSi interfacial layer. A theoretical model taking into account the synergistic effect of phonon confinement and compressive stress is adopted to calculate the frequency and FWHM of the Ge–Ge optical phonon mode. Good agreement is achieved between theory and experiments. This work shows that the GeSi interface plays a crucial role in the Ge–Ge optical phonon behavior.

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