Bandgap expansion and dielectric suppression of self-assembled Ge nanocrystals

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The bandgap and optical properties (dielectric functions and optical constants) of dome-shaped Ge nanocrystals (nc-Ge) with average sizes of ~6 nm in height and ~13 nm in diameter have been investigated using spectroscopic ellipsometry based on the Forouhi-Bloomer optical dispersion model. As compared to bulk crystalline Ge, the nc-Ge exhibited a bandgap expansion of ~0.2 eV and a significant reduction in the dielectric function. The bandgap expansion and dielectric suppression are discussed in terms of the quantum confinement effect as well as the bond contraction model. © 2011 American Institute of Physics. [doi:10.1063/1.3554833]

I. INTRODUCTION

Ge nanocrystals (nc-Ge) have attracted a lot of interest, due to their promising applications in electronic and optoelectronic devices, such as nonvolatile memory devices1,2 and light emitting devices.3–5 The synthesis of nc-Ge is usually focused on being embedded in an insulator layer, most popularly SiO2, with various techniques, such as ion implantation,2,5–7 cosputtering4,8 and chemical vapor deposition.9,10 Some studies on the optical properties of the nc-Ge embedded in an insulator layer have been reported. In the present work, self-assembled nc-Ge without being embedded in an insulator layer was synthesized through the rapid thermal annealing of an ultra-thin Ge film deposited on a thermally oxidized Si substrate. The optical properties and bandgap of the self-assembled nc-Ge were measured using spectroscopic ellipsometry (SE) in the wavelength range of 350–1100 nm. The optical properties of the nc-Ge were found to be well modeled by the Forouhi-Bloomer (F-B) formulism11,12 and the modeling using the F-B formulism enabled the determination of the bandgap of the nc-Ge. The bandgap obtained from the F-B modeling matched the bandgap obtained from absorption measurement, thus proving the accuracy of the bandgap obtained. The nc-Ge exhibited a bandgap expansion which can be explained by the quantum confinement effect13,14 and the bond contraction model.15–17 In addition, the nc-Ge showed a reduction in the dielectric function, which could be attributed to the change in the surface bonding.15–17

II. EXPERIMENT

The synthesis procedure of the self-assembled nc-Ge is as follows. First, a 3 nm SiO2 layer was grown on the cleaned p-type (100) Si substrate using dry oxidation at 950 °C for 1 h. A 3 nm thick Ge layer was deposited on the SiO2 layer using electron beam evaporation under the base pressure of 5 × 10−6 mbar with the deposition rate of 0.07 nm/s. In order to form nc-Ge, the sample underwent a rapid thermal annealing (RTA) in nitrogen ambient at 450 °C for 50 s. With the existence of the SiO2 layer, possible reaction between the deposited Ge layer and the Si substrate during the annealing process can be avoided. The formation of the nc-Ge is clearly demonstrated by the comparison of the atomic force microscopy (AFM) image (planar view) of the Ge layer before the RTA with that after the RTA, as shown in Figs. 1(a) and 1(b). In addition, the transmission electron microscopy (TEM) measurement shows that the self-assembled nc-Ge has a dome-shape with average size of ~6 nm in height and ~13 nm in diameter. Figure 1(c) shows the TEM image of the nc-Ge layer covered by a thick SiO2 capping layer of about 70 nm (note that the capping layer is used for the TEM measurement only). The formation of nc-Ge can be explained by the stress relaxation, dispersion force and surface energy minimization during the annealing process.18,19

The SE measurements on the above nc-Ge sample were carried out using a variable angle ellipsometer (J.A.Woollam Inc. HS-190) in the wavelength range of 350–1100 nm (i.e., 1.13–3.54 eV) with a step of 5 nm at the three incident angles of 70°, 75°, and 80° at room temperature. Figure 2 shows the SE spectra obtained at the three incident angles. On the other hand, absorption measurement of the nc-Ge fabricated on a fused silica substrate was also carried out using a UV-VIS spectrophotometer (Shimadzu UV2450) for the comparison of the nc-Ge bandgap with the SE measurements. Note that the nc-Ge on the fused silica substrate was fabricated using the same procedure and conditions as described above. Figure 1(d) shows the AFM image of the nc-Ge formed on the fused silica substrate. A calculation based on the AFM images shown in Figs. 1(b) and 1(d) yields that the mean nc-Ge sizes for the Si substrate and the fused silica substrate are 6.2 and 6.9 nm, respectively, indicating that the nanocrystal formation on the two substrates is similar.

III. SE ANALYSIS, RESULT AND DISCUSSION

In the SE analysis for the nc-Ge on the SiO2 layer thermally grown on the Si substrate, the four-phase model, i.e., air/nc-Ge layer/SiO2 layer/Si substrate, which is shown in the inset of Fig. 2, was used. The nc-Ge layer comprised of
voids and nc-Ge. Its effective dielectric function \( \varepsilon_i \) (where \( N_i \) is the complex refractive index of the layer) can be modeled with the Bruggeman effective medium approximation.

\[
\frac{\varepsilon_{nc-Ge} - \varepsilon_f}{\varepsilon_{nc-Ge} + 2\varepsilon_f} f + \frac{\varepsilon_{void} - \varepsilon_f}{\varepsilon_{void} + 2\varepsilon_f} (1 - f) = 0, \tag{1}
\]

where \( \varepsilon_{nc-Ge} \) is the refractive index and extinction coefficient of the nc-Ge, \( f \) is the volume fraction of the voids in the layer, and the effective dielectric function \( \varepsilon_{void} \) of the voids is 1.

In order to obtain the optical constants (i.e., refractive index \( n \) and extinction coefficient \( k \)) of the nc-Ge from the spectral fittings to the measured ellipsometric angles (\( \psi \) and \( \Delta \)), an appropriate optical dispersion model is required. The F-B optical dispersion model has been successfully applied to both bulk crystalline Ge and ultra-thin Ge films. As demonstrated in the present work, the F-B model is also applicable to the nc-Ge. It has been found from the spectral fittings of this work that the following three-term F-B model satisfactorily describes the optical constants of the nc-Ge:

\[
k(E) = \left( \frac{3}{\sum_{i=1}^{3} A_i E_i^2 - B_i E + C_i} \right) (E - E_g)^2, \tag{2}
\]

\[
n(E) = n(\infty) + \sum_{i=1}^{3} B_0 E + C_0. \tag{3}
\]

where

\[
E_g = \frac{A_i}{Q_i} \left( \frac{B_i^2}{2} + E_B E_i - E_g^2 + C_i \right),
\]

and

\[
Q_i = \frac{1}{2} (4C_i - B_i^2)^{\frac{1}{2}}.
\]

\( A_i, B_i, \) and \( C_i \) (\( i = 1, 2, 3 \)) are some parameters related to electron transitions in the nc-Ge, \( n(\infty) \) is the refractive index of the nc-Ge when photon energy \( E \rightarrow \infty \), and \( E_g \) is the energy bandgap of the nc-Ge. It should be pointed out that although two terms in the F-B formulas were sufficient in describing the optical constants of Ge thin films, three terms were required for the nc-Ge. It was found that three terms are sufficient for the nc-Ge as more terms do not make any significant difference in the spectral range of the current work. Note that more terms may be needed if spectral range is extended.

The spectral fittings to the measured ellipsometric angles (\( \psi \) and \( \Delta \)) in the wavelength range of 350-1100 nm at the three incident angles of 70°, 75°, and 80° were carried out by freely varying the volume fraction of the voids in the nc-Ge layer and the effective thickness of the layer, the F-B model parameters \( A_i, B_i, \) and \( C_i \) (\( i = 1, 2, 3 \)), \( n(\infty) \) and the nc-Ge bandgap \( E_g \) to minimize the mean-square-error (MSE) function. Figure 2 shows the fittings to the SE spectra measured at the three angles of incidence. As can be seen in this figure, the
spectra of both $\psi$ and $\Delta$ in the whole wavelength range for all the three angles of incidence were fitted excellently which is also demonstrated by the very small MSE (0.0121) of the fittings. The volume fraction of nc-Ge in the nc-Ge layer and the effective thickness of the layer yielded from the fittings are 55.79% and $\sim$6 nm, respectively. The result agrees with the TEM measurement from which the effective thickness and the volume fraction can be estimated based on the average diameter and height of nc-Ge. This indicates that the F-B model well described the dispersion of the optical constants of the nc-Ge and the fitting procedure is effective.

The values of the F-B model parameters $A_i$, $B_i$, and $C_i$ $(i = 1, 2, 3)$, $n(\infty)$ and the nc-Ge bandgap $E_g$ yielded from the spectral fittings are listed in Table I. Compared to the values of $A_i$, $B_i$, and $C_i$ of the four-term F-B model used for bulk crystalline Ge,11 $A_2$ of the nc-Ge is much smaller than that of bulk crystalline Ge, while the other parameters of the nc-Ge are generally close to that of bulk crystalline Ge. As the second term is the dominant term for bulk crystalline Ge,11 this could explain why both the $\varepsilon_1$ and $\varepsilon_2$ of the nc-Ge are significantly smaller than that of bulk crystalline Ge, as shown in Fig. 3.

Perhaps the most important parameter yielded from the spectral fittings based on the F-B model is the bandgap of the nc-Ge. As given in Table I, the value of the bandgap of the nc-Ge formed on Si substrate is 0.92 eV, which is consistent with the absorption measurement of the nc-Ge formed on fused silica substrate. Figure 4 shows the Tauc plot of $(\alpha E)^{1/2}$ versus $E$ yielded from the absorption measurement (note that $\alpha$ is the absorption coefficient). The bandgap of the nc-Ge formed on fused silica substrate obtained from the linear extrapolation of the Tauc plot is 0.86 eV. Therefore, it could be concluded that the nc-Ge has a bandgap expansion of $\sim$0.2 eV as compared to bulk crystalline Ge (note that the bandgap of bulk crystalline Ge is 0.66 eV). The bandgap expansion could be explained by the quantum confinement effect13,14 as well as the bond contraction model15–17. A fit to the result of the calculation of the exciton energy of Ge quantum dot (QD)14 based on the quantum confinement effect presented in Ref. 13 yields

$$E_x(R) = E_x(\infty) + C/R^b,$$  

(4)

where $R$ is the radius of the Ge QD in nm, $E_x(R)$ is the exciton energy of the Ge QD in eV, $E_x(\infty) = 0.66$ eV, $C = 6.46$, and $b = 1.99$. A simple calculation using Eq. (4) yields $E_x = 0.85$ eV for $R = 6$ nm. In the present work, the average diameter of the nc-Ge is $\sim$12 nm (i.e., $R \approx 6$ nm). The exciton energy of 0.85 eV is close to the bandwidth values obtained from both the spectral fittings and the absorption measurement. This suggests that the bandgap expansion could be explained by the confinement effect of electrons and holes in the nc-Ge with the nanometer dimensions. On the other hand, the bond contraction model15–17 also predicts a bandgap expansion. According to the bond contraction model,15–17 the bandgap expansion ($\Delta E_g$) can be expressed as

$$\frac{\Delta E_g}{E_g} = \gamma_1(\varepsilon_1^{-m} - 1) + \gamma_2(\varepsilon_2^{-m} - 1) + \gamma_3(\varepsilon_3^{-m} - 1),$$  

(5)

TABLE I. Values of parameters $A_i$, $B_i$, $C_i$ $(i = 1, 2, 3)$, $n(\infty)$ and $E_g$ for the nc-Ge obtained from the spectral fittings based on the three-term F-B model.

<table>
<thead>
<tr>
<th>$A_i$</th>
<th>$B_i$ (eV)</th>
<th>$C_i$ (eV$^2$)</th>
<th>$n(\infty)$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1001</td>
<td>4.654</td>
<td>5.389</td>
<td>2.607</td>
<td>0.92</td>
</tr>
<tr>
<td>0.0096</td>
<td>6.888</td>
<td>11.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0261</td>
<td>9.577</td>
<td>23.193</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 3. (Color online) Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function of the nc-Ge, obtained from the spectral fittings based on the F-B model. The dielectric function of bulk crystalline Ge is included for comparison.

FIG. 4. (Color online) Tauc plot of $(\alpha E)^{1/2}$ versus $E$ yielded from the absorption measurement for the nc-Ge formed on fused silica substrate. The bandgap of the nc-Ge obtained from the linear extrapolation of the Tauc plot is 0.86 eV.
where \( \gamma_i = \frac{3c_i}{K} \) \((i=1,2,3)\),

\( K = \frac{R}{a} \) (\( R \) is the diameter or height of nc-Ge and \( a \) is the diameter of a Ge atom) is the number of atoms lined along the shortest length in the dimensions of nc-Ge. For the nc-Ge with \( \Delta E_g = 0.2 \) eV in the present work, \( a = 0.2732 \) nm, \( c_1 = 0.87, c_2 = 0.93, c_3 = 1, \) and \( m = 5.4 \). As the \( m \) value, which describes the nature of the bond, is larger than 1, the bonds between the Ge atoms have contracted at the surfaces of the nanocrystals.\(^{17}\)

The optical constants (i.e., refractive index, \( n \) and extinction coefficient, \( k \)) of the nc-Ge can be calculated with the F-B model using the values of the parameters given in Table I. The real (\( = n^2-k^2 \)) and the imaginary part (\( = 2nk \)) of the complex dielectric function of nc-Ge can also be obtained, and the results are shown in Fig. 3. For comparison, the dielectric functions of bulk crystalline Ge is also included in Fig. 3. A strong dielectric suppression can be observed for the nc-Ge with respect to bulk crystalline Ge. For example, at the wavelength of 400 nm, the real and the imaginary part of dielectric function of nc-Ge are lower than that of bulk crystalline Ge by 30% and 76%, respectively. It has been well established that reduction of dimensions of a quantum confined physical system such as quantum dots and nanowires, leads to a decrease in its static dielectric constant.\(^{23-26}\) The dielectric suppression can be attributed to the opening of the bandgap,\(^{12}\) which should lower the polarizability. However, it was also suggested that the size induced dielectric suppression is due to the breaking of polarizable bonds at the surface rather than the opening of the bandgap induced by the confinement.\(^{27}\) The effect of the surface bonds is consistent with the bond contraction model,\(^{15-17}\) which was able to relate both the bandgap expansion and the dielectric suppression. In the bond contraction model, the dielectric depression is proportional to the inverse square of bandgap.\(^{15,17}\) It was also shown that based on the single-oscillator model, a bandgap expansion can lead to a reduction in dielectric function.\(^{28}\)

IV. SUMMARY

In summary, self-assembled dome-shaped nc-Ge with average sizes of \( \sim 6 \) nm in height and \( \sim 13 \) nm in diameter were synthesized through the RTA of an ultra-thin Ge thin film deposited on a thermally oxidized Si substrate. The optical properties and bandgap of the nc-Ge have been obtained from the SE spectral fittings based on the F-B model. The nc-Ge exhibits a bandgap expansion of \( \sim 0.2 \) eV as compared to bulk crystalline Ge, while the dielectric functions of nc-Ge also showed significant reductions, as compared to bulk crystalline Ge, as a result of quantum size effect and surface bond contraction.

ACKNOWLEDGMENTS

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