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<td>Author(s)</td>
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Optical properties of silicon nanocrystals embedded in a SiO₂ matrix

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Optical properties of isolated silicon nanocrystals (nc-Si) with a mean size of ~4 nm embedded in a SiO₂ matrix that was synthesized with an ion beam technique have been determined with spectroscopic ellipsometry in the photon energy range of 1.1–5.0 eV. The optical properties of the nc-Si are found to be well described by both the Lorentz oscillator model and the Forouhi-Bloomer (FB) model. The nc-Si exhibits a significant reduction in the dielectric functions and optical constants and a large blueshift (~0.6 eV) in the absorption spectrum as compared with bulk crystalline silicon. The band gap of the nc-Si obtained from the FB model is ~1.7 eV, showing a large band gap expansion of ~0.6 eV relative to the bulk value. The band gap expansion is in very good agreement with the first-principles calculation of the nc-Si optical gap based on quantum confinement.

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I. INTRODUCTION

Silicon nanocrystals (nc-Si) embedded in a SiO₂ matrix are extensively studied as they provide the possibilities for applications in Si-based optoelectronic devices, memory devices, and single electron devices with the advantage of being compatible with the mainstream complimentary metal-oxide-semiconductor (CMOS) process.¹-⁷ One of the promising techniques to form such a nc-Si structure is the implantation of silicon ions into a SiO₂ matrix followed by thermal annealing.⁵-⁷ In this paper, we present a study on the optical properties of the nc-Si embedded in a SiO₂ matrix synthesized with this technique. Such a study is obviously important to the fundamental physics as it is concerned with a system of quasiparticles with a size of less than ~5 nm isolated by a dielectric matrix, and it is also necessary to optoelectronic and photonic applications of the nc-Si.

Some theoretical calculations of optical properties of semiconductor nanocrystals have been reported. There are calculations of optical properties of nc-Si using various methods such as the empirical-pseudopotential approach and ab initio technique.⁸-¹⁰ Recently, first-principles calculations of optical properties of Si and Ge nanocrystallites have been reported.¹¹-¹³ In contrast, few experimental studies of optical properties of nc-Si have been reported. Especially, it is difficult to experimentally determine the optical properties of nc-Si embedded in a dielectric matrix. Some experimental studies of the optical properties of a continued silicon nanocrystal thin film¹⁴ and SiO₂/nanocrystalline Si multilayers¹⁵ have been reported recently. In our preliminary studies, we have also reported the optical properties of nc-Si embedded in a SiO₂ matrix in the photon energy range of 1.1–3.1 eV.¹⁶,¹⁷ Nevertheless, a comprehensive experimental study of the optical properties in a wider photon energy range and a proper modeling to the optical properties are still lacking. In this work, the optical properties including optical constants, absorption coefficient, and dielectric functions of the nc-Si embedded in a SiO₂ matrix in the photon energy range of 1.1–5.0 eV have been determined with spectroscopic ellipsometry (SE). The optical properties of nc-Si are modeled with the Lorentz oscillator model¹⁸ and the Forouhi-Bloomer (FB) formulism.¹⁹ The modeling based on the Lorentz oscillator model gives the information related to electron transitions, while the FB modeling yields the energy band gap of the nc-Si. A strong dielectric suppression and a large band-gap expansion are observed for the nc-Si.

II. EXPERIMENT

The nc-Si embedded in a SiO₂ matrix was synthesized by Si⁺ implantation with a dose of 1 × 10¹⁷ atoms/cm² at an energy of 100 keV into a 550-nm-thick SiO₂ film thermally grown on a p-type Si substrate. A thermal annealing at 1000 °C for 30 min in nitrogen gas was carried out for the formation of Si nanocrystals. Figure 1 shows the high-resolution transmission electron microscopy (HRTEM) image of the nc-Si embedded in the SiO₂ matrix. The average

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FIG. 1. HRTEM image of nc-Si embedded in SiO₂.
size of nc-Si determined from the broadening of the Bragg peak in the x-ray diffraction (XRD) spectrum is ~4.2 nm, which is consistent with the HRTEM measurement. The SE measurements were carried out in the wavelength range of 250–1100 nm with a step of 5 nm, and the incidence angle was set to 75°.

The nc-Si distribution in the SiO\textsubscript{2} thin film can be determined from the secondary ion mass spectroscopy (SIMS) measurement. The SIMS intensity \(I(x)\) due to the excess silicon in the Si\textsuperscript{+}-implanted region at a given depth \(x\) can be obtained by deducting the Si SIMS signal of the pure SiO\textsubscript{2} region from the measured total Si SIMS signal (which is from both the excess Si and the SiO\textsubscript{2}) at the depth. The amount of excess Si at depth \(x\) should be proportional to the intensity \(I(x)\). The volume fraction of nc-Si at the depth should be proportional to the amount of the excess Si at the depth. Thus, the volume fraction \(f(x)\) of the nc-Si embedded in SiO\textsubscript{2} at depth \(x\) can be expressed as

\[
f(x) = \frac{Q I(x)}{N_{Si} \int_{0}^{d_{\text{max}}} I(x) dx},
\]

where \(Q\) is the dose of implanted Si ions in the unit of atoms/cm\(^2\), \(d_{\text{max}}\) is the maximum depth in SiO\textsubscript{2} beyond which no excess Si can be detected, and \(N_{Si}\) is the Si density in the unit of atoms/cm\(^3\). In this study, \(Q\) is equal to \(1 \times 10^{17}\) atoms/cm\(^2\), and \(N_{Si}\) is \(5 \times 10^{22}\) atoms/cm\(^3\).

### III. Modeling and Discussions

The volume fraction of the nc-Si in the SiO\textsubscript{2} calculated from the SIMS measurement as a function of the depth is shown in Fig. 2. As can be seen in this figure, the nc-Si distributes from the surface of the SiO\textsubscript{2} film to a depth of 250 nm and there is almost no nc-Si in the SiO\textsubscript{2} film beyond a depth of 250 nm. Therefore, the thin film system can be divided into two layers, namely, the first layer (depth \(\leq 250\) nm) of nc-Si distributed in SiO\textsubscript{2}, and the second layer (depth > 250 nm), which is just a basically pure SiO\textsubscript{2} layer without nc-Si. In the first layer, the optical properties vary with the depth as the volume fraction of the nc-Si varies with depth. In order to model the optical properties of the first layer, it is divided into \(m\) sublayers with equal thickness \(d_{0}\) (\(m = 25\) and \(d_{0} = 10\) nm in this study). Each sublayer has a nc-Si volume fraction \(f_{i}\) which can be calculated from the SIMS measurement, and the nc-Si volume fraction is considered to be constant within each sublayer. Each sublayer has its own effective dielectric function \(\varepsilon_{i}\) due to its own nc-Si volume fraction. As such, the optical system in the SE analysis can be described with the multilayer model shown in Fig. 2. Each sublayer can be optically schematized as an effective medium, in which the SiO\textsubscript{2} is the host matrix while the nc-Si is an inclusion embedded in the SiO\textsubscript{2} matrix, represented by the Maxwell-Garnett effective medium approximation (EMA)

\[
\varepsilon_{i} - \varepsilon_{\text{SiO}_2} = \varepsilon_{\text{nc-Si}} - \varepsilon_{\text{SiO}_2} f_{i}.
\]

In Eq. (2), \(\varepsilon_{i}\) (\(=N_{i}\), where \(N_{i}\) is the complex refractive index of the \(i\)th sublayer) is the effective complex dielectric function of the \(i\)th sublayer, \(\varepsilon_{\text{SiO}_2}\) is the dielectric function of SiO\textsubscript{2} matrix, \(\varepsilon_{\text{nc-Si}}\) (\(=n_{\text{nc-Si}}^{2} - ik_{\text{nc-Si}}^{2}\), where \(n_{\text{nc-Si}}\) and \(k_{\text{nc-Si}}\) are the refractive index and extinction coefficient of the nc-Si, respectively) is the complex dielectric function of the nc-Si, and \(f_{i}\) is the volume fraction of nc-Si in the \(i\)th sublayer. As the volume fraction \(f_{i}\) and \(\varepsilon_{\text{SiO}_2}\) are known from Eq. (2), the effective complex dielectric function \(\varepsilon_{i}\) (and thus the effective complex refractive index \(N_{i}\)) for the \(i\)th sublayer \((i = 1, 2, ..., m)\) can be expressed in terms of \(\varepsilon_{\text{nc-Si}}\) (or the refractive index and extinction coefficient of nc-Si). Therefore, in the SE analysis, the ellipsometric angles (\(\psi\) and \(\Delta\)) can be expressed as functions of the optical constants of the nc-Si, although these functions cannot be displayed with analytical formulas due to their complexity. Based on these functions, a spectral fitting to the experimental data of \(\psi\) and \(\Delta\) can yield the dielectric function and optical constants of the nc-Si at various wavelengths. In the spectral fitting, an appropriate optical dispersion model should be used to describe the spectral dependence of dielectric function and the optical constants of the nc-Si. In the present work, two optical dispersion models, the Lorentz oscillator model\textsuperscript{19} and the four-term Forouhi-Bloomer (FB) model,\textsuperscript{19} were used to carry out the spectral fitting.

It is found that a combination of four Lorentz oscillators with different resonant energies is necessary to describe the spectral dependence of optical properties of the nc-Si embedded in SiO\textsubscript{2} over the wavelength range of 250 to 1100 nm.
TABLE I. Values of the parameters $A_i, E_i, \Gamma_i$ (i = 1, 2, 3, 4), and $\varepsilon_1(\infty)$ of the Lorentz oscillator model for both bulk crystalline silicon and the nc-Si embedded in SiO$_2$.

<table>
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<tr>
<th></th>
<th>$A_i$</th>
<th>$E_i$ (eV)</th>
<th>$\Gamma_i$ (eV$^2$)</th>
<th>$\varepsilon_1(\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk crystalline silicon</td>
<td>10.1124</td>
<td>3.4423</td>
<td>0.1407</td>
<td>3.803</td>
</tr>
<tr>
<td></td>
<td>45.9013</td>
<td>3.7005</td>
<td>0.4823</td>
<td></td>
</tr>
<tr>
<td></td>
<td>92.2078</td>
<td>4.3172</td>
<td>0.5289</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.5679</td>
<td>5.3233</td>
<td>0.3823</td>
<td></td>
</tr>
<tr>
<td>Si nanocrystals embedded in SiO$_2$</td>
<td>30.8123</td>
<td>3.5560</td>
<td>0.4313</td>
<td>6.209</td>
</tr>
<tr>
<td></td>
<td>13.7089</td>
<td>4.0151</td>
<td>0.3681</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.4209</td>
<td>4.0529</td>
<td>0.2242</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.3012</td>
<td>5.1616</td>
<td>0.8173</td>
<td></td>
</tr>
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</table>

The Lorentz oscillator model can be expressed as

$$
\varepsilon(E) = \varepsilon_1(\infty) + \sum_{i=1}^{4} \frac{A_i}{E_i^2 - E^2 - i\Gamma_i E},
$$

where $\varepsilon(\infty)$ refers to the dielectric constant at very large photon energies, $A_i$ is the amplitude of the $i$th oscillator with the unit of (eV)$^2$, $\Gamma_i$ is the damping factor of the $i$th oscillator with the unit of eV, and $E_i$ is the resonant energy with the unit of eV.

Besides the Lorentz oscillator model, the four-term FB model is found to be another choice to get a reasonable spectral fitting. It should be pointed out that the FB model can yield not only the information of optical constants and dielectric functions, but also the band gap of the isolated nc-Si embedded in the SiO$_2$ matrix. The information of the nc-Si band gap is very important because a band-gap expansion (if any) is direct evidence of the quantum confinement effect. Based on the four-term FB model, the optical constants including the refractive index and extinction coefficient of the nc-Si are given by

$$
k(E) = \left( \frac{\sum_{i=1}^{4} \frac{A_i}{E_i^2 - B_i E + C_i}}{E - E_g} \right) (E - E_g)^2,
$$

$$
n(E) = n(\infty) + \sum_{i=1}^{4} \frac{B_{0i} E + C_{0i}}{E^2 - B_i E + C_i},
$$

where

$$
B_{0i} = \frac{A_i}{Q_i} \left( -\frac{B_i^2}{2} + E_g B_i - E_{g}^2 + C_i \right),
$$

$$
C_{0i} = \frac{A_i}{Q_i} \left( C_i \frac{B_i^2}{2} - 2E_g C_i \right),
$$

$$
Q_i = \frac{1}{2} \left( 4C_i - B_i^2 \right)^{\frac{1}{2}},
$$

where $A_i, B_i$, and $C_i$ (i = 1, 2, 3, and 4) are some parameters related to electron transition, $n(\infty)$ is the refractive index when photon energy $E \rightarrow \infty$, and $E_g$ is the energy band gap of the nc-Si.

The spectral fitting is carried out by freely varying the parameters of the models to minimize the following mean-square error (MSE):

$$
MSE = \frac{1}{2N - M} \sum_{i=1}^{N} \left[ \left( \psi_i^{\text{cal}} - \psi_i^{\text{exp}} \right)^2 + \left( \frac{(\Delta_i^{\text{cal}} - \Delta_i^{\text{exp}})}{\sigma_i^{\text{exp}}} \right)^2 \right],
$$

where $N$ is the number of data points in the spectra, $M$ is the number of variable parameters in the model, $\sigma$ is the standard deviation on the experimental data points, $\psi^{\text{exp}}$ and $\Delta^{\text{exp}}$ are the measured values of the $\psi$ and $\Delta$, while $\psi^{\text{cal}}$ and $\Delta^{\text{cal}}$ are the corresponding calculated values. For an efficient spectral fitting, the initial values of parameters of the two models are taken equal to that of bulk crystalline silicon listed in Tables I and II. An excellent spectral fitting based on the above approach in a wide wavelength range of 250 to 1100 nm has been obtained, as shown in Fig. 3, in which the best-fit spectra based on the FB model and Lorentz oscillator model are both included. As can be seen in this figure, all the complicated spectra features of both $\psi$ and $\Delta$ are fitted excellently.

The fittings can yield reasonable values of all the parameters of the models. The best-fit parameters for the nc-Si based on the Lorentz oscillator model and four-term FB model are given in Tables I and II, respectively. For comparison, the corresponding values for bulk crystalline silicon are also shown in the tables. For the Lorentz oscillator model, similar to bulk crystalline silicon, the nc-Si also has four oscillators with some small shifts in the resonant energies relative to that of bulk crystalline silicon. On the other hand, the most important finding from the FB modeling is the large band-gap expansion of the nc-Si. The band gap of the nc-Si is 1.74 eV, which shows a band-gap expansion of ~0.6 eV as compared to the band gap of bulk crystalline silicon. A discussion on the band-gap expansion will be given later.

Using the values of the parameters of the nc-Si shown in Tables I and II, the complex dielectric function and the optical constants of the nc-Si are calculated with Eq. (3) for the Lorentz oscillator model or Eqs. (4) and (5) for the FB model. The dielectric function and optical constants of the nc-Si are shown in Figs. 4 and 5, respectively, in which the
results calculated with the above two optical dispersion models are both included. The dielectric function and the optical constants of bulk crystalline silicon are also included in the two figures for comparison. As can be seen in Figs. 4 and 5, the overall spectral features of optical properties of nc-Si are similar to that of bulk crystalline silicon. However, the nc-Si shows a significant reduction in the optical constants and dielectric function as compared with bulk crystalline silicon. It has been well established that reduction of the static dielectric constant becomes significant as the size of the quantum confined physical systems, such as quantum dots and wires, approaches the nanometric range.\textsuperscript{8,20–22} However, the origin of the reduction in the static dielectric constant with the size is still not fully understood. It is often attributed to the opening of the gap, which should lower the polarizability, but it is also shown that the reduction is due to the breaking of polarizable bonds at the surface and is not due to the opening of the band gap induced by the confinement.\textsuperscript{23}

In addition to the above comparison of dielectric function between the bulk crystalline Si and the nc-Si, it is also interesting to have a comparison to other nanostructured Si ma-
The spectral features of the nc-Si embedded in SiO$_2$ and bulk crystalline Si are similar. However, they are quite different from those of the porous Si layer and the nc-Si layer. This could be explained as below. For the porous Si layer, its dielectric function is affected by the pores and SiO$_2$ existing in the layer; for the nc-Si layer, although the porosity of the layer has been taken into account, the dielectric function is still affected by the native oxide of the nanocrystals. In contrast, in the determination of the dielectric function of nc-Si embedded in the SiO$_2$ matrix, the effect of SiO$_2$ has been separated and there are no pores involved.

As mentioned previously, the nc-Si embedded in SiO$_2$ has a band-gap expansion of $\sim 0.6$ eV as compared to bulk crystalline silicon. The band-gap expansion is consistent with the blueshift of the plot of $(\alpha E)^{1/2}$ vs $E$ (where $\alpha$ is the absorption coefficient and $E$ is the photon energy), as shown in Fig. 7. The band gap of the nc-Si obtained by extrapolating the linear portion of the plot is $1.73$ eV, which is almost the same as the value ($1.74$ eV) given in Table II. The band gap obtained in this work is in very good agreement with the first-principles calculation of the optical gap of silicon nanocrystals based on quantum confinement.

$$E_g(D) = E_{g0} + C/D^n$$

where $D$ is the nanocrystal size in nm, $E_g(D)$ is the band gap in eV of the nanocrystal, $E_{g0}=1.12$ eV is the band gap of bulk crystalline Si, $C=3.9$, and $n=1.22$. For the nc-Si size of 4.2 nm of this work, Eq. (10) gives a band gap of 1.79 eV, which is very close to the band-gap values mentioned above. The band gap of the nc-Si is also comparable to the energy of the photoluminescence (PL) peak. Figure 8 shows the room temperature PL spectrum of the nc-Si embedded in SiO$_2$. As shown in this figure, the PL intensity peaks at the photon energy of 1.61 eV, being similar to the result reported by Valenta and the situation of 18% nc-Si in SiO$_2$ reported in Ref. 27. The band gap is larger than the PL peak energy by $\sim 0.13$ eV. This energy difference is about the same as the energy ($0.134$ eV) of the Si-O vibration peak (the Si-O stretching frequency is $\sim 1083$ cm$^{-1}$) of the system of nc-Si embedded in SiO$_2$ matrix. This may suggest that the interface of nc-Si/SiO$_2$ plays an important role in the light emission.
IV. SUMMARY

In summary, we have developed an approach to determine the optical properties of nc-Si embedded in a SiO$_2$ matrix with spectroscopic ellipsometry based on the Maxwell-Garnett effective medium approximation as well as the SIMS measurements. Optical constants, absorption coefficient, and dielectric function of the nc-Si have been obtained in the photon energy range of 1.1–5.0 eV. The optical properties of the nc-Si are found to be well described by the four-term Forouhi-Bloomer model and the Lorentz oscillator model. The nc-Si shows a significant reduction in the optical constants and dielectric function as compared with bulk crystalline silicon. The band gap of the nc-Si is $\sim$1.7 eV, showing a large band-gap expansion of $\sim$0.6 eV. The band-gap expansion is in very good agreement with the first-principles calculation of the optical gap of silicon nanocrystals based on quantum confinement effect. The difference between the band gap and the PL peak is found to be about the same as the energy of the Si-O vibration peak, implying the role of the interface of nc-Si and/or SiO$_2$ in photoluminescence.

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