**Thickness effect on the band gap and optical properties of germanium thin films**

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The band gap and optical properties (dielectric functions and optical constants) of Ge thin films with various thicknesses below 50 nm, which were synthesized with electron beam evaporation technique, have been determined using spectroscopic ellipsometry and UV-visible spectrophotometry. The optical properties are well described with the Forouhi–Bloomer model. Both the band gap and optical properties show a strong dependence on the film thickness. For film thickness smaller than ~10 nm, a band gap expansion is observed as compared to bulk crystalline Ge, which is attributed to the one-dimensional quantum confinement effect. However, a band gap reduction was observed for thickness larger than ~10 nm, which is explained in terms of the amorphous effect in the Ge layers. © 2010 American Institute of Physics. [doi:10.1063/1.3291103]

I. INTRODUCTION

Germanium (Ge) has been a popular material of study as its properties benefit many applications. Ge was the choice of material used in the first bipolar transistor which was invented in 1949 by Bardeen, Brattain, and Shockley; hence proving its electrical functionality. Due to its small energy band gap (0.66 eV), Ge is also popularly used in optical and optoelectronic devices. Examples of optoelectronic devices that use Ge are photodetectors, solar cells, and waveguides. However, the challenge to design a light source based on Ge has not been solved as Ge is known to be a poor light emitter, but the scaling of materials towards nanoscale, which will change its properties as the thickness is reduced, has shed some ray of hope for Ge to emit light. Hence, it is necessary to study the physical properties of Ge in nanoscale. Previous studies on the optical properties of Ge films were usually focused on the films thicker than 100 nm and also in longer wavelengths (2–200 μm). In this paper, we present a study on the optical properties and band gap of Ge thin films in nanoscale regime (thinner than 50 nm), using spectroscopic ellipsometry (SE) in the wavelength range of 350–1100 nm. The optical properties of the Ge thin films are well described by the Forouhi–Bloomer (FB) model, and the modeling using the FB formula yields the energy band gap of the Ge thin films. The values of the band gap yielded from the modeling are in good agreement with those obtained from the measurement of ultraviolet-visible (UV-visible) spectrophotometry. The ultra-thin Ge films (2.6, 4.7, and 8.2 nm) exhibits a band gap expansion as compared to bulk crystalline Ge, showing the one-dimensional quantum confinement effect. However, a band gap reduction was observed for thicker films (15.3, 22, and 46 nm), which is attributed to the influence of the Urbach band tails arising from the amorphous effect.

II. EXPERIMENT DETAILS

Initially, a 30 nm SiO2 layer was grown on the cleaned surface of p-type (100) Si substrate using dry oxidation at 950 °C for 1 h. A Ge layer of different thicknesses (with nominal values of 3, 5, 8, 15, 20, and 50 nm) was then deposited on the SiO2 layer using the electron beam evaporation method. To examine the amorphous degree of the Ge thin films, Raman spectroscopic measurement was conducted using the Renishaw 1000 Ramascope system with the 633 nm line of He–Ne laser. The actual thicknesses of the Ge thin films were determined by the SE spectral fitting with the surface roughness taken into account. The SiO2 layer, which acts as a buffer layer for the deposition of the Ge layer, can prevent the formation of SiGe alloy and also avoid possible strains or defects occurring at the interface between the Ge layer and the Si substrate. The SE measurements were carried out using a variable angle ellipsometer (J.A.Woollam Inc., Model HS-190) in the wavelength range of 350–1100 nm (1.13–3.54 eV) with a step of 5 nm. The measurements were conducted at three different angles of incidence (65°, 70°, and 75°). The absorption measurements of Ge layer deposited on fused silica substrate were carried out using a UV-visible spectrophotometer (Shimadzu UV2450) in the wavelength range of 350–900 nm with a step of 5 nm. All measurements were conducted in room temperature environment.

III. MODELING AND DISCUSSIONS

Figure 1(a) illustrates the five-phase model (i.e., air/surface-roughness layer/Ge layer/SiO2 layer/Si substrate) used in the SE analysis. The inclusion of surface roughness of the Ge layer is supported by the three-dimensional atomic force microscopic (AFM) image of the Ge layer shown in Fig. 1(b). The AFM measurement shows the existence of the
surface roughness of 0.8 nm. The phase of the surface-roughness layer is modeled by the Bruggeman effective medium approximation

\[
\frac{e_{\text{eff-Ge}} - e_i}{e_{\text{eff-Ge}}} f + \frac{e_{\text{void}} - e_i}{e_{\text{void}}} (1 - f) = 0,
\]

where \(e_i\) (=\(N^2\), where \(N\) is the effective complex refractive index of the surface-roughness layer) is the effective dielectric function of the surface roughness layer, \(e_{\text{eff-Ge}}\) is the Ge dielectric function, \(f\) is the volume fraction of Ge in the surface-roughness layer, and the void dielectric function \(e_{\text{void}}\) is 1.

In the SE analysis, based on the model in Fig. 1(a), the ellipsometric angles (\(\Psi\) and \(\Delta\)) can be expressed as functions of the optical constants and the thickness of the Ge layer. However, due to their complexity, these functions cannot be displayed as analytical formulas. These functions are used in the spectral fitting to the experimental data of \(\Psi\) and \(\Delta\), in order to obtain the optical constants and thickness of the Ge layer. In the spectral fitting, an appropriate optical dispersion model should be used to describe the spectral dependence of the optical constants of the Ge layer. In this work, the FB model\(^\text{16,17}\) was used. The two-term FB model is found to be able to yield a reasonable spectral fitting in the whole wavelength range of the SE measurements at different angles of incidence. Based on the two-term FB model, the optical constants including the refractive index \((n)\) and extinction coefficient \((k)\) of the Ge layer are given by\(^\text{14,16,17}\)

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

\[
n(E) = n(\infty) + \sum_{i=1}^{2} \frac{B_i}{E^2 - B_i E + C_i}, \quad (3)
\]

where

\[
B_0 = \frac{A_i}{Q_i} \left(\frac{-B_i^2}{2} + E_g B_i - E_g^2 + C_i\right),
\]

\[
C_0 = \frac{A_i}{Q_i} \left(E_g^2 + C_i \frac{B_i^2}{2} - 2E_g C_i\right),
\]

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

where \(A_i\), \(B_i\), and \(C_i\) \((i = 1, 2)\) are some parameters related to electron transition, \(n(\infty)\) is the refractive index when photon energy \(E \to \infty\), and \(E_g\) is the energy band gap of the Ge layer.

The spectral fitting was carried out by freely varying both the parameters of the two-term FB model of the Ge layer with the values of their counterparts, bulk crystalline Ge used as the initial values; and also by freely varying the thickness of the Ge layer as well, in order to minimize the mean-square error\(^\text{13}\) for the SE measurements at the three angles of incidence (i.e., 65°, 70°, and 75°). Excellent spectral fittings in the whole wavelength range of the SE measurements at the three angles of incidence have been achieved for all the samples. As an example, Fig. 2 shows the spectral fittings for the Ge layer with nominal thickness of 3 nm at the angles of incidence of 65°, 70°, and 75°, respectively. The values of the parameters of the two-term FB model obtained from the spectral fittings for some of the Ge layers were given in Table I. For comparison, the corresponding values for bulk crystalline Ge is also shown in the table. The thicknesses of the Ge layers with the nominal values of 3, 5, 8, 15, 20, and 50 nm obtained from the spectral fittings are 2.6, 4.7, 8.2, 15.2, 22, and 46 nm, respectively. The thickness values obtained from the SE fittings are close to the nominal values which were set for the electron-beam evaporation based on a standard calibration procedure. In addition, they are also in good agreement with the AFM measurement. On the other hand, it is worthy to mention that the volume fraction of Ge in the surface-roughness layer is about 60%.

The most important parameter for the FB modeling is the energy band gap of the Ge layers. As can be seen in Table I, the band gap of the 2.6 nm Ge layer is 1.03 eV, showing a large band gap expansion of 0.37 eV as compared to the band gap (0.66 eV) of the bulk crystalline Ge, however, the 46 nm Ge layer have a band gap of 0.33 eV, which is...
significantly smaller than the value of the bulk crystalline Ge. The band gap values obtained from the above spectral fittings based on the FB model are consistent with the results from the absorption measurements of the corresponding Ge layers deposited on fused silica substrate with the UV-visible spectrophotometer. As examples, Fig. 3 shows the plots of $\alpha E^{1/2}$ versus $E$ where $\alpha$ is the absorption coefficient obtained from the absorption measurement and $E$ is the photon energy for the 2.6 nm and 46 nm Ge layers. The values of the band gap obtained by extrapolating the linear portion of the plots for all the samples are shown in Fig. 4, and they are also compared to the values obtained from the spectral fittings based on the FB model in the figure. As can be seen in the figure, there is a good agreement between the two techniques, indicating that the results from the SE study are reliable.

Another important finding from Fig. 4 is the thickness dependence of the band gap. When the film thickness is smaller than $\sim 15$ nm, the band gap increases as the thickness decreases, and it is even larger than the band gap of bulk crystalline Ge when the thickness is less than $\sim 10$ nm, showing a band gap expansion. However, when the thickness is larger than $\sim 10$ nm, the band gap is smaller than the value of bulk crystalline Ge. As discussed below, the thickness dependence of the band gap can be explained with the one-dimensional quantum confinement effect and the amorphous effect in the Ge thin films.

The very thin Ge films (e.g., the thickness less than $\sim 15$ nm) could be considered as a one-dimensional confined system. In such a two-dimensional system, elementary excitations will experience quantum confinement resulting in finite motion in the confinement direction (i.e., the thickness direction) and infinite motion in other two directions. It has been well known that as the confining dimension decreases, typically in nanoscale, the energy spectrum turns to discrete and thus the band gap of a semiconductor becomes size dependent. For one-dimensional confinement, the quantization energies increase when the size along the confinement direction (i.e., the film thickness in the present case) decreases, as described by

\[ (\alpha E)^{1/2} = \text{constant} \]

### Table I: Values of parameters $A_i$, $B_i$, $C_i$, $n(\infty)$, and $E_g$ of the FB model of some Ge layers obtained from the spectral fittings. The values of bulk crystalline Ge are included for comparison.

<table>
<thead>
<tr>
<th>Dominant effect</th>
<th>Size</th>
<th>$A_1$</th>
<th>$B_1$</th>
<th>$C_1$</th>
<th>$n(\infty)$</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td></td>
<td>0.0140</td>
<td>7.4019</td>
<td>13.6767</td>
<td>2.4738</td>
<td>0.66</td>
</tr>
<tr>
<td>Amorphous effect</td>
<td>46 nm</td>
<td>0.0686</td>
<td>8.6418</td>
<td>18.7880</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>22 nm</td>
<td>0.3432</td>
<td>3.3081</td>
<td>3.1303</td>
<td>2.3007</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3172</td>
<td>5.8803</td>
<td>10.1510</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0964</td>
<td>2.7755</td>
<td>2.2746</td>
<td>2.1714</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.6566</td>
<td>4.6818</td>
<td>7.6074</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-dimensional quantum confinement effect</td>
<td>4.7 nm</td>
<td>0.1082</td>
<td>3.8072</td>
<td>4.8970</td>
<td>2.2328</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>2.6 nm</td>
<td>0.1077</td>
<td>6.2906</td>
<td>11.2363</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0529</td>
<td>7.1618</td>
<td>13.2426</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( a \) is the thickness of the layer and \( m \) is the effective carrier mass. Equation (7) can generally explain the band gap expansion with reduction of film thickness, but it cannot quantitatively describe the result shown in Fig. 4 because the amorphous effect also affects the band gap significantly as discussed below.

Figure 5 shows the Raman spectra of the Ge layers with different thicknesses. A broad Raman band at around \( \sim 270 \text{ cm}^{-1} \) is observed for all samples, and the situation is similar to that of amorphous Ge films.\(^{22,23}\) It is been reported that scattering of local transverse optical phonons leads to a broad Raman band at around 275 \text{ cm}^{-1}.\(^{22,23}\) The result of the Raman measurement indicates that all the Ge layers under study are amorphous or at least present a high degree of structural disorder. The situation is expected as the substrate temperature was maintained below 50 °C during the Ge evaporation and there was no postevaporation annealing.\(^{7}\) In an amorphous or structurally disordered film, the imperfection in the film causes the bands of localized states to get broadened, and a band gap reduction may occur due to the Urbach edge.\(^{9,24}\) The band gap reduction shown in Fig. 4 indicates that the amorphous effect is dominant for film thickness larger than \( \sim 10 \text{ nm} \). However, for film thickness smaller than \( \sim 10 \text{ nm} \), the one-dimensional quantum confinement effect is dominant, and thus the band gap increases when the film thickness is reduced.

On the other hand, the optical constants \((n, k)\) of the Ge layers can be calculated with Eqs. (2)–(6) by using the values of the parameters of the FB model given in Table I, and for a clear presentation, only the results for the thinnest layer (2.6 nm) and the thickest layer (46 nm) are shown in Fig. 6. The real part \((=n^2-k^2)\) and imaginary part \((=2nk)\) of the complex dielectric functions of the Ge layers can be obtained also, and the results are shown in Fig. 7. For comparison, the optical constants and dielectric function of bulk crystalline Ge are also included in Figs. 6 and 7, respectively.\(^{25}\) The broadened structures in the dielectric function spectra observed in Fig. 7 are due to the amorphous or disorder structures presented in the Ge layers. It is worth mentioning that as can be seen in Fig. 6, the dielectric function of the 2.6 nm Ge layer is much lower than that of the bulk crystalline Ge. This phenomenon could be related to the quantum size effect as a large band gap expansion has been observed as a result of the quantum confinement in the 2.6 nm Ge layer. It has been well established that the static dielectric constant decreases as the size of quantum confined physical systems is of nanometric range\(^{14,26}\) although the detailed mechanism is still not fully understood. The reduction in dielectric constant has been attributed to the opening of the gap which should lower the polarizability\(^{27}\) or the break-
band gap expansion is observed, however, for thickness larger than \( \sim 10 \) nm, the amorphous effect is dominant, leading to a reduction in the band gap.

**ACKNOWLEDGMENTS**

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