C incorporation in epitaxial Ge$_{1-y}$C$_{y}$ layers grown on Ge(001): An ab initio study

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Ab initio density-functional calculations, employing the generalized-gradient approximation, have been used to determine formation energies $U$ and the strain associated with different C lattice site configurations in fully coherent Ge$_{1-y}$C$_{y}$ layers grown on Ge(001). Calculations using strained 64-atom supercells show that substitutional C, for which $U=2.40$ eV, is the most stable configuration involving only one C atom per configuration. The bond-centered interstitial and the Ge-C split interstitial configurations have formation energies which are 2.9 and 1.78 eV higher, respectively. However, [001]-oriented C pairs and C triplets are even more stable than substitutional C, by 0.17 and 0.80 eV per C atom, indicating a strong tendency for C atoms to cluster during Ge$_{1-y}$C$_{y}$ growth. Calculated C-induced strain coefficients provide insight for interpreting Ge$_{1-y}$C$_{y}$ x-ray diffraction results and macroscopic strain measurements.

C-containing group-IV alloys, especially Si$_{1-x}$Ge$_{x}$C$_{y}$, are of both technological and scientific interest due to the potential they offer for band-gap and strain-state engineering of layers used in microelectronic and optoelectronic devices compatible with Si integrated circuit technology. There are, however, severe challenges associated with their growth. First, the equilibrium solubility of C in Si and Ge is extremely low, $\approx 10^{17}$ and $10^{8}$ cm$^{-3}$, respectively. Low-temperature growth under highly constrained conditions is required to take advantage of the fact that surface solubilities are orders of magnitude larger than bulk values, while simultaneously inhibiting bulk phase separation during deposition. Another obstacle to be overcome is the large lattice constant mismatch, 34% and 37%, between diamond (a$_{c}$=3.5668 Å) and the group-IV semiconductors Si (a$_{Si}$ = 5.4310 Å) and Ge (a$_{Ge}$=5.6576 Å), respectively.

Si$_{1-x}$Ge$_{x}$C$_{y}$ has been widely studied experimentally and theoretically, but C incorporation into Ge$_{1-y}$C$_{y}$ alloys has received very little attention. Most reported experimental investigations have focused on the growth of Ge$_{1-y}$C$_{y}$ layers (y < 0.1) on Si(001). However, Ge$_{1-y}$C$_{y}$/Si(001) layers typically have highly defective microstructures containing large concentrations of misfit dislocations which can act as sinks for incorporated C.

There are few reports of the successful growth of metastable Ge$_{1-y}$C$_{y}$ alloys on Ge(001). Duschl et al. employed molecular-beam epitaxy (MBE) to grow 30-50 nm thick Ge$_{1-y}$C$_{y}$/Ge superlattices with y = 0.012 and 0.021 at temperatures $T_s$ = 200 and 300 °C. Based upon x-ray diffraction (XRD) measurements of the macroscopic strain state, they concluded that the fraction of incorporated C at substitutional sites was only 0.3 at $T_s$ = 200 °C and 0.1 at $T_s$ = 300 °C. Yang et al. reported the growth of epitaxial Ge$_{0.95}$C$_{0.05}$ on Ge(001) by MBE at $T_s$ = 300 °C but noted that the layers contained stacking faults and exhibited rough 113-faceted surfaces. Raman spectroscopy indicated that only a small fraction of the C was on substitutional sites giving rise to a weak local vibrational mode at 530 cm$^{-1}$ (Ref. 8). This is in good agreement with results of Hoffman and co-workers who used infrared absorption spectroscopy to characterize Ge wafers implanted with $^{12}$C$^{1+}$ and $^{13}$C$^{1+}$ ions at energies and doses chosen to provide a uniformly doped 0.7-μm-thick region with y = 0.007. They observed a Ge-C stretch mode at a frequency of 531 cm$^{-1}$, consistent with predicted values obtained from ab initio local-density functional cluster calculations yielding a vibrational mode frequency between 516 and 563 cm$^{-1}$ for substitutional C in Ge.9 Analyses of ion channeling rocking curves about the (100), (110), and (111) axes suggested that up to 31 ± 3% of the incorporated C was in substitutional sites.

We recently reported the epitaxial growth of Ge$_{1-y}$C$_{y}$/Ge(001) from hyperthermal beams. The films were coherent with the Ge substrate, did not contain misfit dislocations, and were in a state of in-plane compression due primarily to the formation of Ge-C split interstitials during growth.10 The proposed pathway for the formation of the split interstitials involves the reaction in the near-surface region between incorporated substitutional C atoms and Ge self-interstitials, the latter produced by fast incident neutral Ge atoms during deposition.

Two recent theoretical investigations have focused on substitutional C in Ge$_{1-y}$C$_{y}$. Kelires investigated the bulk and surface structure of Ge$_{1-y}$C$_{y}$ alloys using atomistic Monte Carlo simulations within the empirical potential approach. He found that nearby substitutional C atoms prefer to occupy third-nearest-neighbor sites and that C-C dimers on the surface of Ge$_{0.98}$C$_{0.02}$/Ge(001) are more favorable than Ge-C dimers. Guedj et al. employed an anharmonic Keating model to investigate lattice distortions and local vibrational modes in Ge$_{1-y}$C$_{y}$ alloys. They found that the alloy lattice constant follows Vegard’s rule for y < 3% and confirmed that the third-nearest-neighbor arrangement is most stable.

All experimental reports indicate that only a small fraction of incorporated C atoms occupy substitutional sites in Ge$_{1-y}$C$_{y}$. There is, however, no conclusive experimental evidence regarding the lattice site(s) occupied by the remaining C and previous theoretical investigations have only considered the substitutional configuration.
In this paper, we present the results of initial investigations of the formation energies associated with C incorporation into single and multiple lattice site configurations in Ge$_{1-y}$C$_y$. We employ density-functional-theory-based \textit{ab initio} calculations for fully strained epitaxial Ge$_{1-y}$C$_y$ layers on Ge(001). A comparison of the formation energies per C atom shows that substitutional C atoms are energetically less favorable than C triplets. We also calculate the strain coefficients $\alpha$ since they can be used for direct comparison with experimental XRD results.

The calculations were performed using the Vienna \textit{ab initio} simulation package,\textsuperscript{13} which employs pseudopotentials and a plane-wave basis set to calculate the Kohn-Sham ground state. Both the generalized-gradient approximation (GGA) of Perdew and Wang\textsuperscript{14} and the local density approximation (LDA) (Ref. 15) were used to obtain the exchange-correlation functional. Calculations with gradient corrections generally yield more accurate cohesive energies\textsuperscript{15-18} and we therefore emphasize the results obtained from the GGA calculations while the LDA results are presented in Table I for comparison and in order to estimate the uncertainty introduced by the exchange-correlation functional.

Ultrasonic Vanderbilt-type pseudopotentials,\textsuperscript{19} with core radii of 2.58 and 1.81 a.u. for Ge and C, respectively, provided good total energy convergence with an energy cutoff of $E_{\text{cut}}=287$ eV for the plane-wave basis set expansion. Ge$_{1-y}$C$_y$ configurations were calculated in the neutral charge state using 64-atom supercells. In order to compare with experimental data for the pseudomorphic growth of Ge$_{1-y}$C$_y$ on Ge(001), the unit-cell shape was chosen to be tetragonal, with $a_1 = a_2 = a_{\text{Ge}}$. The Ge equilibrium lattice constant $a_{\text{Ge}}$ was obtained by fitting the calculated total energy versus volume with the Murnaghan equation of state.\textsuperscript{20} We obtain values of 5.759 Å (5.625 Å) using GGA (LDA). This is slightly above (below) the experimental value $a_{\text{Ge}} = 5.6576$ Å as commonly observed when employing GGA (LDA).\textsuperscript{21} The equilibrium total energies $E$ and lattice constants perpendicular to the film surface $a_z$ were obtained for each Ge$_{1-y}$C$_y$ configuration by relaxing the ionic positions using a conjugate-gradient algorithm for a minimum set of three different unit-cell sizes obtained by changing the value of $a_z$ by 1% increments. The total energy as a function of $a_z$ was then fit by a parabola.

$k$-space sampling was performed according to the method of Monkhorst and Pack\textsuperscript{22} using a $4\times4\times4$ grid which corresponds to, depending on the symmetry of the configuration, 6 to 20 $k$ points in the irreducible wedge of the Brillouin zone.

Free energies of formation $U$ presented here are obtained from the calculated total energy $E$ of a given configuration with $N_{\text{Ge}}$ Ge and $N_C$ C atoms, according to the expression

$$U = E - N_{\text{Ge}} \mu_{\text{Ge}} - N_C \mu_C.$$  

The Ge and C chemical potentials $\mu_{\text{Ge}}$ and $\mu_C$ are $-4.54$ and $-9.12$ eV ($-5.20$ and $-10.16$ eV with LDA), respectively, as determined by calculating the total energy of pure Ge and diamond, and using the same pseudopotentials, unit-cell size, $E_{\text{cut}}$, and $k$-space sampling as for the Ge$_{1-y}$C$_y$(001) calculations. Correcting the resulting chemical potentials with the corresponding atomic spin energy of Ge and C yields cohesive energies for Ge and diamond of 3.83 and 7.80 eV (4.63 and 8.91 eV with LDA), respectively, in very good agreement with values obtained by Fuchs \textit{et al.}\textsuperscript{16}

$U$ was found to converge to within 0.05 eV with respect to $E_{\text{cut}}$ and $k$-space sampling for all C configurations investigated. The validity of the C pseudopotential cutoff radius was confirmed by performing calculations with an even larger cutoff radius $r_c = 2.12$ a.u. This resulted in $U$ changing by only 0.1 eV. The total computational uncertainty in $U$ is therefore estimated to be <0.1 eV.

Equilibrium configurations were determined by relaxing several initial configurations with the same number of Ge and C atoms and then choosing the one with the lowest total relaxed energy. This approach is feasible when $N_C$ is small and there are only a limited number of different geometries. We considered $\approx 30$ different initial configurations and found the equilibrium configurations for $N_C = 1, 2,$ and 3, with $N_{\text{Ge}} = 63$ and 64, as presented in Fig. 1. We use the labels $C_{\text{N}}^L$ for C in Ge configurations in which $\lambda = (64 - N_{\text{Ge}})$ is the number of Ge atoms missing from the original bulk Ge supercell. The bond lengths are obtained from the GGA calculations, corrected by 1.8% for the overestimated relaxed Ge lattice constant. The corrected LDA bond lengths agree reasonably well with the GGA values; deviations are $\approx 2\%$.

The results are summarized in Table I in which calculated formation energies $U$ and formation energies per C atom, $\bar{U} = U/N_C$, are given for both GGA and LDA. Table I also shows calculated ratios $a_z/a_{\text{Ge}}$ and strain coefficients $\alpha$ associated with each C configuration in order to determine the strain state of a corresponding Ge$_{1-y}$C$_y$ layer on Ge(001). We define $\alpha$ through the expression

$$a_z = a_{\text{Ge}} (1 + \alpha y).$$

### Table I. Formation energy $U$, formation energy per C atom $\bar{U}$, strain ratio $a_z/a_{\text{Ge}}$, and strain coefficient $\alpha$, obtained using GGA and LDA for relaxed C configurations in pseudomorphic fully strained Ge$_{1-y}$C$_y$ layers ($a_z = a_{\text{Ge}} = a_{\text{Ge}}$) on Ge(001).

<table>
<thead>
<tr>
<th>Configurations</th>
<th>$U$ (eV)</th>
<th>$\bar{U}$ (eV)</th>
<th>$a_z/a_{\text{Ge}}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substitutional</td>
<td>GGA</td>
<td>LDA</td>
<td>GGA</td>
<td>LDA</td>
</tr>
<tr>
<td>Split interstitial</td>
<td>$C_1^2$</td>
<td>2.40</td>
<td>2.44</td>
<td>2.40</td>
</tr>
<tr>
<td>C pair</td>
<td>$C_2^0$</td>
<td>4.18</td>
<td>4.50</td>
<td>4.18</td>
</tr>
<tr>
<td>Double interstitial</td>
<td>$C_2^1$</td>
<td>4.45</td>
<td>4.88</td>
<td>2.23</td>
</tr>
<tr>
<td>C triplet</td>
<td>$C_3^1$</td>
<td>4.74</td>
<td>5.43</td>
<td>2.37</td>
</tr>
</tbody>
</table>
FIG. 1. Relaxed C configurations in pseudomorphic Ge$_{1-x}$C$_x$ with in-plane lattice constants $a_y = a_z = a_{Ge}$. $N_C$ and $\Lambda$ in configuration $C_N^{\Lambda C}$ correspond to the number of incorporated C atoms and the number of Ge atoms missing from the original bulk Ge supercell, respectively.

It is important to note that we consider fully coherent Ge$_{1-x}$C$_x$/Ge(001) layers in which $a_x = a_y = a_z = a_{Ge}$ and only $a_z$ varies with C configuration and concentration. In the case of fully relaxed Ge$_{1-x}$C$_x$ with randomly oriented C configurations, $a_x = a_y = a_z = a_o$, the relaxed lattice constant $a_o$ is given by

$$a_o = a_{Ge}(1 + \beta \gamma),$$  \hspace{1cm} (3)

where

$$\beta = \frac{aC_{11}}{C_{11}+2C_{12}}.$$  \hspace{1cm} (4)

The strain coefficient $\beta$ is proportional to $\alpha$ and, using the elastic constants for pure Ge, $C_{11} = 129$ GPa and $C_{12} = 48$ GPa,\textsuperscript{22} we obtain $\beta = 0.57 \alpha$.

Figure 1(a) shows the most stable configuration involving one C atom, direct substitution on a Ge lattice site, with $U = \bar{U} = 2.40$ eV. The C-Ge bond length is 2.08 Å, 15% smaller than the Ge-Ge bond length, 2.45 Å, in bulk Ge and in good agreement with previously reported Ge-C bond lengths of 2.05 and 2.13 Å from Refs. 11 and 12, respectively. This configuration results in a 1.1% in-plane tensile strain in the 64-atom supercell. The calculated strain coefficient $\alpha$ is $-0.71$, slightly less than the Vegard’s rule value of $-0.64$ and indicative of negative bowing in the alloy lattice parameter.\textsuperscript{11}

The Ge-C split interstitial, shown in Fig. 1(b), consists of a Ge-C pair aligned along [001] and occupying a single Ge lattice site. This configuration, labeled $C_1^0$, is 0.3 and 2.9 eV more stable than a Ge-C split interstitial aligned along [011] and a bond-centered interstitial C, respectively. It is also 0.7 eV more stable, due to the additional strain energy, than the Ge-C pair aligned along the strained [100] or [010] directions in heteroepitaxial Ge$_{1-y}$C$_y$ on Ge(001). The Ge-C split interstitial configuration has a formation energy $U = 4.18$ eV and is therefore almost 2 eV less stable than the $C_1^1$ substitutional C-atom configuration.

Figures 1(c) and 1(d) show the equilibrium configurations involving two C atoms with $\Lambda = 1$ ($C_1^1$) and $\Lambda = 0$ ($C_2^1$), respectively. The $C_1^1$ configuration consists of a C pair along [001], similar to the Ge-C split interstitial [Fig. 1(b)]. The alignment along [001] is 0.3 eV more stable than a C pair along [111], a geometry that has been proposed for C defects in Si.\textsuperscript{24} The bond length between the C pair atoms is 1.35 Å. This configuration induces only a small in-plane compressive strain, expanding the 65-atom cell by 0.6% and corresponding to $\alpha = 0.18$. The $C_2^1$ formation energy is 4.45 eV with $\bar{U} = 2.23$ eV per C atom. The substitutional C-pair configuration is, therefore, slightly, by 0.17 eV, more stable than substitutional C atoms. LDA formation energies for these two configurations are, however, identical. We consider the GGA values more reliable since GGA corrects the LDA tendency for overbinding.\textsuperscript{16}

The $C_2^0$ configuration [Fig. 1(d)] consists of two neighboring bond-centered C interstitials, which themselves form a C-C bond along the [110] direction with a bond length of 1.28 Å. This double interstitial configuration expands the lattice constant of the supercell by 1.8%, corresponding to $\alpha = 0.63$. The formation energy per C atom is $\bar{U} = 2.40$ eV, slightly higher than that of the $C_1^1$ pair configuration.

Other possible two-C-atom configurations $C_2^2$ (not shown) include two substitutional C atoms on first-, second-, or third-nearest-neighbor sites corresponding to formation energies per C atom of 2.77, 2.47, and 2.30 eV, respectively. These configurations are thus energetically less favorable than the C pair $C_1^1$. First- and second-nearest-neighbor configurations are also less favorable than a single substitutional C atom ($\bar{U} = 2.40$ eV). However, the third-nearest-neighbor arrangement has a lower formation energy than the $C_1^1$ configuration. This is in agreement with reported C-C pair correlation functions\textsuperscript{11} which indicate a repulsive interaction between C atoms occupying first- and second-nearest-neighbor sites and a preference for third-nearest substitutional sites in Ge$_{1-y}$C$_y$. We also find that C atoms on neighboring sites do not form a strong bond (along the [111] direction), resulting in a C-C distance of 3.64 Å, which is considerably larger than the 2.45 Å Ge-Ge distance in bulk Ge.

A three-C-atom $C_3^1$ configuration on a single lattice site is shown in Fig. 1(e). The C atoms are aligned along the [001] direction, partially filling the Ge vacancy volume. This results in a relatively small in-plane compressive strain with an out-of-plane lattice constant increase of 1.7% and $\alpha = 0.37$. The formation energy of this C triplet is 4.80 eV with $\bar{U} = 1.60$ eV, considerably ($\sim 0.7$ eV) less than the values obtained for the most stable one- and two-C configurations.

Another possible 3-C configuration ($C_3^2$, not shown) consists of two neighboring substitutional C atoms with a bond-
centered interstitial C between them. That is, the three C atoms are aligned along [111]. This configuration is 0.62 eV less stable than the $C_1^3$ triplet. However, its formation energy per C atom, $\bar{U} = 1.81$ eV, is still lower than configurations with $N_C=1$ and 2.

Comparing the formation energies per C atom for all configurations considered with $N_C=1, 2, 3$ clearly indicates that it is energetically favorable for C atoms to form small clusters. This trend is shown in Fig. 2, a plot of $\bar{U}$ as a function of $N_C$. The lowest energy two-C configuration $C_2^2$ is 0.17 eV more stable than the lowest energy one-C configuration $C_1^1$. Adding a third-C atom further reduces the formation energy per C atom by an even larger amount, 0.63 eV. We expect that configurations with $N_C=4, 5, 6, \ldots$ will continue to exhibit smaller formation energies with increasing $N_C$ and we therefore conclude that C in Ge$_{y}$C$_{1-y}$ has a strong tendency to form clusters with a stable minimum nuclei size of only two C atoms.

In summary, our results show that during the growth of Ge$_{y}$C$_{1-y}$ layers, C complexes with $N_C>1$ are energetically favored to form whenever diffusing C atoms encounter another C atom or C multimer. Therefore, the technologically interesting case for Ge$_y$C$_{1-y}$ growth with C incorporated primarily on substitutional sites is only possible under highly kinetically limited growth conditions, where both surface and bulk$^{25}$ C atom encounters are negligible. Thus, only growth under conditions of low temperature, low C concentration, and low C surface segregation will yield films with fully substitutional C. This is consistent with experimental results,$^7,8,10$ which indicate that only a small fraction of the incorporated C in Ge$_y$C$_{1-y}$ occupies substitutional sites and that the substitutional fraction increases with decreasing growth temperatures, from 0.1 at $T_s = 300$ °C to 0.3 at 200 °C for Ge$_{0.985}$C$_{0.012}$ and Ge$_{0.975}$C$_{0.025}$. Finally, we note that the computational results presented here provide insights into expected atomic configurations for C in nonsubstitutional sites and the calculated strain coefficients can be used for direct comparisons with high-resolution XRD results.

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25. Based upon the annealing experiments presented in Ref. 7, we expect the bulk diffusivity of C in Ge to be negligible for Ge$_{y}$C$_{1-y}$ growth temperatures <450 °C.