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C incorporation in epitaxial $\mathrm{Ge}_{1-y}\mathrm{C}_y$ 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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$ 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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$ growth. Calculated C-induced strain coefficients provide insight for interpreting $\mathrm{Ge}_{1-y}\mathrm{C}_y$ x-ray diffraction results and macroscopic strain measurements.

C-containing group-IV alloys, especially $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$, 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, $\simeq 10^{17}$ and $10^{8}\,\mathrm{cm}^{-3}$, respectively.[1] Low-temperature growth under highly kinetically constrained conditions is required to take advantage of the fact that surface solubilities are orders of magnitude larger than bulk values,[2] while simultaneously inhibiting bulk phase separation during deposition. Another obstacle to be overcome is the large lattice constant mismatch, 34% and 37%, between diamond ($a_{\mathrm{C}}=3.5668$ Å) and the group-IV semiconductors Si ($a_{\mathrm{Si}}=5.4310$ Å) and Ge ($a_{\mathrm{Ge}}=5.6576$ Å), respectively.

$\mathrm{Si}_{1-y}\mathrm{C}_y$ has been widely studied experimentally[3] and theoretically,[4] but C incorporation into $\mathrm{Ge}_{1-y}\mathrm{C}_y$ alloys has received very little attention. Most reported experimental investigations have focused on the growth of $\mathrm{Ge}_{1-y}\mathrm{C}_y$ layers ($y\leqslant 0.1$) on Si(001).[5,6] However, $\mathrm{Ge}_{1-y}\mathrm{C}_y$/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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$ alloys on Ge(001). Duschl *et al.*[7] employed molecular-beam epitaxy (MBE) to grow 30 periods of 3-nm/10-nm $\mathrm{Ge}_{1-y}\mathrm{C}_y$/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.*[5] reported the growth of epitaxial $\mathrm{Ge}_{0.95}\mathrm{C}_{0.05}$ on Ge(001) by MBE at $T_s=200$ °C but noted that the layers contained stacking faults and exhibited rough 113 facetted 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[9] who used infrared absorption spectroscopy to characterize Ge wafers implanted with $^{12}\mathrm{C}^{1+}$ and $^{13}\mathrm{C}^{1+}$ 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 $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ axes suggested that up to $31\pm 3\%$ of the incorporated C was in substitutional sites.

We recently reported the epitaxial growth of $\mathrm{Ge}_{1-y}\mathrm{C}_y$/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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$. Kelires[11] investigated the bulk and surface structure of $\mathrm{Ge}_{1-y}\mathrm{C}_y$ 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 $\mathrm{Ge}_{0.98}\mathrm{C}_{0.02}$/Ge(001) are more favorable than Ge-C dimers. Guedj *et al.*[12] employed an anharmonic Keating model to investigate lattice distortions and local vibrational modes in $\mathrm{Ge}_{1-y}\mathrm{C}_y$ alloys. They found that the alloy lattice constant follows Vegard's rule for $y\leqslant 3\%$ 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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$. 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.

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

		U (eV)		$\tilde{U}$ (eV)		a_z/a_{Ge}		α	
Configurations		GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
Substitutional	C_1^1	2.40	2.44	2.40	2.44	0.989	0.989	−0.71	−0.68
Split interstitial	C_1^0	4.18	4.50	4.18	4.52	1.015	1.014	0.95	0.90
C pair	C_2^1	4.45	4.88	2.23	2.44	1.006	1.005	0.18	0.17
Double interstitial	C_2^0	4.74	5.43	2.37	2.72	1.018	1.017	0.63	0.61
C triplet	C_3^1	4.80	5.65	1.60	1.85	1.017	1.017	0.37	0.37

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 $\mathrm{Ge}_{1-y}\mathrm{C}_y$. We employ density-functional-theory-based *ab initio* calculations for fully strained epitaxial $\mathrm{Ge}_{1-y}\mathrm{C}_y$ layers on Ge(001). A comparison of the formation energies per C atom shows that substitutional C atoms are energetically less favorable than substitutional C pairs, which are in turn less favorable than C triplets. We also calculate the strain coefficients α since they can be used for direct comparison with experimental XRD results.

The calculations were performed using the Vienna *ab initio* simulation package,[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[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[16–18] 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.

Ultrasoft Vanderbilt-type pseudopotentials,[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 $E_{\mathrm{cut}} = 287\,\mathrm{eV}$ for the plane-wave basis set expansion. $\mathrm{Ge}_{1-y}\mathrm{C}_y$ configurations were calculated in the neutral charge state using 64-atom supercells. In order to compare with experimental data for the pseudomorphic growth of $\mathrm{Ge}_{1-y}\mathrm{C}_y$ on Ge(001), the unit-cell shape was chosen to be tetragonal, with $a_x = a_y = a_{\mathrm{Ge}}$. The Ge equilibrium lattice constant a_{Ge} was obtained by fitting the calculated total energy versus volume with the Murnaghan equation of state.[20] We obtain values of 5.759 Å (5.625 Å) using GGA (LDA). This is slightly above (below) the experimental value $a_{\mathrm{Ge}} = 5.6576\,\text{Å}$ as commonly observed when employing GGA (LDA).[21] The equilibrium total energies E and lattice constants perpendicular to the film surface a_z were obtained for each $\mathrm{Ge}_{1-y}\mathrm{C}_y$ 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[22] using a $4 \times 4 \times 4$ 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_{Ge} Ge and N_{C} C atoms, according to the expression

$$U = E - N_{\mathrm{Ge}}\mu_{\mathrm{Ge}} - N_{\mathrm{C}}\mu_{\mathrm{C}}. \tag{1}$$

The Ge and C chemical potentials μ_{Ge} and μ_{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_{cut}, and *k*-space sampling as for the $\mathrm{Ge}_{1-y}\mathrm{C}_y(001)$ 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 *et al.*[16]

U was found to converge to within 0.05 eV with respect to E_{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 $\simeq 30$ different initial configurations and found the equilibrium configurations for $N_{\mathrm{C}} = 1$, 2, and 3, with $N_{\mathrm{Ge}} = 63$ and 64, as presented in Fig. 1. We use the labels $C_{N_{\mathrm{C}}}^{\Lambda}$ for C in Ge configurations in which $\Lambda = (64 - N_{\mathrm{Ge}})$ 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 $\simeq 2\%$.

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

$$a_z = a_{\mathrm{Ge}}(1 + \alpha y). \tag{2}$$

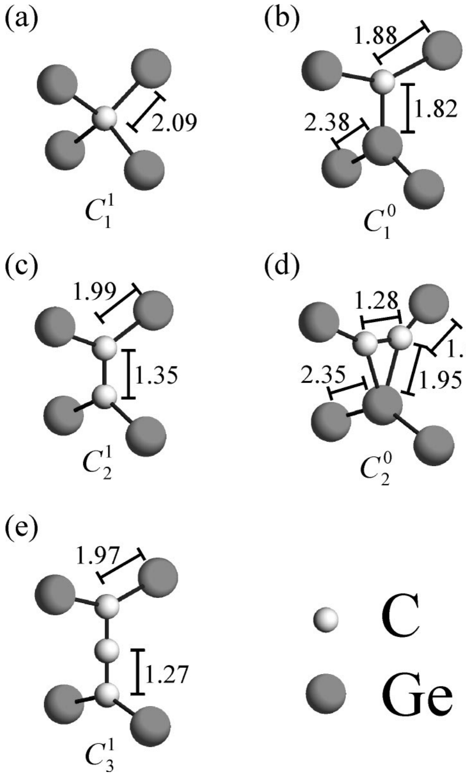

FIG. 1. Relaxed C configurations in pseudomorphic $Ge_{1-y}C_y$ with in-plane lattice constants $a_x = a_y = a_{Ge}$. N_C and Λ in configuration $C_{N_C}^{\Lambda}$ correspond to the number of incorporated C atoms and the number of Ge atoms missing from the original bulk Ge supercell, respectively.

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

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

where

$$\beta = \frac{\alpha C_{11}}{C_{11} + 2C_{12}}. \tag{4}$$

The strain coefficient β is proportional to α and, using the elastic constants for pure Ge, $C_{11} = 129$ GPa and $C_{12} = 48$ GPa,[23] 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 $U = \tilde{U} = 2.40$ 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 α is -0.71, slightly less than the Vegard's rule value of -0.64 and indicative of negative bowing in the alloy lattice parameter.[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 0.1 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_2^1) and $\Lambda = 0$ (C_2^0), respectively. The C_2^1 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.[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 $\tilde{U} = 2.23$ 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.[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 $\tilde{U} = 2.40$ eV, slightly higher than that of the C_2^1 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_2^1. First- and second-nearest-neighbor configurations are also less favorable than a single substitutional C atom ($\tilde{U} = 2.40$ 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[11] which indicate a repulsive interaction between C atoms occupying first- and second-nearest-neighbor sites and a preference for third-neighbor 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 $\tilde{U} = 1.60$ eV, considerably ($\simeq 0.7$ 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-

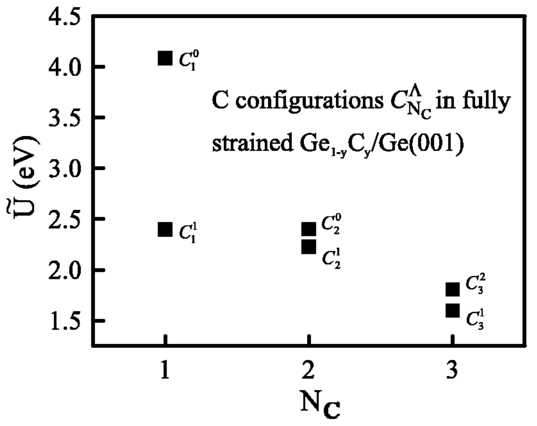

FIG. 2. Formation energy $\tilde{U}$ per C atom vs the number of C atoms N_C in relaxed C configurations in pseudomorphic fully strained $Ge_{1-y}C_y$ layers ($a_x = a_y = a_{Ge}$) on Ge(001).

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_3^1 triplet. However, its formation energy per C atom, $\tilde{U} = 1.81$ 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, and 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 $\tilde{U}$ as a function of N_C. The lowest energy two-C configuration C_2^1 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_yC_{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_yC_{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_yC_{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_yC_{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 $Ge_{0.988}C_{0.012}$ and $Ge_{0.979}C_{0.021}$.[7] 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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