# Chemical Vapor Deposition Growth of Graphene on 200 mm Ge(110)/Si Wafers and Ab Initio Analysis of Differences in Growth Mechanisms on Ge(110) and Ge(001)

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# INTRODUCTION

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Graphene films are highly appealing to microelectronics.<sup>1-4</sup> However, in efficient integration schemes, graphene should preferably be grown directly on CMOS-compatible substrates, ideally on a dielectric layer, which still remains a challenge. Although the carrier mobility in graphene transferred from copper to hexagonal boron nitride (hBN) can be as high as  $3 \times$  $10^5$  cm<sup>2</sup>/Vs,<sup>5</sup> this process scheme is unsuitable for mass production because it requires hBN to be exfoliated and the resulting graphene consists of submicrometer "pads" instead of a closed film.<sup>6,7</sup> Direct growth of graphene on dielectric substrates, such as Al<sub>2</sub>O<sub>3</sub>, sapphire, SiO<sub>2</sub>, MgO, and Si<sub>3</sub>N<sub>4</sub>, has also been attempted.<sup>8-10</sup> Due to poor catalytic properties of dielectric substrates, the results indicated that graphene films are affected by defects. The direct growth on a CMOScompatible semiconductor would be of interest. Silicon as a common substrate material for CMOS processing forms carbide when brought into contact with carbon, which hampers graphene growth.<sup>11</sup> Germanium, which is akin to Si and fully compatible with Si CMOS, does not form carbides.<sup>12</sup> It catalyzes the decomposition of hydrocarbon precursors,<sup>13</sup> and it is a promising substrate for graphene growth. Wrinklefree graphene, attributable to small differences of thermal expansion coefficients between Ge and graphene, was reported on this material.<sup>13</sup> On the other side, graphene films develop

wrinkles when the thermal expansion coefficient of graphene and the underlying substrates, such as copper, differs.<sup>14</sup> Aside from growing wrinkle-free graphene, graphene transferred from Ge is free from metallic contamination, which further ensures the compatibility of the graphene/Ge systems with mainstream silicon technology.<sup>15</sup>

Several works have been devoted to growing graphene on the most technologically relevant (001) orientation of Ge,<sup>15–28</sup> including the growth on Ge(001) deposited on 8 inch sized Si(001) substrates used in standard CMOS processing.<sup>15</sup> However, the graphene/Ge(001) stack has several issues. As graphene is growing on Ge substrates, the morphology of the Ge(001) surface changes: (107) nanofacets appear.<sup>15–18,22,28</sup> One of the consequences is the quantum-mechanical interaction between graphene and the substrate, which is different on the ridges and in the valleys of the facets, leading to the electrical inhomogeneities of the film.<sup>16,18,23</sup> Further-

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Figure 1. (a) XPS C 1s and (b) Raman spectra of as-grown graphene on Ge(110).

more, Ge-Ge bonds change direction by  $90^{\circ}$  in each (001) layer of Ge, so that two families of orientational domains appear in graphene, each associated with the underlying  $2 \times 1$ or  $1 \times 2$  dimerization of the surface atoms and rotated by  $30^{\circ}$ with respect to one another.<sup>16,18,19</sup> The resulting grain boundaries cause significant structural defects and decrease the film integrity, as exemplified by the observation that oxidation of graphene-covered Ge wafers is initiated.<sup>23,29-31</sup> The presence of interfacial oxygen atoms negatively impacts the electrical and mechanical properties of graphene.<sup>15,29</sup> Even if perfectly reconstructed, the grain boundaries are expected to adversely affect the electrical mobility of graphene by scattering mechanisms. On the contrary, the "seamless" stitching of grains can be achieved by the growth of graphene on Ge(110). This leads to the improved quality graphene films<sup>13,32,33</sup> as high electrical mobility in the range from about  $1 \times 10^4$  cm<sup>2</sup>/  $Vs^{13}$  to nearly  $3 \times 10^4$  cm<sup>2</sup>/Vs<sup>33</sup> and reduced oxidation of the underlying Ge(110) surface were demonstrated.<sup>29,31</sup> Most significantly, the surface of Ge(110) underneath the graphene layer remains flat: in contrast to graphene/Ge(001), there are only random surface steps, and no faceting was observed.<sup>13,23,28,32</sup> Also, Ge(11L) vicinals (L > 3) of Ge(001)respond to the CVD of graphene with the formation of (107)facets, while Ge(113) and Ge(111) surfaces remain stable.<sup>21</sup>

To the best of our knowledge, the reason why Ge(001) responds to the CVD of graphene by faceting while Ge(110) remains flat has not yet been disclosed. Therefore, this study addresses this question by applying ab initio density functional theory (DFT) to disclose the mechanisms of the faceting/ nonfaceting behaviors of the corresponding Ge surfaces. The previous model of the Ge(001) faceting<sup>15</sup> is augmented by new insights. This can help to further understand and improve the properties of graphene grown by CVD on Ge surfaces.

Another important aspect of this work is to explore the possibility to grow graphene by CVD on 8 in. Ge(110) wafers. Up to now, the growth has been demonstrated only on Ge(110) wafers up to 4 inches in diameter.<sup>13,33</sup> This work presents a systematic study to grow graphene on large 8 inchsized Ge(110) films deposited on Si(110) substrates by optimizing various growth parameters using a CVD method. By applying various characterization methods, such as Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and Hall measurements, an assessment and determination of graphene quality and electrical properties was done. The growth experiments have been performed in the standard 200 mm Si pilot line, which further contributes toward explorations, developments, and

routes of integrating graphene toward novel proof-of-concept graphene devices.

#### METHODS

**Experimental Methods.** Graphene layers were deposited by the CVD method in a Black magic BM300T system (Aixtron). The substrates for graphene growth were prepared by depositing epitaxial, 2  $\mu$ m-thick Ge(110) films on 8 inch Si(110) substrates by a CVD method. The growth of graphene was performed at 885 °C under the pressure of 700 mbar for 1 h. Methane (10 sccm) and H<sub>2</sub> (200 sccm) were used as precursor and carrier gas. More details about the growth could be found in ref 15. The samples were characterized by X-ray photoelectron spectroscopy (XPS), using an Al K $\alpha$  source (*E* = 1486.6 eV). The energy calibration was performed with Au 4f 7/2 and Cu 2p 3/2, and the pass energy was 58.700 eV. The peak fitting procedure was performed using Shirley backgrounds along with Gaussian Lorentzian (Voigt) line shapes, except for graphene peaks, which were fitted with an asymmetric (LF) shape.

Furthermore, the surface morphology of the graphene/Ge systems was examined by scanning electron microscopy (Merlin, ZEISS), scanning tunneling microscopy (SPECS Aarhus 150), and atomic force microscopy (Park NX20, Park Systems). After that, graphene was transferred on isolating wafers by the electrochemical delamination procedure, employing polymethylmethacrylate as intermediate support. A NaOH electrolyte solution was employed where the PMMA/graphene/Ge/Si was used as the cathode and graphite plate as the anode. Further details could be found in ref 34. Graphene's electrical properties were then extracted using a Lakeshore 7600 Hall system using Hall bar structures. Raman study was conducted using an excitation wavelength of 532 nm, a 100× objective, a laser spot size of about 1  $\mu$ m, and a step size of 1  $\mu$ m for area mapping. The distribution of Raman peak intensity ratios was fitted using the ECM algorithm.<sup>35,36</sup>

**Theoretical Methods.** Ab initio calculations within the plane wave pseudopotential density functional theory (DFT) were conducted on the JUWELS cluster<sup>37</sup> using Quantum ESPRESSO.<sup>38,39</sup> Meta-GGA rVV10 functional<sup>40,41</sup> and pseudopotentials of PBE type<sup>42</sup> were employed, yielding a satisfactory description of the reference materials: graphene lattice constant of 2.461 Å (0.01%), graphite interlayer spacing of 3.385 Å (1.1%), bulk Ge lattice constant of 5.658 Å (0.00%), and Ge bulk modulus of 64 GPa (-15%).

For surface energy calculations, periodic slabs with a thickness of up to 20 atomic layers separated by a vacuum of varying width were used. The results were extrapolated to infinite slab and vacuum thickness. The slabs representing the bulk were passivated by hydrogen. They were then halved, and the exposed surfaces were allowed to reconstruct.

The calculations assume dimerization of Ge(001) atoms. At temperatures above about 850  $^{\circ}$ C, this structure appears to be destroyed.<sup>43</sup> Yet, we observed that interaction of Ge with C atoms, also with those on graphene edges, can open the dimers and the energy changes involved are small to moderate. Moreover, the high-



Figure 2. Raman study of graphene (a) histogram of the  $I_D/I_G$  ratio, (b) micro-Raman map of FWHM of the 2D band, (c) histogram of the 2D-FWHM, and (d) 2D versus G peaks position.

temperature disorder may be related with the presence of Ge adatoms<sup>44</sup> and/or subsurface interstitials,<sup>45,46</sup> which alter the appearance of the surface but do not remove the dimers to substitute them by entirely different structural elements. We thus suppose that the simplifying assumption of dimerized Ge(001) may be acceptable.

The structure of Ge(110) "8 × 10" was optimized by assuming the positions of the adatom pentamers at the sites indicated by STM images<sup>47,48</sup> and placing additional adatoms at various sites on the remaining area. More than hundred structures were considered. Because of varying number of adatoms, the surface energy depends on the chemical potential  $\mu$  of Ge. Equilibrium with the bulk was thus assumed, whereby  $\mu$  was obtained from energies of slabs with various thicknesses. The "8 × 10" order is lost at high temperatures,<sup>49</sup> but the pentamers are needed to counter-balance the adatom-induced strains; hence, both elements should survive the heating.

# RESULTS AND DISCUSSIONS

**Experimental Results.** In the first step, the as-grown graphene/Ge(110) samples were investigated by XPS; the C 1s spectrum is shown in Figure 1a. The spectrum exhibits a typical asymmetric graphene peak at the binding energy around 284.5 eV, confirming the presence of graphene. The binding energy of the graphene peak is in agreement with the previous study.<sup>13,16,17</sup> The absence of the C 1s signal at lower binding energy demonstrates the lack of germanium carbides.<sup>13</sup> However, some peaks at higher bonding energies around 285.0 (C–H), 286.0 (C–O), 287.0 (C=O), and 289.0 eV (O–C=O) corresponding to adventitious contaminations can be observed.

The quality of the as-grown graphene layers was examined by Raman spectroscopy. A typical Raman spectrum of graphene comprising 2D, G, and D Raman bands is shown in Figure 1b. It can be observed that the D peak that requires the presence of defects for its activation exhibits the low intensity of  $I_D/I_G \approx 0.06$ , demonstrating that the crystallographic quality of the film is high. This is in contrast to what is observed in CVD graphene on Ge(001) where two domain orientations of graphene leads to much higher D to G intensity ratios of up to 0.7.<sup>15,20</sup> Under the assumption that grain boundaries are the main source of the D peak, the mean size  $L_{\text{grain}}$  of graphene grains is measured by the relative strength of the G band:

$$L_{\rm grain} = 2.4 \times 10^{-10} \lambda^4 \frac{I_{\rm G}}{I_{\rm D}}$$
(1)

where  $\lambda$  (nm) is the wavelength of the laser used ( $\lambda$  = 532 nm) and  $I_G/I_D$  is the ratio of the intensity of the G and D Raman bands.<sup>50</sup>

The grain size distribution was examined by performing micro-Raman mapping over a  $10 \times 10 \,\mu\text{m}^2$  area. The measured ratio (Figure 2a) was fitted with a log-normal distribution. The fit reveals the major mode (the higher peak in Figure 2a) with an average grain size of about 300 nm ( $I_D/I_G = 0.06$ ) and the secondary one (the smaller peak in Figure 2a) with an average grain size of around 1  $\mu$ m. The grain sizes estimated for our graphene on Ge(110) are thus much larger than the diameter of 80 nm estimated for graphene on Ge(001).<sup>29</sup>

The full width at half-maximum (FWHM) of the 2D band (Figure 2b,c) is known to increase with the number of graphene layers due to the splitting of the 2D peak into multiple components because of the interlayer coupling.<sup>50</sup>

Therefore, the width of the 2D peak can be used to determine the thickness of graphene film.  $^{\rm 50}$  A Raman mapping of the 2D-FWHM is displayed in Figure 2b. The FWHM of the 2D band lies within the range of 28 to 39  $\text{cm}^{-1}$ . The histogram of the 2D-FWHM (Figure 2c) indicates the presence of two distinct modes, at about 32 and about 38 cm<sup>-1</sup>, possibly related to the two mean grain sizes (Figure 2a). More detailed Raman and elipsometry measurement details have been reported previously.<sup>15</sup> The observed range of 2D-FWHM is below the 46-48 cm<sup>-1</sup> reported previously for the same system.<sup>51</sup> The FWHM range of 28-39 cm<sup>-1</sup> is also below the 32 to 44 cm<sup>-1</sup> range reported previously for Ge(001).<sup>15,16</sup> It may be tempting to attribute the mode with the smaller width of the 2D band to monolayer graphene<sup>52</sup> and the other mode to a thicker and/or more defective graphene. However, SEM does reveal no signs of the presence of multilayer graphene domains (Figure 3a). More detailed analysis toward large area graphene has been reported previously.<sup>15,25,29,53-56</sup>



**Figure 3.** (a, b) SEM and AFM micrographs of graphene/Ge(110). (c, d) SEM and AFM micrographs of graphene/Ge(001).

In addition, the 2D bandwidths are still much higher than the widths of about 17 cm<sup>-1</sup> observed for monolayer graphene on hBN.<sup>5,52</sup> This is likely to be associated with the nanometerscale strain variations in the graphene film within the laser's spot size.<sup>57,58</sup> The information on the strain and at the same time on the doping may be obtained by plotting the position of 2D and G peaks (Figure 2d) and applying the method of vector decomposition.<sup>58</sup> The data points in Figure 2d are scattered mostly along the strain axis, indicating significant strain variations in graphene and relatively homogeneous doping. The strain in graphene is compressive; assuming that the strain is biaxial, it can be estimated to be approximately -0.19%. The origin of this compressive strain may reflect the difference between the thermal expansion coefficients of Ge  $(5.75 \times 10^{-6} \text{ K}^{-1})$  and graphene  $(-6 \times 10^{-6} \text{ K}^{-1})$ .<sup>24</sup> The Ge lattice contracts upon cooling from high graphene growth temperature, causing the compression of the graphene layer constrained by the friction force to the dimensions of the substrate wafer. In addition, one can observe that some of the data points are positioned in the "forbidden" region on the left side of the strain axis. This is attributable to the substrateinduced screening, which shifts the neutrality point,<sup>52</sup> and its occurrence indicates that the doping level is low. Assuming the neutrality point of suspended graphene, we estimate that our graphene films are p-type doped (~ $0.1 \pm 0.1$ ) × 10<sup>13</sup> cm<sup>-2</sup>. This clearly differs from the graphene/Ge(001) system, for which a higher compressive strain of about  $-0.3\%^{15,16,19}$  and higher p-type doping levels of about  $3 \times 10^{13}$  cm<sup>-2</sup> were reported.15,

The surface morphology of graphene/Ge(110) was investigated with the help of SEM and AFM. It can be seen in the SEM micrograph in Figure 3a that the Ge(110) surface does not reconstruct into nanofacets and remains flat underneath the graphene film. The same is evident in AFM topography (Figure 3b), which in addition reveals a low surface roughness of Ra = 0.2 nm. The flat surface morphology of Ge(110) is in agreement with previous reports.<sup>13,23,26,28,32</sup> This is, however, opposite to the morphological behavior of Ge(001) orientation that reconstructs into (107) facets during the graphene growth process, as shown in Figure 3c,d. The faceted Ge(001) surface is also rougher (Ra = 1.0 nm) as compared to the flat Ge(110) surface.

In the next step, graphene was transferred onto a silicon dioxide substrate. Then, the samples were again investigated by performing SEM and Raman analysis. In Figure 4a, the SEM micrograph shows that the transferred graphene is free from visible defects, such as cracks, holes, wrinkles, etc. However, a defect or D mode attributable to the transfer process in the Raman spectrum can be seen in Figure 4b.

In addition, the electrical properties of the transferred graphene were also extracted from Hall measurements using the Hall bar structure, as shown in Figure 4c. The measured



Figure 4. Graphene transferred from Ge(110) onto SiO<sub>2</sub>. (a) SEM image. (b) Raman spectrum. (c) Optical image of a Hall bar structure.

electron mobility ( $\mu$ ) and sheet resistance ( $R_s$ ) are around 2700  $\pm$  100 cm<sup>2</sup>/Vs and 800  $\pm$  50  $\Omega$ /sq, respectively. In contrast, a lower mobility of graphene in the range from 300 to 2500 cm<sup>2</sup>/Vs has been reported on Ge(001).<sup>15,16,21</sup> On the other hand, it has also been shown that graphene's mobility can be reached up to 10,000 cm<sup>2</sup>/Vs after flattening the surface of Ge(001) by annealing treatment.<sup>25</sup>

**Theoretical Results.** We now turn attention to the fact that  $Ge(001)^{15-18,22}$  and  $Ge(110)^{13,23,26,32}$  respond to the same CVD process of graphene growth by radically different changes of the surface morphology: while Ge(001) roughens and develops nanofacets, Ge(110) tends to flatten out (Figure 3). This dramatic difference may contribute to the observed differences in the electrical properties of the graphene layers.<sup>25,33</sup> On the basis of DFT calculation results, we conclude that it stems from three major factors: (1) the difference in the response of both surfaces to the loss of Ge atoms by sublimation and/or by hydrogen etching, (2) the difference in the way the graphene sheet nucleates and expands itself, and (3) the energetic proximity of Ge(107) and Ge(001).

The first factor is associated with a different character of the surface reconstruction. On Ge(001), due to the reconstruction being simple and occurring solely by local adjustment of atomic coordinates (Figure 5a,c), even narrow terraces



**Figure 5.** Ge(001) and Ge(110) surfaces and their reconstructions. The broken lines indicate primitive  $1 \times 1$  cells of truncated bulk. The atoms of the truncated bulk are indicated in sepia; fog is used for depth cueing. (a) Unreconstructed Ge(001)  $1 \times 1$ . (b) Unreconstructed Ge(110)  $1 \times 1$ . (c) Dimerized Ge(001)  $p2 \times 2$ . (d) Ge(110) "8 × 10" with adatoms (blue) and adatom clusters: dimers (green) and pentamers (red). Single adatoms and adatom dimers reduce the dangling bond density; adatom pentamers maintain low surface strain.

separated by monatomic steps may acquire low energy. The surface energies of some Ge(001) vicinal are, for this reason, not much higher than that of Ge(001),<sup>59</sup> and the surface becomes susceptible to roughening when step pinning centers (here, Ge–C bonds) appear. This scenario is less accessible on Ge(110), where the reconstruction involves a complex arrangement of many Ge ad-atoms (Figure 5b,d). Consequently, it may be easier for surface vacancies on Ge(110) to erode the unpinned step edges of the existing terraces (and to reduce the surface roughness in this way) rather than to enhance the roughness by constantly creating new terraces that expand and eventually accumulate around the pinning centers

so that a system of low-energy vicinal facets appears. Note that this reasoning may be formulated in more general terms: if low-energy surface reconstructions are closely related to truncated bulk, involving only local distortions (like dimerization), new terraces are easily formed during sublimation and the surface roughens around pinning centers, while in the opposite case, sublimation is more likely to erode unpinned steps and the surface flattens out. The argument may thus be applicable even when the temperature approaches the melting point, since these features of Ge(001) and Ge(110) are likely to prevail.

The second factor responsible for the observed difference in the surface morphology after the growth of graphene, the difference in the way the graphene sheet nucleates expands itself, is associated with different dimensions of the primitive surface cells (Figure 5) and may be strengthened by the differences in the energy of the step-edge bonding (Figure 7).

The distances between Ge atoms are such that a graphene flake with its armchair axis or its zigzag axis rotated by a small angle of  $\alpha \approx 4^{\circ}$  with respect to any of the two surface primitive translation vectors of Ge(001) is lattice-matched to the substrate along the primitive cell diagonal, i.e., along (010), which is also the direction of (107) facet ridges.<sup>15</sup> This match facilitates the expansion and coalescence of grains along the facet ridges, irrespective of the substrate temperature. In addition, a rugged edge can make chemical bonds to the substrate along graphene "fingers" (Figure 6a) perpendicular to the direction of future facet ridges (Figure 6d).



**Figure 6.** Expansion of unstrained graphene on Ge(001) and formation of facets. The atoms involved in Ge–C bonds are enlarged; Ge(001) domains are red and blue. (a) Graphene fingers creeping across Ge dimer rows. (b) STM image of the boundary between faceted and nonfaceted area after graphene growth at 850 °C from 10 mbar CH<sub>4</sub>. (c) The fingers make bonds also to dimer vacancies (blue), so that the creeping continues across monatomic steps to the lower terrace, i.e., to the other domain of Ge(001). (d) Graphene edge bonded to Ge(107).

These fingers are predicted to form when the temperature is high enough, and the  $H_2$  partial pressure is low enough (we estimate that 900 °C and 500 mbar are well within this region). They creep on the surface by attaching C atoms to their tips filling the space between the fingers by these atoms, as in the middle of Figure 6a. This may be more efficient than collecting carbon from the substrate by the graphene edge that is hydrogenated and floats above the substrate. The finger motion is not stopped by attachment of Ge vacancies to the step (Figure 6c), and it may also continue on a Ge(107) facet (Figure 6d).

Formation of the fingers is supported by the rotation angle  $\alpha$  being small (as this maintains shear stresses on a low level). When the fingers creep on the surface, the flake grows wider. Incomplete coverage of Ge(001) with graphene may thus result in faceted "islands" surrounded by nonfaceted area, as indeed is sometimes the case (Figure 6b). The faceting during the growth of graphene is therefore supported by the dimensions of the Ge(001) primitive cell and by the close relation between surface vacancies and terraces on this surface.

Furthermore, it is known that on Ge(110), the graphene armchair edge aligns itself perfectly with the  $[\overline{110}]$  axis of the substrate.<sup>32,60</sup> This is associated with the preferential bonding of graphene edge to monatomic steps running in this direction.<sup>32</sup> The atomic structures reported so far have been computed assuming that the armchair edge is lattice-matched to <011> zigzags of Ge atoms<sup>32</sup> (Figure 7a). In reality, there is



**Figure 7.** Bonding of graphene to straight steps on Ge, top view with fog used as depth queuing. Atoms belonging to the  $[\overline{110}]$  Ge zigzag on the Ge(110) step are sepia (panels a and b); atoms of the two Ge(001) domains are red and blue (panels b and c); C atoms from rings attached to Ge atoms are black; atoms involved in Ge–C bonds are enlarged; and of the remaining atoms, only their bonds are shown. (a) Ge atoms on a  $[\overline{110}]$  Ge zigzag step of Ge(110). (b) Graphene bonded to a  $[\overline{110}]$  step on Ge(110), (c) to S<sub>B</sub> step on Ge(001), and (d) to S<sub>A</sub> step on Ge(001).

a substantial mismatch of 6.1% when measured along these directions. This lattice mismatch (5.8% in the DFT model) has been taken into account in the current work so that the complex bonding configuration obtained here (Figure 7b) is likely to be closer to reality than the simple 1-to-1 case with a C armchair dimer placed between each two Ge atoms on one side of the step zigzag. As in the previous work,<sup>32</sup> our calculations also employed periodic boundary conditions, but instead of one Ge(110) and one graphene unit, we used 16 Ge(110) and 15 graphene units, resulting in nearly unstrained graphene on an unstrained substrate.

The alignment of the graphene armchair edge along a [110] zigzag step of Ge(110) is optimal in the sense that it allows the graphene edge and Ge(110) to make a chemical contact along the direction of their maximal chemical activity. Indeed, these are the directions of the highest linear density of dangling bonds on the graphene edge and on a Ge(110) monatomic step.

Moreover, Ge atoms in the zigzag  $\langle 011 \rangle$  step (Figure 7a) are flexible enough to adjust themselves to the relatively rigid lateral spacing of C atoms on the armchair edge (Figure 7b). The step-edge atoms rearrange from a straight zigzag into several quasi-random groups. In spite of this, the edge of graphene makes stronger bonds to the Ge(110) step than to straight monatomic steps on Ge(001): by 0.26 eV/nm with respect to the  $S_B$  step (Figure 7c) and 0.72 eV/nm to the  $S_A$ step (Figure 7d). This strength with which graphene bonds its armchair edge with the straight zigzag of Ge(110) atoms diminishes the tendency-observed on Ge(001) (Figure 6d)—to trade by rotation the number and strength of Ge–C bonds for the possibility of strain relaxation, as it happens on Ge(001) (Figure 6d). This expectation is corroborated by the previous DFT results: in spite of the lattice mismatch being neglected, the graphene/step bonding energy density has its minimum when the armchair edge is parallel to the Ge zigzag.<sup>32</sup>

The third factor contributing to the (lack of) stability of the surface during the growth of graphene by CVD is related with surface energies. Interestingly, the most direct contribution of surface energy to the surface morphology after growth, the difference in the adhesion of graphene to the flat surface and to a facet, seems to play a negligible role. Indeed, the computed surface energy of Ge(107) is by 0.022 J/m<sup>2</sup> higher than that of Ge(001), while the computed adhesion energy of graphene to these surfaces is the same within  $0.002 \text{ J/m}^2$ . Of importance is however that when the surface energy difference between the basal and the vicinal planes is sufficiently small and when the surface area of interest is densely covered by small flakes, as it may be the case for the "carbon precursor" phase in the early stage of graphene CVD on Ge(001),<sup>27</sup> slow attachment of carbon directly from the gas phase to the edges of these flakes may be accompanied by enlargement of the substrate surface area caused by faceting. This is thermodynamically favorable if the Gibbs free energy gained by conversion of more molecules from the gaseous precursor into graphene when more substrate area becomes available in the course of facet formation overweighs the energy needed to create the facets.

Figure 8 illustrates schematically the role of these three factors in the morphology evolution of Ge(110) and Ge(001) during CVD growth of graphene on these surfaces.

#### CONCLUSIONS

This work reported the growth of graphene on 200 mm Ge/ Si(110) wafers by CVD and an analysis of graphene nucleation and growth mechanisms based on DFT calculations inspired by these results. Uniform monolayer graphene can be grown over a large area, verified by Raman spectroscopy. In addition, the low density of defects indicated the good quality of the obtained graphene. Indeed, Hall measurements showed that graphene exhibits high electrical mobility ( $\sim$ 2700 cm<sup>2</sup>/Vs) and low sheet resistance (~800  $\Omega/sq$ ). From SEM and AFM investigations, it was found that the Ge(110) layer underneath the grown graphene remains flat in comparison to the surface of Ge(001), which is composed of (107) facets. Given the DFT outcome, it was argued that the main factors responsible for the observed difference in the behavior between these two surfaces of Ge are (1) the difference in the response of both surfaces to the loss of Ge atoms (by sublimation and/or by hydrogen etching), (2) the difference in the way the graphene sheet nucleates and expands itself, and (3) relation between the substrate surface energy distance from the basal plane to

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Figure 8. Factors governing the response of Ge(110) and Ge(001) to graphene growth.

the kinetically accessible system of vicinal planes, compared to the graphene surface energy gained by conversion of the gaseous precursor into graphene.

The simplicity of the Ge(001) reconstruction, as opposed to the complexity of the Ge(110) reconstruction, is responsible for the first one of these three factors, while the different dimensions and shapes of the primitive surface cell and also the strong bonding of graphene edge to straight Ge(110) steps account for the second one. The third of these factors comes into play during the phase when relatively small and densely spaced flakes coalesce slowly enough to allow for more carbon to be still incorporated along their boundaries. Figure 8 summarizes these observations.

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#### Notes

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