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Inhibiting molecular array formation on Si(111)-7 × 7 using site-selective Ge/Si exchange

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The Si(111)-7 × 7 surface reconstruction can be used to template an array of mesitylene (1,3,5-trimethylbenzene) molecules in which each molecule bridges a corner Si adatom and a neighboring Si rest atom. The molecules adsorb in corner sites to minimize a weak steric interaction associated with nearest-neighbor bridging sites. We demonstrate that the formation of the molecular array can be blocked by adding submonolayer amounts of Ge to the surface. The Ge atoms block the formation of the array because they substitute preferentially for Si adatoms located in corner sites, and the Ge–C bond strength is ≈0.8 eV weaker than the Si–C bond strength.

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To utilize the optical and biofunctional properties of organic molecules in hybrid devices, it would be advantageous to have at our disposal a wide range of techniques to grow high-quality Si-organic interfaces.[1,2] However, Si surfaces are reactive and one cannot, for example, draw on the large body of knowledge that has been acquired from studying surface-confined supramolecular assembly on weakly reactive noble-metal surfaces.[3,4] This has prompted an intensive study of organic-Si interfacial physics and chemistry,[5–12] producing a much improved understanding of interface formation. Nevertheless, there is still a practical need to control the growth of organic mono- and multilayers on Si.[9]

Inspired by the work of Hamers *et al.*,[11,13] who demonstrated that monolayers of alkenes and dialkenes can be self-assembled on Si(001)-2 × 1 by [2 + 2] cycloaddition, we recently developed a method for self-assembling a molecular array on Si(111)-7 × 7 using [4 + 2] cycloaddition and steric hindrance. Proof of principle was demonstrated with mesitylene, and subsequent theoretical studies[14] using *ab initio* methods suggest that array formation should not be limited to this molecule.

In this paper, we demonstrate that mesitylene array formation can be blocked by adding Ge atoms to the 7 × 7 surface and our total-energy calculations, together with the results of previous studies of the Ge/Si(111)-7 × 7 system, suggest a possible mechanism. Because Ge is compatible with Si growth technology and because it can be patterned onto the 7 × 7 surface using, for example, a shadow mask or a nanostencil, this approach may also allow organic arrays, like mesitylene, to be patterned.

The surface-templated molecular array that self-assembles when Si(111)-7 × 7 surfaces are exposed to mesitylene is illustrated in Fig. 1.[15,16] To associate the model [Fig. 1(b)] with the scanning tunneling microscopy (STM) image [Fig. 1(a)], it is necessary to know that mesitylene chemisorption occults or darkens the Si adatom that bonds to the molecule. The occultation of the adatom is produced by a chemisorption-induced modification of the surface electronic structure that lowers the surface-state density in the energy window accessible to the tunnel current. Consequently, the bright features in the image are the Si adatoms, colored blue in Fig. 1(b), located at the edge of the half cell that *do not* form covalent bonds with the chemisorbed molecules. Twelve edge adatoms form a hexagonal ring, the dominant motif of the constant-current topographical image.

Studies of Ge growth on Si(111)-7 × 7[17–21] found that at substrate temperatures in the range 100–300 °C, in contrast with adsorbates like hydrogen which attach to Si adatoms and rest atoms.[22] Ge atoms substitute for Si adatoms which are known to be in highly strained geometrical configurations. For example, for a corner Si adatom in the unfaulted half cell, we calculate that the angle between the backbonds to the substrate to be ≈16° smaller than the tetrahedral angle (109.5°), characteristic of sp^3 hybridization. Moreover, the STM study performed by Wang *et al.*[18] at 150 °C found the ratio of corner-to-edge adatom sites to be 64/36, 80/20, and 73/27 at Ge coverages of $\theta_{\mathrm{Ge}} = 0.02$, 0.08, and 0.10 monolayers (MLs), respectively, and, furthermore, the preference for corner sites is clearly illustrated in Fig. 1 of Ansari *et al.*[21] Consequently, Ge atoms prefer adatom sites located at the corner of the half cell and a number of commonly occurring structures involving three,[18,20,21] five,[18,20] and six substituted Ge atoms per half cell have been identified,[21] with the latter forming a hollow-centered hexagonal Ge cluster. Because the Ge atoms show a preference for corner sites and because the Ge–C bond strength is ≈0.8 eV lower than that of Si–C (3.29 and 2.47 eV, respectively[23,24]), we decided to investigate the possibility of blocking the covalent attachment of the molecules to the surface and subsequent array formation by adding submonolayer amounts of Ge to the 7 × 7 surface.

We prepared a 7 × 7 surface by heating a Si(111) wafer at 1250 °C for 40 s, and then annealing it at 850 °C for 120 s. It was subsequently cooled at a rate of 1 °C/s. After the 7 × 7 surface reconstruction was formed, up to 0.33 ML of Ge was deposited with the surface temperature at 500 °C. After Ge deposition, the sample was annealed at this temperature for another 300 s. Each Ge/Si(111) surface was exposed

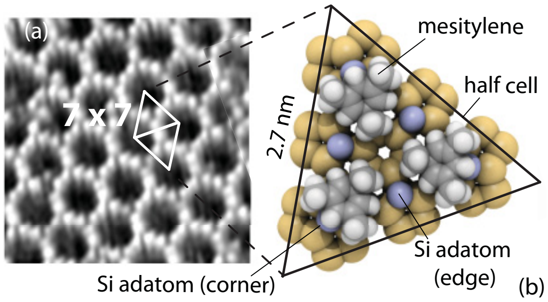

FIG. 1. (Color online) (a) Mesitylene array on Si(111)-7 × 7 surface reconstruction.[15,16] Image details: −0.8 V and 0.7 nA. (b) A model showing a 7 × 7 half cell with three mesitylene molecules located in the corner bridging sites. In the STM image, it is the Si adatoms (colored blue) in edge (middle or center) positions that appear bright forming a honeycomb-like network.

to the same amount of mesitylene (0.170 L, where 1 L ≡ 1×10^{-6} Torr s) and imaged with STM.[25]

Figure 2 illustrates what happens when Si(111) surfaces with different amounts of Ge are exposed to the same amount of mesitylene (0.170 L); the samples with higher Ge coverages (θ_{Ge}) show a reduced mesitylene uptake. As mentioned earlier, the signature of mesitylene adsorption is a dark or missing Si adatom, and this behavior will be investigated further in Fig. 3. When a saturation coverage of six molecules per 7 × 7 cell is adsorbed onto the surface up to 92% of the molecules occupy corner bridging sites [Fig. 3(a)] with the remainder occupying edge bridging sites. With as little as $\theta_{\mathrm{Ge}} = 0.08$ ML [Fig. 3(a)], the effect of Ge substitution is already evident, but the characteristic motif of the molecular array, the ring structure, is preserved in some regions of the image. At coverages of 0.16 ML [Fig. 3(b)] there are few rings present, and at coverages of 0.33 ML [Fig. 3(c)], there is less than one molecule per 7 × 7 cell. Also, as Ge is added to the surface, the number of mesitylene molecules in corner sites decreases rapidly [Fig. 2(d)]. Consequently, this sequence of images clearly shows that the formation of the mesitylene array can be blocked by adding submonolayer amounts of Ge to the surface.

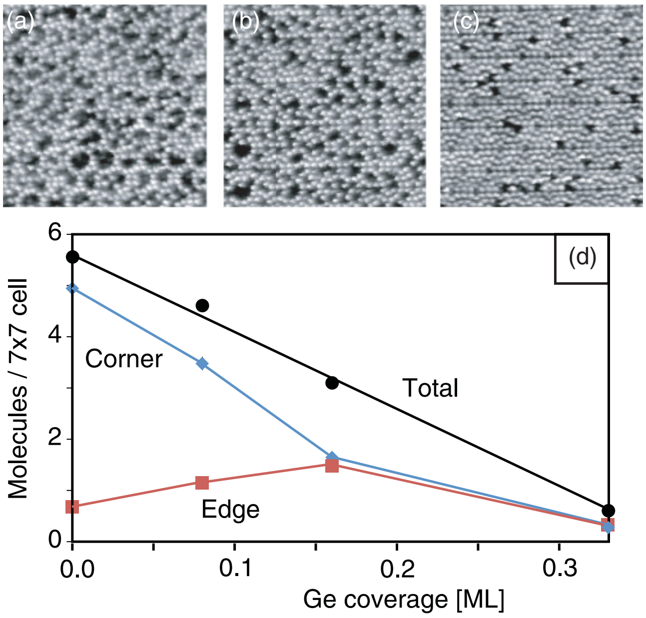

FIG. 2. (Color online) Si(111) surfaces with increasing amounts of Ge were exposed to 170 mL of mesitylene. The Ge concentrations θ_{Ge} were (a) 0.08, (b) 0.16, and (c) 0.33 ML. Panel (d) shows that the mesitylene coverage calculated from the number of missing Si adatoms (see text), in units of molecules per 7 × 7 unit cell, decreases as the Ge coverage increases.

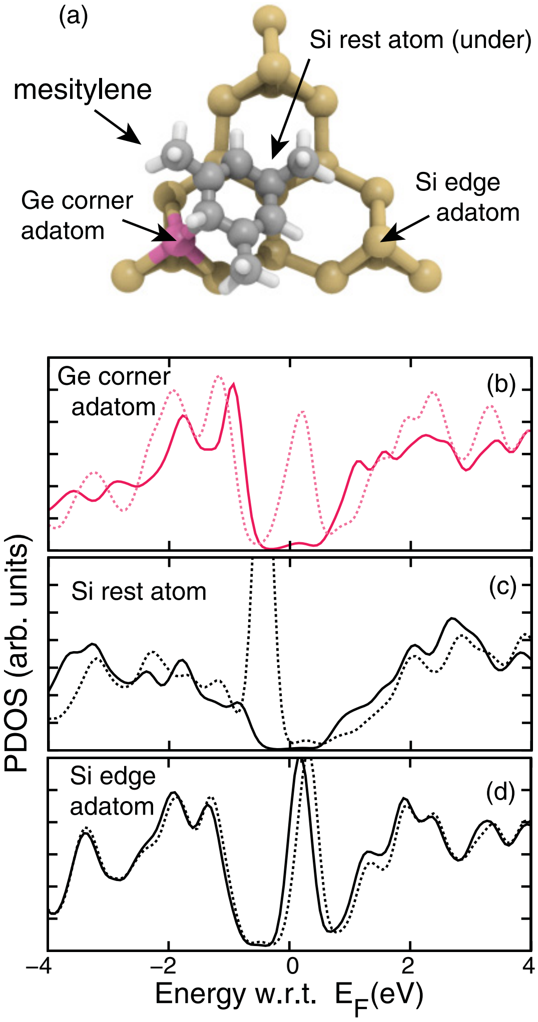

FIG. 3. (Color online) (a) Model of mesitylene adsorbed in stable corner bridging site with Ge adatom colored pink. The calculated partial density of states (PDOS) is shown for (b) the Ge corner adatom, (c) the Si rest atom, and (d) the neighboring Si edge adatom. The dotted lines represent the PDOS before attachment. The calculated PDOS indicate that the molecule (not shown; see Ref. 16) and the adatoms it attaches to should appear dark in STM images.

To develop a deeper understanding of the blocking mechanism, total-energy calculations were performed within density functional theory.[16] Ge/Si substitution was examined by comparing the total energies of the four nonequivalent $\mathrm{Ge}_{\mathrm{Si}}$ adatom substitution geometries (FC, FE, UC, and UE where F and U are faulted and unfaulted, respectively, and C and E are corner and edge, respectively). $\mathrm{Ge}_{\mathrm{Si}}$ FC is the most likely configuration, by ≈40 meV per 7 × 7 cell, in

TABLE I. Calculated binding energies (E_B) for molecules located in the faulted-edge (FE), faulted-corner (FC), unfaulted-edge (UE), and unfaulted-corner (UC) bridging sites. The calculations were performed for a single molecule per 7 × 7 cell.

Si Adatom	E_B (eV)	Ge Adatom	E_B (eV)
UE_r	0.687	UE_r	0.342
FE_r	0.662	FE_r	0.310
UC_r	0.649	UC_r	0.286
FC_r	0.632	FC_r	0.254

agreement with the experimental observation that Ge_{Si} FC is most abundant.[18,19,21] Also, in the equilibrium geometry, the substituted Ge_{Si} atom is ≈0.2 Å higher than the other corner Si adatoms, contributing to the bright appearance of the Ge adatoms in STM images.[17–21] The total-energy differences between the three other geometries (FE, UC, and UE) are less than 10 meV per 7 × 7 cell.

Previously,[16] we found the most stable attachment geometry for a single mesitylene molecule on 7 × 7 to be the UE_r geometry, where the molecule bridges a Si adatom atom located at the edge of the unfaulted half cell and a neighboring rest atom. In the UE_r geometry, the molecule is oriented such that the C atom bound to the rest atom has a methyl group attached to it [Fig. 3(a)]. At saturation coverage, six molecules per 7 × 7 cell [Fig. 1(b)], the preference changes to corner to minimize a steric interaction between the molecules. Once we obtained a suitable description of Ge/Si(111)–7 × 7, the energetic stability of the attachment sites was investigated by comparing the binding energy (E_B) of the molecule adsorbed on the Si(111)–7 × 7 surface with the binding energy of the molecule adsorbed on the Ge/Si(111)–7 × 7 surface. Following the calculation procedure described earlier,[16,26] the binding energy was obtained by comparing the total energies of the isolated molecule and the isolated surface with the total energy of the combined system. Table I summarizes the binding energies of single mesitylene molecules in each of the four binding sites with both Si and Ge adatoms.

The calculated binding energy for the most stable UE_r attachment geometry is 0.687 eV, and it was found that exchanging the Si adatom for a Ge atom reduces the binding energy to 0.342 eV. Similarly, for mesitylene in the FC_r site, exchanging the Si adatom for a Ge atom reduces the binding energy to 0.254 eV. Consequently, neither can be regarded as stable chemisorption geometries at room temperature. The averaged binding energy $\bar{\varepsilon}$, which is defined in Refs. 16 and 26, was also calculated and found to be 0.268 eV lower for the UE_r binding geometry when the Si adatom was substituted with a Ge atom.

TABLE II. Calculated bond lengths (Å). Si_1 is the Si adatom and Si_2 is the neighboring Si rest atom.

Si Adatom	C–Si_1	C–Si_2	Ge Adatom	C–Ge_1	C–Si_2
UE_r	2.03	2.03	UE_r	2.18	2.03
FE_r	2.03	2.04	FE_r	2.19	2.05
UC_r	2.02	2.03	UC_r	2.17	2.03
FC_r	2.03	2.04	FC_r	2.18	2.04

The calculated values for the equilibrium bond lengths are summarized in Table II. The C–Ge bond lengths (2.18 Å) are slightly larger than the sum of the C (0.77 Å) and Ge (1.22 Å) covalent radii and also their C–Si counterparts. Because the C–Ge bond lengths are longer than the C–Si bond lengths, the deformation of the C_6 ring is less (more) when the molecule bridges a Ge (Si) adatom and a Si rest atom. For example, considering the isolated molecule, one finds that the total energy of the molecule in the UE_r attachment geometry, with a Ge adatom, is 1.93 eV larger than the total energy of an isolated and fully relaxed molecule. A similar calculation for UE_r geometry, with a Si adatom, provides a total-energy difference of 2.16 eV. Consequently, despite the fact that our calculations indicate that the presence of the Ge atom in the Si adatom site reduces the mesitylene binding energy, the longer C–Ge bond lengths result in less deformation of the mesitylene molecule.

By adding Ge atoms to a Si(111)-7 × 7 surface, the formation of an organic corner array is blocked because the Ge atoms preferentially substitute for corner Si adatoms and the Ge–C bond is substantially weaker than the Si–C bond. Consequently, at room temperature, adatom sites containing Ge atoms can no longer be considered to be stable covalent attachment sites and the delicate energy balance that supports the kinetic processes that allow the molecular array to form is destroyed.

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