Patterned Growth of Nanoscale In Clusters on the Si(111)-7×7 and Si(111)-Ge(5×5) Reconstructions

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Abstract. Results of a study designed to investigate the possibility of using the Si(111)-Ge(5×5) surface reconstruction as a template for In cluster growth are described. As with Si(111)-7×7, the In adatoms preferentially adsorb in the faulted half-unit cell, but on Si(111)-Ge(5×5) a richer variety of cluster geometries are found. In addition to the clusters that occupy the faulted half-unit cell, clusters that span two and four half-unit cells are found. The latter have a triangular shape spanning one unfaulted and three, nearest neighbor, faulted half-unit cells. Triangular clusters in the opposite orientation were not found. Many of the faulted half-unit cells have a streaked appearance consistent with adatom mobility.

Despite numerous studies of adsorption on Si(111)-7×7, only recently has it been found that this surface reconstruction can be used as a template for cluster growth. Low adatom fluences and relatively low substrate temperatures produce arrays of identical six-atom clusters for a variety of adatom species including: the Group III metals Al (Kotlyar et al. 2002, Jia et al. 2002), Ga (Lai & Wang 2001) and In (Li et al. 2002), and the alkali metals Na (Wu et al. 2003) and K (Wu et al. 2005).

Figure 1. The bright triangular features are 6-atom In clusters located in faulted halves of the Si(111)-7×7 unit cell. Image size; 16.7 nm × 16.7 nm. Bias = +1.02 V (empty states). Current = 0.86 nA.
On the related Ge(111) surface, the stable surface reconstruction is $c(2\times8)$; the dimer-adatom-stacking fault (DAS)-$7\times7$ reconstruction is metastable and the DAS-$5\times5$ reconstruction is unstable. Nevertheless, when 2-6 monolayers (ML) of Ge are deposited on Si(111)-$7\times7$, a $5\times5$ surface reconstruction is stabilized (Becker et al. 1985) by the compressive strain from the underlying Si substrate (Gossmann et al. 1985). Studies of Si and Ge cluster growth on Si(111)-Ge($5\times5$) have recently been performed (Asaoka et al. 2005). The diffusion of Si and Ge adatoms on both Ge($5\times5$) and Ge($7\times7$) has also been studied (Cherepanov & Voigtländer 2004) and it was found that the effective diffusion lengths of both species are ten times larger on the Ge surfaces than on the corresponding Si surfaces (Cherepanov & Voigtländer 2004).

![Diagram of DAS-5×5 reconstruction](image)

**Figure 2.** Top view of DAS-$5\times5$ with the faulted half on the left and the unfaulted half on the right. The unit cell is the area enclosed by the red line.

The goal of the present study was to investigate whether Si(111)-Ge($5\times5$) could be used as a template for In cluster growth. On Si(111)-$7\times7$, there are a number of closely spaced In adsorption sites, local minima in the total energy, located around the rest atoms that form ‘basins’ (Cho & Kaxiras 1997). It was not known whether basins form around the rest atoms on Ge($5\times5$).

In addition to studying the system with scanning tunneling microscopy (STM), the binding energy of a single In atom was calculated for a number of different adsorption sites within the Ge($5\times5$) unit cell using *ab initio* methods. Details are published elsewhere (MacLeod et al. 2006). In good qualitative agreement with earlier theoretical studies of adatom adsorption on Si(111)-$7\times7$, an energy basin centered around the rest atom (R) was found. An In atom located above the rest atom has a higher energy than an In atom located in the surrounding basin. Regarding cluster formation, the basin is large enough to accommodate a number of In atoms. The In binding energies in the basins on the faulted and unfaulted half-unit cells are very similar. The absolute minimum energy is found to be at the three-fold hollow site (H3) in the basin of the faulted half-unit cell. It is 0.15 eV lower than the corresponding site in the unfaulted half-unit cell. Small energy barriers were found for closed path diffusion in a basin involving the T4-H3-B2-T4-... sites. Commensurate results have been reported for similar systems (Cho & Kaxiras 1997). These barriers are between 0.15 eV and 0.35 eV on the unfaulted half-unit cell and 0.36–0.42 eV on the faulted half-unit cell. Large energy barriers were found for diffusion between the basins in the faulted and unfaulted half-unit cells across the dimer rows.

Fig. 3 shows the calculated total energy of systems with an In atom adsorbed near selected high-coordination sites in the faulted and unfaulted unit cell halves. The sites are indicated in the inset and standard labeling (e.g. see (Cho & Kaxiras 1997, Cho & Kaxiras 1998)) is used. Additionally, the symbols $A$ and $b$ denote the adatoms and adatom backbonds respectively.
Figure 3. Calculated total energy of the adsorbed In atom as a function of position. Solid and dashed lines indicate continuous and discontinuous paths respectively. Inset: adsorption sites located around the restatom and along a path crossing into an adjacent half-unit cell.

Sites along a path crossing into an adjacent half-unit cell between two dimer rows are indicated by $E$ and $D$.

Figure 4. Si(111)-Ge(5×5). a. A Ge coverage of 5.8 ML. Image size 30 nm x 30 nm. Bias = 1.99 V (empty states). b. Bias = -1.99 V (filled states).

Ge(5×5) surfaces were created by depositing Ge onto Si(111)-7×7, held at $T \approx 500$ °C, at rates between 0.2 and 0.6 ML/min. Indium was then deposited using a recipe that has produced six-atom clusters on Si(111)-7×7 (Li et al. 2002); 0.06 - 0.24 ML of In deposited, at a rate of $\approx 0.15$ ML/min, onto a substrate held at a temperature of $\approx 150$ °C. We found at Ge coverages $> 3$ ML, in agreement with previous studies (Motta 2002), that the entire surface converted to 5×5 (Fig. 4). In the filled-state image, Fig. 4b, variations in the brightness of the adatom features can be seen, particularly in the faulted half-unit cells (see later).

Fig. 5a is an image of the Si(111)-Ge(5×5) surface after 0.06 ML of In had been deposited. The addition of 0.06 ML does not destroy the 5×5 periodicity of the substrate. Indium atoms typically appear, Fig. 5b, as bright features occupying: i) a single faulted half-unit cell, ii) an entire unit cell, or iii) a large four half-unit cell triangle, as identified in the figure. Additionally, some unfaulted half-unit cells appear darkened (iv), and some faulted half-unit cells contain streaks (v). It is not clear if the darkened half-unit cells are produced by the In adatoms because darkened features are also observed on Si(111)-Ge(5×5) (Fig. 4a). The streaks in the faulted halves also appear in empty-state images (bias = +0.88 V, not shown). In contrast,
Figure 5. Si(111)-Ge(5×5) with various In coverages. Before depositing In, the Si(111)-7×7 surface was heated to 500 °C and exposed to ≈3 ML of Ge. a. Indium coverage of 0.06 ML. Image size 30 nm × 30 nm. Bias = -2.32 V (filled states). Current = 3.0 nA. b. In coverage of 0.11 ML. Representative feature types: i. single half-unit cell cluster, ii. full unit cell cluster, iii. four half-unit cell cluster, iv. darkened unfaulted and v. streaked faulted half-unit cells. Image size 30 nm × 30 nm. Bias = -1.50 V (filled states), current = 1.3 nA. c. Indium coverage of 0.23 ML. Image size 30 nm × 30 nm. Bias = -1.50 V (filled states). Current = 1.5 nA.

Streaks were not observed in any unfaulted halves in either filled or empty-state images.

The large triangular features (iii) comprise one unfaulted and three nearest-neighbor faulted half-unit cells. Individual atoms in the center of the triangular feature were not resolved. However, a division of the feature into three sections, corresponding to the three faulted halves in the Ge(5×5) substrate, was observed. The relative brightness of these three regions varies from triangle-to-triangle. In contrast, the clusters occupying two half-unit cells (ii) possess much less variability in their appearance.

The same In features were observed, at different areal densities, on surfaces with coverages of 0.06 and 0.23 ML (Figs. 5a and 5c). Fig. 6 is a graph of the populations of In-related features in each of these images, based on a counting analysis of the ≈440 half-unit cells, showing that the In-related features are located predominantly in the faulted halves. No unfaulted half-unit cells were observed to contain streaks. Nearly all of the ‘filled’ unfaulted halves occurred as part of feature (ii), occupying a full unit cell, or the four half-unit cell feature (iii). The relative population of these filled unfaulted half-unit cells increased linearly as the coverage was approximately doubled; a similar trend was observed for the four half-unit cell features. The number of streaked faulted half-unit cells increased as the coverage increased from 0.06 to 0.11 ML, where nearly half the faulted half-unit cells were streaked. Between 0.11 and 0.23 ML, the percentage of streaked half-unit cells dropped considerably, and the number of filled faulted half-unit cells increased by nearly the same proportion.

The STM images of In on Ge(5×5) show In features predominantly in faulted half-unit cells. This suggests that clusters, as was found to be the case on Si(111)-7×7, are bound more strongly in the faulted half-unit cells. The simulations provide support for this result for single atoms. The major differences between In adsorption on Si(111)-Ge(5×5) and Si(111)-7×7 are the multiple half-unit cell clusters and the streaked faulted half-unit cells found on the former. In explaining the multiple half-unit cell clusters, the composition of the substrate may be an important factor. It has been previously reported (Fukuda 1996), and again seen in our images, that the adatoms in the Si(111)-Ge(5×5) layer have variable brightness. This has previously been attributed to Si-Ge intermixing (Fukuda 1996), although intermixing is known to be less important for Si(111)/Ge than for Si(001)/Ge (Cherepanov & Voigtländer 2004). The effect of intermixing on In adsorption and In cluster formation would be worthy of further theoretical study. Studies of In adsorption at lower substrate temperature are also planned. Features similar to the streaked faulted half-unit cells seen in Fig. 5 have been observed by several groups who
Figure 6. Approximate populations of In-related features on Si(111)-Ge(5×5) with different In coverages. The populations were obtained from single-image counting analyses performed on filled-state images with size 30 nm × 30 nm, corresponding to ≈440 half-unit cells per image. FHUC; faulted half-unit cell. UHUC; unfauluted half-unit cell.

attributed the streaking to adatom diffusion (Gómez-Rodríguez et al. 1996, Sato et al. 1999, Wu et al. 2004). Moreover, the reduced population of streaked faulted half-unit cells between 0.11 and 0.23 ML suggests that the diffusing atoms precipitate into clusters at higher In coverages.

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