

Surface Reconstruction and the Nucleation of Palladium Silicide on Si(111)

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(Received 13 January 1988)

Scanning tunneling microscopy has been used for real-space imaging of the initial interaction of palladium with the Si(111)-(7×7) surface at room temperature. The nucleation of silicide is spatially localized and occurs only in the faulted half of the (7×7) unit cell. Large-scan-area images have been statistically analyzed to determine the subsurface extension of the silicide nuclei and the nature of growth as a function of coverage and island size. Steps are found to have no influence on the nucleation at this temperature.

PACS numbers: 68.55.Wy, 61.16.Di, 68.35.Bs

Knowledge of the atomistics of the initial stages of silicide formation is of importance in the understanding of Schottky-barrier formation as well as the nature of epitaxial growth. The detailed surface structure as well as the presence of steps or other defects is widely considered to play a role in these processes. The reaction of palladium with Si(111) provides a model system to address these questions and has been widely studied by electron diffraction,^{1,2} ion scattering,^{3,4} photoemission and Auger-electron spectroscopies,^{1,5} and electron energy-loss spectroscopy.⁶ There is general agreement that room-temperature deposition leads to a silicidelike compound which has a Pd₂Si stoichiometry and electrical properties expected of a silicide.¹⁻⁶ To examine the initial nucleation and growth process we have performed scanning tunneling microscopy (STM) at various coverages and have performed a statistical analysis. Our results reveal several new features of this growth process including a spatially selective nucleation phenomenon occurring on the atomic level.

These experiments were performed in a small UHV chamber (base pressure 1×10^{-10} Torr) containing STM, LEED optics, and a sample-transfer assembly. The type of scanning tunneling microscope and experimental apparatus used in these studies is described elsewhere.⁷ The Si(111) samples were 6-mΩ-cm Sb-doped wafers which were cleaned *in situ* by thermal removal of the native oxide at 1050°C after careful degassing of the sample at 700°C. This procedure reproducibly produces large surface areas (typically $2000 \times 2000 \text{ \AA}^2$) displaying a nearly perfect Si(111)-(7×7) superstructure and permits the statistical analysis of the growth phenomena we report here. The Pd depositions were done *in situ* from a resistively heated Pd filament and controlled by a sensitive deposition monitor. A large distance between Pd filament and sample ensures that the sample temperature remains below 40°C during deposition. Absolute coverage calibration for each sample was done afterwards with a standard Rutherford-backscattering measurement (accurate to 0.1 ML). All STM images shown here are obtained with a 2-V positive sample bias (tunneling into

empty surface states) and a tunneling current around 1 nA. Positive- and negative-bias images of the silicide deposits reveal the same features. The Pd coverages are given in monolayers of the Si(111) surface (1 ML Pd = 7.83×10^{14} atoms/cm²). LEED shows the gradual disappearance of the substrate (7×7) structure with increasing Pd dosage as found previously.²

Figure 1 shows tunneling images from a sequence of Pd depositions at room temperature. At the lowest coverage, 0.25 ML [Fig. 1(a)], a large fraction of the surface still shows the substrate (7×7) reconstruction, on top of which are small well-separated protrusions having no distinguishable atomic structure of their own. STM does not allow detailed chemical identification but, as mentioned above, it is well known that even at room temperature a silicidelike compound is formed with a stoichiometry close to Pd₂Si.^{3,5} Thus the protrusions on top of the (7×7) structure likely correspond to islands of amorphous silicide. Analysis of our large-area scans ($1000 \times 1000 \text{ \AA}^2$) shows that only $(9 \pm 2)\%$ of the surface is covered with these small nuclei. From the known Pd coverage we can deduce that each nucleus contains on average ≈ 13 Pd atoms. The Si (7×7) structure in the uncovered regions is nearly undistorted showing a defect density comparable to the starting clean (7×7) surface. This means that Pd atoms do not react with the Si surface where the atoms impinge on the surface, but must migrate via some kind of precursor state to cluster into larger islands.

At 1-ML Pd coverage [Fig. 1(b)] the silicide nuclei have grown bigger, and the underlying substrate lattice is still visible. $(42 \pm 6)\%$ of the surface area is now covered. The islands start to touch each other, but do not yet form a continuous silicide layer. The 7×7 substrate has completely disappeared after 1.8-ML Pd dosage [Fig. 1(c)]. This surface now shows a continuous net of connected islands. Histograms over the height distribution of this continuous layer give a surface roughness of 3–5 Å, which is in good agreement with a variation in layer thickness of 3 Å as determined by ion scattering.³

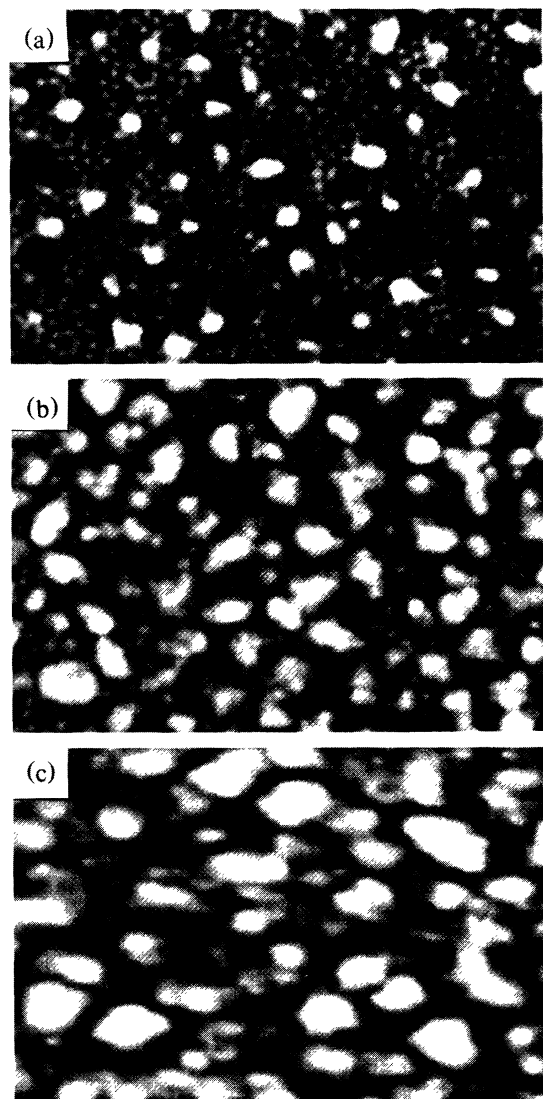


FIG. 1. Sequence of STM topographic images showing a $260 \times 190\text{-}\text{\AA}^2$ area of Si(111)-(7 \times 7) with Pd-silicide nuclei for (a) 0.25-ML Pd, (b) 1.0-ML Pd, and (c) 1.8-ML Pd.

Insight into the initial nucleation process can be best understood from a statistical analysis of the submonolayer results. Using $1000 \times 1000\text{-}\text{\AA}^2$ area scans we determine the density of silicide nuclei by directly counting (with a computer) the bumps in the images. For the 0.25-ML Pd coverage we get a value of $(1.5 \pm 2.0) \times 10^{13}/\text{cm}^2$. Increasing the coverage to 1.0 ML yields an island density of $(1.2 \pm 0.2) \times 10^{13}/\text{cm}^2$. Hence there is basically a fixed number of possible nucleation sites which are mostly occupied already at submonolayer coverages. (At higher coverages the decrease in island density arises because of the start of island coalescence.) Comparison of the above island densities with the density of Si (7 \times 7) unit cells, $1.6 \times 10^{13}/\text{cm}^2$, suggests roughly one nucleation site per Si (7 \times 7) unit cell.

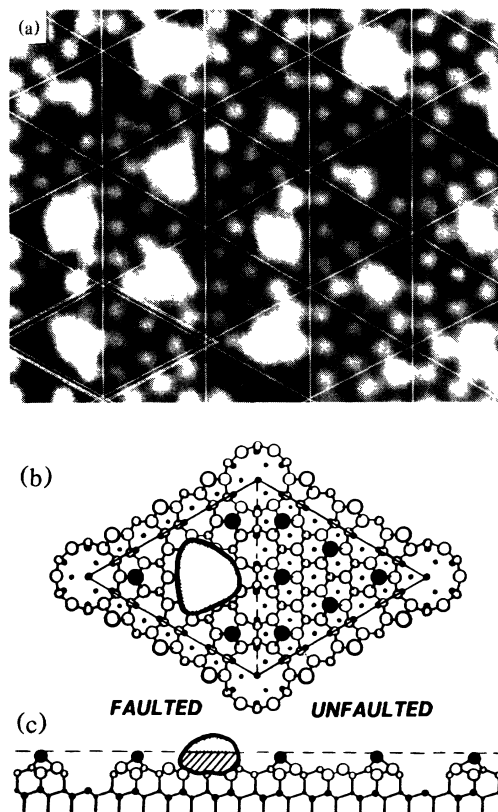


FIG. 2. (a) STM topograph of a $115 \times 95\text{-}\text{\AA}^2$ area of Si (7 \times 7) with 0.25-ML Pd. A grid is overlaid to indicate the substrate (7 \times 7) lattice. The size of one (7 \times 7) unit cell is highlighted in the lower-left corner. (b) Top view of the dimer-atom-stacking-fault model for the Si(111)-(7 \times 7) reconstruction indicating the location of the Pd-silicide cluster within the faulted half of the unit cell. (c) Cut through the long diagonal of the (7 \times 7) unit cell showing the vertical extension of the Pd-silicide nucleus. Only the part above the dashed horizontal line is visible for STM. [The orientation of the sample and the location of the stacking fault are determined from bias-dependent tunneling into the filled states nearest E_F on the pure 7 \times 7 surface (Ref. 8).]

In Fig. 2(a) a more highly resolved image of the 0.25-ML palladium-covered surface is displayed. A grid is overlaid to indicate the Si (7 \times 7) unit cells. What the statistical analysis suggests is now readily seen. There is almost always one small silicide island in each unit cell. In addition it is obvious that the clusters are not randomly distributed within the (7 \times 7), but are all located on one half of the unit cell. Figure 2(b) shows a schematic top view of the now well-confirmed dimer-atom-stacking-fault model for the Si(111)-(7 \times 7) reconstruction.^{8,9} The most important feature in our case is that a stacking fault occurs on the left (faulted) side of the unit cell.⁸ We find that 95% of the palladium silicide islands have nucleated on the faulted half as indicated in Fig. 2(b). To the best of our knowledge this is the first exam-

ple showing the influence of the Si(111)-(7×7) subsurface stacking fault on adsorption. The quasicrystalline arrangement of the amorphous silicide nuclei at low coverage has the same periodicity as the substrate and is difficult to distinguish by LEED. At higher coverages, as seen in Fig. 1(c), the (7×7) periodicity of the nuclei disappears, consistent with LEED observations.²

The electronic difference between the two halves of the Si (7×7) superstructure is considered to be one of the main reasons for this selective nucleation behavior. Density-of-states calculations show that the chemical bond in the Pd₂Si is mainly due to Si-*p* and Pd-*d* interactions.¹⁰ For the Si(111)-(7×7) the Si-adsorbate-induced surface states are mainly derived from interaction between adsorbate *p* orbitals and dangling-bond orbitals of the first Si bilayer.¹¹ Thus, these adsorbate dangling bonds are the logical sites for the initial bonding (and reaction) to occur. Spectroscopic images of these adsorbate dangling-bond states⁸ suggest a significantly higher state density on the adsorbates on the faulted side than on the unfaulted side of the unit cell. Previous photoemission measurements¹² of adsorbed rare gases on Si(111)-(7×7) support the idea that these differences in nucleation or spectroscopic images are not associated with different electrostatic potentials on the faulted and unfaulted areas of the (7×7) unit cell. This seems to indicate that the localized nucleation of palladium silicide is driven by a Pd-Si adsorbate bond on the faulted half of the unit cell. It should be mentioned that there can also be a geometric contribution to the initial nucleation process associated with the different stacking sequences on the faulted and unfaulted halves of the unit cell shown in Figs. 2(b) and 2(c). The Si lattice on the unfaulted side has an atom in the second bilayer sitting directly in the middle of the ring of six atoms making up the first bilayer. This leads to a fairly closed structure. In contrast, on the faulted half, the first bilayer is rotated 180° to line up with the second bilayer. This openness may make it physically easier for palladium atoms to intermix with the first bilayer to form a nucleus for further silicide formation.

The STM images reveal only the topology of the silicide islands lying above the level of the Si (7×7) adsorbates. To address the amount of buried silicide we consider the relation between the palladium coverage and the fraction of the surface covered by silicide islands. Consider, for example, the 1-ML Pd coverage, 7.83×10^{14} Pd atoms/cm². To form a silicelike compound with a Pd₂Si stoichiometry one needs 3.92×10^{14} Si atoms/cm². The Si (7×7) provides 8.63×10^{14} Si atoms/cm² if one includes the 54 atoms comprising the adsorbates and next layer of Si atoms in each unit cell. Hence only 45% of the Si surface is needed to form Pd₂Si. This value is in very good agreement with the previously mentioned 42% measured for the 1-ML coverage. Thus the (7×7) adsorbates and only a half of the first

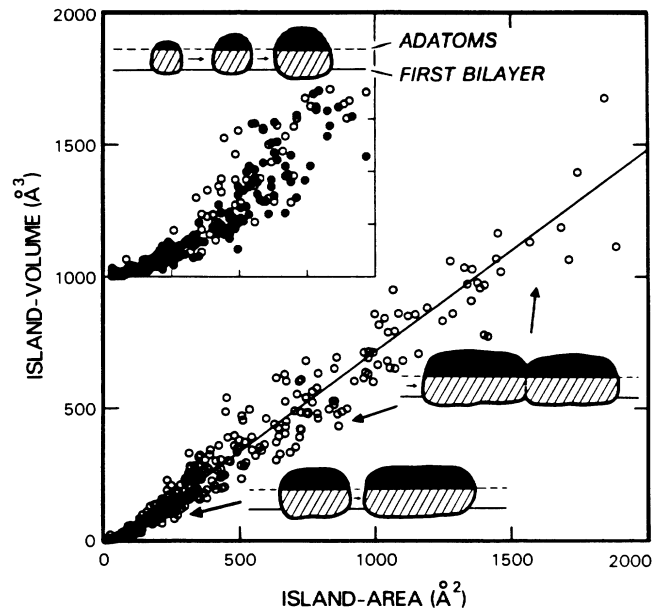


FIG. 3. Plot of the island volume vs island area. Inset: Magnification of the region below 200 Å². The filled circles are from 0.25-ML images and the open circles from 1.0-ML Pd. The island growth mechanism for the different regions is schematically indicated.

Si bilayer are sufficient to saturate the adsorbed Pd. For this reason the depth of the silicide islands is believed to extend on average only down to the first Si bilayer as displayed in Fig. 2(c), which corresponds to 2.3–2.5 Å beneath the adsorbates.^{11,13}

Images obtained by tunneling from filled surface states and by tunneling into empty surface states show essentially the same shapes and heights for the silicide islands. Hence our tunneling images should reflect their real geometric extension without a large influence from electronic effects. This further enables us to utilize the statistical correlation between island area and island volume visible above the Si-adsorbate level to achieve further insight into the growth of the silicide islands following nucleation. Figure 3 shows a plot of the island volume versus the island area obtained from STM images for 0.25- and 1.0-ML palladium coverages. The data show a lot of scatter, further confirming that palladium silicide formed at room temperature is not epitaxial but an amorphous compound. Nevertheless there are three regimes of growth that we can identify and that we have schematically indicated in Fig. 3. For very small islands with an area smaller than 100 Å² we find a power-law dependence of the island volume, *V*, on island area, *A*, where $V \sim A^n$ with $n = 1.6 \pm 0.1$. A power-law dependence with $n = 1.5$ is expected for the uniform growth of nuclei in all directions. Islands larger than 100 Å² display a linear relation between island area and volume. Here compound formation by lateral growth keeps the

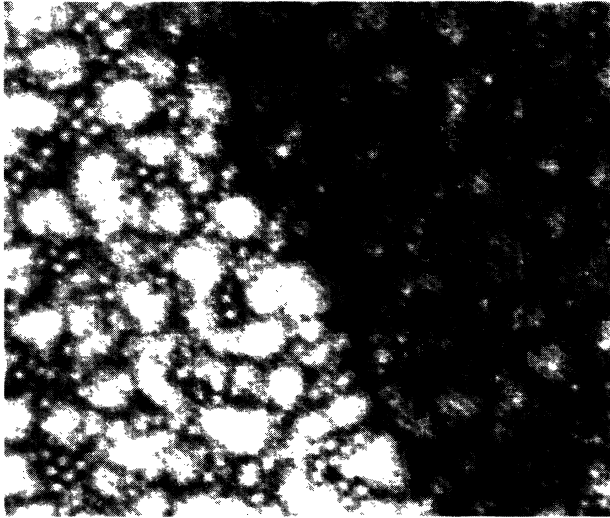


FIG. 4. STM topograph of Si(111)-(7 \times 7) with 1.0-ML Pd containing a monatomic step.

ratio of volume to area constant. Islands larger than 300 \AA^2 also show a linear correlation between volume and area, likely because they then exceed the area of the Si (7 \times 7) half cell and start to coalesce. We have also studied island size distributions as a function of coverage, but we do not discuss this here.

Finally the influence of gross surface imperfections, such as steps, on the initial nucleation is found to be negligible for this reactive silicide. Figure 4 shows a Si-surface region containing a monatomic step covered with 1 ML of palladium. It is obvious that there is nothing special about nucleation and growth near this step as the cluster density and size are unaffected. The high density of possible nucleation sites provided by the substrate superstructure seem to limit surface diffusion so that trapping and pileup at gross surface imperfections never occurs.

In conclusion, we have shown that it is possible to achieve useful statistical information with the STM.

The initial nucleation of palladium silicide at room temperature is entirely driven by the intrinsic local structure of the substrate reconstruction. Nucleation occurs almost exclusively in the faulted half of the Si (7 \times 7) unit cell. The extension of the nuclei below the surface and their growth behavior have been modeled by our making simple assumptions. Initial compound formation seems to include only the outermost Si layer. Steps and other surface imperfections play a minor role in this particular nucleation process. The subsequent behavior of the Pd-Si system upon annealing to form an epitaxial silicide has also been studied and will be discussed elsewhere.

The authors gratefully acknowledge useful discussions with R. M. Tromp and J. G. Clabes.

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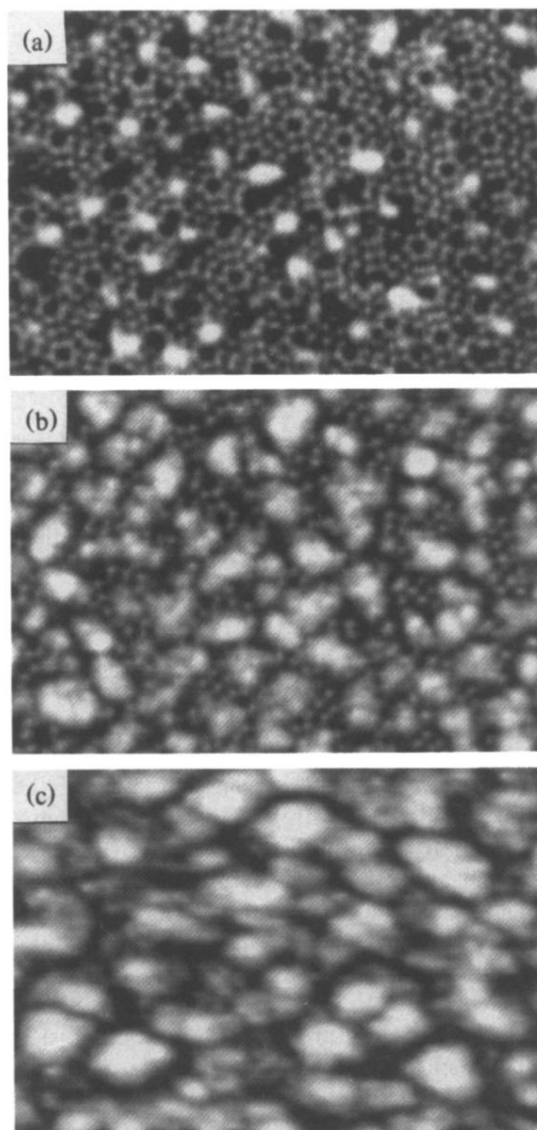


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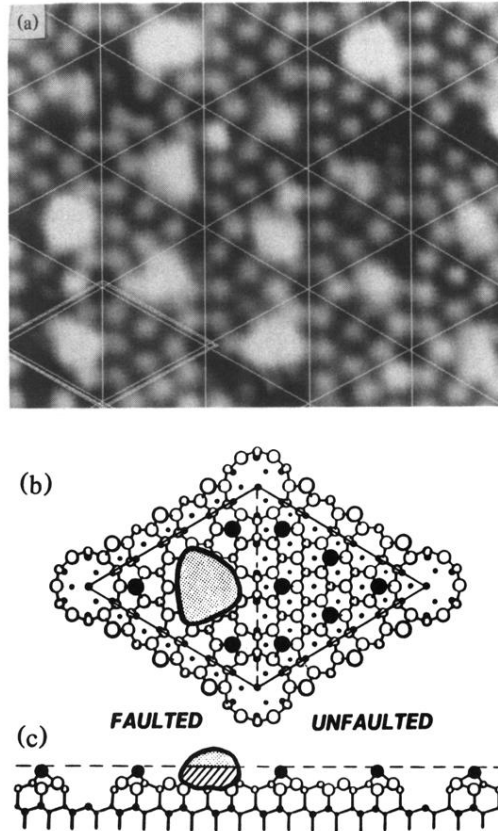


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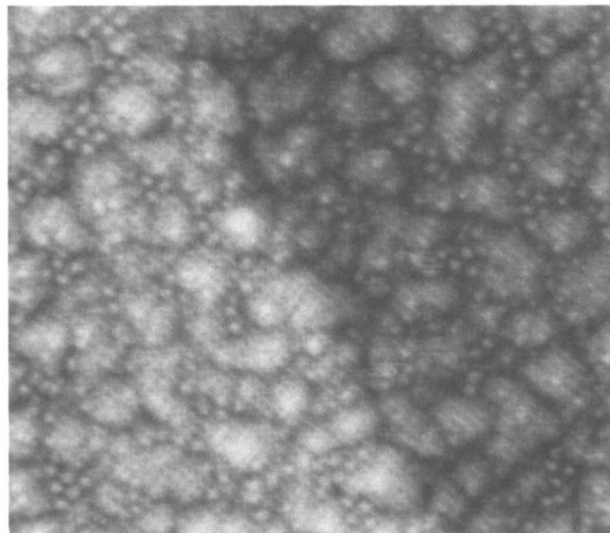


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