Epitaxial growth of manganese on silicon: Volmer-Weber growth on the Si(111) surface

M. M. R. Evans, J. C. Glueckstein, and J. Nogami
Department of Physics and the Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201
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Mn forms islands with a $\sqrt{3}\times\sqrt{3}$ reconstruction and a minimum thickness of 4 Å on Si(111). When up to 4 ML Mn is deposited at room temperature and annealed, Mn displays a modified Volmer-Weber growth mode with $\sqrt{3}\times\sqrt{3}$ islands surrounded by partially ordered silicon adatom arrangements similar to those of quenched Si(111). Mn deposited at an elevated temperature also forms $\sqrt{3}\times\sqrt{3}$ islands, but the surrounding clean Si preserves the 7×7 arrangement. At coverages of Mn above 4 ML, the surface is almost completely covered with a $\sqrt{3}\times\sqrt{3}$ overlayer.

INTRODUCTION

Mn on Si(111) was studied using LEED (low-energy electron diffraction) by Jona, who found that 4 ML of manganese deposited on Si(111) was needed to make the 7×7 LEED pattern of the Si(111) disappear.[1] Below this coverage substrate spots were still visible. Upon annealing, LEED gave a strong $\sqrt{3}\times\sqrt{3}$ pattern. Our own LEED studies found that samples with coverages below 4 ML, when annealed, show 7×7, $\sqrt{3}\times\sqrt{3}$, and diffuse 2×2 LEED spots as shown in Fig. 1. Samples above 4 ML show a pure $\sqrt{3}\times\sqrt{3}$ LEED pattern, which reproduces Jona's results. There is a question of why it takes 4 ML for the surface to be entirely covered by a $\sqrt{3}\times\sqrt{3}$ phase, unlike many other metals, such as Ag,[2,3] Au,[4–6] or Al,[7–9] which need 1 ML or less to produce a pure $\sqrt{3}$ surface. Also under investigation is the origin of the diffuse 2×2 LEED pattern occurring for coverages below 4 ML, at relatively lower annealing temperatures.

The persistence of the substrate LEED spots with coverage, and the diffuse 2×2 LEED pattern, are found to be due to a Volmer-Weber growth mode for the Mn overlayer. This is unusual for metals deposited on Si(111), with virtually all other metals growing in a Stranski-Krastanov mode. The agglomeration of the metal into three-dimensional islands is seen to affect the surrounding bare substrate in different ways, depending on the growth conditions. This paper presents details of the behavior at coverages up to 4 ML, a region where the Mn overlayer coexists with the regions of bare substrate.

SAMPLE PREPARATION

The samples were prepared by flashing Si(111) wafers to at least 1150 °C for 15 s, holding them at 1000 °C for 10 min, then cooling over 10 min. This gave a clean 7×7 surface, as seen by LEED and scanning tunneling microscopy (STM), Manganese was deposited by heating the evaporant in a W basket. Deposition rates were recorded with a crystal monitor which gave readings between 0.04 and 0.13 ML/min, and coverages were determined by timed exposures to the sample. (1 ML$=7.88\times10^{14}$ atoms/cm$^2\approx1$ Å for Mn). The samples were then heated with either a filament heater, or dc current. No difference was seen between the two methods. Annealing temperatures were measured by IR pyrometry above 600 °C, and by a calibration of the sample temperature vs filament heater current below 600 °C. The experiments took place in an UHV chamber with a base pressure of 1×10^{-10} Torr, equipped with LEED and a commercial STM.[10]

RESULTS

Mn covers the entire Si(111) surface when deposited at roughly room temperature (RT), forming clusters whose size corresponds roughly to the half 7×7 unit cells with no preference between the faulted and unfaulted halves, as can be seen in Fig. 2. When a sample with less than 4 ML of Mn is annealed to temperatures between 325 and 450 °C, the surface is a combination of irregular clusters, tabular islands with a $\sqrt{3}\times\sqrt{3}$ termination, and bare Si with a variety of structures, including 5×5, 7×7, $c(2\times4)$, and $c(2\times8)$, as shown in Fig. 3. The minimum height of the $\sqrt{3}$ islands is 4 Å, independent of the Mn coverage. Thicker islands are seen, and the height distribution depends on the annealing time and temperature.

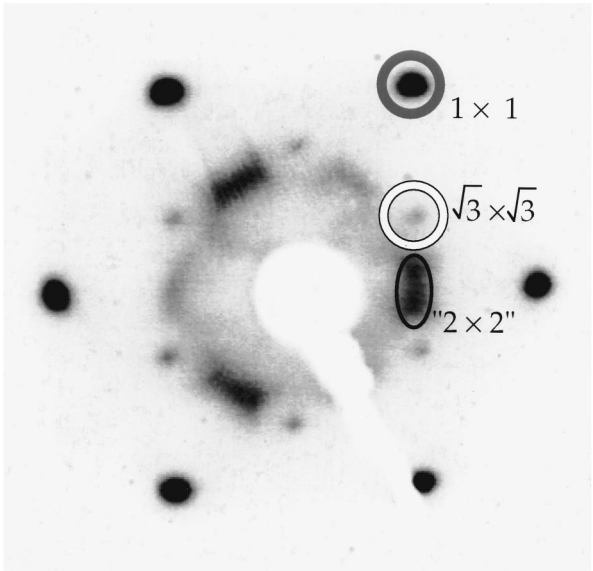

FIG. 1. A LEED pattern of 2.7-ML Mn on Si(111) annealed at 350 °C shows $\sqrt{3}\times\sqrt{3}$, 7×7, and 2×2 spots at 36 eV. The LEED intensities have been inverted black to white.

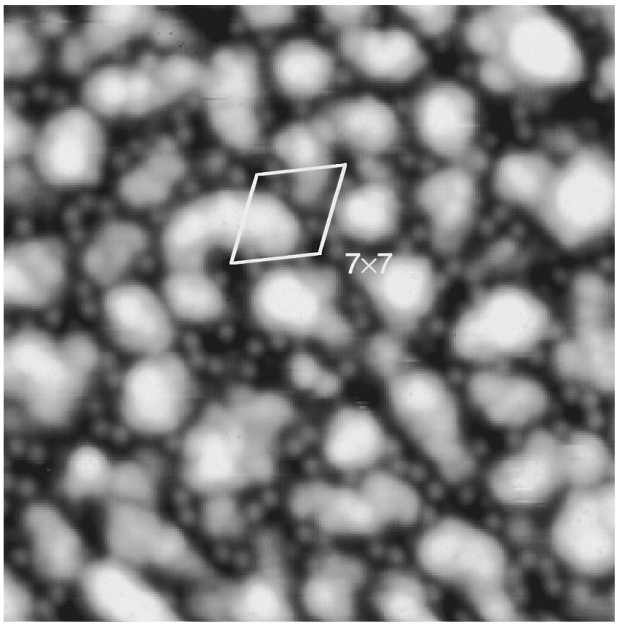

FIG. 2. The deposition of 1 ML of Mn onto a room-temperature Si(111) surface yields a uniform distribution over the entire surface, with small clusters roughly marking the location of the 7×7 half unit cells (300×300 Å^2).

The percentage of the surface covered in these islands increases with the Mn coverage. This fact, along with the appearance of the surrounding areas which can be attributed to bare Si, allows us to conclude that the Mn is incorporated into the $\sqrt{3}$ islands and the irregular clusters. At annealing temperatures closer to 450 °C, all clusters have been converted to $\sqrt{3}$ islands.

The volume of the islands at a given coverage, calculated by multiplying their height and area, depends on annealing temperature and time, but is approximately equal to the bulk volume of the Mn deposited. However, the structure of these islands makes it clear that they are not simply bulk metal, and could either be a bulk metal with surface-segregated Si, or a bulk compound. Further experiments with other analytical techniques are under way to determine the exact nature of these tabular islands.

Figure 4 shows the surface of a tabular island and some surrounding Si. The atomic structure of the island and the disordered silicon are clearly seen. (The corrugation has been enhanced by a slight addition of the data curvature to the greyscale in this image). The islands have a $\sqrt{3}\times\sqrt{3}$ surface termination, and images indicate that there is one maximum per unit cell in both the positive and negative biases which is in the same location at both polarities. The point defects on the $\sqrt{3}$ surface corrugation do not have the simple appearance of anomalously bright or dim or missing maxima, indicating that this $\sqrt{3}$ surface is not a simple adatom-induced phase such as for group-III elements on Si(111) [B,[11–16] Al,[7,8,17] Ga,[18–21] and In (Refs. 22 and 23)].

We now turn our attention to the behavior of the Si. Figure 2 clearly shows that 1 ML of Mn deposited on the Si(111) surface does not disturb the 7×7 periodicity, and that it also covers the entire surface with irregular clusters. With coverages of 1.9 ML of Mn at RT, the 7×7 is completely buried, similar to metals like Pd.[24] The continuing presence of the 7×7 unit cell indicates that the Mn atoms have not

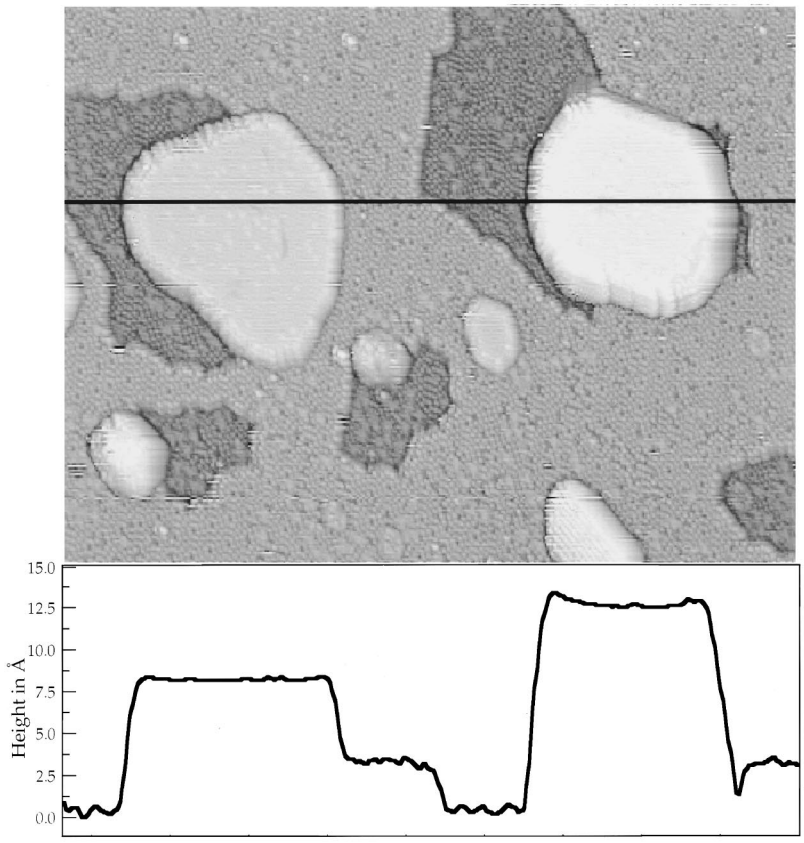

FIG. 3. Annealing 1 ML of Mn on Si(111) leads to the partial coverage of the surface by raised islands of minimum height 4 Å displaying a $\sqrt{3}\times\sqrt{3}$ structure. The surrounding bare Si areas have split into two levels, separated by a Si bilayer step. The horizontal line shows the location of the cross section shown in the lower panel (1400×1100 Å^2).

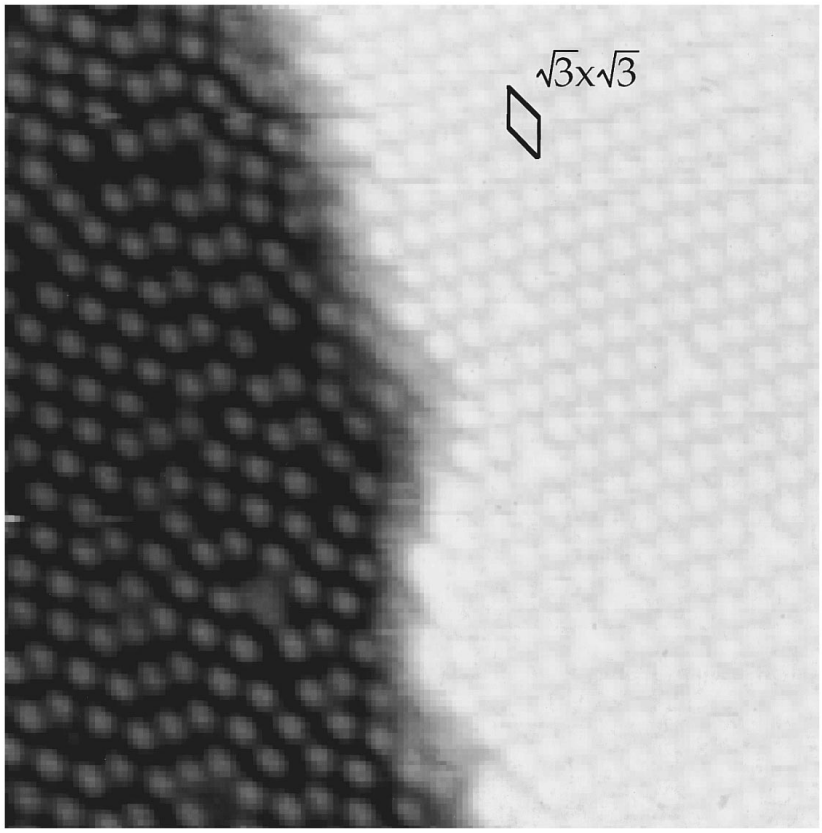

FIG. 4. A detailed view of the surface of 1-ML Mn annealed to 475 °C showing the atomic structure of the $\sqrt{3}\times\sqrt{3}$ phase with one maximum per unit cell. An adjacent area of bare Si on the left-hand side shows disordered adatom arrangements similar to 7×7 (130×130 Å^2).

substantially reacted with the surface Si at room temperature. At the same time, the Mn is not very mobile, and tends not to cross the 7×7 unit cell boundaries, and thus forms clusters of a characteristic size.

Annealing less than 4 Å of Mn forms $\sqrt{3}$ islands and areas of bare Si. The fact that Mn originally covered the entire surface after deposition means that the Mn atoms have moved across the surface, and the effect of this movement is readily apparent in the nature of the uncovered Si. The bare silicon left behind when the sample was annealed to temperatures less than 350 °C exhibits many different features. There are occurrences of 5×5, 7×7, 9×9, 11×11, $c(2\times4)$, and $c(2\times8)$, as well as disordered Si. These features, seen in Fig. 5, are similar to those seen on quenched silicon,[25] and can be attributed to either Si adatoms arrangements or DAS (dimer-adatom-stacking fault) structures. The $c(2\times8)$, 2×2, and 2×4 features are similar to those in Ge(111),[26] and in fact the LEED intensity centered about the $\frac{1}{2}$ positions has an elongated ''bowtie'' appearance, also similar to that of disordered Ge(111).[27]

Annealing temperatures above 450 °C lead to a recrystallization of the 7×7 structure on the bare silicon. At the same time the total volume for the $\sqrt{3}$ islands decreases. Whether the loss of island volume is due to indiffusion of Mn, loss of Mn, or other effects will have to be determined by other analytical techniques. Details of these annealing results will be presented elsewhere.

The overall growth mode can be considered modified Volmer-Weber growth. Volmer-Weber growth is characterized by immediate nucleation of islands coexisting with the bare substrate at lower coverages. In this modified Volmer-Weber growth mode the Mn originally covers the surface, and upon annealing the Mn forms three-dimensional (3D) islands and also perturbs the surrounding bare substrate surface. To our knowledge, this is the first time that Volmer-Weber growth of a metal has been observed on a Si(111) surface.

Depositions of 4 ML or more and annealing temperatures at 350 °C yield a virtually complete $\sqrt{3}\times\sqrt{3}$ surface film.

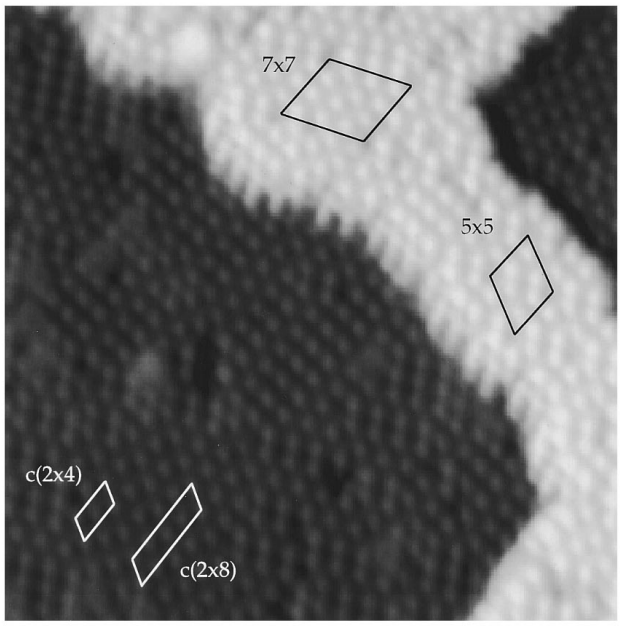

FIG. 5. Bare Si areas show considerable disorder at lower annealing temperatures ($T\approx350$ °C) with 7×7, 5×5, $c(2\times4)$, and $c(2\times8)$ structures, similar to those found on quenched Si. The Si uncovered by the annealing and motion of the overlayer has not had a chance to recrystallize (130×130 Å^2).

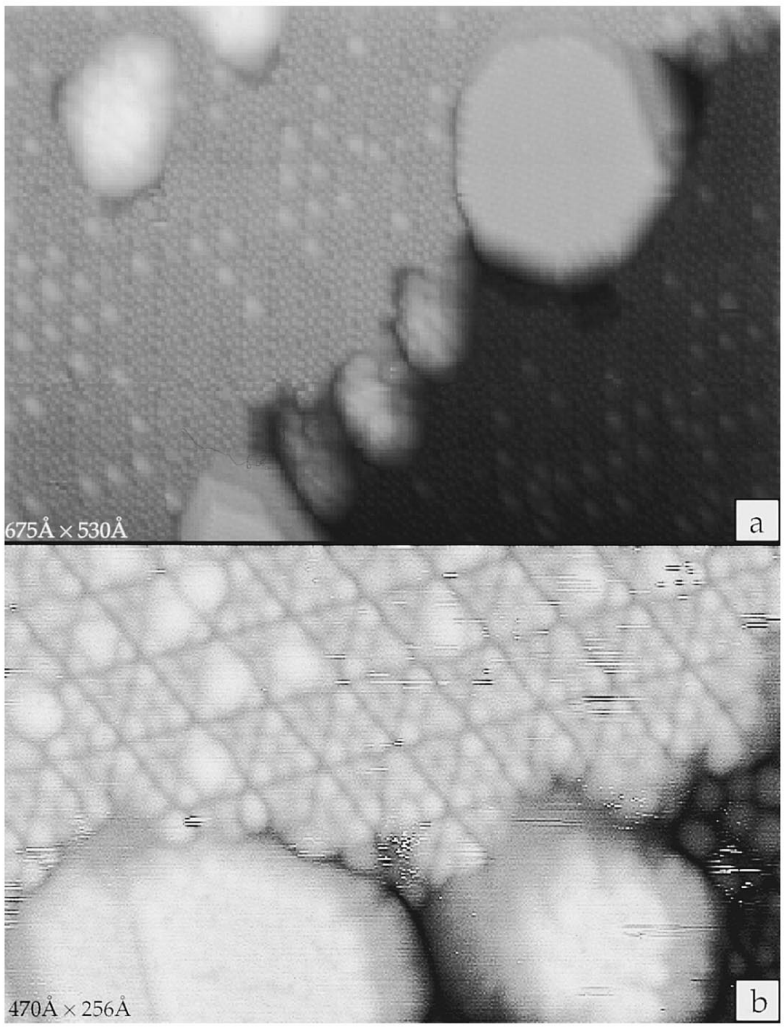

FIG. 6. (a) Deposition of 0.8-ML Mn onto Si(111) at $T=325$ °C leads to the formation of $\sqrt{3}\times\sqrt{3}$ islands, and small clusters of Mn on the faulted half of some 7×7 unit cells. (b) This filled-state image shows the atomic structure of a $\sqrt{3}$ island nucleated at a step edge, as well as a closer view of the small Mn clusters. In this image the faulted half of the 7×7 unit cells are pointing upwards.

Small holes in these complete films show disordered Si features at the bottom, and are a minimum of 4 Å in depth, the same as the minimum height of islands at lower coverages which provides support for the idea of a minimum stable thickness for the $\sqrt{3}$ overlayer. The reason for this minimum stable thickness is not known, particularly since we have no information about the bulk structure of the islands. Effects such as the strain between the islands and substrate as well as charge balance in the island itself (if it is a bulk silicide) might play a role.

When Mn is grown on a heated substrate, the results are subtly different than RT deposition at the same coverage and subsequent annealing at the same temperature. Figure 6 shows the result of growing 0.8 ML of Mn onto a substrate at $T=325$ °C. With the elevated substrate temperature the silicon between the islands is undisturbed, whereas post-deposition annealing of a RT film at the same temperature produces disordered Si. The 7×7 reconstruction is clearly seen, as well as $\sqrt{3}\times\sqrt{3}$ islands and large irregular clusters at the step edge. Much of the Mn moves about the surface of the Si, creating $\sqrt{3}\times\sqrt{3}$ islands and clusters at the steps. However, there are small Mn clusters in some of the 7×7 half-unit cells.

These small clusters of Mn occur most frequently on the faulted half of the Si(111)-7×7 unit cell, as seen in Fig. 6(b), similar to Ag.[28] One can also notice that there is a tendency for these small clusters to be less densely located near step edges and $\sqrt{3}\times\sqrt{3}$ islands where it is apparently more favorable for the Mn to migrate to an island, or to a step edge with an island.

The question arises as to the reason for the difference between RT growth with post annealing, and elevated temperature growth. The deposition onto the heated substrate most probably involves diffusion of monomers on the surface, which might be able to move across the surface without disrupting the 7×7 structure. In contrast, Mn deposited at RT has already formed sizable clusters, and annealing of these clusters evidently causes enough reaction with the surface to disrupt the 7×7. Further evidence for this disruption is the splitting of the uncovered Si into several bilayers, which is a signature of substantial rearrangement of the substrate material during growth.[29]

There is a precedent for the metal cluster size dependent reactivity on Si(111). Shibata, Kimura, and Takayanagi[30] have shown, with *in situ* high-temperature measurements of Ag growth on Si(111), that a minimum cluster size of Ag is necessary to nucleate areas of the Ag-induced $\sqrt{3}$ structure, a process that also involves substantial movement of Si. Smaller clusters of Ag do not disturb the 7×7 structure.

CONCLUSIONS

We have studied the growth of Mn on the Si(111) surface. The Mn forms a well-ordered $\sqrt{3}\times\sqrt{3}$ reconstruction after the deposition and annealing of 4 ML. This reconstruction is the surface termination of islands with a minimum thickness of 4 Å (≈4 ML). Therefore, at coverages of less than 4 ML, $\sqrt{3}$ islands coexist with bare areas of silicon. In this respect the initial growth of Mn on Si(111) is Volmer-Weber.

The nature of the uncovered silicon depends on the details of the growth. RT deposition results in complete coverage of the surface, and agglomeration of Mn by annealing leaves behind disordered silicon. As the annealing temperature is increased the silicon recrystallizes into the 7×7 structure. In contrast, growth at elevated substrate temperatures allows the formation of $\sqrt{3}$ islands without disruption of the 7×7 structure in surrounding areas.

The STM images of the $\sqrt{3}$ structure show one maximum per unit cell, but this is not a simple adatom-induced phase. It is probably the surface of a bulk manganese compound. At high coverages of Mn, above 4 ML, the surface is almost completely covered with this compound.

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