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We have investigated the properties of Mn clusters deposited on clean semiconductor surfaces using an ultrahigh vacuum scanning tunnelling microscope. The clusters were formed using a gas aggregation source and were deposited on Si(111)-7×7 and Si(111)-7×7 terminated by a C_{60} monolayer. A distribution of cluster widths was observed with a most frequent value of 2.6 nm. There was no evidence of either cluster coalescence or preferential bonding sites. The clusters had an irregular shape, but did not appear to be grossly deformed upon adsorption onto the surface. The clusters could be selectively removed from the C_{60} terminated surface during scanning at negative sample bias. © *1997 American Institute of Physics.* [S0003-6951(97)02816-7]

The study of aggregates of atoms known as clusters has expanded rapidly over the last few years. The number of atoms in a cluster ranges from less than 10 up to >10 000 atoms, equivalent to a particle with a diameter of several nanometers. Much of the recent research has been driven by the expectation that clusters could have physical properties which are qualitatively different from those of the bulk form of the same element (see, for example, Ref. 1). Novel solids formed by an array of clusters have also been proposed and demonstrated.[2–5] It may be possible to tailor the electrical, optical, and magnetic properties of such a solid by controlling the size of the constituent clusters. In addition, manipulation of clusters on surfaces has been demonstrated [6–8] with a view to the fabrication of nanometer scale electronic devices. For all these applications the interaction of clusters with a solid substrate is of great importance.

In this letter, we discuss the properties of Mn clusters deposited on Si(111)-7×7 and C_{60} terminated Si(111)-7×7. We have investigated the cluster size, shape, and height, using an ultrahigh vacuum (UHV) scanning tunnelling microscope (STM) operating at room temperature. In addition, we have established that the STM tip can be used to modify the cluster distribution. In particular, we have found that clusters can be removed from C_{60} /Si(111)-7×7 by scanning under the appropriate bias conditions, although this was not possible for clean Si(111)-7×7. Manipulation of somewhat larger (>10 nm) semiconductor[6] and noble metal clusters[7,8] has previously been demonstrated using an atomic force microscope (AFM) at atmospheric pressure. In that work, it was found that the cluster-substrate interaction was extremely weak and the clusters could be moved rather easily. In contrast for the metal clusters discussed below, which are deposited, imaged and manipulated under UHV conditions, the substrate interaction is found to be much stronger and is determined by the chemistry of the surface.

Our experiments were carried out using a commercially supplied STM.[9] Pieces of Si(111) wafer (5×3) mm^2 were introduced into the UHV/STM system, outgassed at ~800 °C overnight, and then flash annealed to ~1200 °C for ~120 s. This procedure resulted in the (7×7) surface reconstruction. W tips were electrochemically etched and then cleaned in UHV by electron bombardment. The clean Si(111)-7×7 surface was held at room temperature while C_{60} was sublimed at a rate of ~0.05 monolayers/min. A single complete C_{60} monolayer was prepared by depositing ~2 monolayers of C_{60} and then annealing at ~300 °C for 10 min, causing the second monolayer to desorb.[10,11]

The clusters were produced in a gas aggregation source[12–14] by evaporating Mn from an alumina crucible held at ~1000 °C into a stream of inert He gas. The gas/particles pass through several differential pumping stages and then impinge on the Si(111)-7×7 surface. During deposition of the Mn clusters, the pressure in the UHV system rose to $\sim 10^{-5}$ Torr but upon isolating the source the pressure fell to $\sim 10^{-10}$ Torr. A typical deposition rate was 10^3–10^4 clusters/μm^2/min. The cluster source is equipped with a mass filter but this was not used for the set of experiments described below.

The images in this letter were acquired using the STM in constant current mode. During the experiment, the UHV system was connected to large, noisy rotary pumps which led to a slight degradation in image quality. Figure 1 shows an

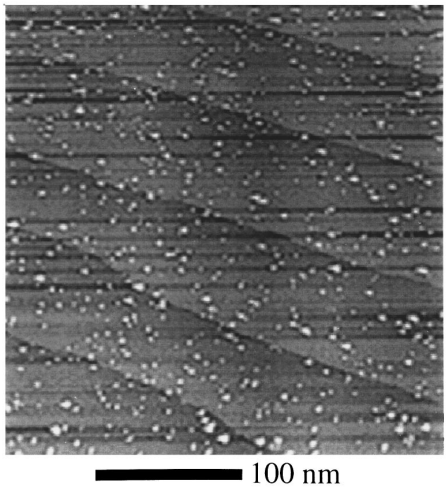

FIG. 1. Constant current STM image of Mn clusters adsorbed on a Si(111)-7×7 surface. Scan parameters are +0.9 V (sample bias), 0.25 nA (tunnel current).

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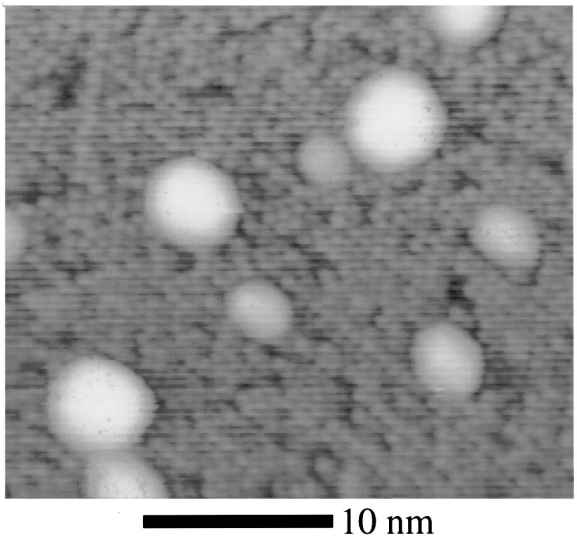

FIG. 2. Constant current STM image showing distinct cluster edges. Scan parameters = +2 V, 0.1 nA.

STM image of Mn clusters on the Si(111)-7×7 surface. The clusters appear as bright topographic features in both filled and unfilled state STM images and are unaffected by STM scanning. Bilayer terrace steps of height 0.31 nm running from left to right may also be resolved in the image. The clusters are distributed randomly over the surface and we find no evidence for preferential bonding sites. In particular, we do not observe an increased density of clusters near terrace step edges, nor the coalescence of clusters. This implies that the interaction between the adsorbed clusters and the Si(111)-7×7 reconstruction is sufficiently strong that cluster diffusion is small.

Figure 2 is a smaller area image in which the shapes of the clusters may be resolved. It is noticeable in Fig. 2 that some of the clusters do not appear round, and have distinct straight edges. Also apparent are the diamond shaped unit cells as well as the adatoms of the 7×7 reconstruction in the background. Our STM images indicate that cluster adsorption does not affect the surrounding (7×7) reconstruction as there is no increase in surface defect concentration in the vicinity of the clusters.

The distribution of apparent cluster sizes has been measured from an image containing ~500 clusters and is shown in the form of a histogram in Fig. 3. The width is taken as the full width at half-height. The width distribution fits a log-normal distribution[15] with a most frequent apparent width of

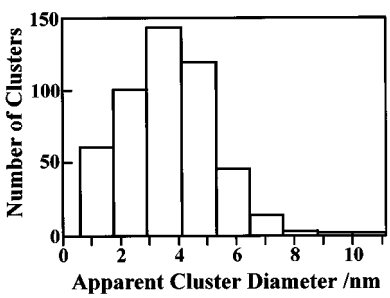

FIG. 3. Histogram of the apparent cluster width.

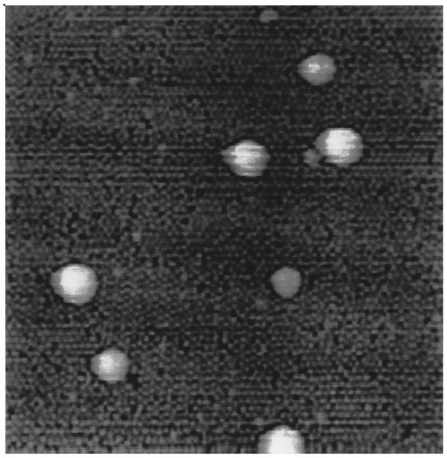

FIG. 4. STM image of Mn clusters on a C_{60} terminated Si(111)-7×7 surface. Scan parameters are −4 V and −0.2 nA.

3.6 nm. To determine the true width of the clusters, we need to take account of the broadening due to the nonzero radius of curvature of the tip. The simplest model for the effects of tip convolution (in which the tip and cluster are assumed to be spherical) gives unphysical values for the cluster widths and tip radius of curvature. As an alternative, we take an empirical approach and assume the following simple relationship[6] between d_a, the apparent cluster width, and d_o, the true cluster width, $d_a \sim d_o - 2w$ (w is a broadening parameter which is assumed to be constant for clusters of approximately the same size) and use for calibration purposes our previous STM images[16] of C_{60}. This molecule has an aspect ratio and diameter which are well known and are comparable to the Mn clusters. The apparent width of C_{60} on Si(111)-7×7 is 2.0±0.1 nm. This measurement is consistent over the course of many experimental runs and is in good agreement with the data of other groups [17,18] and provides a means of calibration. The hard sphere diameter of C_{60} is known to be 1.0 nm. This gives a most frequent corrected diameter of 2.6 nm, close to the value of 2.2 nm found in a previous experiment using the same source.[11] Using the bulk density for Mn (7.4×10^3 kg m^{-3}) gives a value of 750 for the number of atoms in the most frequent cluster.

We have also measured the distribution of cluster heights and find a mean height of 0.93 nm and a standard deviation of 0.45 nm. The clusters are not spherical and it might be expected that a given cluster would take up an orientation which would maximize its contact area with the surface. This would lead to an average height:width ratio less than 1 as observed. An alternative explanation for the departure of the height:width ratio from 1 would be that the cluster has been distorted on impact with the substrate. On the basis of the above discussion, we believe that our data imply that there is no gross distortion of the cluster on impact, although some deformation cannot be ruled out.

We have also investigated the properties of Mn clusters on C_{60}/Si(111)-7×7. This surface has been chosen since it is known to be chemically unreactive[10] and provides an interesting comparison with the more reactive Si(111)-7×7 reconstruction. Figure 4 shows an image of Mn clusters depos-

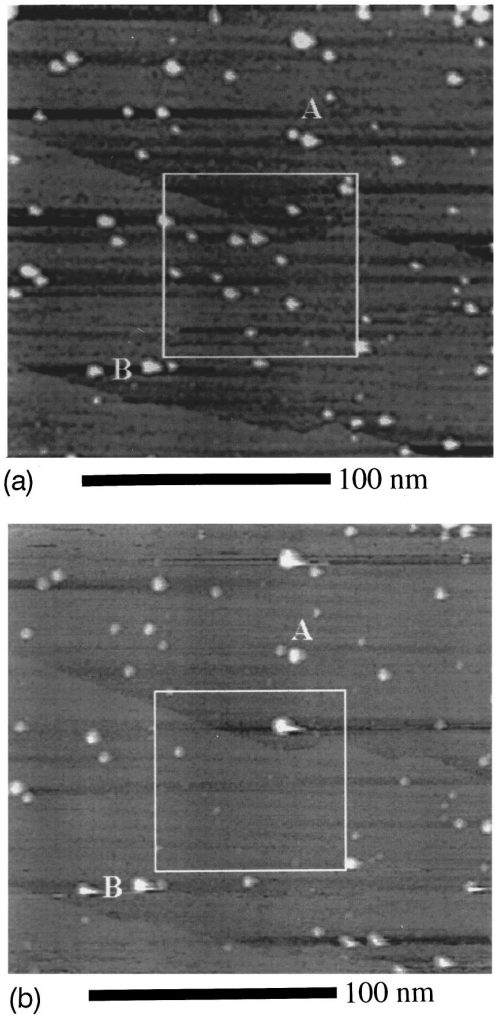

FIG. 5. STM induced removal of clusters from the C_{60} terminated surface: (a) image of the surface prior to removal. Scan parameters −4 V, −0.1 nA. Following acquisition of this image the central area within the white box was scanned 5 times with the same scan parameters. (b) STM image of the surface after the 5 smaller scans showing that many of the clusters in the central area have been removed. Scan parameters =−4 V, −0.1 nA.

ited on a complete monolayer of C_{60}. Also resolved in this image are the C_{60} molecules hexagonally ordered in two possible domain orientations (see Refs. 10, 19, and 20 for a discussion). The cluster size distribution was found to be similar to that for clean Si(111)-7×7 with no coalescence or higher density at step edges observed. The sample was annealed to temperatures up to ~600 °C after which there was no observed change in cluster statistics.

For the clean Si(111)-7×7, we have observed no modification of cluster position even under application of the manipulation procedures which we have recently developed.[16] However, we have found that for the C_{60} terminated Si the clusters are strongly affected by scanning the tip of the STM and may be removed from the surface under certain bias conditions. This is illustrated in Figs. 5(a) and 5(b). After acquisition of Fig. 5(a), the area shown within the white box was repeatedly (5 times) scanned. Figure 5(b) was acquired following these scans and reveals that of the 17 clusters originally present within the white box 9 have been removed. We did not observe any new clusters appearing in the images, indicating that the clusters have been transferred to the tip but are not redeposited. The resolution of the tip is found to vary as clusters are transferred to it from the surface. This effect is revealed from a comparison of Figs. 5(a) and 5(b) and implies that the exact configuration of the tip is modified by cluster adsorption. The ability to remove clusters from the surface is found to be intermittent but has so far been observed only when scanning with a negative bias applied to the sample. We have tried scanning with different biases and applying voltage pulses in an effort to remove clusters from the tip without success.

We have used this effect to remove a cluster from the surface and inspect its adsorption site. This was found to be identical to the surrounding region and therefore unaffected by either the removal process or cluster adsorption (we assume that the clusters do not diffuse after adsorption as implied by the lack of cluster coalescence and adsorption at step edges). The fact that the clusters may be removed from the C_{60} terminated surface but not from the Si(111)-7×7 surface strongly suggests that, as expected, the bonding to the C_{60} surface is much weaker.

We have studied the deposition of Mn clusters on Si(111)-7×7 and C_{60} terminated Si(111)-7×7. There was no evidence of coalescence or preferential adsorption sites on either of the surfaces. The cluster-surface interaction is found to be much stronger than that reported in previous studies[6–8] and could be controlled by the chemistry of the surface.

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[1] A. J. Cox, J. G. Louderback, S. E. Apsel, and L. A. Bloomfield, Phys. Rev. B **49**, 12 295 (1994).
[2] V. Paillard, P. Melinon, V. Dupuis, J. P. Perez, A. Perez, and B. Chanpagnon, Phys. Rev. Lett. **71**, 4170 (1993).
[3] K. Sattler, G. Raina, M. Ge, N. Venkateswaran, J. Xhie, Y. X. Liao, and R. W. Siegel, J. Appl. Phys. **76**, 546 (1994).
[4] C. B. Murray, C. R. Kagan, and M. G. Bawendi, Science, **270**, 1335 (1995).
[5] V. Dupuis, J. P. Perez, J. Tuaillon, P. Mélinon, A. Perez, B. Barbara, L. Thomas, S. Fayeulle, and S. M. Gay, J. Appl. Phys. **76**, 6676 (1994).
[6] T. Junno, K. Deppert, L. Montelius, and L. Samuelson, Appl. Phys. Lett. **66**, 3627 (1995).
[7] D. M. Schaefer, R. Reifenberger, A. Patil, and R. P. Andres, Appl. Phys. Lett. **66**, 1012 (1995); B. Schleicher, T. Jung, and H. Burtscher, J. Colloid Interface Sci. **161**, 271 (1993).
[8] T. Junno, S. Anand, K. Deppert, L. Montelius, and L. Samuelson, Appl. Phys. Lett. **66**, 3295 (1995).
[9] The STM, control software and electronics provided by Oxford Instruments SPM Groups (originally WA Technology).
[10] A. W. Dunn, P. Moriarty, M. D. Upward, and P. H. Beton, Appl. Phys. Lett. **69**, 506 (1996).
[11] D. Chen, and D. Sarid, Surf. Sci. **318**, 74 (1994).
[12] C. Binns, C. Norris, S. H. Baker, A. M. Keen, and S. N. Mosley (unpublished).
[13] A. M. Keen, C. Binns, S. H. Baker, S. Mozley, C. Norris, and S. C. Thornton, Surf. Sci. **352**, 715 (1996).
[14] S. J. Riley, E. K. Parks, C. -R. Mao, L. G. Pobo, and S. Wexler, J. Phys. Chem. **86**, 3911 (1982).
[15] C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. **47**, 2200 (1976).
[16] P. H. Beton, A. W. Dunn, and P. Moriarty, Appl. Phys. Lett. **67**, 1075 (1995).
[17] Y. Z. Li, M. Chander, J. C. Patrin, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **45**, 13 837 (1992).
[18] X. D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nashina, and T. Sakurai, Jpn. J. Appl. Phys. 1 **31**, L983 (1992).
[19] D. Chen, J. Chen, and D. Sarid, Phys. Rev. B **50**, 10 905 (1994).
[20] H. Xu, D. M. Chen, and W. N. Creager, Phys. Rev. Lett. **70**, 1850 (1993).