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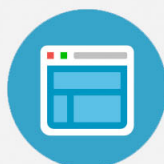
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We have used an ultrahigh vacuum scanning tunneling microscope to investigate the deposition of mesoscopic iron clusters from a gas aggregation source. The size of the clusters was found to be in the range 1–7 nm. The effect of exposure of the iron clusters to the atmosphere results in a significant increase in cluster size, which we believe is consistent with total oxidation of the clusters. A specially designed quadrupole mass filter is incorporated inside the cluster source. We have investigated the sizes of the clusters deposited using different quadrupole settings and find that it is possible to size select the clusters prior to deposition. Finally we have studied the effect of sample surface reactivity and annealing on cluster distribution. © 2000 American Vacuum Society. [S0734-211X(00)10606-7]

I. INTRODUCTION

In recent years there has been intense interest in nanometer scale clusters. Mesoscopic clusters, which have diameters of ~1–10 nm and contain 10–1000 s of atoms, represent the transition between particles whose properties are described by atomic or molecular physics and those whose are described by solid state physics. Consequently, the properties of an individual cluster are critically dependent upon its size.¹ This size dependence may enable cluster-based materials to be produced with novel optical, magnetic, or electronic properties.^{2–4} It may be envisioned that the properties of such cluster-based materials may be determined by careful selection of the size of the constituent clusters. One critical requirement for the production of these materials is the ability to mass or size select the clusters prior to deposition onto a substrate. Another important consideration is the behavior of the cluster upon adsorption on the surface. For instance it has been demonstrated⁵ that high energy clusters (with energies >1 eV/atom) can have their structure considerably altered upon impact with the surface. It has also been shown⁶ that small clusters can diffuse and coalesce to form larger clusters. Both of these effects are undesirable for the manufacture of cluster based materials.

In this article we discuss an ultrahigh vacuum scanning tunneling microscopy (UHV-STM)⁷ study of nanometer scale Fe clusters produced using a high temperature gas aggregation source.⁸ Fe clusters are of particular interest in fields of research such as catalysis, magnetic sensing, and data storage. We present results of the cluster size distribution, mass selection of clusters, and oxidation of clusters.

II. EXPERIMENT

Gas aggregation sources^{8,9} are particularly suited to the production of continuous beams of clusters of up to thousands of atoms. The gas aggregation source used in these experiments is described in detail elsewhere.⁸ Briefly, metal is evaporated from an alumina crucible (held at a tempera-

ture of ~1600 °C) into a chamber filled with cold He gas. The supersaturated vapor formed above the metal then nucleates and coalesces to form clusters. These clusters are found to have a smoothly varying size distribution⁹ that is fitted well by a lognormal distribution, and determined primarily by collision statistics.^{9,10} A stream of He and clusters then passes out of this chamber through various differential pumping stages and then through a quadrupole mass filter. During these experiments the gas aggregation source was connected directly to the deposition chamber of the STM-UHV system. This enabled the clusters to be studied *in situ*, without exposure to ambient conditions. In practice, during cluster depositions the pressure in the UHV chamber rose from its normal base pressure of ~10⁻¹¹ mbar to around 10⁻⁵ mbar. However this pressure increase was mostly due to the He bath gas; the principal contaminant, carbon monoxide was present with partial pressures of ~10⁻⁸ mbar. The pressure in the deposition chamber returned to the 10⁻¹¹ mbar range within a few minutes of isolating the cluster source.

The samples used in these experiments were 7×3 mm pieces cut from a single crystal B doped Si(111) wafer (resistivity >1 Ω cm). The samples were introduced and degassed at ~600 °C overnight by direct current heating. They were then annealed at ~1200 °C for ~60 s resulting in a 7 × 7 reconstructed surface with a low defect density.

III. RESULTS

Figure 1 is a typical STM image of Fe clusters on the Si(111) surface following a 15 min deposition, with a typical deposition rate of 500 clusters/μm²/min. The quadrupole mass filter was not in operation during this deposition and so there is no size selection of clusters. In the STM images the clusters appear as isolated topographic features that are randomly distributed across the surface. The terrace steps of the underlying surface are resolved in the background. We did not observe an increased density of clusters at step edges or any large groups of clusters. This suggests that there is a

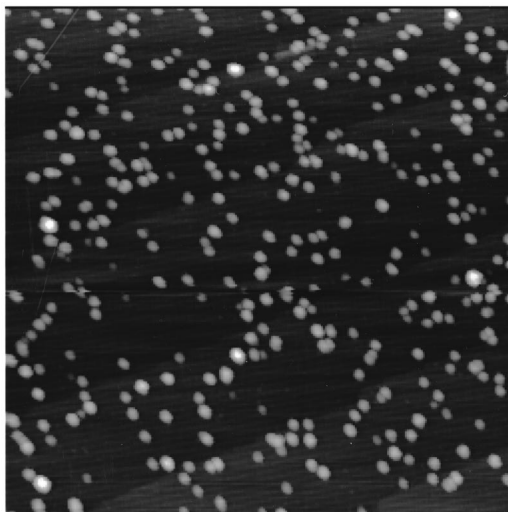


FIG. 1. Fe clusters adsorbed on the Si(111)- 7×7 surface. Image parameters $200\times 200\text{ nm}^2$, sample voltage 2.5 V, tunnel current 0.25 nA.

strong interaction between the clusters and the surface, which inhibits cluster diffusion. These results are in good agreement with an earlier study of mesoscopic Mn clusters on the same surface.¹¹ Higher magnification images of clusters reveal that when two clusters are in contact with one another they remain separate and do not coalesce into a single, larger cluster. The cross sections of adsorbed clusters are not circular and show some evidence of faceting.

The height and width of the clusters have been measured from several STM images by analyzing line profiles through the clusters. The width of the cluster was taken to be the full width at half maximum height. Figure 2 shows three graphs of cluster sizes measured from ~ 1200 clusters. Figure 2(a) is a scatter plot of cluster height versus measured width. There appears to be a general trend for the cluster height to be approximately proportional to the apparent width, although there is a considerable spread in the results. Figures 2(b) and 2(c) are histogram plots of the cluster heights and widths, respectively. Both graphs have a clear peak in the size distribution. Also plotted on these two graphs are lognormal distributions fitted using a Levenberg–Marquardt algorithm. Theoretical studies of gas aggregation sources predict^{9,10} that the cluster size distribution should be lognormal in shape. It can clearly be seen here that the fitted distribution agrees well with the experimental results, with the exception of large cluster heights. The fitted distributions give mean heights and apparent widths of 2.0 and 3.8 nm.

There is a broadening of the apparent lateral dimensions of an object when imaged with STM due to the finite radius of curvature of the STM tip. As in an earlier study of Mn clusters¹¹ we estimate that this broadening leads to an increase in the measured width of order 1 nm. Including this correction gives a typical height:width ratio of 1:1.4 for the clusters. This ratio implies that the shape of Fe clusters deposited using this source is much closer to spherical than the Mn clusters, which we have studied previously for which the height:width ratio is $\sim 1:2.5$.

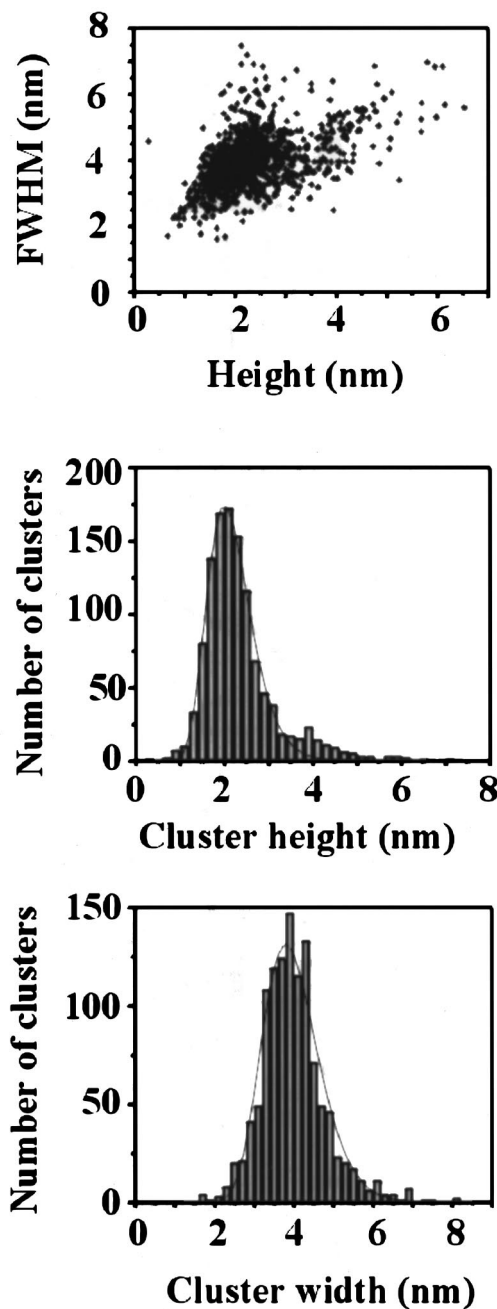


FIG. 2. Scatter plot and height and width histograms of the size distributions of Fe clusters on the Si(111)- 7×7 surface.

There are many structural and functional properties of free clusters which are of interest but require transfer of a sample through atmosphere. Figure 3 shows the results of an investigation of the stability of clusters to atmospheric exposure. In Fig. 3 we show STM images of a sample prepared in a similar manner, but with a slightly longer exposure time, to that shown in Fig. 1. Figure 3(a) is a STM image taken immediately after cluster deposition and the mean height and full width half maximum (FWHM) of clusters are 2.1 and 3.8 nm, respectively. The STM image in Fig. 3(b) was acquired after the sample was removed from the UHV system and exposed to ambient conditions for 2 min. Figures 3(a)

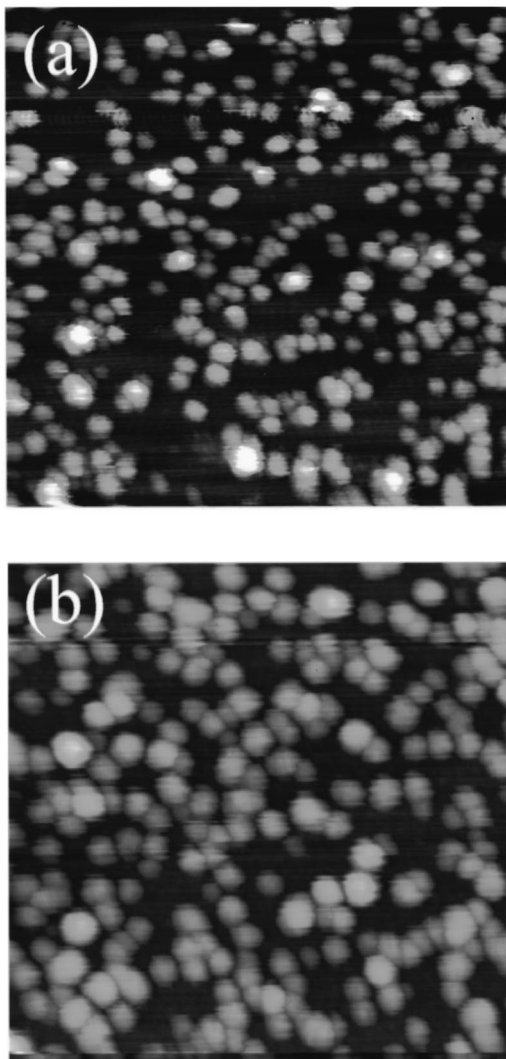


FIG. 3. STM images showing Fe clusters on the Si(111)- 7×7 surface before (a) and after (b) exposure to atmospheric conditions for 2 min. Image parameters (a) $95\times 95\text{ nm}^2$, 2.5 V, 0.2 nA; (b) $100\times 100\text{ nm}^2$, 2 V, 0.1 nA.

and 3(b) are similar size images and allow the size of the clusters before and after exposure to be compared. It is clear that the clusters have increased in size. Height and FWHM size distributions of the exposed clusters are found to be lognormal with mean heights and widths of 2.5 and 5.1 nm, giving approximately the same height:width ratio as measured prior to atmospheric exposure.

Clearly the increase in size is due to oxidation. Dupuis *et al.*¹² have studied thin (<100 nm) films of Fe formed from 2 to 6 nm diam clusters. Using Mössbauer spectroscopy they determined that 20% of their sample had been converted to iron oxide. Two different oxide phases were found to be present Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The oxidation of Fe to Fe oxide requires the addition of oxygen to the cluster, explaining the increase in cluster size. We have used the densities of bulk Fe and Fe_2O_3 (the most abundant Fe oxide) to estimate the increase in size of an Fe cluster when completely oxidized. These calculations predict that the means of the height and width distributions should increase to 2.7 and 4.9 nm, re-

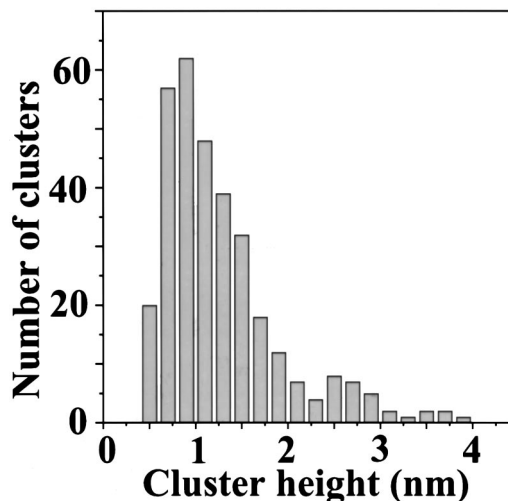


FIG. 4. Histogram of the cluster height distribution of mass selected clusters.

spectively. These values are in reasonably good agreement with the measured size distributions following exposure. These results highlight the importance of *in situ* studies of clusters produced from reactive materials.

As mentioned above the construction of cluster based materials requires clusters that have been size selected prior to deposition. We have investigated the distribution of cluster sizes produced from the gas aggregation source when operating the quadrupole mass filter with two different settings. The beam of clusters produced from the cluster source includes a considerable percentage of neutrally charged particles; these particles are not removed by the mass filter. To deposit only mass selected clusters the sample was moved 20 mm to one side of the neutral beam and the selected, charged particles were deflected onto it using a set of steering plates at the end of the quadrupole.

During this experiment the quadrupole variables were set to select particles in the size range 1.6–2.8 nm (assuming that the clusters have the same density as bulk Fe). Figure 4 shows the cluster height distributions measured from these two experiments. It can clearly be seen that the peak is now much narrower than that observed in the absence of mass selection. Most significantly it has been possible to almost entirely remove the very large number of clusters with diameters of 2–4 nm found in the unselected cluster beam. Thus the quadrupole has been effective at size selecting the clusters prior to deposition on the surface. Recent modifications to the cluster source mean that it is now possible to produce a much higher cluster flux. This should allow mass selection experiments with narrower ranges of cluster sizes to be performed in the near future.

In all of the experiments discussed so far clusters have been deposited on the reactive Si(111)-(7×7) surface to inhibit cluster diffusion. However it is also interesting to deposit clusters onto less reactive surfaces which might be compatible with cluster diffusion or manipulation.^{13–16} We have found that various adsorbates which are strongly bound to the Si(111)-(7×7) surface are free to diffuse on the Ag

terminated Si(111) surface.¹⁷ This surface has a single monolayer of Ag atoms bonded within a reconstructed surface which has $(\sqrt{3}\times\sqrt{3})R30^\circ$ periodicity. The surface was prepared by depositing Ag onto a clean Si sample which was held at $\sim 500^\circ\text{C}$.¹⁷ The resulting surface is much less reactive than the (7×7) surface, primarily because the only dangling bonds present are found at step edges and at surface defect sites. However we have found no evidence that clusters are preferentially adsorbed at such sites. In a further attempt to induce cluster diffusion and modification the sample was annealed at 325°C for 5 min. The cluster distribution following annealing was not significantly different from the arrangement beforehand. This indicates that the clusters are firmly bonded to the surface. Furthermore the height and width distributions of the clusters were measured before and after annealing. The clusters sizes were unchanged providing further evidence that the clusters may be considered as stable nanoparticles which experience a strong interaction with the surface.

IV. SUMMARY

In conclusion, we have analyzed the size distributions of Fe clusters produced from a gas aggregation source and found that they agree well with theoretical predictions. The clusters increase in size following exposure to atmospheric conditions. The size of the clusters following exposure is consistent with total oxidation of the clusters. We have found that it is possible to alter the size range of clusters deposited by using a quadrupole mass filter built into the cluster

source. Finally we have observed that even when deposited on a much less reactive surface the clusters are still unable to diffuse freely, both at room temperature and elevated temperatures.

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