Vacancy island creation and coalescence using automated scanning tunneling microscopy

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We demonstrate that scanning tunneling microscope tip-surface crash events can be utilized as an efficient means for the creation of predefined island configurations for diffusion studies. Using this method, islands of varying size can be created and placed in close proximity, increasing the probability of initiating and observing coalescence events. Data obtained from crash initiated events on a Ag(111) surface are presented. Relaxation time exponents extracted from these data confirm that our method gives results consistent with previous, sputter-obtained island coalescence studies. We also describe an instrument-control routine developed for these measurements that utilizes commercial imaging and off-the-shelf automation software to automate the tracking of islands or other features by the microscope. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2818777]

INTRODUCTION

Time-resolved studies of nanometer-scale vacancy and adatom island motion on single crystal metal surfaces have proven to be a useful method for elucidating the underlying atomic diffusion mechanisms that drive surface evolution and relaxation.[1–4] In particular, scanning tunneling microscopy measurements have been used to extract the exponents of the size-dependent power laws that are predicted to govern the diffusion of such islands.[5] The island movement is Brownian in nature and can be measured using time-resolved images, with the root mean square displacement varying according to the standard Einstein relation

$$\langle \mathbf{r}^2 \rangle = 4D\Delta t, \tag{1}$$

where D and Δt are the island diffusion coefficient and the time step between images, respectively.

In practice, one obtains D by imaging islands of similar size, with $\langle \mathbf{r}^2 \rangle$ representing the root mean square displacement between the center of mass of each island. This method alleviates inherent drift and point-of-reference complications that would otherwise inhibit the use of the scanning tunneling microscope or STM. The power law obtained from such measurements for an island of characteristic size d is $D \propto d^{-\beta}$, with $\beta=2$ and $\beta=3$ corresponding to the cases of terrace- and periphery-limited diffusion, respectively.[1,4] An alternative and equivalent method of extracting diffusion-related exponents is to follow the time evolution of coalescing islands as they combine and move toward an equilibrium shape. In this case, a characteristic time τ, with a size dependence of $\tau \propto d^{\alpha}$, governs the evolution of the larger, coalesced shape as it reforms.[6]

In the two methods described above, there are intrinsic constraints in terms of the surface preparation and time resolution that can be achieved in a given measurement. Specifically, the primary method to date for the creation of vacancy/adatom island pairs has been through low dose sputtering. Following the sputter cycle, the sample is repeatedly imaged with the STM until suitable island pairs are found. The pairs are then tracked as they either diffuse across the surface, giving a measurement of $\langle \mathbf{r}^2 \rangle$ or coalesce and evolve, giving a measurement of τ. In either case, there is a significant time penalty incurred as the STM is scanned about the surface to search for appropriate island pairs. Moreover, the necessity of using low dose sputtering to create the islands lowers the probability that closely spaced islands can be found within a reasonable experimental time frame.

In this paper we demonstrate an alternative method that allows for the creation of predefined island configurations for diffusion studies by utilizing controlled STM tip-surface crashes. Using this method, islands of varying size can be created and placed in close proximity, increasing the probability of initiating and observing a coalescence event. In the sections that follow we discuss our experimental setup and present data obtained from tip-surface crash initiated coalescence events on a Ag(111) surface. We also describe an instrument-control routine developed for these STM measurements that utilizes commercial imaging and off-the-shelf automation software to automate the tracking of islands or other features by the microscope. Finally, we present relaxation time exponents extracted from our observed events which confirm that our method gives results consistent with previous, sputter-obtained island coalescence studies.

EXPERIMENT

Setup

These experiments were carried out on an Omicron Nanotechnology variable temperature scanning tunneling microscope (VT-STM).[7] The microscope is mounted in a load-locked ultrahigh vacuum (UHV) system. The main chamber of this system has a base pressure of 10^{-10} Torr and is pumped using a combination of turbomolecular, ion, and titanium sublimation pumps. Various surface preparation and

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analysis tools are attached to the main chamber, including a sputter ion gun, sample heating stage, and low energy electron diffraction (LEED) system. The chamber is also equipped with a rotating carousel stage so that multiple tips and/or samples can be held in UHV, enabling quick turn around for imaging studies. The single crystal metallic substrate used here was a $2\times3\times9$ mm^3 Ag(111) crystal obtained from MaTeck.[8] The sample was mounted in a standard Omicron VT holder incorporating an on board boron nitride (BN) heater for sample annealing.

The Ag(111) crystal was prepared using a standard sputter-anneal cycle that consisted of 600 eV Ar^+ sputtering at normal incidence followed by annealings with the BN heater to 350 °C. Surface structure following the annealed portion of the cycle was verified by LEED images. Additionally, high resolution STM images confirmed the (111) crystal structure as well as sample cleanliness and minimal step bunching. Typical imaging parameters used with the STM and Ag(111) crystal were a gap voltage $U_{gap}=0.07$ V and tunnel current $I_t=0.25$ nA. The STM tips were fabricated by electrochemical etching in an aqueous 4.0*M* NaOH solution using 0.25 mm diameter W wire from Refining Systems[9] and an electrochemical etching apparatus by Obbligato Objectives.[10] During the imaging portion of these measurements, the scan time per image was held constant at $t=30.15$ s. Scanning parameters (U_{gap}, I_t, t) of the order used here have been shown not to modify the topography of the Ag(111) surface,[1,11] which is a requirement for diffusion studies. Scan ranges were varied between $(100\text{ nm})^2$ and $(150\text{ nm})^2$ in area.

Tip-surface crash

The creation of vacancy islands at the Ag(111) surface was achieved through controlled tip-surface crash events. There is some precedent for this method in the field of diffusion studies, as the first observations of atomic diffusion with the STM occured following the creation of a slight surface depression with the microscope tip on Au(111).[12] Nanoindentation has also been used as a novel way to make and characterize surface defects and fabricate dislocations.[13,14] More recently, this method has been used as an efficient source of substrate material for low temperature studies of bottom-up atomic manipulation.[15] In our work, the standard procedure adopted involved positioning the tip above the surface at imaging height and turning off the imaging feedback loop. We then advanced the tip a predetermined distance toward the sample for the crash, retracted it back to imaging height, and reset the feedback loop.

The positioning of each tip-crash event, the cycling of the feedback loop, and the tip approach/retract were all controlled using a macrocode written in the native batch programming language provided with the Omicron SCALA control program.[7] Within a range of 1–4 nm, we found that the tip could be repeatedly crashed into the Ag surface without significantly lowering our image quality. In many cases, the image quality was improved, presumably due to a Ag coating on the end of the tip, as was observed in low temperature studies.[15]

Automated tracking

As noted above, vacancy islands diffuse across the surface at room temperature. Therefore, imaging islands created by a tip-surface crash over a finite time interval required a periodic recentering of the STM scan range. Although this was achieved initally under user control, we found it necessary to implement an automated tracking routine to keep an island under observation for long time periods. The method we arrived at relied on performing a Fourier correlation of sequential image scans to arrive at a spatial offset between the two images. This offset was then used to generate a new recentered coordinate for the microscope scan frame.[16] As implemented on our system, the automated tracking method involved the coordinated execution of three software codes. The first was the SCALA code, which controls the microscope scan parameters.[7] The second was the commercial imaging and analysis software SPIP,[17] and the third was an off-the-shelf software automation tool, MACRO SCHEDULER.[18] The SCHEDULER software coordinated the tracking operation by loading sequential SCALA-saved images into SPIP and initiating the Fourier correlation there. The shift generated by the correlation was then read by the SCHEDULER software and used to generate a new set of centered coordinates which it passed into SCALA to recenter the scan frame. This cycle was repeated on successive images to achieve automated tracking. The use of successive images allowed the tracking routine to follow islands even as they coalesced and gave images that were significantly different than those taken in the initial time step.[19]

DISCUSSION/ANALYSIS

Vacancy island creation

The tip crash procedure we have outlined above was used to create various initial adatom/vacancy island pairs at the Ag(111) surface. A typical STM image taken following a tip crash event is shown in Fig. 1. The adatom islands created in each crash event were observed to be short lived, dissipating rapidly, and disappearing from the image frame.[20,21] The vacancy islands which remained were generally between 1 and 3 ML deep, and the island perimeter at each depth quickly assumed the equilibrium hexagonal shape expected for this (111) surface. The stability of the vacancy islands can be qualitatively attributed to the Ehrlich-Schwoebel barrier on the Ag surface: an effective uphill gradient preventing adatoms from returning to their original positions in the vacancy.[3,22,23]

The size and depth of the vacancy created in a tip-crash event were strongly dependent on the distance the tip was advanced during the crash sequence. For our imaging parameters, we observed that advancing the tip approximately 3 nm gave vacancy islands that were 1–2 ML deep and that were large enough to be observed and tracked before they moved out of the scan frame by diffusion. Although tip crashes beyond this depth gave vacancy islands of larger size, the islands were typically more than two layers deep and the tip often became unstable and/or unusable for imaging. In order to create vacancy islands that were large and shallow, we found that the coalescence of small islands could

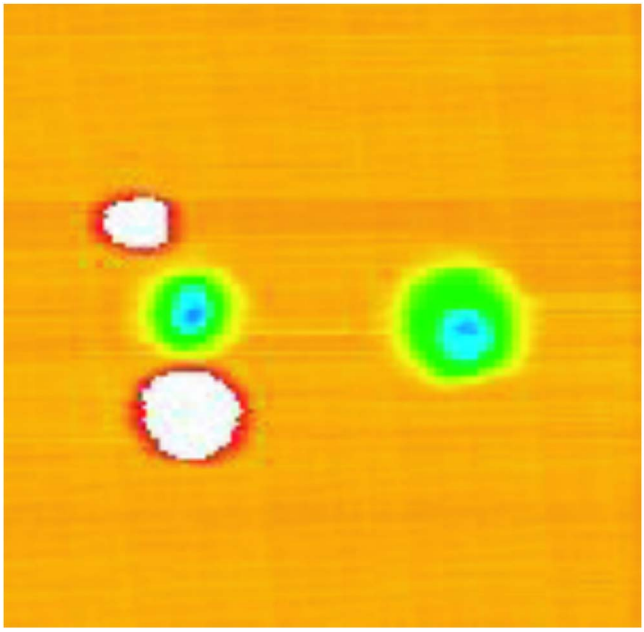

FIG. 1. (Color online) STM image obtained immediately after a tip-crash event. The vacancy island created on the left is surrounded by adatom islands formed by material ejected from creation site. Adatom islands on the Ag(111) surface decay rapidly, leaving behind the as-created vacancy islands, such as the isolated island that appears on the right. The scan range is $(100\ \text{nm})^2$.

be used. That is, coalescence events were highly probable over a short time period for islands created within 50 nm of each other. Therefore, multiple shallow islands could be created in close proximity and then allowed to diffuse, collide, and coalesce, forming a larger, shallow vacancy island.

Vacancy island coalescence

In order to demonstrate that tip-surface crash vacancy island creation is a viable method for studying atomic diffusion, we analyzed the relaxation times of several vacancy island coalescence events. An example of such an event is shown in Fig. 2. Tracking and recording the shape of an out-of-equilibrium coalesced island as it approached its equilibrium hexagonal configuration, we could extract power law exponents related to the underlying atomic diffusion.

The beginning of a coalescence event t_0 was recorded as the first STM image that showed that the adatom barrier between two vacancies had broken apart. A sequence of timed images was then recorded of the irregular, coalesced island shape until it had relaxed into an equilibrium hexagonal configuration. Typical observation times of island coalescence events were between 250 and 1000 s. Analysis of this type of event was made using in-house image thresholding and edge-detection software. All image pixels that were below half the depth of 1 ML of the Ag(111) surface were thresholded and marked as part of the vacancy island. The thresholded image provided a two-dimensional binary image of the island location. A center of mass was then established for the vacancy island, weighting each vacancy pixel equally. The equilibration of this thresholded island shape was followed through successive images or time steps by establishing observed long ($d_{\max}$) and short ($d_{\min}$) diameter values.[24] These values were found at each time step by drawing straight lines from each pixel location on the island perimeter through the center of mass to a pixel location on the opposite side of the island. To account for the irregular shape of the evolving island, the $d_{\max}$ and $d_{\min}$ were averaged over a range of $\pm 11°$ about their initial positions on the island shape. A typical plot of these diameter values as a function of time for one coalescence event is shown in Fig. 3. As the shape evolves forward in time from t_0 and toward a hexagon, the two diameters approach a fixed equilibrium value. A

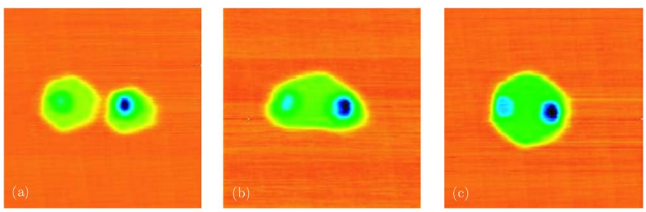

FIG. 2. (Color online) Coalescence event measured in successive STM scans [(a)–(c)] with area of $(100\ \text{nm})^2$ were recorded at $t=0$ s, $t=30.15$ s, and $t=60.3$ s.

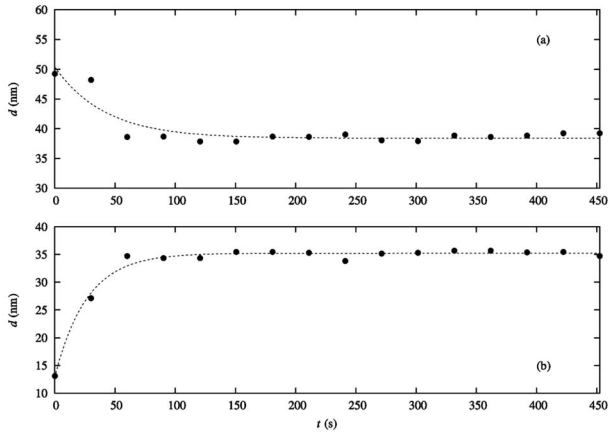

FIG. 3. Plot of the maximum (a) and minimum (b) diameters of a coalescing vacancy island shape as it approaches equilibrium. The characteristic time for the event is $\tau=36\pm7$ s, and the final diameter of the relaxed shape is $d=36.8\pm0.2$ nm.

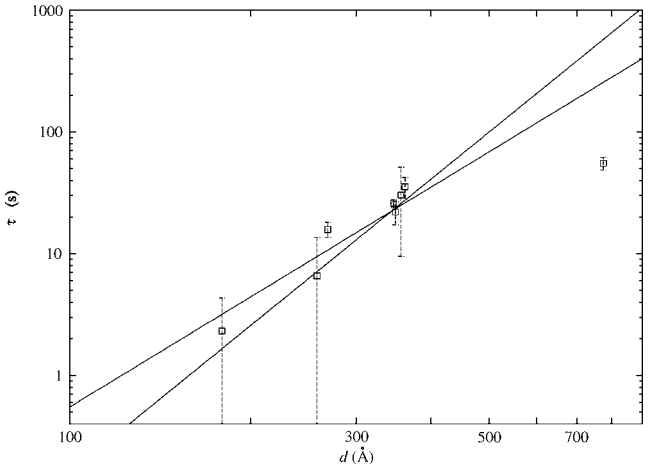

FIG. 4. Characteristic time (τ) as a function of final island diameter (d). The two lines represent the classical scaling exponents $\alpha=3$ (terrace-limited diffusion) and $\alpha=4$ (periphery-limited diffusion).

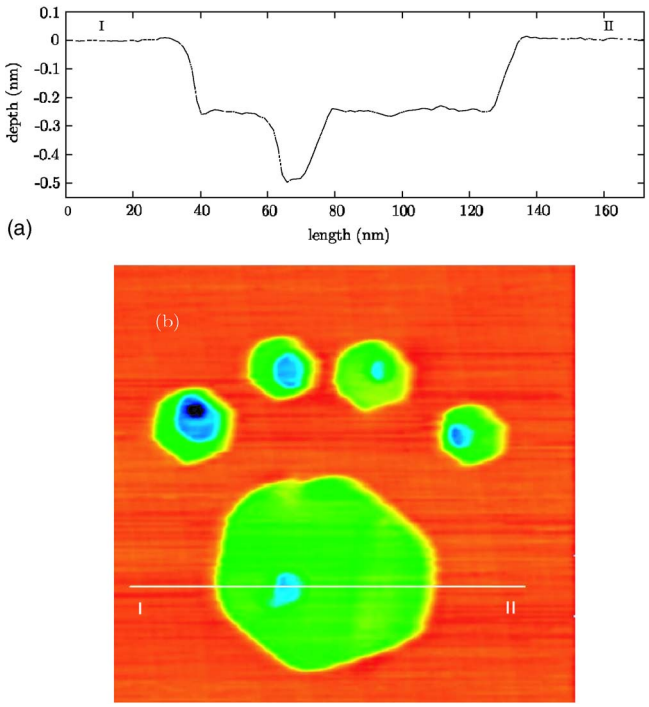

FIG. 5. (Color online) A $(200\ \text{nm})^2$ area STM image of a vacancy island configuration fabricated by multiple controlled tip crashes to represent the authors' university logo. The islands are 2 ML deep at the lowest level.

characteristic time τ was found for the observed diameter evolution of each coalescence event by fitting to an exponential curve with an equilibrium diameter d_0. As the change of both the long and short diameters for a given island should evolve according to one time constant, we averaged the τ values obtained from the fits for each diameter.[2]

The τ values obtained from multiple tip crash initiated coalescence events for islands with equilibrium diameters of 179–775 Å are plotted in Fig. 4. The slope obtained from this log-log plot gives a scaling exponent of $\alpha=2.4\pm0.6$, assuming that $\tau\propto d^{\alpha}$ as discussed above. Comparing this exponent to the expected value for β, we obtain $\beta=1.4\pm0.6$, a result that is consistent with that obtained by Eßer *et al.* Although this result suggests that island diffusion is limited by the movement of atoms across the terraces, it is well known that classical scaling exponents are not definitive proof that the movement of atoms is governed by a specific atomistic mass transport channel for these temperature and island size ranges. In fact, it has been proposed that the movement of vacancy islands on the surface of Ag(111) is limited instead by atomic diffusion about the islands' peripheries.[25] By demonstrating in this work that we can obtain island statistics consistent with those obtained stochastically, we now have the ability to utilize our own self-initiated coalescence events to test the limits of the classical diffusion theory description. As Fig. 5 demonstrates, we can now create small, closely spaced island distributions of desired complexity that would have a low probability of being observed in a time-constrained stochastic measurement.

IV. SUMMARY

We have introduced the method of controlled tip-surface crashes as a viable alternative for creating vacancy islands in diffusion studies. By crashing the STM tip only a few nanometers into the surface, we can construct 1–2 ML deep vacancy islands within a narrow size range. Utilizing the inherent diffusion of these islands, we can place them in close proximity to initiate island coalescence events. The resulting nonequilibrium shapes are observed to equilibriate toward hexagonal configurations on our Ag(111) surface, and the power law exponents extracted from such events agree with previous studies that utilized sputter-created islands. Control over island placement provides us with a new ability to study the coalescence of complicated predefined island patterns spaced only a few nanometers apart and increases the likelihood that islands of a given size and relative proximity to other surface features, including other islands, can be observed within reasonable experimental time scales.

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