Nanoscale Surface Structures

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Island decay on the anisotropic Ag(110) surface

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ABSTRACT

We have investigated the decay of two-dimensional islands on the anisotropic Ag(110) surface using variable-temperature scanning tunneling microscopy. Contrary to predictions from traditional Ostwald ripening theory, a quasi-one-dimensional decay mode is observed at low temperatures (175-220 K). A surprisingly sharp transition to the quasi-two-dimensional decay mode is observed around 220 K. This transition is accompanied by a fast equilibration of the island shape. These findings have tentatively been rationalized within a simple model to identify the underlying rate limiting atomistic processes.

INTRODUCTION

In recent years the development of fast scanning tunneling microscopes (STM) has triggered the investigation of changes in surface morphologies that were deliberately created far from equilibrium [1-10], as well as thermal fluctuation around equilibrium-shaped structures [11,12] in high temporal resolution. Model studies of the decay of islands, i.e., structures of monatomic height consisting of up to several thousand atoms, on metal surfaces [1-10] allow one to predict the limits of stability of atomic systems using a common theory for both metals and semiconductors which are the main components of microtechnology nowadays. In this paper we discuss fundamental laws of the stability of nanostructures on an anisotropic surface, thereby summarizing earlier publications on this subject [13].

Studies of the decay of quasi-isotropic islands have led to an improved understanding of the physical properties and processes involved in their decay. It has been shown that a common theory based on the classic Ostwald ripening theory [14] can be used for island decay on metal and semiconductor surfaces [2-4]. The importance of short-ranged island interaction for Ostwald ripening has been pointed out (Si(100) [2,3], Ag(111) [10]). Based on this knowledge, energetic barriers have been measured (Si(111) [7], Ag(111) [9]). Finally, the dominating coarsening mechanisms for different coverage (Ag(100) [5]) and the rate limiting step for ripening between islands on the same terrace (Cu(100) [6]) and on top of each other (Cu(111) [8]) have been determined.

The majority of these studies were carried out on isotropic surfaces, whereas the material of choice of the semiconductor industry, Si(100), has a higher complexity, being anisotropic due to dimerization. The relevant processes on anisotropic surfaces are however less well understood, because the only studies on this surface [2,3,7] were performed at temperatures well above the predicted crossover temperature from isotropic to anisotropic island growth [15]. Indeed, the anisotropy does not influence the Ostwald ripening in the temperature range investigated [3].

To elucidate the effects of anisotropy on island decay, we investigate islands on an anisotropic surface at lower temperatures. For silver islands on the Ag(110) surface in a temperature

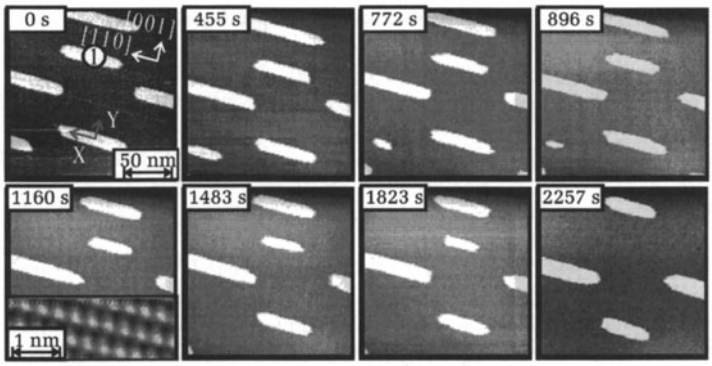


Figure 1. Series of STM images recording the development of adatom islands on Ag(110) at 235 K, U = -2.1 V, I = 0.1 nA; Inset: atomic resolution image showing the orientation of the close-packed rows, U = -2.0 V, I = 0.32 nA.

range between 155 K and 255 K, we find three different decay behaviors with transitions at T_l = (175 ± 5) K and T_c = (220 ± 10) K, respectively. Below T_l no island decay is observed. Between T_l and T_c, we find a quasi-one-dimensional decay mode, contrary to predictions of conventional Ostwald ripening theories [16]. In spite of the high energy for detachment of adatoms out of a [-110] step [17], a quasi-isotropic decay of the islands sets in already at T_c. Above T_c the island shrinks in both dimensions, and the decay can be described within the framework of the Ostwald ripening theory.

EXPERIMENTAL

The experiments were performed in a UHV system equipped with a home-built, fast-scanning, variable-temperature STM as well as standard facilities for sample preparation and characterization [18].The Ag(110) surface is prepared by several sputtering (1 keV Ne^+) and annealing cycles below the roughening transition temperature [19] (623 K) followed by a slow cool down (10 K/min). This procedure results in a clean, well-ordered surface as shown in Figure 1 (inset). The anisotropic Ag(110) surface consists of close-packed atom rows with an atomic distance of 0.289 nm running in the [-110] direction. The rows are separated in the [001] direction by 0.409 nm.

Recipes were developed to prepare three different types of monatomic high adatom islands on this surface:

(a) Deposition of silver from a tungsten basket with sample temperatures of 250-270 K for up to 3 min results in equilibrium-shaped islands (Figure 1) with an aspect ratio of R_{eq} := X/Y = 2.9 ± 0.4. These islands have their longer axis parallel to [-110], i.e., parallel to the direction of fast diffusion. This is in contrast to semiconductor epitaxy on Si(100), where the island elongation driven by anisotropy in bonding is perpendicular to the direction of fast diffusion [20].

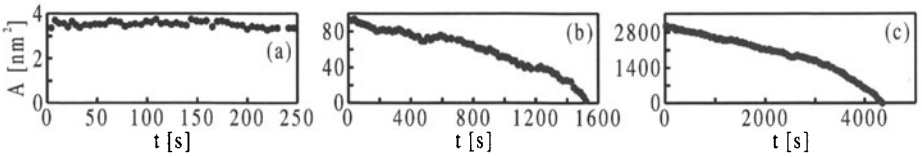


Figure 2. Evolution of island area at different temperatures T: (a) T = 169 K (b) T = 212 K (c) T = 255 K.

(b) Silver deposition at 180-200 K results in islands with an aspect ratio larger than R_{eq}. Islands with even larger aspect ratios have been predicted for this temperature range [21].
(c) Sputtering with 1 keV Ne^+ ions at 190-200 K for 1-2 sec without any Ag deposition results in islands with $R < R_{eq}$.

After preparation of the desired islands, the sample is transferred to the STM for imaging at the appropriate temperature. With fast-scanning STMs it is possible to visualize the change in surface morphology with high temporal and spatial resolution in consecutive STM images, so-called STM movies, which typically contain a few tens to over a thousand images. When recording the STM movies we employ a dynamic drift compensation mode that practically eliminates thermally-induced drift and allows us to monitor the decay of individual islands over extended periods of time. The position of a non-moving feature (e.g. a kinked step edge) is located in each image using a home-written pattern recognition software routine. During acquisition of the next image, the necessary offset voltages are added to the scanning voltages to keep the feature at the same place in the image. The achieved stability is typically ±1 pixel over several hours. Images with 256 x 256 pixels are recorded at time intervals between 5 and 70 seconds, according to the decay rate. Special care was taken to insure that the STM data are not influenced by the imaging process [9,10,22].

RESULTS

Excerpts from an STM movie recording Ostwald ripening in an ensemble of islands at 235 K are shown in Figure 1. Ostwald ripening on a surface refers to the coarsening of an ensemble of differently sized islands via the diffusion of adatoms between them. For equilibrium-shaped islands, small islands have a larger curvature and thus a larger adatom concentration in their vicinity than large islands. This difference in chemical potentials induces a net flux of material from small to either larger islands or pre-existing terrace step edges by diffusion of adatoms through the adatom gas phase.

In Figure 1, the island marked '1' decays within 40 min. From this type of image we determined the area A of isolated decaying islands that are situated on terraces so that they do not communicate directly with neighboring islands, i.e., usually, the next step in [001] is a terrace step with terrace widths of 200 to 400 nm. In [-110] the next islands are typically at a distance of 50 to 200 nm. Examples are shown in Figure 2. At temperatures below $T_l = (175 \pm 5)$ K, no island decay is observed at 169 K (Figure 2a). From atom-resolved STM movies, it is concluded that the silver adatoms are simply not able to detach from the island edges at these temperatures. Above T_l adatom detachment from the island is possible, and the islands decay (Figs. 2b and c).

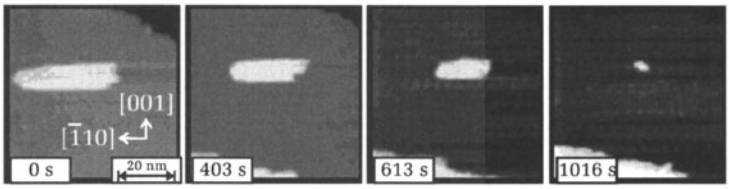


Figure 3. Series of STM images recording adatom island decay on Ag(110) at 218 K, U = -0.53 V, I = 0.11 nA.

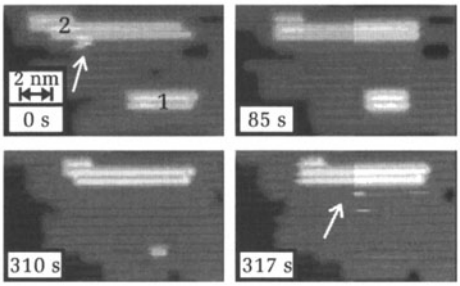


Figure 4. Excerpts of a high resolution movie at 186 K showing that adatoms from island '1' diffuse perpendicular to the rows towards island '2'; arrows mark diffusing atoms that are only partly imaged as they diffuse faster than the tip scans an atomic row; U = -0.5 V, I = 1.18 nA.

The decay curves of the islands are not linear in time. At all temperatures the islands decay faster the smaller they are. Furthermore, the overall decay rate increases with temperature. For the particular islands shown, the decay rate is 0.07 nm^2/s at 212 K (Figure 2b) and 0.70 nm^2/s at 255 K. The decay rate of islands of the same size should be compared for comparison. For instance, when the island at 255 K has reached the size of 100 nm^2, it decays with 1.9 nm^2/s.

In the following, we will argue that the island decay is qualitatively different below T_c = (220 ± 10) K (e.g., at 212 K in Figure 2b) and above T_c (e.g., at 255 K in Figure 2c). If we compare STM movies of the island decay in both temperature ranges (cf. Figs. 1 and 3) we find that below T_c the island length decreases with constant width, while above T_c both the island's width and length decrease. This is corroborated by measuring the aspect ratio R. Indeed, for island decay with initial aspect ratios between 1.25 and 10, the aspect ratio changes differently below and above T_c. Above T_c, the islands equilibrate, i.e., R decreases if the initial value is larger than R_{eq}, while it increases if the initial value is smaller than R_{eq}. Subsequently, R fluctuates within the error bars around R_{eq}. In contrast, for islands decaying below T_c, R changes towards smaller values regardless of R_{eq}. For this one-dimensional decay atoms can only detach from the open step edge. STM movies, however, reveal that the subsequent migration of the released silver adatoms on the Ag(110) terrace is not confined to one specific direction, but occurs isotropically (see Figure 4).

To analyze the decay quantitatively we recall that the continuum theory of Ostwald ripening for two-dimensional islands can be used to determine the rate limiting step of the island decay. It states that the area A of the island follows a power law of the form [23]:

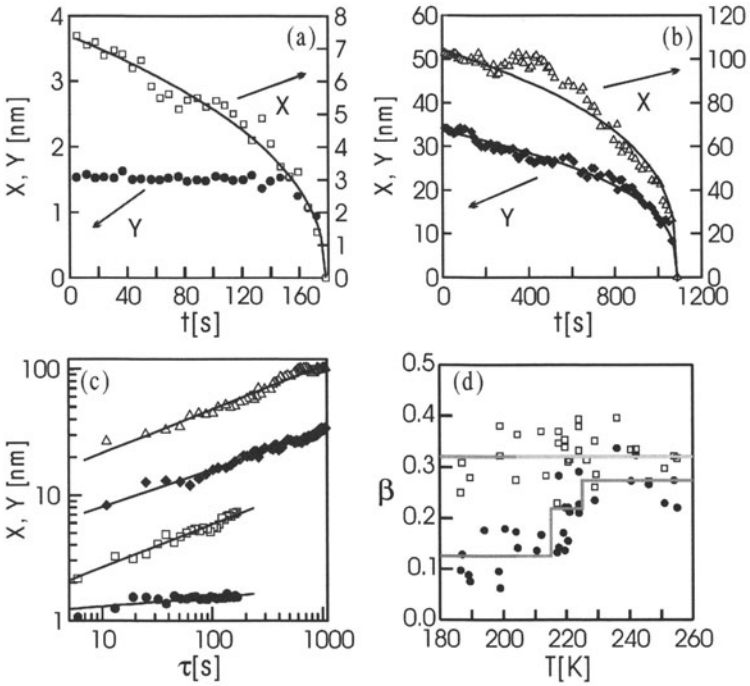
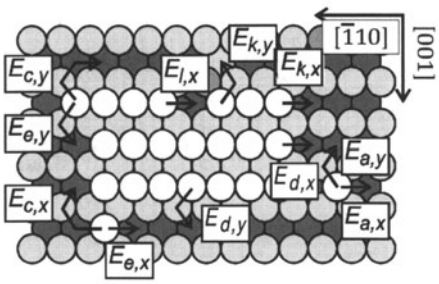


Figure 5. (a,b) Evolution of *X* (open symbols) and *Y* (filled symbols) extension at different temperatures T: (a) T = 199 K (b) T = 242 K; (c) double logarithmic *X,Y* - vs. - decay time of (a,b) with linear fit. (d) Exponents β - vs. - T determined via Equation 2; open squares β_X; filled circles β_Y; horizontal solid lines represent mean values in the regions they are drawn.

$$A \sim \tau^{2\beta}, \qquad (1)$$

τ being the decay time (τ (A = 0) = 0), and β an exponent, that depends on the ratio of the activation energies for terrace diffusion and reattachment to the island. The island decay is either diffusion-limited with β =1/3 or attachment-detachment limited with β =1/2 [24]. This continuum theory is generally valid for equilibrium-shaped islands and is *not* restricted to isotropic surfaces as anisotropy manifests itself in the prefactor and leaves the exponent unaltered. For the interface limit Bartelt *et al.* [3] calculated explicitly the prefactor by including the anisotropy in the calculation of the chemical potential. With $X \equiv \sqrt{A \cdot R}$, $Y \equiv \sqrt{A/R}$, the extensions of the islands along the long/short axis parallel to the [-110]/[001] directions (see Figure 1), respectively, we therefore expect for equilibrium-shaped islands, i.e., for X ~ Y, throughout the decay:



	a,x	e,x	c,x	a,y	k,x	l,x	d,x	e,y	c,y	k,y	d,y
E_{calc} [eV]	0.28	0.29	0.38	0.39	0.44	0.45	**0.45**	**0.53**	**0.56**	**0.56**	**0.85**
T_{onset} [K]	**110**	**115**	**151**	**156**	**173**	**175**	**178**	**209**	**220**	**220**	**333**

Figure 6. Hard sphere model of an island indicating the processes relevant in island decay, energy barriers calculated with EMT potentials [26], and corresponding onset temperatures. For all processes perpendicular to the close-packed rows ($E_{*,y}$), the exchange process with a substrate atom is found energetically favorable over the hopping over the row. Some of the energies have previously been calculated by Hontinfinde *et al.* [17] based on the RGL potential. Besides process $E_{d,y}$, for which they give the energy for the hopping mechanism (1.05 eV), the energies differ only slightly (in the order of 5 %).

$$X \sim \tau^{\beta x}, \qquad Y \sim \tau^{\beta y} \tag{2}$$

At low temperature the island length *X* decreases continuously, while the island width *Y* stays approximately constant until the island has almost disappeared (Figure 5a). At high temperature both *X* and *Y* decrease continuously (Figure 5b). Moreover, the decay rate for *X* is found to be about three times higher than for *Y*, with R_{eq} being conserved throughout the decay. Double logarithmic plots (Figure 5c) reveal that the parameters *X,Y* indeed follow the power laws of X, Y in Equation 2 above T_c, while below T_c only *X* follow the power law scaling, while *Y* is apparently constant. We determine the exponents β_X and β_Y by fitting Equation 2 to the *X(t)* and *Y(t)* data (Figs. 5a,b). We find that β_X is approximately constant with 0.32 ± 0.04 over the whole temperature range; β_Y has a similar value above 230 K (0.27 ± 0.04) but drops to a much lower value below 210 K (see Figure 5d) [25].We have repeated these measurements for vacancy islands on Ag(110) and find a similar conclusion but with a transition temperature of (205 ± 10) K.

To summarize our experimental results: Below T_l = 175 K the island size stays constant. Between T_l and T_c = 220 K the islands are not equilibrium-shaped and decay in a preferred direction by adatom detachment from the [001]-oriented step. Above T_c the islands equilibrates and decay two-dimensionally. The decay parameters β ($\beta_X \approx 1/3 \approx \beta_Y$) indicate a diffusion-limited decay process qualitatively equivalent to the decay on isotropic metal surfaces [4].

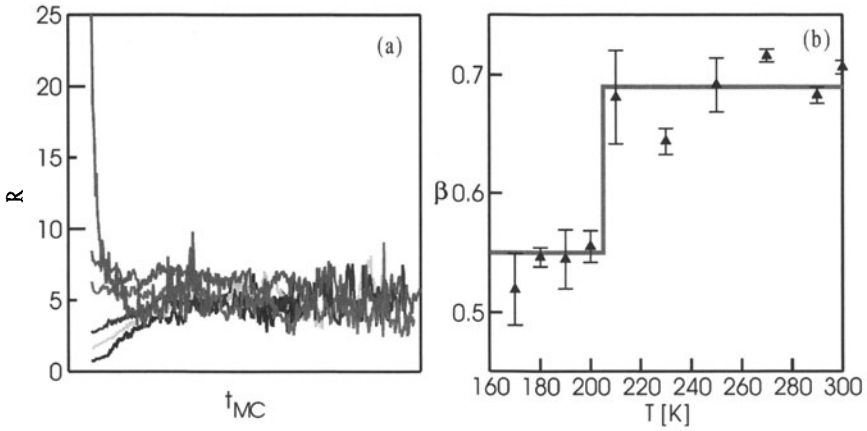


Figure 7. kMC calculation: average of 10 runs. (a) Aspect ratio *R* for islands of 145 atoms each with different initial aspect ratios during their decay at 500 K (b) Exponent $\beta = \beta_X + \beta_Y$.

DISCUSSION

To rationalize these results and to understand the atomic processes underlying the two different decay modes, we have performed molecular dynamic calculations of activation energies for a variety of elementary processes (Figure 6) relevant for the decay of silver islands on Ag(110), using approximate effective medium theory (EMT) potentials [26]. With the EMT theory the energy of an atom in a free structure is a simple function of the nearest neighbor (nn) and next-nearest neighbor (nnn) coordination numbers for in this case Ag atoms in the topmost surface layers.

To compare the calculated energies to the experimental results, we recall that calculations based on approximate potentials like EMT tend to underestimate the energy barriers. Agreement with experiments can be achieved by multiplying all energies with the same factor [26]. Under the assumption of equal prefactors for all processes, the calculated energies are therefore proportional to the lowest temperature at which the processes occur. We scale the calculated energies to the experimental onset temperature of $T_l = (175 \pm 5)$ K for island decay, i.e., the adatom detachment from the [001] step ($E_{k,x} = 0.44$ eV and $E_{d,x} = 0.45$ eV). With the resulting calibration factor $C = (378 \ldots 410)$ K/eV we calculate the onset temperatures $T_{onset} := C \cdot E_{calc}$ depicted in Figure 6.

First, we discuss the two-dimensional decay of equilibrium-shaped islands above T_c. An effective way for an island to evolve into its equilibrium shape is adatom diffusion along its perimeter. On anisotropic surfaces this implies that the atoms are able to diffuse along the [001] and the [-110] steps *and* to diffuse around the corners in *both* directions [27]. The migration of adatoms along the [001] steps, ($E_{e,y} = 0.53$ eV, 208 K), as well as the corner rounding from [001]

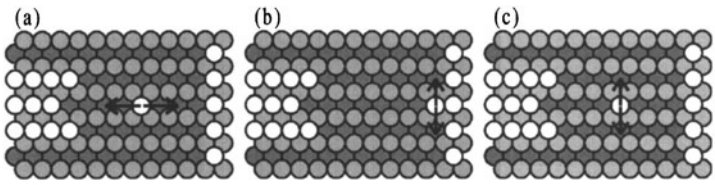


Figure 8. Hard sphere model illustrating possibilities for one-dimensional decay.

steps to [-110] steps ($E_{c,y}$ = 0.56 eV, 220 K) set in around T_c, whereas diffusion along the [-110] step ($E_{e,x}$ = 0.29 eV, 115 K) and corner diffusion from [-110] to [001] steps ($E_{c,x}$ = 0.38 eV, 151 K) set in well below T_c.

The observed two-dimensional island decay behavior should imply that atoms can detach from *both* step edges. The detachment from a close-packed straight [-110] step ($E_{d,y}$ = 0.85 eV) should however not occur until about 330 K, and thus this process is not considered relevant here. Instead, we propose that detachment preferentially occurs from kink sites next to vacancies on the [-110] step facet. The onset temperature for this process ($E_{k,y}$ = 0.56 eV, 220 K) is indeed close to T_c. Such a process is, however, only relevant if a sufficient number of kinks exists along the [-110] step of the islands. The following three observations make the existence of a sufficient number of kinks very plausible: (a) a low activation energy for the formation of vacancies in the outermost row ($E_{k,x}$ = 0.44 eV, 173 K) (b) a low activation energy for their subsequent diffusion along the [-110] direction, ($E_{l,x}$ = 0.45 eV, 175 K) and (c) the elliptic form of the islands. Based on the atomic arrangement on fcc(110) surfaces we propose the coincidence of the same onset temperature for edge diffusion (allowing shape equilibration) and detachment out of kink sites (allowing two-dimensional decay) to be a general phenomena. Generally, the difference in energy between $E_{k,y}$ and $E_{c,y}$ should be negligible as the atomic arrangements of both initial and final positions do not differ in the number of their nearest neighbors. Kinetic Monte Carlo kMC) simulations based on the calculated EMT energies [26] of islands of identical size but with different aspect ratios, confirm that the islands evolve into their equilibrium shape above T_c (Figure 7a).

We will now discuss the situation below T_c, where the island width remains approximately constant. The detachment from a [-110] step even at a kink site ($E_{k,y}$ = 0.56 eV, 220 K) is energetically impossible and atoms can only detach from the [001] step.

Figure 8a shows the situation considered in textbooks [16] for a fcc(110) surface. The adatom migration is strictly one-dimensional, i.e. constrained to the close-packed [-110] rows. Within this row the adatoms sense the same chemical potential on both ends, the driving force for ripening is missing, and Ostwald ripening theories predict no decay at all [16]. This is, however, inconsistent with the observed one-dimensional island decay. Between islands there is no potential gradient if all islands have the same dimension in the *Y*-direction, so that the total length of both [001] steps and [-110] steps never change when atoms are transferred from one island to another. A chemical gradient, on the other hand, exists between islands of different *Y*-dimension.

We exemplify this in the extreme case of an island end being perpendicular to an infinitely long step. When an island looses a complete row of atoms its perimeter and thereby the total step energy are decreased, whereas atoms attaching at an infinitely straight step do not change the step length. Such an adatom flux becomes possible if the adatoms can diffuse perpendicular to