Kinetic Mechanism for Island Shape Variations Caused by Changes in the Growth Temperature

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By using energy calculations and kinetic Monte Carlo simulations we find a kinetic mechanism that appears to control the shape of the islands formed by the aggregation of Pt atoms adsorbed on Pt(111).

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Atoms adsorbed on a single crystal surface aggregate and form islands. Often these have a well defined shape, which depends on the particular system and the deposition conditions. Si atoms on the Si(100) surface assemble—with practically no error—into thin, long dimer rows [1] oriented parallel to each other. Deposition of 0.1 to 0.3 monolayer (ML) of Pt on Pt(111) leads [2,3] to triangular islands, if the surface temperature is 425 K; nearly regular hexagons are formed if the deposition takes place at 450–470 K; triangles with a different orientation appear for deposition at 550 K and hexagons with threefold symmetry at 700 K. At room temperature Fe atoms on Au(111) (0.2–0.5 ML) [4] and Co atoms on Ru(0001) (0.2 ML) [5] form triangles. Even vacancies seem to have preferences: On Pt(111), the holes produced by the missing atoms aggregate to form hexagonal patterns [6].

During deposition and growth each atom moves randomly and independently along the surface. It is difficult to understand how this chaotic motion is capable of forming, with an overwhelming probability, islands having precise shapes [7]. The fact that a very small change in the growth temperature can cause a change in the shape and the symmetry (e.g., from triangles to hexagons) of the aggregates is even more enigmatic.

In this Letter we report a kinetic mechanism that leads to triangles and shape switching on surfaces having triangular symmetry. Our simulations suggest that this shape change, observed only on Pt/Pt(111) so far, is likely to be a general process.

We have a tendency to think of triangles and hexagons as qualitatively different objects. Because of this a transition from triangles to hexagons seems discontinuous. No discontinuity is involved if we assume that the shapes observed experimentally are hexagons of the kind shown in Fig. 1. They have two types of edges, A and B, having a length l_A or l_B, respectively. If l_A/l_B is large, the shape is the "triangular hexagon" shown in Fig. 1(a); $l_A/l_B=1$ gives a regular hexagon; $l_A/l_B<1$ leads to an inverted "triangular hexagon" like the one shown in Fig. 1(c). Within this scheme the triangles observed experimentally are hexagons having either very large or very small values of l_A/l_B.

One can express this geometric idea in kinetic terms. The experiments and our calculations show that edges tend to stay straight during growth and remain parallel to their earlier orientation as they advance into the terrace. Because of this we can define edge advancement velocities, v_A and v_B, for each type [8]. The experimental observations on the Pt/Pt(111) system [3] can then be described as follows: At low surface temperature $v_B \gg v_A$ and a small hexagonal island will evolve into the triangular hexagon shown in Fig. 1(a); at higher temperatures $v_A \gg v_B$ and a small regular hexagon will evolve into a triangular hexagon like the one shown in Fig. 1(c). Shape switching is achieved continuously if v_B/v_A changes continuously with the growth temperature, from values larger than 1 to values less than 1.

There are thus two requirements for achieving the kind of growth seen in the experiments: a tendency of the arriving atom to spread along the edge and keep it flat (the atoms "wet" the edge) and a v_B/v_A ratio which goes from values greater than 1 to values smaller than 1 as the temperature increases. It is amusing to note that the edge having a higher propagation velocity will become shorter; excessive rates of growth will make an edge grow itself out of existence.

To turn this idea into a kinetic mechanism we must answer a number of questions. Why are the sides of a hexagon different? What are the kinetic consequences of this difference? How do they control the rates v_A and v_B of edge propagation?

The positions of the atoms forming a hexagonal island on top of a surface with triangular symmetry [e.g., a Pt island on Pt(111)] are shown in Fig. 2. It is easy to see that the surface atoms (empty circles in Fig. 2) neighboring edge A have different positions than those neighboring edge B. This means that the properties (e.g., binding energy, barrier to diffusion, etc.) of an atom bound to

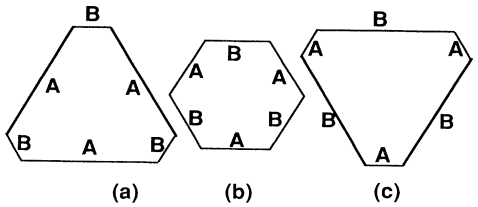

FIG. 1. A schematic representation of the island shapes mentioned in the text.

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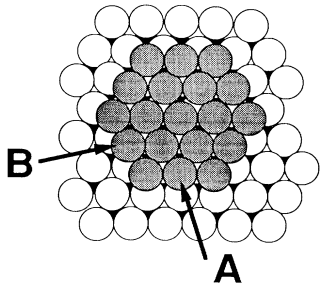

FIG. 2. The location of the atoms in the island (gray circles), the first surface layer (empty circles), and the second layer (black patches between three empty circles).

edge A differ from those on B.

To simplify the presentation we confine all our remarks to the temperature range from 400 to 600 K and introduce the following nomenclature. We call a hexagonal island with straight edges a "closed shell" island. All others are "open shell" islands. Furthermore, since the atoms present on the same edge tend to bind to each other, they will form linear clusters along the edges; we call these clusters rows. We argue below that an island grows essentially row by row and its shape is controlled by the tendency of these rows to grow more frequently on one type of edge.

We begin this argument by examining the elementary processes that are essential to the growth mechanism. Then we show how these processes work together to control the shape. Our results are based on kinetic Monte Carlo (KMC) simulations using energy barriers close to those calculated with Norskov's effective medium theory [9] (EMT).

The barrier opposing the migration of a single atom on the Pt(111) surface is very low (~0.13 eV) [10]. The first atoms deposited on the surface have no difficulty meeting each other to form low mobility dimers, trimers, etc., having strong bonds [10]. The atoms deposited a little later will manage (due to their high mobility and the low deposition rate) to find the small clusters formed previously on the surface and stick to them, rather than form new clusters. Thus, clusters formed in the earliest stage of deposition serve as centers for further island growth. Continuing the deposition will lead to the formation of a small number of large islands.

We are not interested here in the details of small island growth in the early stages of the deposition, which will be examined in Ref. [10]. We assume that each island is, at some time during its growth, a hexagonal, closed shell island, and follows its fate as the deposition continues and new atoms arrive on its edges.

The energy barriers preventing the diffusion of an atom along an edge is 0.44 eV for edge A, and 0.40 eV for edge B. These values are given by $E^{\alpha}-E_{\alpha}$ with $\alpha=a$ or b and the EMT values given in Table I. The barrier preventing the transfer of an atom from one edge to another is ~0.5 eV. This is obtained from $E^{c}-E_{\alpha}$ and the EMT values given in Table I. These numbers tell us that, for the temperature range and the deposition rate of interest here, an atom landing on the edge of an island can run around it several times before another atom arrives.

TABLE I. E_{α} is the minimum energy for an atom sticking to the edge α. E^{α} is the maximum energy for an atom adsorbed on edge α and moving along the edge. $E^{\alpha}-E_{\alpha}$ is the energy barrier to diffusion along the edge α. E^{c} is the maximum energy encountered by an atom going from one edge to another. $E^{c}-E_{\alpha}$ is the barrier preventing an atom from going from edge A to edge B. $E^{c}-E_{b}$ prevents jumps from B to A. E_{d}^{a} is the energy barrier preventing an atom from leaving a row of atoms (dimer, trimer, etc.) on the edge α. The symbol α can be a or b, indicating edge A or edge B, respectively.

Parameter sets	Simulation (eV)	Pt/Pt(111) (EMT) (eV)
E_{a}	−0.02	−0.003
E^{a}	0.44	0.44
E_{b} (reference energy)	0	0
E^{b}	0.40	0.40
E^{c}	0.54	0.54
E_{d}^{a}	0.73	0.73
E_{d}^{b}	0.70	0.70

The atoms stuck to a closed shell island tend to bind to each other and form rows along the edges. The atoms at the end of a row can "dissociate"; the barriers preventing this breakup are $E_{d}^{a}=0.73$ eV and $E_{d}^{b}=0.70$ eV. This process, even though less frequent than others, turns out to be essential for the formation of sharp triangles.

The energy barrier preventing an atom from moving from the edge onto the terrace is ~0.82 eV. We simplify our KMC simulation by ignoring this process.

Atoms landing on top of an incomplete row have little difficulty in descending and adding themselves to the end of the row. This is why the atoms "wet" the edge, and the edges observed experimentally tend to be straight.

The deposition rate is 0.01 ML per second [2,3]. By dividing the number of atoms falling on a given area per second by the number of islands on that area, we determine the mean number of atoms reaching an island per second. When the islands are large some of the incident atoms will fall on top of them. The mobility of these atoms is high and the barrier preventing them from descending on the surface on which the island is growing is small [10], so that we can assume that all atoms falling on top of an island will descend from it and join its border.

The energy barriers calculated here show that, compared to all other kinetic events of interest, the arrival of a new atom at the edge of an island is a rare event. For example, a single atom makes more than one million site-to-site hops along the island's edge before a new atom joins the island. This is not always the case: At low

temperatures (e.g., 200 K) the mobility along the surface is practically suppressed and the islands grown at these temperatures are very rough.

Now we can describe how the elementary kinetic steps specified above work together. Since the arrival of new atoms is infrequent, as compared to the other kinetic processes, the first two atoms landing on the island have plenty of time to run around, meet each other, and pair up. If the bond between them was strong enough to prevent their dissociation before the third atom arrives to join them, etc., than a whole row will be completed on the edge where the first two atoms met to form a pair. We have performed simulations assuming infinite binding energies between the atoms of a row and found that they lead to shape switching, if the binding energy and the diffusion barriers on A and B are slightly different. Triangular hexagons are formed at high and low temperatures and nearly regular hexagons at the intermediate one (l_A/l_B varied from 1.23, to 1 and to 0.85). However, we could find no reasonable parameter values that lead to sharp triangular hexagons. To obtain sharp triangles we had to allow the atoms at the end of a row to dissociate.

Once the breakup of the atoms at the end of a row is allowed, the life of the atoms joining a closed shell island becomes more interesting. It is useful to realize that if we mark one atom and follow its travels, the other atoms act as traps; the marked one is slowed down by temporary bonds to other atoms. The first two atoms meeting on an edge dissociate and recombine many times before a third atom joins the island. Thus, the trimer formed when a third atom joins them is not on the edge where the dimer was first formed. When the fourth atom arrives the quadrimer is not necessarily formed where the trimer appeared first. At the lower temperature ($\sim$400 K) there is some correlation between the edges where the first dimer, and trimer and quadrimer, etc., are formed; this is diminished when the temperature is raised. As the number of atoms is increased the behavior of the populations on different edges becomes more predictable. If the number of atoms on a given edge goes up, it takes longer for all of them to clear the edge. First, an atom that leaves the populated edge is likely to rejoin it. This can be prevented only if a newly deposited atom or another atom that breaks away from the populated edge meets and traps the lone walker. Both events are, however, less probable than the return of the lone walker to the populated edge. Second, the walk along an edge is one dimensional and only the two atoms at the end of a row have a chance to leave the edge; the others must queue behind them. Thus, after a sufficiently large number of atoms have congregated on an edge, the subsequent arrivals tend to join them and accumulate there until the whole row is completed. A closed shell island is formed and the whole process can start over. If this would always happen we would have a row by row growth.

However, this is a statistical process which depends on temperature. We observe that at the lower temperatures often a whole row is completed on the edge where a trimer or a quadrimer was first formed. But we also observe with some frequency, especially at higher temperatures, that two edges become populated and they compete with each other for population. Often the row with a high population manages to acquire all the atoms. This happens for a simple reason. Imagine that we make the two edges identical by giving the atoms the same binding energies and barriers to diffusion. Then the two edges have roughly the same probability of gaining or losing an atom. If there were no fluctuations the populations of the edges will stay constant. However, the fluctuations are fairly large especially when the number of atoms involved in the game is small. As the edges trade atoms during the random kinetic process, it is easier to have a deviation from the mean kinetic process that depletes completely the edge having fewer atoms. Once that edge is depleted the rules of the game are completely changed: There is only one populated edge and, as explained above, a runaway atom is very likely to return to the edge of origin. This is why the edges with a large population tend to acquire the atoms of a sparsely populated edge. Nevertheless, this relies on fluctuations, which are fickle and can work both ways. In our simulations we see occasionally that an edge with a smaller population wins and gains all the atoms from a more populous edge. Such events become more frequent as the temperature is raised closer to 600 K.

We give now the results of KMC [11] simulations using the parameters shown in Table I. The differences of the relevant energies on the two edges (i.e., A and B) are very small and we do not assume that the EMT method gives such differences accurately. Therefore we varied the energies slightly around the values given by EMT. Because the calculations are time consuming and the number of parameters is large we did not attempt to optimize the simulation and get the best fit to the experiment. To describe the shape of the islands we give the ratio L_a/L_B where L_a is the total length of all the edges A and L_b has a similar meaning. We obtained $L_a/L_b=34$ (for $T=500$ K), $L_a/L_b=0.93$ (for $T=550$ K), and $L_a/L_b=0.05$ (for 600 K). The temperatures are not exactly those of the experiment; however, a slight rescaling of the energies in the model will bring the two in agreement. We do not expect energy accuracy of 100 K and do not intend to determine the precise transition temperature.

The triangles generated by the simulations at low and high temperatures are similar to the ones seen experimentally [Figs. 3(a) and 3(b)]. The intermediate temperature case is, however, very strange. Even though the ratio L_a/L_b is very close to 1 in all simulations, the shapes are far from being regular hexagonal. The three faces of the same kind have widely different lengths. Since all A faces have identical mean properties the difference in

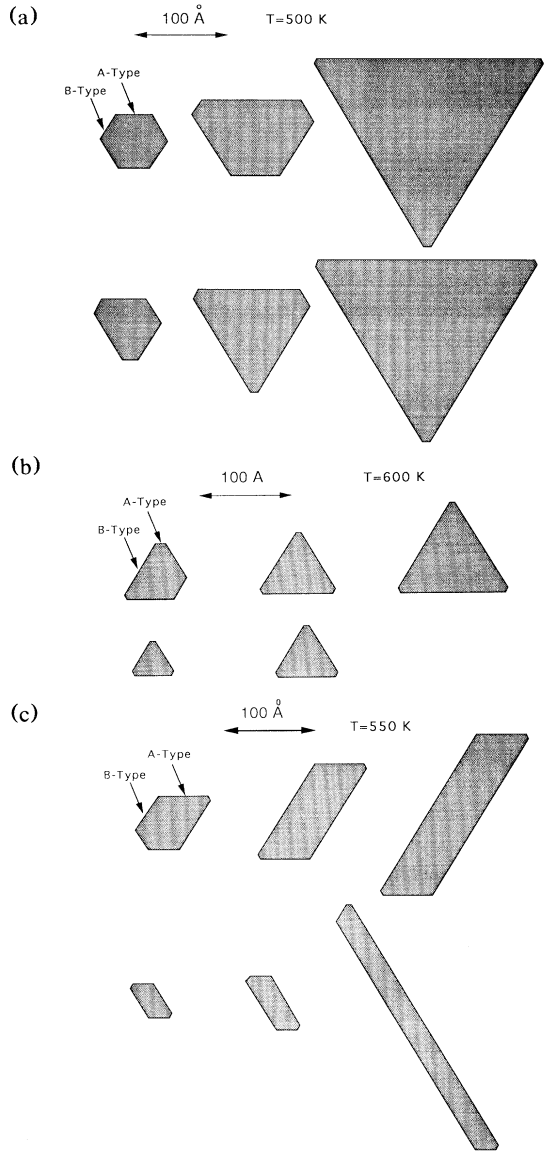

FIG. 3. The islands generated by the kinetic Monte Carlo simulations using the energies specified in Table I. In each figure we show two independent MC runs using identical starting conditions and parameters. (a) Low temperature islands, (b) high temperature shapes, and (c) shapes obtained at intermediate temperature. The number of atoms deposited goes down with temperature.

their length must be attributed to fluctuations taking place during the growth process. This notion is supported by the fact that, at the intermediate temperature, different runs lead to different shapes [see Fig. 3(b)]. Experimenting with the simulations indicates that the kinetics used in the model tends to make small edges grow much faster. Thus unavoidable fluctuations in the size of the same kinds of edges, which are rather likely when the islands are small, are amplified by this propensity; an edge which is slightly shorter by accident will be made even shorter by the kinetics. This helps generate sharp triangles when we need them, but it also makes the regular hexagon shape very unstable during the growth. We plan to study this instability in future work. The shapes predicted here at the intermediate temperatures have not been observed experimentally.

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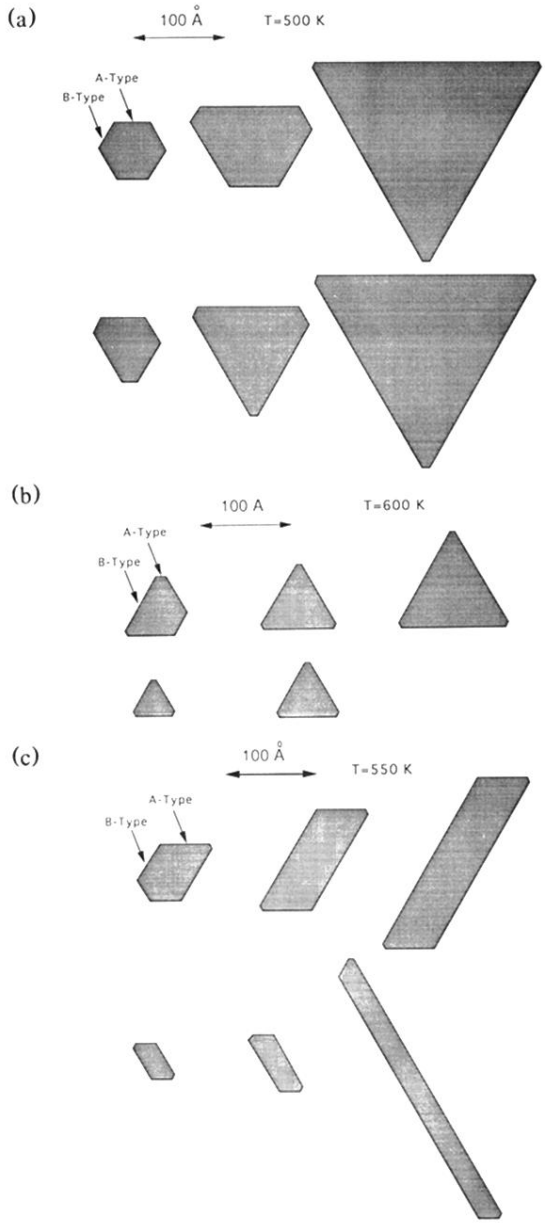

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