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Quantum Size Effect on Adatom Surface Diffusion

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Using scanning tunneling microscopy, we demonstrate that the nucleation density of Fe islands on the surface of nanoscale Pb films oscillates with the film thickness, providing a direct manifestation of the quantum size effect on surface diffusion. The Fe adatom diffusion barriers were derived to be 204 ± 5 and 187 ± 5 meV on a 21 and 26 monolayer (ML) Pb film, respectively, by matching the kinetic Monte Carlo simulations to the experimental island densities. The effect is further illustrated by the growth of Fe islands on wedged Pb films, where the Fe island density is consistently higher on the odd-layer films than on the even-layer films in the thickness range of 11 to 15 ML.

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One prominent feature of nanoscale metallic structures is the quantum size effect (QSE), which has been recognized since the mid 1960s [1,2]. QSE may manifest itself in various properties of a small metallic structure, such as stability [3], optics [4], magnetism [5], transport [6], and superconductivity [7]. Recently, QSE on epitaxial growth properties of nanometer-thick metallic thin films, in particular, ultrathin Pb films grown on Si(111) substrate, has attracted considerable interest [7–13]. The incidental "perfect" matching between the Pb Fermi wavelength and its interlayer spacing in the [111] direction, i.e., the growth direction, has led to a striking odd-even oscillation in the film electronic structure and hence its stability. These pioneering studies have greatly enriched our fundamental understanding of epitaxial growth of metallic thin films. The study of QSE in metallic thin films will certainly also impact the fabrication of metallic nanostructures and nanodevices.

The epitaxial growth process is generally controlled by the competition between thermodynamic and kinetic factors. Naturally, one may expect that the QSE will affect not only growth thermodynamics but also kinetics. However, existing studies of the QSE on the growth of nanoscale metal thin films have focused mostly on thermodynamics [7–13], e.g., the film energetics and stability. Little attention has been paid to the possible QSE on growth kinetics. Here, we demonstrate an example of QSE on growth kinetics, i.e., surface diffusion through the measurement of island nucleation density at the early stage of growth.

Surface diffusion is the most fundamental kinetic rate constant in controlling the epitaxial growth process, and hence a subject of extensive studies [14]. On the surface of a very thick metal film, surface diffusion coefficient is generally a constant, characteristic of the given metal surface. It is well known that QSE has a profound impact on the stability of ultrathin metal films [7–13]. In a simple free-electron-like picture, the finite dimension in the growth direction (normal to substrate surface) confines the electrons and introduces a set of discrete quantum-well electronic states, which modulates the electron energy levels and electron filling as a function of film thickness. Consequently, many physical properties of the film, such as work function, surface energy, and film stability, display an oscillatory behavior with increasing film thickness, manifesting the QSE. Intuitively, however, it is more difficult to rationalize how QSE would change surface diffusion.

One way to derive the surface diffusion coefficient is by measuring island nucleation density at the early stage of growth in the submonolayer regime [15–17], using, e.g., scanning tunneling microscopy (STM) [16]. We have applied this method to explore the QSE on surface diffusion, using nucleation or growth of Fe islands on Pb thin films of different thickness. We deduce that the surface diffusion barrier on a 21 and 26 monolayer (ML) Pb film is respectively 204 ± 5 and 187 ± 5 meV, by performing kinetic Monte Carlo (kMC) simulations to match the measured island densities. As a further illustration, we carried out growth experiments on wedged Pb films of different layer thickness, where the density of Fe islands exhibits an oscillatory behavior, being consistently higher on the odd-layer film than on the even-layer film in the thickness regime from 11 to 15 ML.

Our experiments were carried out in a commercial Omicron UHV-MBE-STM system with the pressure maintained at 2×10^{-10} mbar. The Si substrate (n-type with a resistivity of 2–3 Ω cm) was prepared by well-established flashing procedures [18]. The atomically flat Pb films were first grown by evaporating Pb from a Knudsen cell onto the Si(111)-(7×7) surface at low temperature (LT) ~150 K via a two-step growth method [13,19]. Subsequently, Fe islands were grown on top of the Pb films at both LT and room temperature (RT) by evaporating Fe from a tantalum boat using direct current heating. The deposition rate was

~0.08 ML/ min. *In situ* STM measurements were conducted at RT.

Because of the low solubility and large surface energy difference between Fe and Pb, the Fe islands nucleate and grow into a conglobated shape at both LT and RT. At a very low coverage, the islands grow in a 2D shape having a ML height of ~0.32 nm. With increasing coverage, the islands grow into a fractal shape with increasing ramification and into a 3D shape with their height gradually saturating at 2 ML of ~0.67 nm.

Figures 1(a) and 1(b) show STM images of Fe islands grown on atomically flat 21 and 26 ML Pb films, respectively, up to the same nominal coverage of 0.24 ML. In both images, there are smaller islands decorating the step edges and concentrating at some local corrugated surface regions, indicating nucleation is more favorable at those locations. But overall, it is evident that the island density (number of islands per surface area) is higher on the 21 ML Pb film [Fig. 1(a)] than on the 26 ML Pb film [Fig. 1(b)], while the average island size is smaller on the 21 ML film than on the 26 ML film.

To obtain a statistical average of island density, we have selectively counted the islands in the open flat (step- and strain-free) surface areas from 20–25 STM images as Figs. 1(a) and 1(b), in a total number of 350—450 islands. Figure 1(c) shows the counting results. The average island density on the 21 ML film (~1.53×10^{11} cm^{-2}) is nearly 2 times of that on the 26 ML film (~0.73×10^{11} cm^{-2}). We have also checked the average island size on the two films; the island size on the 21 ML film (~54 nm^2) is about one-half of that (~93 nm^2) on the 26 ML film. Given the same island height (0.67 nm), this is consistent with the same nominal Fe coverage of 0.24 ML on the two films.

According to the classical mean-field nucleation theory [15–17], the island density (N) depends on deposition rate (F) and surface diffusion coefficient (D). For isotropic surface diffusion and the critical nucleus size of one, they follow the scaling relation of $N \propto (F/D)^{1/3}$ [15–17]. Thus, the different island density on the 21 and 26 ML film is believed to be originated from the different surface diffusion coefficient on the two films, because other growth parameters, especially the deposition rate, were kept same. Using the measured island densities, the Fe adatom diffusion barrier is estimated to differ by up to 28 meV on these two film surfaces. The most possible cause for the thickness-dependent surface diffusion coefficient is the QSE. So, these experiments provide not only a direct manifestation of QSE on surface diffusion but also a quantitative measure of diffusion-barrier difference induced by QSE.

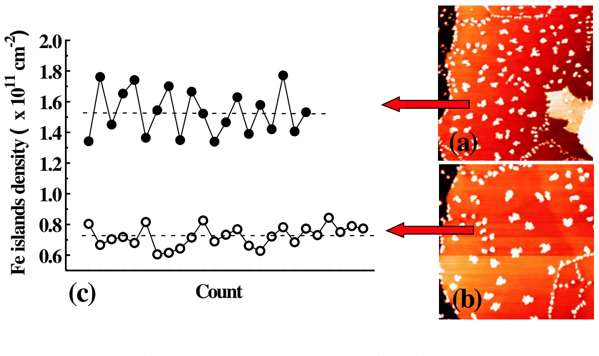

FIG. 1 (color online). STM images of Fe islands grown at LT on (a) a 21 ML and (b) a 26 ML Pb film, respectively, up to the same coverage of 0.24 ML. Both images are 200×200 nm^2 taken with a tip bias of -2.67 V and tunneling current of 20 pA. (c) Counted Fe island density on a 21 ML (solid circles) and a 26 ML (open circles) Pb film.

Although the mean-field analysis (MFA) has sufficiently demonstrated the essential physical nature of QSE on diffusion, it can give only an estimate of diffusion-barrier differences and not absolute barriers. There are also other limitations associated with the MFA. The island density scales strictly with adatom density, so that individual collision events between two adatoms are neglected. The analysis is based on 2D islands and neglects island coalescence, while experimental islands are 3D and may coalesce if two islands happened to be close. Therefore, to further augment our theoretical analysis, we have performed kMC simulations that remove some limitations of the MFA, to derive the absolute diffusion barriers by matching the simulated densities to the experiments [16,17].

Normally, one simulates island density as a function of temperature (i.e., an Arrhenius plot) on a single surface with constant diffusion barrier. Here, instead, we simulate the island density as a function of diffusion barrier at the given deposition rate and temperature, since the experiments were performed on different surfaces with different diffusion barriers. We used a solid-on-solid model and a simulation cell of 164×142 hexagonal grid (100×100 nm^2). The choice of using a hexagonal cell was made based on recent first-principles calculations [20] which showed that the adatom surface diffusion on Pb(111) takes effectively a hexagonal pathway with the hcp and fcc hollow sites being, respectively, the minimum energy and the saddle point. The critical size for island nucleation was assumed to be one. In accordance with the experiments, we used the hit-and-stick model neglecting island edge diffusion so that the islands take a fractal shape. We simulated 3D islands of 2 ML height by letting an atom have a 50% chance of sticking to the island edge and a 50% chance of jumping up to the second layer. 2D islands of 1 ML height were also simulated for comparison.

The simulations were carried out at the growth temperature of 150 K, using a deposition rate of 0.08 ML/ min up to a total coverage of 0.24 ML. We used the n-fold way algorithm [21], with a variable time step $\Delta t = -(\ln\eta)/\Gamma$, where η is a random number between 0 and 1, and Γ is the sum of the rates of all atomic events at the given time. The attempt frequency for adatom diffusion was set at $kT/h = 3.128 \times 10^{12}$ s^{-1}. For each given diffusion barrier, simulations were repeated 8 times to obtain the statistical average island density and error bars.

Figure 2 shows the simulated island density as a function of diffusion barrier in a semilog plot. The solid line is the linear fit to the simulation data (solid dots) of 3D islands. The dashed line is the linear fit to the simulated data (not shown) of 2D islands, for comparison. By matching the simulated island densities to the two experimentally measured values on the solid line (i.e., the linear fit of 3D islands data), we obtain the Fe surface diffusion barriers on the 21 and 26 ML Pb film to be respectively 204 ± 5 and 187 ± 5 meV, with a difference of ~17 meV. Note that this difference is much smaller than the mean-field estimate (~28 meV), indicating that the simple mean-field scaling of experimental densities would overestimate the barrier difference.

Comparing the solid line (3D island results) with the dashed line (2D island results) in Fig. 2, one sees that the dashed line has a slightly smaller slope. This is caused by the coalescence of laterally larger 2D islands at higher densities as shown by the simulations. But the overall difference between the 3D and 2D island simulations is small, indicating that the nucleation density is largely determined by the adatom-adatom collision rate, with the critical size of one, and less dependent on the shape that the island grows into. We note that in our analysis and simulation, we assumed critical nucleation size of one atom independent of film thickness. One can imagine that if QSE can strongly change the binding between adatoms and hence the critical size, then it may also induce oscillation in island density. This could be a very interesting subject for future studies.

To further illustrate the QSE on surface diffusion, we carried out another set of experiments depositing Fe islands on wedged Pb films on a vicinal Si(111) substrate consisting of a staircase of steps. The wedge Pb film has a flap top, so its thickness changes by one atomic-layer height when passing over a substrate step. Consequently, Fe islands will simultaneously nucleate on one flat surface of Pb film but of different underlying film thickness. This allows a direct comparison of island densities in different surface regions, as illustrated in Fig. 3. It shows a typical STM image of ~0.08 ML nominal Fe deposition at RT on a wedged Pb island of varying thickness from 10 to 16 ML.

Evidently, the Fe island density displays an interesting odd-even oscillation, with higher densities on the surface regions of the odd-layer film (11, 13, and 15 ML) than those of the even-layer film (10, 12, 14, and 16 ML). Island counting on a number of such samples shows that the average island density on the odd-layer film surface ($\sim 2.95 \times 10^{10}$ cm^{-2}) is ~55% higher than that on the even-layer film surface ($\sim 2.03 \times 10^{10}$ cm^{-2}), excluding the two outmost layers, i.e., 10 and 16 ML in Fig. 3, on which the island density is much lower because deposited adatoms have diffused out of island edges.

However, we found it is difficult to derive the diffusion barriers by matching the kMC simulations to these experimental data due to the following complications. First, about 75% adatoms have diffused out of the wedged film. The final coverage is, respectively, 0.024 and 0.016 ML on the odd- and even-layer films, which are much smaller than the nominal deposition (~0.08 ML). Second, first-principles calculations [20] showed that in addition to diffusion barriers, the QSE modulates the adatom binding energies. This causes an apparent difference in the adatom chemical potentials in different surface regions, leading to nonuniform surface coverage. Third, the QSE may also change the step edge barriers in different surface regions of different film thickness. All these factors will affect the island nucleation densities, making the quantitative derivation too ambiguous.

Nevertheless, the experiments suggest qualitatively the surface diffusion barriers on the odd-layer films are higher than those on the even-layer films in the given film thick-

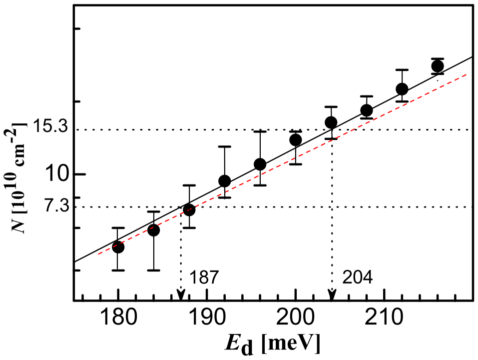

FIG. 2 (color online). Island nucleation density (N) as a function of surface diffusion barrier (E_d), obtained from kMC simulations. The solid line is the linear fit to the 3D island data (solid dots). The two dotted horizontal lines mark the experimental densities, from which the surface diffusion barriers were derived as indicated on the x axis. For comparison, the dashed line is the fit to the 2D island data, which were not shown for better clarity.

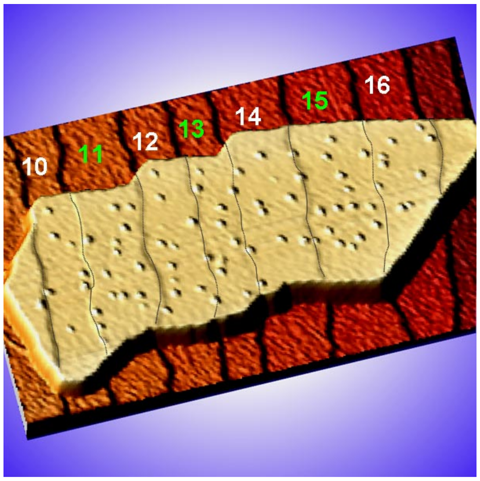

FIG. 3 (color online). A 1200×800 nm^2 STM image (acquired at a tip bias of -5.0 V and tunneling current of 20 pA) displays a density oscillation of Fe islands nucleated on a wedged Pb film at RT. The island density on the odd-layer films is consistently higher than that on the even-layer films on the given film thickness regime from 10 to 16 ML.

ness regime from 11 to 15 ML. This is consistent with recent first-principles calculations which show the adatom diffusion barriers are higher on the more stable film surfaces than those on the less stable surfaces [20]. For example, the Pb adatom diffusion barriers are calculated to be higher on the even-layer Pb (111) films in the thickness regime below 9 ML [20] when the even-layer films are more stable [10]. In contrast, due to the quantum beating effect, the odd-layer Pb(111) films become more stable than the even-layer films in the thickness regime from 11 to 15 ML [10]. Consequently, the adatom diffusion barriers are expected to be higher on the odd-layer films in this thickness regime, consistent with our experiments. Future first-principles calculations of Fe adatom diffusion on Pb (111) films will be useful to be compared with our experiments.

We may estimate from the mean-field theory that the average surface diffusion barriers on the odd-layer films (i.e., the 11, 13, and 15 ML) is ~34 meV higher than those on the even-layer films (i.e., the 12 and 14 ML), by attributing the observed island density oscillation solely to being caused by difference in diffusion barrier. This could be compared with the mean-field estimate of the barrier difference of 28 meV between the 21 and the 26 ML film discussed above. The QSE induced barrier difference is larger on the thinner films (from 11 to 15 ML) than that on the thicker films (21 vs 26 ML), consistent with our physical intuition. However, we must caution about the overall overestimation of barrier difference by the mean-field approach and the oversimplification in the analysis of wedged thin films.

Several other recent experiments have also indicated indirectly the QSE on surface diffusion [9,20,22]. For example, it has been observed that the Pb island nucleation on top of a Pb mesa starts from the edge on a 5-layer mesa but from the middle on a 6-layer mesa [9,20], which was attributed to different surface diffusion barrier [20]. However, a more detailed analysis [23] showed that the preferred location of island nucleation on a mesa top is mostly determined by the mesa edge barriers, while the surface diffusion barrier influences only the overall nucleation rate on the mesa top. Furthermore, those experimental phenomena do not allow the quantitative determination of diffusion barriers. In contrast, our experiments here isolate the surface diffusion barrier as the most direct kinetic parameter to be quantitatively determined.

The underlying physical mechanisms giving rise to the QSE on surface diffusion barrier might be rather complex. The experiment [13] has revealed that the highest occupied quantum-well states near Fermi level show an oscillatory behavior in Pb films, which will likely affect the adatom surface binding energies and diffusion barriers. In general, the adatom has lower binding energy and higher diffusion barrier on a more stable film than those on a less stable film.

In conclusion, we have carried out STM experiments of epitaxial growth of Fe on nanoscale Pb films of varying thickness in the submonolayer regime. We show that the Fe island nucleation density is 2 times higher on a 21 ML film than on a 26 ML film, and exhibits an odd-even oscillation on a wedged film of 10 to 15 ML thick having the higher density on the odd films. These observations provide a direct manifestation of QSE on surface diffusion and a quantitative measure of the QSE induced diffusion-barrier difference. Combining the kMC simulations with the experiments, we derive the Fe adatom diffusion barrier to be 204 and 187 meV on the 21 and 26 ML film, respectively. This difference is likely to be even larger on thinner films. We attribute such difference to be originated from the QSE induced oscillation in surface charge density near the Fermi level that modulates the adatom surface binding energies.

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