Adatom Self-Organization Induced by Quantum Confinement of Surface Electrons

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We present a novel mechanism of nanostructure growth based on quantum confinement of surface-state electrons. *Ab initio* calculations and the kinetic Monte Carlo simulations reveal the phenomenon of confinement-induced adatom self-organization in quantum corrals. Our studies indicate that new atomic-scale nanostructures can be engineered exploiting the quantum confinement of surface electrons.

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In the past few years, much effort has been devoted to studying the effect of confinement of conduction electrons on thin film growth. It has been found that in several systems such as Ag/GaAs(110), Ag/Si(111), Pb/Si(111), Pb/Cu(111), Pb/Ge(111), and Ag/Fe(100), quantum confinement of electrons has the decisive influence on the film stability [1–8]. For example, the confined motion of electrons can lead to the existence of critical thickness for smooth film growth [7]. "Magic" heights of nanoislands are also related to the confinement of electrons within islands [5]. The underlying mechanism driving the self-organization of these systems has been revealed by Zhang *et al.* [9]. They have introduced a novel "electronic growth" model for metallic films which emphasizes the importance of quantum electronic confinement, charge spilling, and interface-induced Friedel oscillations in the growth modes. Such quantum growth could be of great importance in engineering of nanostructures at surfaces. Very recent studies have shown that the quantum confinement has a profound effect on the diffusion of Pb adatoms on Pb/Si(111) and the island coarsening in this system [10,11]. Spectroscopic studies have directly demonstrated the confinement of electronic states within atomic chains [12]. The length distribution of gold chains on Si(553) found in the experiments of Crain *et al.* reveals oscillations that presumably indicate quantum growth of chains [13]. Electron confinement to Ag islands on Ag(111) has been shown to affect an adatom island decay [14]. The essential role of electron confinement in ultrathin films on the chemical activity of surfaces has been demonstrated [15].

Noble metal surfaces featuring a surface state are especially appealing substrates to study quantum confinement. It is known that surface-state electrons on (111) noble metal surfaces form a two-dimensional (2D) nearly free electron gas [16]. Particularly fascinating phenomena occur if the surface electrons are confined to closed structures (corrals). The direct observation of standing-wave patterns in the Fe corral on Cu(111) is one of the most spectacular examples demonstrating quantum effects at the atomic scale [17]. The quantum confinement of surface electrons inside corrals can lead to a mirage effect [18–20], i.e., the projection of the electronic structure of adatoms to a remote location. Quantum corrals can be used to tailor the spin polarization of surface electrons and magnetic interactions between adatoms [20,21].

In this Letter, we show that quantum confinement of surface-state electrons, for example, in quantum corrals on metal surfaces, can significantly affect an adatom motion. Our *ab initio* calculations and kinetic Monte Carlo simulations reveal an adatom self-organization inside corrals at low temperatures induced by quantum confinement and long-range surface-state mediated interactions. We concentrate on Co adatoms on Cu(111) and Ce adatoms on Ag(111) confined to quantum corrals, and demonstrate a novel mechanism of quantum growth on metal surfaces.

Our *ab initio* calculations are performed using density-functional theory with exchange-correlation functional determined in the local density approximation. Multiple-scattering of surface-state electrons in corrals is treated by means of the Korringa-Kohn-Rostoker Green function method [20–22]. The consideration of quantum resonators, such as corrals, adatom islands, or vacancy holes, destroys the translational symmetry; therefore, the Green function of such systems is calculated in the real space formulation. The structural Green function of the ideal surface is used as the reference Green function for the calculation of the resonators on surfaces. Details of the method and its first applications for calculations of properties of surface-state electrons in quantum corrals, on adatoms islands, and vacancy islands can be found in our recent works [20,21,23].

In Fig. 1 we show a spatial distribution of the local density of states (LDOS) at the Fermi energy inside a Co corral on Cu(111). The geometry of the corral corresponds to the experimental setup of Manoharan *et al.* [18]. Surface-state electrons are confined within the corral by strong scattering at the corral walls. The quantum interference between electronic waves traveling towards to the corral walls and the backscattered ones leads to the

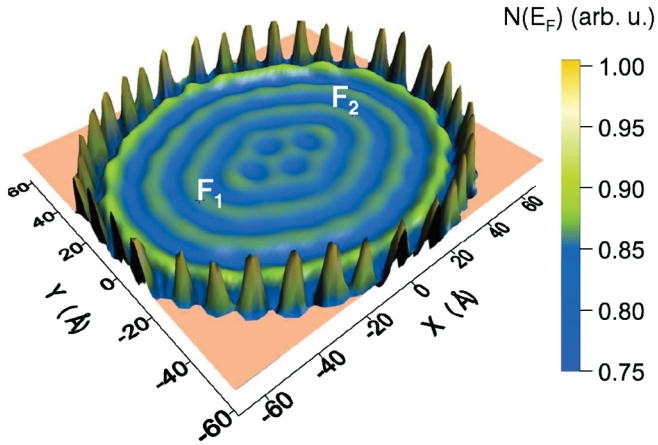

FIG. 1 (color). Standing-wave patterns inside the Co corral on Cu(111). The LDOS at the Fermi energy is shown; geometrical parameters of the corral are the same as in the experimental setup of Ref. [18], i.e., semiaxis $a = 71.3$ Å and eccentricity $\varepsilon = 0.5$.

standing-wave patterns. In other words, strong oscillations in the LDOS manifest the confined surface states.

The interaction of the confined surface electrons with adatoms leads to an interesting effect. We have calculated the energy of the Co adatom placed inside the corral. For large distances between the adatom and the corral walls the interaction energies are calculated in the framework of the frozen potential approximation using single-particle energies instead of total energies [24]. It has been proved that even very small energies can be resolved using such an approach [24].

As an example, the interaction energy along the line between the two foci is shown in Fig. 2. One can see that the energy exhibits an oscillatory behavior and can be attractive or repulsive. For the adatom it appears to be energetically favorable to rest in regions of high LDOS [25]. The above results clearly demonstrate the impact of the quantum confinement of surface electrons on energetics of adatoms.

To gain detailed insight into the physics underlying the behavior of adatoms in corrals, we have calculated the long-range surface-state mediated interaction (LRI) between the Co adatom and the corral walls. It has been demonstrated that such LRI occurs due to the quantum interference of surface electrons [24,26]. Several studies have shown that the LRI can significantly influence the growth of nanostructures [24,26,27].

Our results depicted in Fig. 2 show that the energy of interaction between the Co adatom and the corral walls calculated using the LRI potentials is very close to that determined by the single-particle energies. Note that the interaction between more than two atoms is described by pairwise summation [28]. The above findings unambiguously prove that the surface-state mediated LRI between the adatom and the corral walls is the driving force for the energy oscillations inside the corral. The interaction energies are small and can be relevant only at low temperatures.

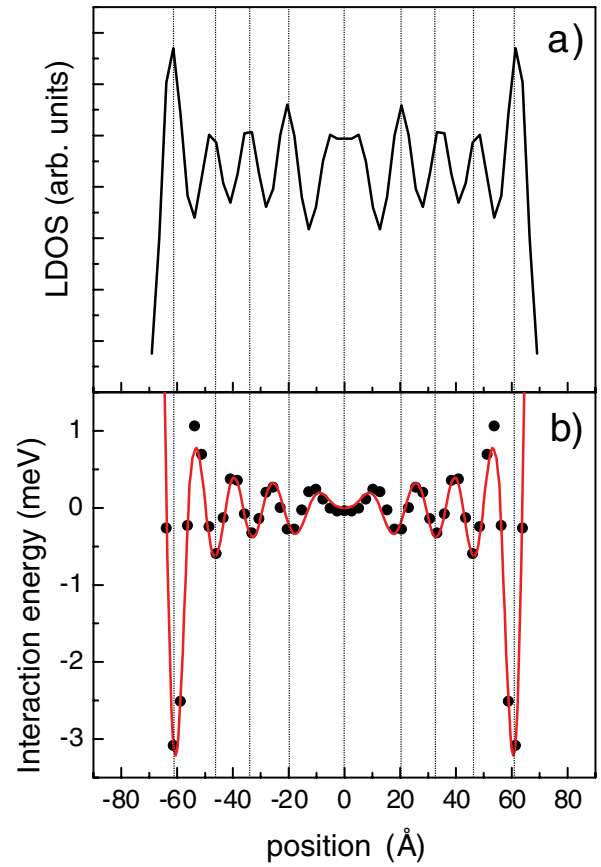

FIG. 2 (color). Effect of the quantum confinement on the interaction energy of a single Co adatom with the Co corral. (a) The LDOS at the Fermi energy along the line between the two foci. (b) The energy of the interaction between the Co adatom and the Co corral: black dots correspond to calculations with single-particle energies; the red curve corresponds to calculations with the LRI potentials.

In order to give clear evidence that an adatom diffusion inside corrals is significantly modified compared to that on an open surface, we perform the kinetic Monte Carlo (KMC) simulations [29] for a single Co adatom randomly deposited inside the Co corral. The hop rate of a single atom from site k to site j is calculated using the ratio $\upsilon_{k\to j} = \upsilon_0 \exp(-E_{k\to j}/k_B T)$. Here T is the substrate temperature, υ_0 is the attempt frequency (about 10^{12} s^{-1}), and k_B is the Boltzmann factor. The influence of the LRI on adatom diffusion is included in the hopping barrier, which takes the form: $E_{k\to j} = E_D + 0.5(E_j - E_k)$ [28], where E_D is the diffusion barrier for an isolated atom on a clean surface [37 meV for Co on Cu(111) [24]]. Despite the fact that the magnitude of the diffusion barrier E_D is significantly larger than $E_j - E_k$, the interaction of a single adatom with the corral walls could be essentially affected by the confinement. This conclusion can be done from a simple analysis of the above equation. The expression can be transformed to $\upsilon_{k\to j} = \upsilon_0 \exp(-E_D/k_B T) \exp[-(E_j - E_k)/2k_B T]$. Now E_D and $(E_j - E_k)$ are included separately. Term $\exp[-(E_D)/k_B T]$ is a constant for all possible

jumps. Together with υ_0, it does not depend on the position of an adatom inside the corral and determines only the characteristic time scale of adatom kinetics. The magnitude of the factor $\exp[-(E_j - E_k)/2k_BT]$ is different for different jumps and, thus, only it determines the relative probabilities to jump from one site to another one.

The adatom probability distribution inside the corral is shown in Fig. 3. It appears that the alternation of atomic behavior at low temperatures (15–20 K) due to the corral is quite significant. There are regions that form different orbits of adatom motion and an empty zone with very low adatom presence probability. These orbits perfectly match with the oscillations of the LDOS (or the interaction energy) shown in Fig. 2. "Allowed" orbits correspond to an attractive (negative) interaction energy between the adatom and the corral.

With respect to possible experiments on adatom motion in corrals, it is important to address the thermal stability of corrals. In order to avoid problems with stability of the corral for nonzero temperatures, we propose to construct the corral from Co dimers. The reason for this is clear: the dimer has a much higher diffusion barrier than the monomer. To check the stability of the corral made of dimers, we have performed the molecular dynamics simulations at finite temperatures. Our results have shown that such a corral is stable up to 200 K. The only effect we have seen was a small rotation of Co dimers around their original positions. This is due to the fact that the barrier for this kind of movement is very small, about 10 meV. We have performed the KMC simulations for adatom motion in the corral made of dimers [the distance between dimers is roughly three atomic sites of the Cu (111) surface]. The distribution of adatoms inside the corral is found to be similar to results presented in Fig. 3. So, we can conclude that the general result of our calculations is not affected by the geometry of the corral walls; i.e., there are "forbidden" regions inside the corral.

The above results suggest that if adatoms are deposited in a corral, the growth process could be profoundly influenced by the surface-state confinement. We have performed the KMC simulations for Co adatoms randomly deposited inside the Co corral. Evidence of lack of order of Co adatoms inside the corral is well seen in Fig. 4: Co adatoms tend to occupy allowed orbits determined by quantum states of the corral (cf. Fig. 3). Dimer formation (which occurs during the deposition process) and the weak LRI of adatoms with the corral walls prevent the atomic ordering in the central part of the corral. Even a small number of dimers can significantly affect the atomic motion inside corrals.

Our systematic studies have shown that an atomic self-organization in corrals is determined by a delicate balance between adatom diffusion barrier, sample temperature, adatom concentration, and the LRI. Variation of substrate and deposited atoms may allow one to tailor the atomic self-organization in corrals. For example, recent experiments have revealed that Ce adatoms on Ag(111) form a well-ordered 2D hexagonal superlattice with a lattice constant of 32 Å [30]. We have performed the KMC simulations for Ce adatoms randomly deposited inside the corral made of Ce dimers on Ag(111). The temperature, the concentration of adatoms, and the parameters of interatomic interactions used in our calculations correspond to the experimental conditions for the superlattice formation [30]. According to the experiment [30] the activation energy for diffusion of Ce atoms on Ag(111) is very low, only

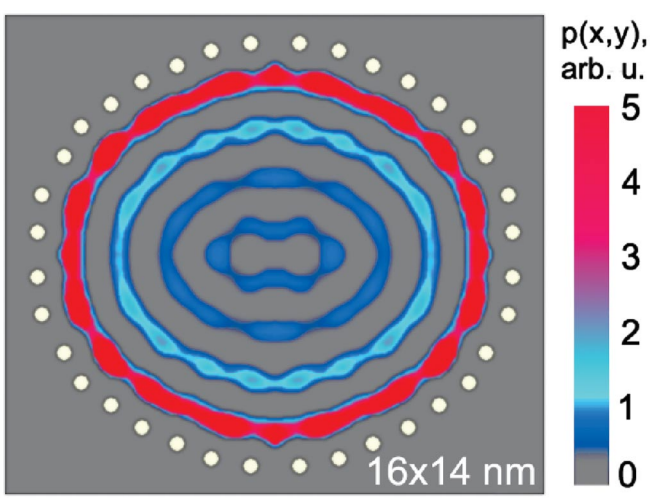

FIG. 3 (color). Adatom diffusion in the Co corral: Results of the KMC simulations for a single Co adatom are presented; the probability to find the Co adatom inside the corral is calculated at 15 K. The corral walls are assumed to be pinned, a situation that can be physically realized by building the corral walls from dimers (see text).

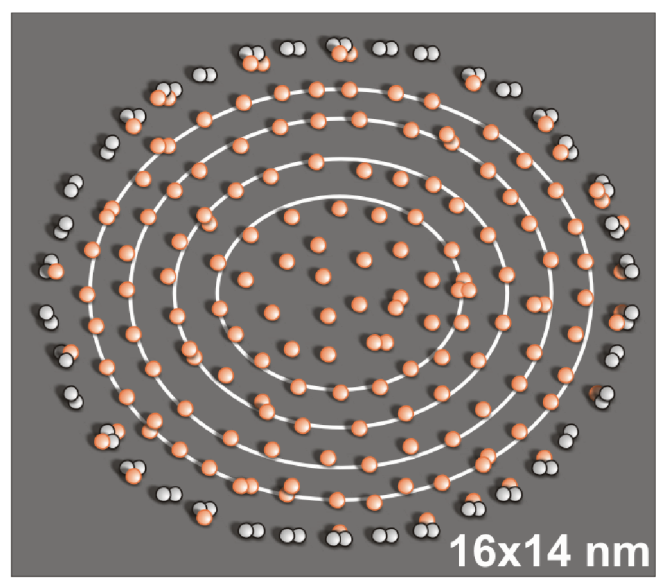

FIG. 4 (color). Self-organization of Co adatoms inside the Co corral made of Co dimers (white balls) on Cu(111). The temperature of the system is 13 K, Co adatom coverage is 0.06 monolayers, and Co adatoms were deposited simultaneously.

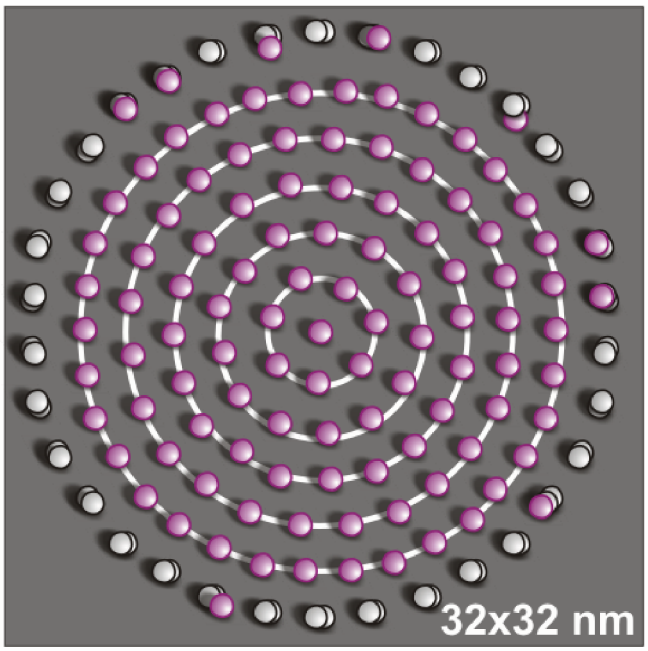

FIG. 5 (color). "Quantum onion": Self-assembly of Ce adatoms inside the Ce corral (semiaxis $a = 150$ Å; eccentricity $\varepsilon = 0$) made of Ce dimers on Ag(111). Temperature of the system is 4 K, Ce adatom coverage is 0.01 monolayers, and Ce adatoms were deposited simultaneously.

9 meV, which accounts for the high mobility of Ce at low temperatures. The results presented in Fig. 5 reveal the self-organization of Ce adatoms into different concentric circular orbits, forming a structure which we call a "quantum onion." The distance between two neighboring orbits (and between two neighboring Ce adatoms) is found to be about 32 Å, which corresponds to the first and deepest minimum of the LRI between Ce adatoms on Ag(111) [30]. Increasing the temperature up to 10 K causes the disappearance of the atomic ordering in the corral [31].

In conclusion, our findings have demonstrated the ability to affect an adatom motion by exploiting the quantum confinement of surface electrons. We have shown that electronic states in quantum corrals can significantly modify the diffusion of adatoms at low temperatures. The self-organization of adatoms inside corrals has been revealed. The quantum confinement of surface electrons and the surface-state mediated long-range interactions are shown to determine the growth process in quantum corrals. In addition, provided that quantum confinement of surface electrons occurs on mesoscopic islands [32] and in vacancy holes [33] on metal surface, we expect our conclusions to hold also for such nanosystems. We believe that quantum growth during a low-temperature deposition of atoms in or on quantum resonators (corrals, vacancy holes, and nanoislands) should be detectable with current STM technology.

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