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Effect of quantum confinement of surface electrons on an atomic motion on nanoislands: *Ab initio* calculations and kinetic Monte Carlo simulations

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Ab initio calculations and kinetic Monte Carlo simulations demonstrate that the quantum confinement of surface electrons to nanoislands can significantly affect the growth process at low temperatures. Formation of empty zones and orbits of an adatom motion is demonstrated for Cu nanoislands on Cu(111).

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Noble (111) metal surfaces support Shockley surface states.[1] These electronic states arise in the inverted L gap of a metal band structure. Electrons occupying the Shockley-type surface states form a two-dimensional (2D) nearly free-electron gas confined in the vicinity of the top layer.[2] Surface electrons scatter at point defects,[3] adsorbates,[4] and steps,[5] leading to standing waves of local density of states (LDOS), which can be detected using scanning tunneling microscopy (STM) technique. These standing-wave patterns contain important information about properties of scattering sites and interaction between the surface electrons and scattering centers. Particularly, scattering of the surface states at adatoms leads to the standing-wave patterns around the adsorbates and to an indirect long-range interaction (LRI) between adatoms.[6] While the first experimental evidence of such type of interactions was reported 35 years ago,[7] quantitatively they have been resolved only recently by means of low-temperature STM studies.[8–10] These remarkable observations have opened a door to creation of macroscopic-ordered 2D (Ref. 11) and one-dimensional (1D) (Ref. 12) nanostructures stabilized by the surface electrons.

Several fascinating phenomena occur if surface electrons are confined to closed nanostructures, such as corrals, vacancy holes, or clusters. Experiments of Manoharan *et al.*[13] and later *ab initio* calculations[14] have demonstrated that the quantum confinement inside corrals induces a mirage effect. It is also possible to tailor spin polarization of surface-state electrons and exchange interaction between magnetic adatoms within the confined nanostructures.[15] Confined surface electrons inside quantum resonators alter diffusion at low temperatures, leading to atomic self-organization.[16] To the best of our knowledge Li *et al.*[17] performed the first quantitative investigation of the quantum confinement of surface electrons on nanoscale Ag islands on Ag(111) by means of STM. These studies revealed the validity of the confinement picture down to the smallest of island sizes. It was proposed[17] that the quantum confinement can arise not only on Ag(111) but on Cu(111) and Au(111). Observation of quantized electronic states in vacancy islands on Cu(111) has been recently reported.[18]

In this Rapid Communication we demonstrate the effect of confined surface electrons on atomic motion in close proximity and on top of nanoislands. The quantum confinement is studied by means of the first-principles Korringa-Kohn-Rostocker (KKR) Green's function method. Our kinetic Monte Carlo (kMC) simulations reveal that confinement-induced electronic states around and on top of nanoislands significantly affect atomic diffusion. Formation of empty zones and orbits of adatom motion is shown. We demonstrate that the quantum confinement dramatically influences the growth process of nanoislands at low temperatures.

Within our study calculations of the electronic interaction between an adatom and a nanoisland are performed using density-functional theory in local spin-density approximation by means of the KKR Green's function method.[19] The basic idea of this method is a hierarchical scheme for the construction of the Green's function of nanostructures on a surface by means of successive applications of Dyson's equation. The bulk, surface, and impurity problems are consequently treated with a perturbative approach. At each stage a fully self-consistent Green's function is obtained, which is then used as a reference for the next step. We treat a surface as a 2D perturbation of an ideal bulk with a slab of vacuum. Taking into account the translational symmetry of the surface geometry, the Green's functions are formulated in momentum space. Adatom and nanoisland are considered as a perturbation of a clean surface. These calculations are performed in real space. The method we use allows one to obtain with a good accuracy (i) a surface-state band edge E_0, (ii) a surface-state Fermi wavelength λ_F,[20] and (iii) to describe in a very good agreement with experiments long-range interactions between adatoms on metal surfaces.[10,21] Previous studies have demonstrated that a spatial modulation of LDOS and interaction energy in closed nanostructures can be calculated within our method.[14,15,18]

As a model system we consider a hexagonal Cu nanoisland placed in fcc hollow sites on a Cu(111) surface[22] and study diffusion of a Cu adatom near and on top of it. Each edge of the island has length of 11 atoms (2.6 nm). Two different kinds of close-packed steps can be distinguished in the nanoisland: the {100}-microfaceted (A) step and the {111}-microfaceted (B) step. We neglect the elastic interaction between the adatom and the island.[23]

At first, we concentrate on the quantum confinement on top of the island. Figure 1 presents the 2D potential-energy map of a Cu adatom placed in different hollow sites. The interaction potential exhibits an oscillatory behavior if one recedes from an edge of the nanoisland toward its center

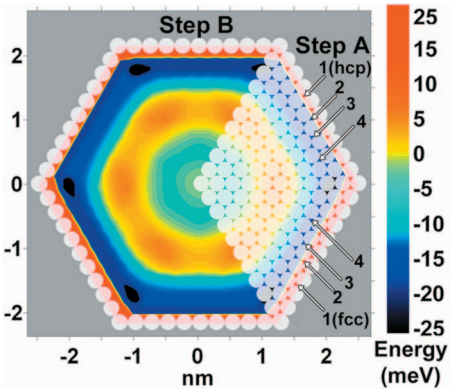

FIG. 1. (Color) The 2D map of the interaction potential between a Cu nanoisland and a Cu adatom placed on top of it. Semitransparent white circles demonstrate the edges of the island and 1/3 part of it. The rows of hollow sites are numerated from the steps (numbers 1–4).

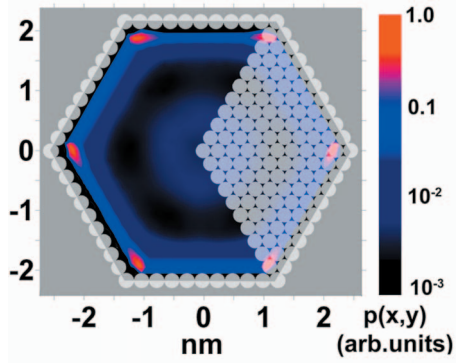

FIG. 2. (Color) Atomic diffusion on top of the nanoisland: results of the kMC simulations for a single Cu adatom. The probability to find a randomly deposited Cu atom is calculated at 60 K. Semitransparent white circles demonstrate the edges of the island and 1/3 part of its surface. The logarithmic scale is used.

along the perpendicular bisector to the edge. When the Cu adatom is located in the first row of hollow sites near A or B step (Fig. 1), the interaction is repulsive, being larger than 30 meV. We attribute this effect due to redistribution of the electron-charge density at steps as was suggested a long time ago by Smoluchowski.[24] When the Cu adatom is located in the second row of hollow sites near B step, the interaction is also repulsive, being 10 meV. Our calculations reveal the attractive minima of −19 meV at 1.5 Å from A step (the second row of hollow sites) and −20 meV at 2.9 Å from B step (the third row). Difference in the positions of the minima with respect to the island edges appears due to the different types of atomic packing at A and B steps. The existence of attractive potential in the vicinity of a descending Cu step is confirmed by experimental observations of Repp *et al.*[8] One of the most fascinating effects of confined surface electrons is quantum interference at the corners (black spots in Fig. 1). The attractive potential in these spots is deeper than at steps, being −25 meV. A similar phenomenon has been already observed for the scattering of surface-state electrons in a "hand-made" triangular corral constructed of Ag adatoms on a Ag(111) surface.[25]

In order to give clear evidence that atomic motion on top of the nanoscale island is substantially modified compared to that on an open surface, we perform the kMC study[26] of behavior of a Cu adatom randomly deposited on top of the island. The hop rate of an adatom from site k to site j is calculated using the formula $\nu = \nu_0 \exp(-E_{k\to j}/k_B T)$, where T is the substrate temperature, ν_0 is the attempt frequency [10^{12} s^{-1} (see Refs. 21 and 27)], and k_B is the Boltzmann factor. The influence of the electronic interaction "adatom-island" (Fig. 1) is included in the diffusion barrier: $E_{k\to j} = E_D + 0.5(E_j - E_k)$, where E_D is the energy barrier for a Cu atom on a clean surface [40 meV (Ref. 28)] and $E_{k(j)}$ is the magnitude of interaction, when the adatom is in the hollow site $k(j)$. Previous studies[21,27] have confirmed the applicability of this approach.

The adatom probability distribution on top of the island is shown in Fig. 2. Contrary to the traditional view, the adatom does not diffuse as it does on a flat surface. Regions marked with the red color correspond to the energy minima of −25 meV in the corners of the island (Fig. 1). The probability to find the adatom in these six spots is significantly higher than that one along the island edges. At the same time a localization of the adatom in a narrow stripe along the steps is more preferable than in the center of the island. Formation of empty zones and orbits of adatom motion takes place.

Now we turn to the effect of the quantum confinement around the island. The 2D potential-energy map caused by the substrate-mediated electronic interaction between the adatom and the nanoisland is presented in Fig. 3. The interaction has an oscillatory behavior, decaying to zero if one recedes from the island along the perpendicular bisector to a step edge. The interaction is strongly attractive (about −1.4 eV) when the Cu adatom is at 2.2 Å from the step; it corresponds to aggregation of the adatom and the island. This energy is originated solely from the short-range chemical bonding between the adatom and the island. Our calculations reveal a concentric repulsive ring of 25 meV at 4–7 Å from the edge of the island. This barrier prevents atomic diffusion toward the steps at low temperatures. At such distances the contribution of the short-range chemical interaction is almost zero, and the repulsive peak is deter-

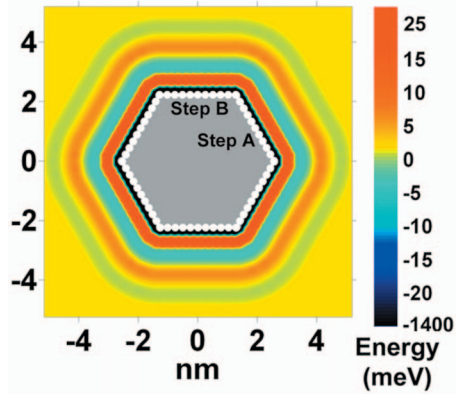

FIG. 3. (Color) 2D interaction potential between a Cu nanoisland and a Cu adatom placed in its vicinity. The edge of the island is marked with the white circles.

mined only by the oscillations of the LDOS around the island. There are a ring of attractive interaction of −5 meV at 8–14 Å and a ring of repulsive interaction of 2 meV at 15–20 Å. The next minima and maxima of energy are less than 1 meV. Concentric rings of negative and positive energies (Fig. 3) lead to the formation of empty zones and "allowed" orbits. Particularly, at low temperatures a migrating adatom prefers to be at about 9 Å from the steps, while the probability to find an adatom at 4–7 Å from the edge of the nanoisland is very low.

The quantum confinement has a dramatic effect on growth of small clusters at low temperatures. To illustrate this statement we perform the kMC simulations of self-organization of Cu atoms on Cu(111) at 14 K for different coverages of deposited atoms ρ_0. As a model system we now consider a hexagonal Cu nanoisland with the length of each edge of 16 atoms (3.8 nm). Within our study the LRI between Cu adatoms[29] is described by a pairwise summation. Previous studies have confirmed that this approximation is well justified at large interatomic separations.[21,27] The interlayer diffusion is not feasible in the considered system.[30]

In Fig. 4 we present histograms of statistically averaged density of adatoms on top of the island and around it as a function of the distance between the adatom and the nearest step. Positive distances r correspond to the area outside the island, while negative ones to that on top of it. At coverage $\rho_0=1\%$ of monolayer (ML) [Fig. 4(a)] there is only one peak of the density on top of the island. It indicates that all adatoms are localized at separations of 1.5–3 Å from the steps, forming the first inner orbit. The first peak outside the island (at $r=2.2$ Å) corresponds to atoms nucleated to the island during deposition. The second maximum of atomic density outside the island is located at $r=8.8$ Å: these atoms form the first outer orbit. The probability to find an adatom on the second orbit (at $r=17-22$ Å) is much smaller. The electronic interaction "adatom nanoisland" at such distances is less than 2 meV (Fig. 3), and the second orbit is stabilized by the LRI with the adatoms placed on the first orbit.

Our simulations indicate that effect of the quantum confinement on atomic self-organization remains significant in a wide range of coverages. The results for $\rho_0=3.5\%$ of ML are presented in Fig. 4(b) and for $\rho_0=5\%$ of ML are given in Fig. 4(c). With increasing coverage the probability of the occupation of the first orbit on top of the island (at $r\sim-2$ Å) increases. The second and the third inner orbits (at $r\sim-12$ Å and at $r\sim-22$ Å, respectively) are formed. The similar phenomenon occurs around the island: adatoms form orbits at $r\sim18$ Å and $r\sim28$ Å, while the atomic density between the orbits is low. Two Cu atoms located on the same orbit are separated by 11–12 Å, corresponding to the position of the local minimum of the LRI between two Cu adatoms.[29]

Finally, we would like to note that empty zones were found in several experimental works of Ehrlich and coworkers. In Refs. 31 and 32 diffusion of an Ir adatom around an Ir cluster on Ir(111) was studied. Empty zone was resolved at separations of 3–7 Å from the edge of the cluster, while the preferable distance between the migrating atom and the step edges was 9–12 Å. With increasing temperature the adatom overcame the empty zone and nucleated with

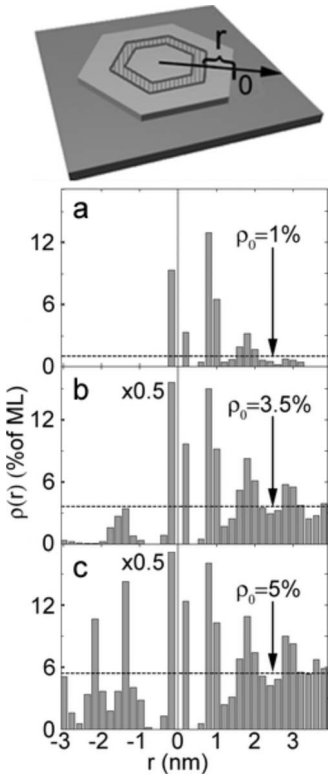

FIG. 4. Surface density of adatoms $\rho(r)$ on top of the nanoisland and around it as a function of the distance r to the nearest island edge. Function $\rho(r)$ is a number of adatoms over the square of a hexagonal concentric ring (marked with a shadow). Positive values of r correspond to the region outside the island, while negative ones to that on top of it. The results of the kMC simulations of self-assembly of Cu adatoms at a presence of Cu nanoisland on Cu(111) are demonstrated. The Cu adatoms are deposited simultaneously at 14 K; the coverage ρ_0 is (a) 1% of ML, (b) 3.5% of ML, and (c) 5% of ML. In (b) and (c) peaks at $r=-2$ Å are rescaled by factor 0.5. Dashed lines correspond to the uniform atomic density at a given coverage.

the cluster. The anisotropy diffusion was also observed for an Ir adatom placed on top of an Ir cluster on Ir(111). The Ir atom was localized near the edge of the cluster with a higher probability than in its central region.[32,33] Diffusion of a Pt atom on top of a Pt cluster on Pt(111) was a subject of study in Ref. 34. It was found that an empty zone (of width of 7 Å) divides the region with uniform atomic distribution in the center of the cluster from the orbit near steps. During migration along the step edges, the preferable location of a Pt adatom was in the corners of the cluster. Results of our study for Cu suggest that phenomena observed by Ehrlich and coworkers could be promoted by the quantum interference of electrons scattered on the cluster, on one hand, and on the adatom, on another hand. However, in order to give a precise answer to this question, further theoretical investigations are required.

In conclusion, we have performed an *ab initio* study of the quantum confinement of surface electrons on top of nanoscale Cu islands on Cu(111) and around them. Formation of concentric rings with positive and negative interaction energies is revealed outside and on top of a nanoisland.

This phenomenon substantially modifies the atomic diffusion at low temperatures, leading to empty zones and orbits of adatom motion. Our results indicate on a profound role of the quantum confinement of surface electrons during growth of metal nanoclusters at low temperatures.

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[20] Our calculations for a Cu(111) surface reveal that $E_0 = -0.50$ eV below the Fermi level and $\lambda_F = 29$ Å, which are in good agreement with experimental values −0.44 eV and 29 Å, respectively (Ref. 35). Similar calculations for Ag(111) demonstrate that $E_0 = -73$ meV and $\lambda_F = 75$ Å. The corresponding experimental values are −63 meV and 77 Å (Ref. 11).
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