

Effect of the long-range adsorbate interactions on the atomic self-assembly on metal surfaces [☆]

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Abstract

Recent experimental studies have demonstrated that short linear chains are often formed in the early stage of heteroepitaxy on the (111) noble metal surfaces at low temperatures. Here, we show that the surface-state mediated long-range interaction between adsorbates is the driving force for the self-organization of adsorbates at very low temperatures. Our kinetic Monte Carlo simulations for Co adatoms on Cu(111) and for Ce adatoms on Ag(111) reveal that these interactions can lead to the formation of linear chains.

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It is well known that the surface-state electrons on the (111) surfaces of noble metals form a two-dimensional (2D) nearly free-electron gas [1]. If an adsorbate is placed in a 2D electron gas, the quantum interference between the electron wave traveling towards the adsorbate and the backscattered one leads to Friedel-type oscillations in the local density of electronic states (LDOS) [2]. The standing wave pattern around adsorbates can be observed with the scanning tunneling microscope (STM) [3]. The ability of adsorbates to scatter surface-state electrons can be used to confine electrons in engineered atomic structures. Recent experiments and *ab initio* calculations demonstrated that surface-state electrons confined in corrals can be exploited to project an electronic structure and the spin-polarization to a remote location [4,5].

The oscillations of the LDOS around adsorbates can lead to a long-range oscillatory interaction (LRI) between them [6–8]. Several theoretical studies have demonstrated

that despite the fact that indirect adsorbate interactions are small, they can affect atomic motion and growth processes. For example, the results of a combined kinetic Monte Carlo (kMC) and the density functional (DFT) study of Fichthorn and Scheffler [9] have shown that the strength of the LRI can be comparable to the diffusion barrier, and they can significantly influence surface diffusion and the growth morphology in thin-film epitaxy. The DFT and the kMC calculations of Bogicevic et al. [10] have revealed a large increase in island density when the substrate-mediated interactions are taken into account. Theoretical studies of Fichthorn et al. [11] have predicted that the intermediate-range, substrate-mediated interactions lead to the formation of repulsive barriers surrounding small islands. Recent experiments performed by means of the STM and the DFT calculations have resolved the LRI between Co adatoms on Cu(111) at large distances [12]. These studies clearly show the oscillatory nature of the LRI with a period of half the Fermi wavelength of surface-state band, linking the LRI to standing-wave patterns in the LDOS.

The LRI can be exploited to create ordered atomic and possibly molecular superlattices [13]. For example, the

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self-assembly of Ce adatoms on Ag(111) into large ordered superlattices has been recently observed in the experiment of the group of Schneider [14,15]. Theoretical studies have predicted that new magnetic nanostructures can be stabilized at low temperatures by the LRI [16]. A nice discussion of substrate-mediated interactions on solid surfaces is presented in a review of Merrick et al. [17].

In this Letter we present the kMC studies of the self-organization of adsorbates caused by the LRI. Our work has been motivated by the experiments of Knorr et al. [8] on Co adatoms on Cu(111), and Silly et al., on Ce adatoms on Ag(111) [14,15]. In both studies short linear chains have been seen in STM images at low temperatures and for a low concentration of adatoms. We demonstrate that the substrate-mediated interaction between adsorbates at intermediated and large distances is the driving force for the formation of metastable linear structures on metal surfaces.

First, we briefly discuss the LRI between adsorbates on metal surfaces. Theoretical study of Hyldgaard and Persson [18] has shown that electronic adsorbate–adsorbate interactions at large distances are caused by the scattering of surface-state electrons by adsorbates. Their theory links the electronic pair interaction $E(r)$ and the scattering properties of the adsorbate

$$E(r) = AE_0 \left(\frac{2 \sin \delta_0}{\pi} \right)^2 \frac{\sin(2k_F r + 2\delta_0)}{(k_F r)^2} \quad (1)$$

Here k_F is the Fermi surface wavevector, E_0 is a surface state band edge, δ_0 is a phase shift, A is the scattering amplitude.

Recent DFT calculations for the interaction between Co adatoms on Cu(111) [12], and for the interaction between Ag adatoms on a compressed Ag(111) [19] have shown that the DFT results follow the trend of the theory of Hyldgaard and Persson [18] for large adatom–adatom separations. It is important to note that the LRI are primarily pair-wise. Interactions between more than two adatoms are described by pair-wise summation. Theoretical studies and a STM study suggest that such approximation is well justified for large distances between adatoms [14,20–22].

A schematic description of the electronic pair interaction energy is depicted in Fig. 1. At intermediated adatom separations a repulsive barrier D can prevent dimer formation at low temperatures. Ab initio studies of the LRI between 3d adatoms on Cu(111) have shown that this barrier changes non-monotonically from about 70–24 meV going from the Ti to the Ni [16]. The interaction energy has been found to oscillate with a period of $\lambda_F/2 = 15 \text{ \AA}$ (λ_F is a surface state Fermi wavelength of Cu(111)) and decays as $1/d^2$ (d is the distance between adatoms). The first minimum has been found to be about 12 Å for all 3d pairs. The experiments of Repp et al. [7] have shown that the copper adatoms on Cu(111) form islands with a local hexagonal structure, and a closest distance between adatoms has been found to be about 12 Å. This proves the existence of an attractive potential minimum B (see

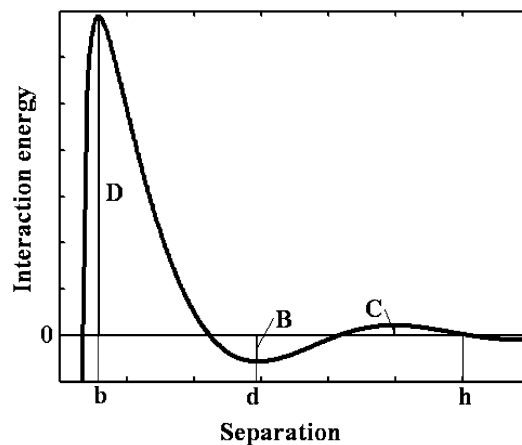


Fig. 1. Schematic description of the interaction energy between adatoms on metal surfaces.

Fig. 1) at about 12 Å. The repulsive barrier C for adatoms on Cu(111) is rather small (in the range between 0.13 and 0.54 meV going from the Ti to the Ni) [16]. Therefore, adatoms may overcome this barrier even at very low temperatures. The depth B of the potential well is about 1–2 meV [16]. To the best of our knowledge, ab initio studies of the LRI on Ag(111) reflecting the surface band structure of Ag(111) have not been performed so far. Experiments of Knorr et al. [8] and Silly et al. [15] have shown that the period of the oscillation of the LRI on Ag(111) is about 38 Å i.e. more than twice larger than for Cu(111). The parameters of the LRI obtained in the above mentioned experiments indicate that the first minimum B (see Fig. 1) is at around 27 Å for Co on Ag(111), and around 32 Å for Ce on Ag(111). The depth of the potential for Co and Ce adatoms has been found to be about 1 meV in both cases. In our kMC simulations for Co adatoms on Cu(111) we use parameters of the LRI determined in our ab initio calculations [16]. Our ab initio approach is based of the DFT and Korringa–Kohn–Rostoker Green’s function method for low dimensional systems [5,12,16,23]. The LRI for Ce adatoms is described using the experimental data of Silly et al. [15].

For simulations we use the rejection-free kMC method of Fichthorn et al. [11,24]. According to this model the hop rate of adatom from the site k to the site j is calculated using the expression $v_{k-j} = v_0 \exp(-E_{k-j}/k_B T)$, where T is a temperature of the substrate, v_0 is a frequency factor and k_B is the Boltzmann constant. The prefactor v_0 is set to 10^{12} (0.9×10^{12}) s^{-1} for Ag (Cu) surface [10,15]. The influence of the LRI on adatoms diffusion is included in the hopping barrier which takes the form [11]: $E_{k-j} = E_D + 0.5(E_j - E_k)$. Here E_D is a diffusion barrier for an isolated atom on a clean surface, $E_{k(j)}$ is the interaction energy when adatom is in the site $k(j)$. For the further discussions we transform the expression for v_{k-j} to the following form:

$$v_{k-j} = v_D \exp(-0.5(E_j - E_k)/k_B T) \quad (2)$$

where $v_D = v_0 \exp(-E_D/k_B T)$ is the average rate of the diffusion of single adatom on the clean surface.

Both fcc and hcp sites on the (111) surfaces are considered in our simulations. The magnitude of the diffusion barrier E_D for a single Co adatom on Cu(111) surface is equal to 37 meV [12,25]. The energy difference between fcc and hcp sites for Co adatom on Cu(111) surface is about 1 meV with the fcc site being energetically more stable [12,25]. The magnitude of E_D for a single Ce adatom on Ag(111) is about 11 meV, and the energy difference between fcc and hcp sites for a Ce adatom is so small that it is unnoticeable in the experiment [14,15]. Therefore, fcc and hcp sites are considered in our simulations to be identical. Three short jumps to the different neighboring positions can occur for each adatom on the (111) surface. If the number of adatoms in the system is equal to N , then for every kMC step $3N$ different hops with the rates v_1, v_2, v_{3N} are possible. The time interval between two steps can be calculated [24]

$$\tau = \frac{-\ln U}{\sum_{i=1}^{3N} v_i} \quad (3)$$

where U is a randomly distributed number in the interval (0, 1).

First, we present results of the kMC simulations for Ce adatoms on Ag(111). The size of the simulation cell is set to be 100×100 nm. To avoid the influence of the finite size of the cell we use the periodic boundary conditions. The cut-off distance for the interaction potential is equal to 6.00 nm. Fig. 2 shows the results of the kMC simulation for 0.2% of monolayer (ML) of Ce adatoms on Ag(111) at the temperature of 4.0 K. One can see that the short linear chains (mainly three atoms in length), crooked chains and small hexagonal clusters are formed. The distance be-

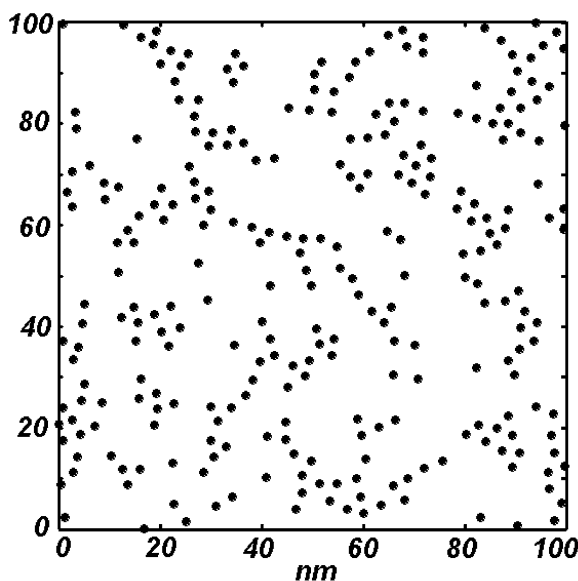


Fig. 2. The kMC simulation of Ce adatoms on Ag(111). The concentration is 0.2% of ML, temperature is 4.0 K. The distance between nearest Ce atoms in chains and clusters is about 3.0 nm.

tween nearest Ce atoms in the clusters and in the chains is about 3.0 nm, and corresponds to the first minimum of the interaction potential for Ce on Ag(111) [15]. These results clearly demonstrate that the self-organization of Ce adatoms is caused by the surface-state mediated LRI. Linear chains formed due to the LRI are metastable structures. Our own calculations [12] and the study of Fichtorn et al. [11] have indicated that although short linear chains can grow more easily than compact ones, they can rearrange to the more stable compact form. For example, the chain-size distribution for 0.2% of ML of Ce adatoms on Ag(111) is shown in Fig. 3 for 4 and 10 K. One can see that as the temperature increases, the average chain length decreases. The relative time scales for the incorporation of adatoms at chain ends and island rearrangement determines the growth process. The parameter v_D characterizing the average rate of the adatom hop can be used to estimate the temperature which is necessary for the stabilization of linear chains. For example, for Ce on Ag(111) at the temperature of 3.0 K the average time $1/v_D$ of a single adatom jump is equal to 30 days. The lifetime for the linear structures in this case is even larger. Linear chains of Ce atoms on Ag(111) surface appear only for a very delicate balance between the adatom concentration and the temperature. If the concentration of Ce adatoms is about 0.03% of ML, we find that they are distributed on the surface almost uniformly with the preferential separations of 3, 7 and 11 nm. These values are very close to the adatom–adatom separations found in the experiment of Silly et al. [15] and correspond to the first three minima of the LRI for Ce adatoms on Ag(111). Our study reveals that Ce chains are formed for the concentration of Ce adatoms in the range 0.10–0.25% of ML. The temperature of the system required for the linear chains formation is found to be between 3.8 and 11 K.

Now we turn to the results for Co adatoms on Cu(111). The size of the simulation cell is 50×50 nm. The cut-off distance for the LRI (Fig. 1) is set to 2.29 nm. Fig. 4 depicts the results of the simulation for the Cu(111) surface with 1.0% of ML of Co adatoms at the temperature of 14 K. One can see that short linear chains, crooked chains and hexagonal clusters occur. The distance between the nearest

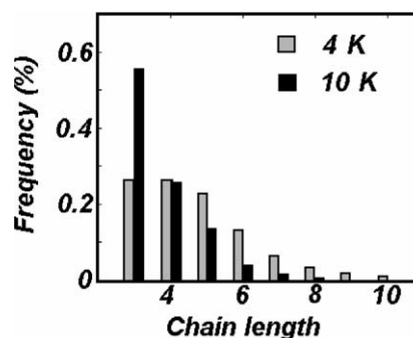


Fig. 3. Chain-size distribution of Ce adatoms on Ag(111). The concentration is 0.2% of ML.

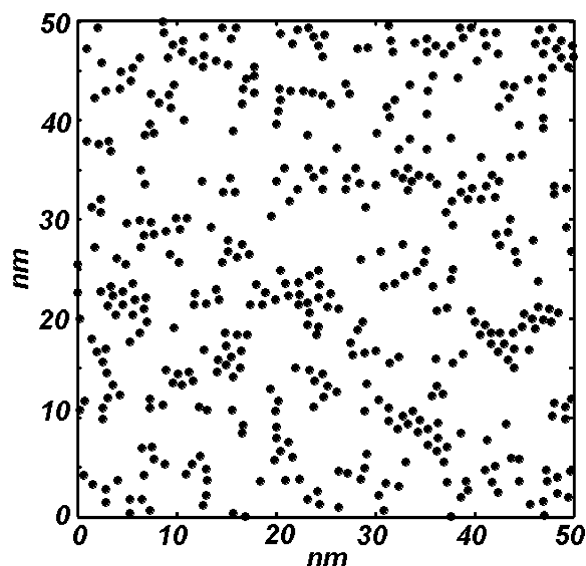


Fig. 4. The kMC simulation of Co adatoms on Cu(111). The concentration is 1.0% of ML, temperature is 13 K. The distance between nearest Co atoms in chains and clusters is about 1.2 nm.

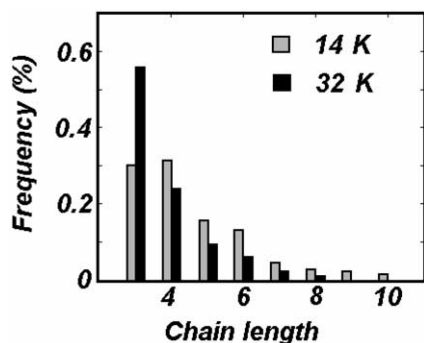


Fig. 5. Chain-size distribution of Co adatoms on Cu(111). The concentration is 1.0% of ML.

Co atoms in these nanostructures is about 1.2 nm, and corresponds to the first minimum of the interaction potential for Co/Cu(111) (Fig. 1) [16]. These results nicely correspond to the experiments [8,12] where chains have been observed. The chain-size distribution for 1.0% of ML of Co adatoms on Cu(111) is shown in Fig. 5 for 14 and 32 K. Similar to our results for Ce adatoms on Ag(111), the fraction of chains with more than three atoms in length decreases as the temperature increases. Our simulations indicate that Co chains on Cu(111) are formed for the con-

centration of the deposited atoms in the range of 0.3–5% of ML. The temperature of the system required for the chains formation is found to be between 13 and 35 K.

In summary, we have performed the kMC studies of an atomic motion caused by surface-state mediated interactions. Our results for Ce adatoms on Ag(111) and for Co adatoms on Cu(111) demonstrate that such interactions can lead to the self-organization of adatoms in short chains. The temperature and the concentration of adatoms are found to be key parameters in this process.

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