Self-organized long-period adatom strings on stepped metal surfaces: Scanning tunneling microscopy, *ab initio* calculations, and kinetic Monte Carlo simulations

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Combined experimental and *ab initio* studies show that the surface-state-mediated adatom-step and adatom-adatom interactions are the driving forces for the self-organization of Fe adatoms on vicinal Cu(111) surfaces at low temperatures. Our scanning tunneling microscope observations and the kinetic Monte Carlo simulations reveal the self-organization of Fe adatoms into atomic strings. The interatomic separation (1.2 nm) in the strings is not determined by the nearest-neighbor distance (0.26 nm) of the Cu atoms along the step edge but by the wavelength of the surface-state charge density oscillations.

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Recent developments in nanoscience make it possible to engineer artificial structures at surfaces and to gain control over matter at the atomic scale.[1–7] To date, two main approaches have been used: atomic manipulation with scanning tunneling microscope (STM) and self-organization techniques. The ability of manipulating atoms on solid surfaces with the STM has opened the door to study local properties in man-made nanostructures. The STM has been used to create quantum corrals[6] and atomic chains,[8–10] to control an atomic motion,[11] and to manipulate single molecules.[12] Many new physical insights and phenomena have been obtained.[6–10] Nowadays, nanosystems of enormous interest are atomic chains,[8–10] nanocontacts,[13] nanowires, and stripes.[14–16] Such one-dimensional (or quasi-one-dimensional) systems are believed to possibly play a leading role in future electronic devices. Because of the giant magnetic anisotropy energy,[17] the one-dimensional (1D) magnetic systems could also be very interesting for spintronics applications. Recent studies suggest that 1D spin chains could be used for quantum communications.[18]

Among self-organization techniques, step decoration of vicinal surfaces with a regular array of steps can be exploited to grow superlattices of quantum wires.[16] The basic idea of this approach is that step edges act as preferential nucleation sites for adatoms due to increased coordination with respect to the terrace sites. In general, the bonding between atoms in atomic chains and nanowires assembled by atomic manipulation or self-organization is caused by direct interatomic interactions. In other words, a strong overlap of atomic wave functions is the driving force stabilizing 1D systems in the above mentioned experiments. Usually, interatomic distances in such low-dimensional systems are close to the intrinsic nearest-neighbor spacing.[8–10,16,25] However, there could be substrate-mediated long-range interactions between adatoms.[19,20] Such interactions have been shown to significantly affect the growth morphology at low temperatures[21] and can be used to create ordered superlattices.[3]

In this Brief Report, we present a "bottom-up" scenario for the self-organization of adatoms on vicinal surfaces into 1D stringlike structures at low temperatures. Our theoretical and experimental studies demonstrate that the surface-state-mediated interactions between Fe adatoms and Cu steps can be exploited to create a well-ordered array of 1D Fe nanostructures on a vicinal Cu(111) surface. Both experiments and *ab initio* calculations reveal that the interatomic spacing in strings grown on the upper terraces along the step edges is far beyond the region of the direct adatom-adatom interactions and close to 1.2 nm. Our results unambiguously prove that the bonding between Fe atoms in strings and their self-organization into 1D arrays are caused by the surface-state electrons.

To understand the underlying physics, we have calculated the interaction energy between an Fe adatom and the step on Cu(111) for the adatom-step separation up to 4.0 nm. We have considered both *A*-type and *B*-type steps on Cu(111) and found that the substrate-mediated interaction energies are essentially the same for both types of steps; therefore, we present only results for *B* steps. We take into account the direct and substrate-mediated interactions of electronic origin. Our studies have shown that while elastic interactions can have a significant impact on an atomic motion near steps, they practically do not affect main results presented here. Our *ab initio* calculations are based on the density functional theory and the multiple-scattering approach in the framework of the Korringa-Kohn-Rostoker (KKR) Green's function method.[20,22] Two approaches have been used to describe the step in KKR method: a vicinal surface has been treated by means of screened KKR Green's function method,[23] and a large cluster has been calculated in the real space representation by KKR Green's function method. The energy of the interaction between adatoms and steps are essentially the same in both approximations.

Our calculations for the interaction energy between the Fe adatom and the Cu step on Cu(111) for the lower and upper terraces are presented in Fig. 1. One can see that the interaction energy in both cases is oscillatory with a period of about 1.5 nm [half the Fermi wavelength of the surface band[19,20] of Cu(111)]. The first minimum of the interaction

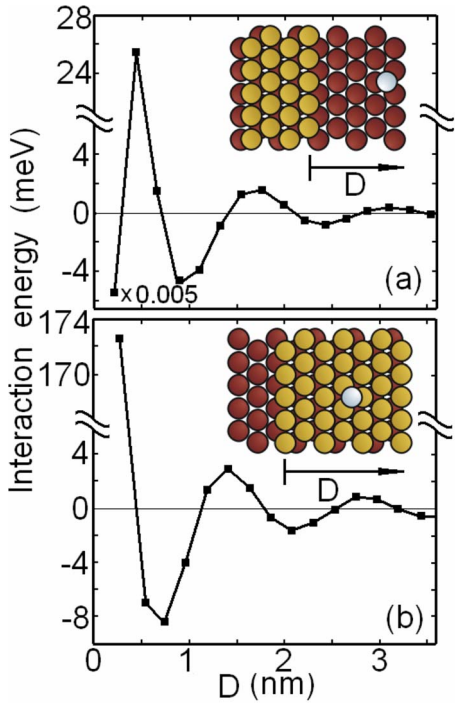

FIG. 1. (Color online) The interaction energy between the Fe adatom and the Cu step on Cu(111): (a) for the lower terrace and (b) for the upper terrace.

energy is found to be ≈0.9 nm on the lower terrace and ≈0.8 nm for the upper terrace. However, the depth of this minimum on the upper terrace (≈8 meV) is more than twice compared to that on the lower terrace (≈4 meV). Our results reveal that the adatom moving toward the step is repelled by the repulsive potential (Fig. 1). For the lower and upper terraces, the first repulsive barrier occurs at distances of about 0.4–0.5 nm from the step. However, the strength of this repulsive potential on the upper terrace is significantly larger (≈173 meV) than that for the lower terrace (≈26 meV). The physics underlying the difference in the behavior of adatoms at the upper and lower terraces seems to be related to a redistribution of the electron-charge density at step edges as was suggested long ago by Smoluchowski.[24] The charge redistribution at step sites, with a flow of electron density from the upper step edge to the step base, is the main factor governing the differing properties between the adatom-step interaction on the upper and lower terraces near the step edge. Our calculations reveal such charge redistribution and show that the reduction of the electron density at the edge of the upper terrace reduces the screening of the direct Coulomb repulsive interaction between the Fe adatom and the step atoms. A repulsion between adatoms and the step could prevent an adatom diffusion toward the step edge at low temperatures. Note that, due to the oscillatory nature of the adatom-step interaction, there are many different repulsive barriers for the adatom diffusion. However, our calculations show (Fig. 1) that such barriers (e.g., for distances between 1.5 and 2.0 nm from the step edge) are significantly smaller (<2 meV) than the first repulsive barrier. The above results imply that it could be possible to find a temperature at which the adatoms are trapped in attractive potential wells near steps on the upper or/and lower terraces. Fe adatoms become quite mobile on Cu(111) at temperatures larger than 10–11 K due to a small barrier for the hopping diffusion [≈25 meV (Ref. 25)]. At such temperatures, adatoms can easily overcome small repulsive barriers. Using a Boltzmann distribution, $\exp(-E_1/k_BT)$ (where T is the temperature of the substrate and E_1 is the depth of the first minimum of the interaction energy; see Fig. 1), one can find that the occupation probability of surface sites in the potential well near the edge of the upper terrace is about 100 times larger than that on the lower terrace at 10–13 K. In other words, it seems likely that the preferential adatom position at such temperatures is on the upper terrace at about 0.8 nm distance from the step edge. Moreover, our *ab initio* calculations predict that, in this region, adatom aggregation is hindered. In Fig. 2, we depict the potential-energy map for the Fe adatom to approach another Fe adatom trapped in the potential well near the edge of the upper terrace. The repulsive area surrounding this adatom is well seen. It is easier for the Fe adatom to approach the step edge within a distance of about 1.2 nm from the first Fe adatom. Consequently, there could be many isolated Fe adatoms near the step edge, forming an atomic string with large interatomic distances. Note that the 1.2 nm separation between adatoms is related to the first minimum of the surface-state-mediated pair interaction potential on Cu(111).[19,20]

The above results suggest that the growth process of Fe on a stepped Cu(111) at low temperatures could be profoundly affected by surface-state electrons. To test this theoretical prediction, we have performed experimental studies of the low-temperature deposition of Fe atoms on a stepped Cu(111) surface.

The experiments are made in an ultrahigh vacuum chamber (5×10^{-11} mbar) which is equipped with a low-temperature STM, an Auger electron spectroscopy (AES) apparatus, and a sputter gun. The high purity Cu(111) crystal is cleaned by repeated cycles of argon ion sputtering (2 kV) and annealing at 700 K until no trace of contaminations could be found in AES. After that, the crystal is transferred into the STM stage and cooled down to 4.7 K. The surface quality is further cross-checked with the STM to ensure low defect concentration. High purity Fe is deposited by means of electron beam evaporation onto the Cu(111) substrate in the STM stage at ≈5 K. The typical rate of deposition is 0.02 monolayer/min. We find that Fe sticks to the Cu surface mostly in a single-atom (monomer) form at the coverage below approximately 0.04 monolayer equivalent (MLE). For this coverage, only a few percent of dimers or clusters are found. With increasing coverage, the concentration of dimers or clusters increases. When the sample is slightly warmed up to ≈10 K, we find that the monomers become mobile, while the dimers remain almost at the same position due to their relatively large diffusion barriers. At the temperature above ≈14 K, we found that the monomers have the tendency to form more dimers and clusters. Therefore, we use 13 K as the annealing temperature for the experiments described below. After annealing, we find that Fe atoms form strings along the step edges. To present this effect more clearly, we explore the Fe atoms' arrangement on an area with high density of step edges, i.e., a vicinal surface. Figure 3 presents a

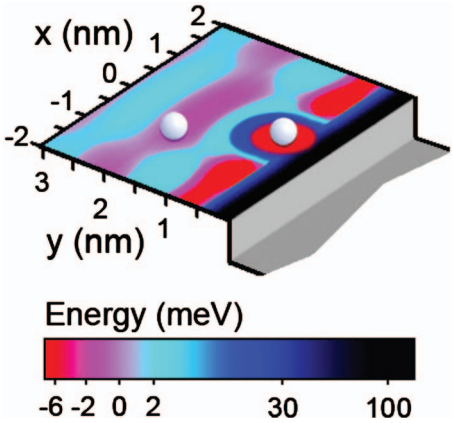

FIG. 2. (Color) The potential-energy map for the Fe adatom to approach another Fe adatom trapped in the potential well near the edge of the upper terrace.

typical topographic image of Fe atoms on a vicinal surface with the average terrace width of about 5 nm after annealing to 13 K. The Fe coverage is about 0.008 MLE. As the image is taken at the sample bias of −0.8 V, which is below the minimum of the surface-state energy of Cu(111), a standing wave pattern is not visible in this graph. As shown in Fig. 3, the Fe atoms reside on the upper step edges and form well-ordered atomic strings with a fixed separation along the step direction. Only a few atoms and/or clusters still exist on top of the terrace. The reason could be the pinning effect of the local defects on the terrace or locally more atoms existing on the wider terraces; however, there is no space to fill in more atoms at the step edges.

To obtain quantitative information about atomic strings, we have made the line profiles along and perpendicular to the string directions as marked in Fig. 4(a). From the line profile along the string direction [*A*-*A'* in Fig. 4(a)], one can see that the Fe atoms are separated by a fixed distance of 1.2±0.1 nm [see Fig. 4(b)]. The line profile perpendicular to the chain direction (*B*-*B'* in Fig. 4) shows that the Fe atoms are typically 0.8±0.1 nm away from the step edges [see Fig. 4(c)]. During deposition process, a few atoms can appear closer to the step edges, as shown in line profile *C*-*C'*.

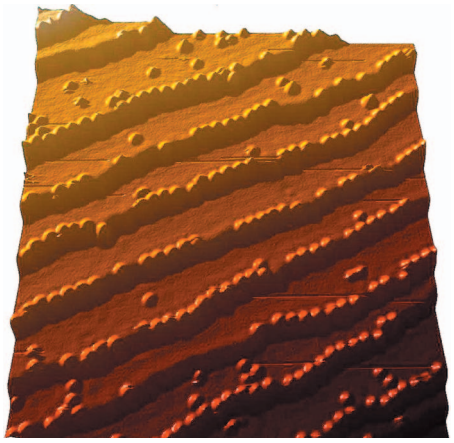

FIG. 3. (Color) The STM image of Fe atomic strings on a vicinal Cu(111) surface. The size is 40×40 nm^2 and the coverage is ≈0.008 MLE. Imaging condition: −0.8 V and 1 nA.

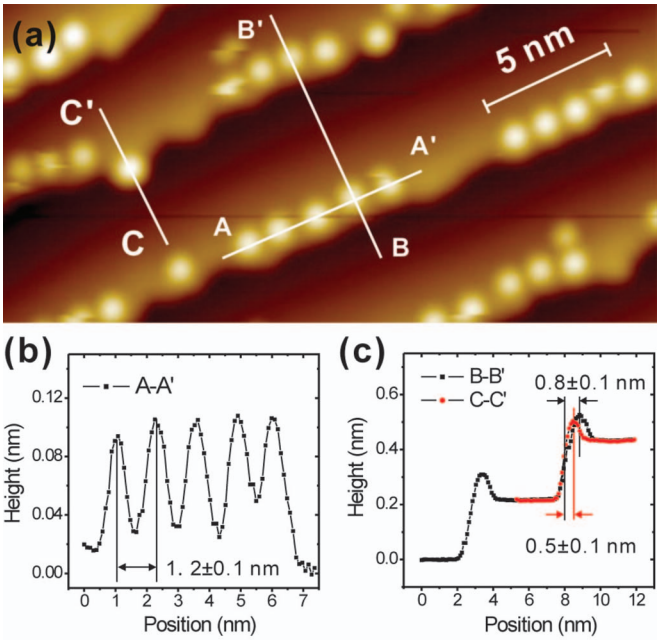

FIG. 4. (Color) (a) A zoomed-in image of Fig. 3. (b) and (c) are the line profiles along and perpendicular to the string directions as marked in (a).

These experimental results perfectly correspond to the theoretical scenario of adatom motion near steps. To provide clear evidence that a proposed mechanism of "bottom-up" self-organization is based on electronic interactions predicted by our *ab initio* studies (Figs. 1 and 2), we carried out the kinetic Monte Carlo (kMC) simulations[26] of the growth process of Fe on a stepped Cu(111) surface. The kMC simulations follow closely the experimental conditions. The effect of the long-range interaction on adatom diffusion is included

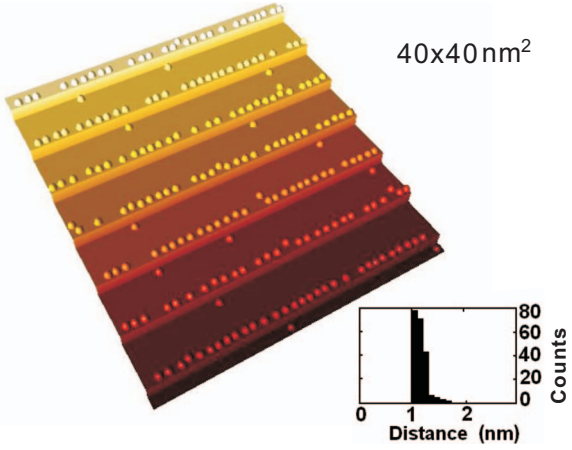

FIG. 5. (Color) The kMC simulations of the self-organization of Fe adatoms on a vicinal Cu(111) into atomic strings. Calculations are performed according to the experiments. The inset shows the statistics of the nearest-neighbor Fe-Fe separation along the step edges. It is centered in a narrow range around 1.2 nm.

in our simulations.[27–29] The results of kMC simulations shown in Fig. 5 nicely demonstrate the self-organization of Fe adatoms into atomic strings at the edge of the upper terraces. The distribution of the interatomic distances in strings (Fig. 5, inset) shows a pronounced peak around 1.2 nm, in good agreement with the experiment. The distance between strings and the step edge is found to be close to 0.8 nm. Results of our kMC simulations unambiguously prove that the surface-state-mediated interactions between adatoms and steps are the driving forces for the self-organization of atomic strings.

In conclusion, we have discovered a way to exploit surface-state electrons on stepped metal surfaces to create a well-ordered array of atomic strings at low temperatures. Our studies reveal that such 1D nanostructures are stabilized by surface-state-mediated long-range interactions. The universal nature of the underlying physics suggests that our bottom-up approach for an adatom self-organization may be of general importance for the growth of 1D nanostructures on different metal substrates supporting an electronic surface state.

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[1] D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).
[2] H. Röder, E. Hahn, H. Brune, J.-P. Bucher, and K. Kern, Nature (London) **366**, 141 (1993).
[3] F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, and W.-D. Schneider, Phys. Rev. Lett. **92**, 016101 (2004).
[4] J. V. Barth, G. C. Costantini, and K. Kern, Nature (London) **437**, 671 (2005).
[5] Y. Pennec, W. Auwärter, A. Schiffrin, A. Weber-Bargioni, A. Riemann, and J. V. Barth, Nat. Nanotechnol. **2**, 99 (2007).
[6] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Science **262**, 218 (1993).
[7] H. C. Manoharan, C. P. Lutz, and D. M. Eigler, Nature (London) **403**, 512 (2000).
[8] N. Nilius, T. M. Walls, and W. Ho, Science **297**, 1853 (2002).
[9] J. N. Crain and D. T. Pierce, Science **307**, 703 (2005).
[10] J. Lagoute, X. Liu, and S. Fölsch, Phys. Rev. B **74**, 125410 (2006).
[11] J. A. Stroscio and R. J. Celotta, Science **306**, 242 (2004).
[12] S.-W. Hla, K.-F. Braun, B. Wassermann, and K.-H. Rieder, Phys. Rev. Lett. **93**, 208302 (2004).
[13] N. Agraït, A. L. Yeyati, and J. M. van Ruitenbeek, Phys. Rep. **377**, 81 (2003).
[14] H. J. Elmers, J. Hauschild, H. Höche, U. Gradmann, H. Bethge, D. Heuer, and U. Köhler, Phys. Rev. Lett. **73**, 898 (1994).
[15] J. Shen, R. Skomski, M. Klaua, H. Jenniches, S. S. Manoharan, and J. Kirschner, Phys. Rev. B **56**, 2340 (1997).
[16] P. Gambardella, A. Dallmeyer, K. Maiti, M. C. Malagoli, W. Eberhardt, K. Kern, and C. Carbone, Nature (London) **416**, 301 (2002).
[17] J. Dorantes-Davila and G. M. Pastor, Phys. Rev. Lett. **81**, 208 (1998).
[18] M. Avellino, A. J. Fisher, and S. Bose, Phys. Rev. A **74**, 012321 (2006).
[19] J. Repp, F. Moresco, G. Meyer, K.-H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. **85**, 2981 (2000).
[20] V. S. Stepanyuk, A. N. Baranov, D. V. Tsivlin, W. Hergert, P. Bruno, N. Knorr, M. A. Schneider, and K. Kern, Phys. Rev. B **68**, 205410 (2003).
[21] M. L. Merrick, W. Luo, and K. A. Fichthorn, Prog. Surf. Sci. **72**, 117 (2003), and references therein.
[22] K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995).
[23] K. Wildberger, R. Zeller, and P. H. Dederichs, Phys. Rev. B **55**, 10074 (1997).
[24] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[25] Y. Mo, K. Varga, E. Kaxiras, and Z. Zhang, Phys. Rev. Lett. **94**, 155503 (2005).
[26] K. A. Fichthorn and W. H. Weinberg, J. Chem. Phys. **95**, 1090 (1991).
[27] K. A. Fichthorn, M. L. Merrick, and M. Scheffler, Phys. Rev. B **68**, 041404(R) (2003).
[28] N. N. Negulyaev, V. S. Stepanyuk, W. Hergert, H. Fangohr, and P. Bruno, Surf. Sci. **600**, L58 (2006).
[29] N. N. Negulyaev, V. S. Stepanyuk, L. Niebergall, W. Hergert, H. Fangohr, and P. Bruno, Phys. Rev. B **74**, 035421 (2006).