Formation of monatomic Fe chains on vicinal Cu(111) surfaces: An atomistic view

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Uniform arrays of monatomic Fe chains are realized on a vicinal Cu(111) surface with a regular step array. Deposited Fe atoms are first embedded into the flat Cu(111) terrace at precisely one-atom distance away from the *upper* edge of a monatomic surface step. The resulting Fe wires, in turn, serve as one-dimensional nucleation lines for the formation of monatomic Fe chains along the upper edges of the steps. The present results, obtained by scanning tunneling microscopy and interpreted with first-principles calculations, unambiguously establish the essential role of embedded Fe atoms as a precursor to monatomic wire growth. The Fe wires present an ideal testing ground for exploring ferromagnetism in the one-dimensional limit.

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One-dimensional (1D) condensed-matter systems display exotic physical properties that are often attributed to enhanced electron correlations, thermodynamic fluctuations, collective excitations, and the pivotal role of defects in low-dimensional systems.[1] For example, the predicted breakdown of Fermi-liquid theory,[2] or the possibility of establishing long-range magnetic order at finite temperatures,[3] are classic topics of recurring interest. With the advent of nanoscience, many concepts of quantum mechanics and statistical mechanics pertaining to low-dimensional systems can be explored at the nanoscale in real space. For instance, scanning tunneling microscopy (STM) has recently provided atomistic descriptions of competing orders and phase transitions in various quasi-1D systems;[4–7] most of these phenomena are intertwined with the local structure and electronic properties.[7]

Nature, unfortunately, rarely provides us with true 1D model systems. A very intuitive approach toward creating a *quasi*-1D system is to use a stepped surface as a template for atom wire growth. The basic idea is that lattice sites along a step edge are far more reactive than those on top of a flat terrace. Hence, deposited atoms should preferentially adsorb at the step edge, leading to nucleation and growth of an atom chain on the lower terrace, along the step edge. Indeed, quasi-1D metallic atom chains have been fabricated on, e.g., vicinal silicon surfaces but the metal atoms are generally incorporated into the terraces, not at the step edges, and often form complex surface reconstructions.[4,5,8] Step edge decoration appears a more viable approach for metal substrates.[9–12] For instance, highly uniform monatomic Co chains have been realized via step edge decoration of Pt(997) (Ref. 9).

The growth of Fe on Cu(111) is a notable exception to the prevailing picture of step edge decoration on metal surfaces. Here, contrary to intuitive expectations, Fe nucleates and grows along the *upper* edges of monatomic steps on vicinal Cu(111) (Refs. 10 and 13) leading to the formation of irregular stripes that are single-monolayer high and several atoms wide. Since this initial observation, an intensive effort has been devoted toward understanding the surprising occurrence of long-range ferromagnetism in such quasi-1D systems,[14–17] but to date the major limitation has been the lack of knowledge on the precise atomic structure as well as the formation mechanism of the Fe wires.

Very recently, density functional theory (DFT) calculations indicated a unique kinetic pathway toward the formation of single-atom-wide Fe wires on a stepped Cu(111) surface.[18] It was predicted that Fe atoms should be incorporated into the upper terrace via an intricate exchange process. In this process, Cu step edge atoms are initially displaced by the incoming Fe atoms but remain located at the lower edge of the step. This is the energetically preferred and kinetically most accessible configuration, regardless of whether the Fe adatom approaches the step edge from the upper or lower terrace. Accordingly, the embedded Fe atoms are located one lattice constant away from the step edge. It was furthermore predicted that embedded Fe atoms will capture other diffusing adatoms, thus providing an elegant explanation for the upper step edge decoration seen in experiments. It should be noted, however, that the experiments employed a rather high coverage of Fe (Refs. 10 and 13). Consequently, the embedded or hidden Fe wire, if present, would have escaped experimental detection. A convincing demonstration of the existence of the embedded atom wire is indispensable for achieving a microscopic understanding of the 1D ferromagnetism from first principles.

In this Brief Report, we report on the experimental realization of monatomic Fe chains on a vicinal Cu(111) substrate. Detailed STM investigations not only confirm the theoretically predicted[18] pathway involving the initial embedding and subsequent trapping of atop Fe atoms, but also elucidate a remarkable wire uniformity that only appears to be affected by the terrace size distribution of the vicinal substrate. The results represent a significant advance from a growth science perspective, leading to near perfect control of shape and uniformity. Furthermore, the highly ordered monatomic Fe wires in a nonmagnetic matrix as achieved here in principle provide an ideal testing ground for exploring magnetism in the 1D limit.

Experiments were performed in an Omicron ultrahigh-vacuum variable temperature STM. We used a nominally flat Cu(111) crystal and a vicinal Cu(111) substrate having a miscut by 4° toward the $[11\bar{2}]$ direction. The crystals were

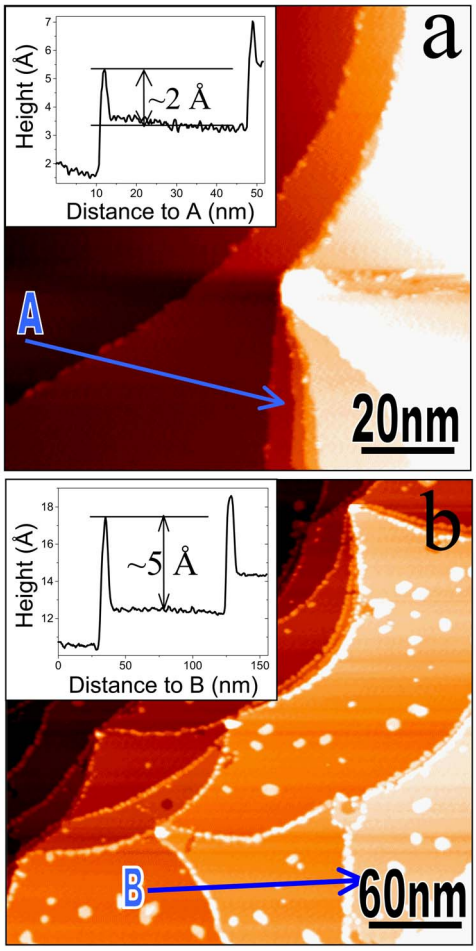

FIG. 1. (Color online) STM images of Fe on Cu(111) with different nominal coverages: (a) 0.03 and (b) 0.10 ML. The inset shows the line profiles of the nanowires across the step edges as indicated in the topographic images.

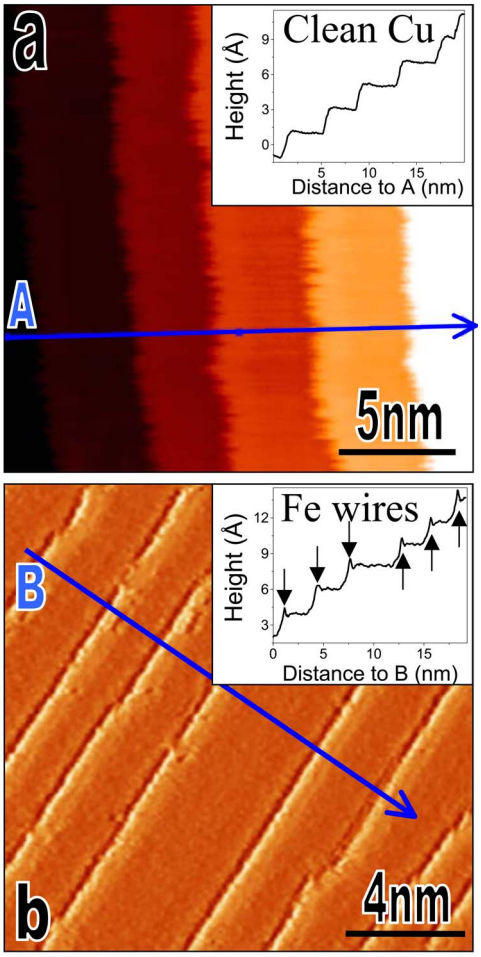

FIG. 2. (Color online) STM images (+30 mV/10 nA) of (a) clean vicinal Cu(111) surface at RT and (b) a Fe nanowire array on the vicinal Cu(111) surface at 60 K. The image in (b) is the first derivative of the topographic image. Insets (both from original images): line profiles showing the existence of monatomic steps on the surface. The arrows in (b) point toward small spikes in the step profile and indicate the presence of embedded Fe atom wires along the upper edges of the steps.

cleaned *in situ* by repeated cycles of Ne^+-ion sputtering and annealing at ~500 °C. The cleanliness of the surfaces was confirmed by low-energy electron diffraction and STM. Fe atoms were dosed onto a cold substrate (120 K) using an e-beam evaporator. The Fe flux was stabilized at ~0.05 monolayer per minute (ML/min). Following the Fe deposition, the sample slowly warmed to room temperature (RT) and was subsequently transferred onto a variable temperature STM stage.

Figure 1 shows a nominally flat Cu(111) surface with monatomic steps decorated by Fe. The Fe atoms line up along the upper edge of the step, forming continuous Fe nanowires with a rather uniform thickness. At low coverage, Fe atoms all nucleate along the upper step edge, forming a line of Fe atoms which protrude ~2 Å above the upper terrace, as shown by the line profile in Fig. 1(a). The Cu(111) terraces are atomically flat and there is no sign of Fe nucleation on the terraces. With increasing coverage, the Fe wires along the step edge continue to grow to a height of about ~5 Å, after which Fe also starts to nucleate on the terraces, as shown in Fig. 1(b). Evidently, there is a reasonably broad coverage window where Fe atoms exclusively nucleate along the step edge. This indicates the possibility of growing atomic Fe wires along the step edges in a highly controlled manner.

Next, we explore the feasibility of creating long and straight nanowires along the edges of a vicinal crystal. Figure 2(a) shows an STM image of the clean vicinal substrate. The line profile indicates monatomic steps (~2.08 Å) with sufficiently regular spacing between the steps. The average terrace width is ~3 nm (~14 terrace atoms), consistent with the nominal miscut angle of 4°. The imaging noise at the step edges originates from the fast kink diffusion on Cu(111) at RT (Ref. 19). Figure 2(b) shows a derivative image of the vicinal Cu(111) surface after depositing ~0.07 ML of Fe. The image reveals a set of parallel, ultrathin Fe nanowires with uniform thickness, orientation, and separation (~3 nm). The presence of Fe is also confirmed by the step line profiles, which consistently show a spike at the upper edge of every step; this spike is absent on the clean surface. From these line profiles, we can estimate the height and width of the atom wires: they are about ~4 Å wide and protrude

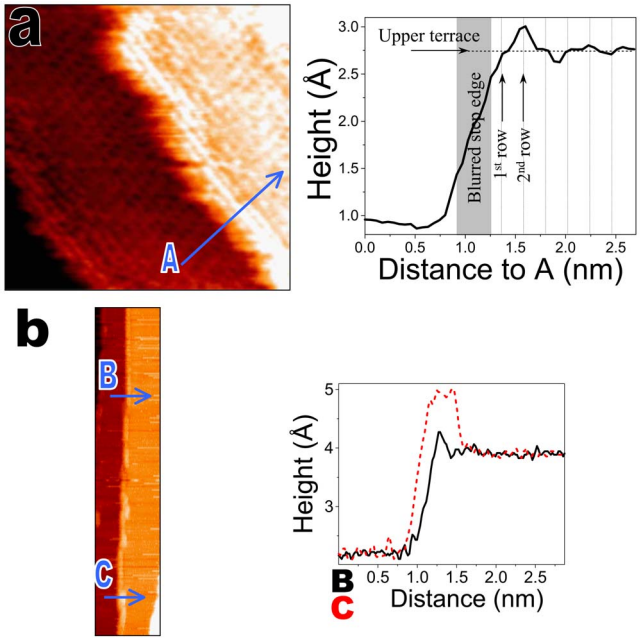

FIG. 3. (Color online) (a) Closeup view STM image (7 nm×7 nm, +1 V/5 nA) of a decorated Cu(111) step. The line profile on the right is an average of 10 line scans at different locations across the step edge. The vertical grid lines indicate the locations of the atoms in the upper terrace. The shaded zone corresponds to the blurred region in the STM topographic image. (b) STM image (4 nm×20 nm, +1 V/3 nA) of the decorated step edge for higher Fe coverage. Additional Fe atoms are attached to the upper edge of the step, thus enhancing the vertical corrugation. Line profiles B (solid line) and C (dashed line) correspond to embedded Fe and atop Fe, respectively.

about ~0.4 Å above the upper terrace. The image contrast is not only influenced by the local topography and electronic structure of the steps, but also by the shape of the W tip, especially at the step edges since the step height of W is comparable to that of Cu along the [111] direction (2.7 Å for W and 2.1 Å for Cu). Considering the fact that these protruding features are heavily convoluted by the structure and electronic structure of the STM tip, it is likely that these wires are indeed single-atom wires. In particular, the ~0.4 Å protrusion of such wires strongly suggests that they are embedded into the upper edge.

Figure 3(a) is a closeup atomic resolution image of the Fe decorated step edge, recorded at RT. The atomic resolution on the terrace allows us to precisely indicate the location of the Cu atom rows in the line profile of the step. The Cu rows are indicated by the vertical grid lines in the line profile diagram. The step edge appears rather blurred; the width of this blurred region is about two atom rows, as indicated by the shaded bar in the line profile diagram. Such blurring at a step edge is not unusual and could be due to the combined effects of tip shape, scanning, and/or kink diffusion. Attempts to obtain sharper images at low temperature were not successful due to instrumental limitations. The region of bright contrast, presumably indicating the location of the Fe atoms,[20] is clearly displaced away from the actual step edge. A visual inspection of the bright region in the topographic image may suggest that it is two atom rows wide. The line profile in Fig. 3(a), however, does show a distinct maximum at a location that is approximately two atomic distances away from the blurred step edge region. Its height protrudes at most 0.3 Å above the upper terrace.[21] Atoms that are located right at the step edge (i.e., indicated as the first row in the line profile diagram), appear to be at exactly the same height level as the Cu atoms on the flat upper terrace, suggesting that they are Cu atoms. The 0.3-Å protrusion in the second row is too small for an atop adsorbate. Instead, these observations [see, also, Fig. 2(b)] are fully consistent with the possibility of an embedded Fe atom, located at one atom distance away from the step edge. However, since the contrast in STM contains both geometrical and electronic contributions, and specifically contributions from the modified charge density near a step edge, we must verify the origin of the contrast, as done below based on first-principles calculations.

Figure 3(b) shows an image of a decorated step edge at a coverage slightly higher (~0.10 ML) than that of Fig. 2(b). The thickness and height of the wires are no longer uniform. The line profiles clearly distinguish between embedded Fe atoms (line profile along B) and atop Fe atoms (line profile along C). These observations are fully consistent with a scenario where the embedded Fe atoms trap additional atoms, which nucleate into an atop wire or an attached nanowire.

In order to elucidate the nature of the step edge contrast, we simulated the STM images and line profiles using DFT for different step geometries. The DFT results are obtained with the VASP code,[22] using the Perdew–Wang 1991 version of the generalized gradient approximation (PW91-GGA) (Ref. 23). Computational details and convergence checks are the same as those in Ref. 18. For the STM image simulations, we used the Tersoff–Hamann method[24] for a six-layer Cu slab with 144 atoms. Each terrace is 4×4 atoms in size. The bottom three layers are fixed at their respective bulk positions during the relaxation. A 4×2×1 mesh in the Brillouin zone of the supercell is used to sample the reciprocal space. The vacuum region separating slabs is equal to 10 Å.

Simulated STM images of the decorated step edges for the three step geometries considered in Ref. 18 are shown in Figs. 4(a)–4(c). To further determine whether the Fe wire is truly embedded away from the step edge, we also simulated the STM image for Fe atom locations at the lower edge of the step [Fig. 4(d)]. The clean Cu step shown in Fig. 2(a), the "buried" wire in Fig. 3(a), and the "attached" wire in Fig. 3(b) are nicely reproduced in Figs. 4(a)–4(c), respectively. On the other hand, the distinction between Figs. 4(b) and 4(d) requires special consideration. In both cases, there is a clear charge density protrusion at the location of the Fe atoms. However, compared to Fig. 4(d), Fig. 4(b) shows a small shoulder to the left of the Fe row, due to the presence of a Cu atom at the lower edge of the step. This shoulder is apparent in the line scan shown in Fig. 3(a). Also, the pronounced dip in the charge density contour at the location of the lower step edge in Fig. 4(d) is not present either in Fig. 4(b) or in experiment. The combined experimental and theoretical results thus overwhelmingly support the picture of initial embedding and subsequent attachment of monatomic Fe wires.

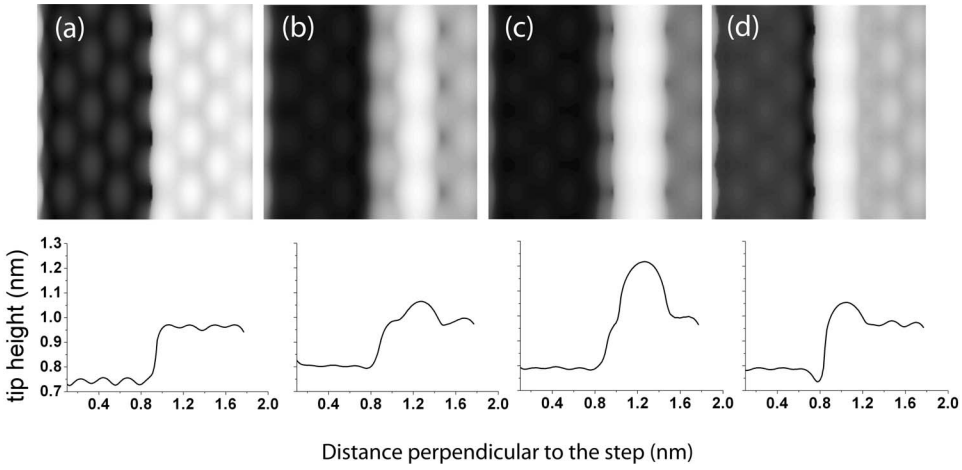

FIG. 4. Upper panel: simulated STM images for (a) a Cu(111) step, (b) a Cu(111) step with one row of Fe atoms embedded one lattice constant away from the step edge, (c) same as (b) except for the addition of an atop Fe wire, and (d) a Cu(111) step with one row of Fe atoms terminating the step. Lower panel: averaged tip height profiles for the corresponding configurations shown in the upper panels. These profiles are plotted along the direction perpendicular to the step and are averaged over 70 different line scans.

As an indication of the general nature of this intriguing growth concept, we have carried out first-principles calculations on the energetics and kinetics of different types of metal adatoms (Co, Cu, and Zn) on vicinal Cu(111) with the monatomic Fe wires embedded one lattice constant away from the step edges. We find that the atop position is at least a local energy minimum, regardless of the type of the adatoms. In particular, it is energetically most favorable for Co to reside on top of the embedded Fe wires, thereby opening the possibility of forming a well-ordered Co-Fe wire. Therefore, the Cu(111) stepped surfaces containing embedded Fe wires can be used as ideal templates for tailoring metal alloy wires with tunable chemical compositions and potentially intriguing magnetic and transport properties.

Before closing, we note that the enhanced stability of the embedded monatomic Fe wires might be attributed to the passivation and protection of the otherwise more reactive Fe atoms by the outer lines of Cu atoms. Specifically, the mechanism of embedding and passivation during the formation of the first Fe wire can be viewed as the 1D analog of related processes in two dimensions, in which an Fe or Co layer grown on Cu(100) is buried by an inert Cu layer upon annealing.[25–27] Precisely how the passivation modifies the magnetic properties of the embedded Fe wire remains a challenging issue for future studies.

In summary, arrays of monatomic Fe chains have been realized using a vicinal Cu(111) surface with a regular step array. Detailed STM investigations aided by DFT calculations firmly establish the initial embedding of Fe into the upper terrace and the subsequent trapping of atop Fe atoms, resulting in the formation of long atom wires along the upper edges of the steps. The atom wires are remarkably uniform and in principle present an ideal testing ground for exploring one-dimensional magnetism from first principles.

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