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Citation: Appl. Phys. Lett. **103**, 081608 (2013); doi: 10.1063/1.4819231
View online: http://dx.doi.org/10.1063/1.4819231
View Table of Contents: http://aip.scitation.org/toc/apl/103/8
Published by the American Institute of Physics

Spectroscopy of self-assembled one-dimensional atomic string: The role of step edge

Rongxing Cao, Zhangfeng Zhong, Jian Hu, Xiaopu Zhang, Bingfeng Miao, Liang Sun, Biao You, Di Wu, An Hu, Weiyi Zhang, and Haifeng Ding[a)]
National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, 22 Hankou Rd., Nanjing 210093, People's Republic of China

(Received 22 April 2013; accepted 12 August 2013; published online 23 August 2013)

Step-edge guided Gd one-dimensional atomic strings on Ag(111) surface are studied by scanning tunneling microscopy and spectroscopy at low temperature. Spectroscopy measurements show a characteristic peak, 65 meV above Fermi level in sharp contrast with tight-binding calculations of a string on a flat terrace. Good agreement can be obtained when the step edges are included in the calculations, revealing their roles on the electronic spectra of the self-assembled strings guided by step edges. The results are further confirmed by the spectroscopy study of Fe strings on a flat terrace and near step edges constructed by atomic manipulation. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819231]

Low dimensional systems are of special interests due to their rich physical properties and potential applications. Atomic manipulation through scanning tunneling microscopy (STM)[1–6] and self-assembly growth[7–13] are two main routes to fabricate the low dimensional structures at atomic scale. Atomic manipulation can build structures in arbitrary geometry, while self-assembly can provide well-ordered structures with relatively large area homogeneity and in an economic way. The low dimensional structures, especially the one-dimensional systems are believed to play important roles in future nanoscale electronic and magnetic devices. Previous theoretical studies revealed general features of electronic structure, magnetic properties, and interactions in one-dimensional nanostructures on metal surfaces.[14–18] The prototype device of nonvolatile information storage has been demonstrated in atomic chains due to the magnetic coupling.[6,11] Moreover, one-dimensional spin chains show strong potentials in quantum communications.[19–23] Especially, the magnetic atomic strings, where the atoms are separated by a fixed distance, are predicted to have both high speed and high fidelity in quantum information transfer.[20,21] The prototype device was recently demonstrated experimentally through the spin strings built by STM atomic manipulation.[22,23] One dimensional Fe atomic strings have also been self-assembled on vicinal Cu(111) surfaces.[13] Surface-state-mediated long-range interactions (LRI) and step-edge guiding were revealed to be the origin for stabilizing this unique one-dimensional atomic structure.[13,14] The electronic properties of the atomic strings, which are critical for their functionalities, however are not explored. This is in sharp contrast with the close-packed atomic chains which were intensively investigated.[4,24–27]

In this letter, we report on the scanning tunneling spectroscopy (STS) investigation of the spectroscopy of both self-assembled Gd strings and atomic manipulated Fe strings on Ag(111) surfaces. At the coverage of 1.0×10^{-3} monolayer equivalent (MLE), Gd atomic strings on the upper terrace and near the step edges are observed. The atomic string has a periodicity of 3.0 nm and stands 2.5 nm away from the step edges on the upper terraces. The differential conductance (dI/dU) spectra of this structure are measured and a characteristic peak above Fermi level (+65 meV) at the interatomic positions is observed. To understand the physical origin, we performed the tight-binding (TB) calculations for atomic strings on a flat terrace following the work by Ternes *et al.*[28] The calculated spectra however only yield a step-like function, in sharp contrast with the experimental findings. Good agreement can be obtained by including the step edges in the calculations, revealing their roles on the spectroscopy of the step-edge-guided one-dimensional atomic string. Moreover, we also studied the electronic property of Fe strings both on a flat terrace and near the step edges constructed by atomic manipulation. The TB calculations with the local environmental effects included can once again reproduce the experimental findings on both cases. Our findings demonstrate that the electron scatterings by both the adatoms of the string and step edges play important roles in the electronic spectra of the self-assembled strings guided by the step edges.

The experiments are performed in an ultrahigh vacuum chamber equipped with a low-temperature STM and a sputter gun. The base pressure is 2.0×10^{-11} mbar. The single-crystal substrate Ag(111) is cleaned by repeated cycles of argon ion sputtering (at 1.5 keV) and annealing (at 870 K). After that, the crystal is transferred into the STM stage and cooled down to 4.7 K. The clean surface with low impurity concentration is checked by STM. The sample can be cooled further down to 3.5 K by pumping liquid He in the cryostat. With a typical deposition rate of 0.002 monolayer/min, high-purity Gd and Fe are deposited utilizing electron beam evaporation onto the Ag(111) substrate in the STM stage at 6 K from thoroughly outgassed rods. Electrochemically etched and *in-situ* e-beam cleaned tungsten tips are used for the STM and STS measurements.[29] The bias voltage, U, refers to the sample voltage with respect to the tip. Spectroscopy measurements are performed via the modulation technique utilizing a 10-mV amplitude and 6.09-kHz frequency.

[a)]Author to whom correspondence should be addressed. Electronic mail: hfding@nju.edu.cn.

Figure 1(a) shows the typical image for 1.0×10^{-3} MLE Gd on Ag(111) obtained at 3.8 K. The scanning conditions are $U = 100$ mV and $I_t = 2$ pA. We find that Gd atoms form well-ordered atomic strings near the step edges on the upper terrace which are similar to Fe atomic strings on vicinal Cu(111) surfaces observed previously, where the surface-state-mediated LRI and the step guiding are revealed to be the driving force.[13,14] The interaction energy between step edges and adatoms on the upper/lower terrace is oscillatory with a period of half the Fermi wavelength of the surface state on substrates. At a proper temperature, the adatoms can easily overcome small repulsive barriers and be trapped in attractive potential wells of interactions with nearby step edges. The adatom moving further towards the step edge is repelled by much larger repulsive potentials existing both on upper and lower terraces with different strengths, which is induced by redistribution of the electron-charge density at step edges.[13,14,30] Adatoms captured near step edges are separated from each other driven by the Gd-Gd LRI,[31] forming the step-edge guided Gd one-dimensional atomic strings. We note that a few atoms also aggregate near the lower step edges (Mark A) and this indicates LRI between adatoms and step exists at both the upper and lower terraces near the step edges. The fact that most of the atomic strings are found near the step edges on the upper terrace is similar to the Fe on stepped Cu(111) surface where the interaction at the upper step is found to have deeper potential well.[13,14] This suggests that it could be a general behavior though more systems, including theory, should be explored to understand the basic mechanism. Moreover, a few single adatoms (Mark B) and locally hexagonal structures (Mark C) are found on the flat terrace. Because the single adatom and hexagonal structures with similar size are typically mobile at this temperature on a flat terrace without defect, we attribute this to the pinning effect induced by the substrate defects and subsequent aggregation near the pinned adatom driven by the Gd-Gd LRI.

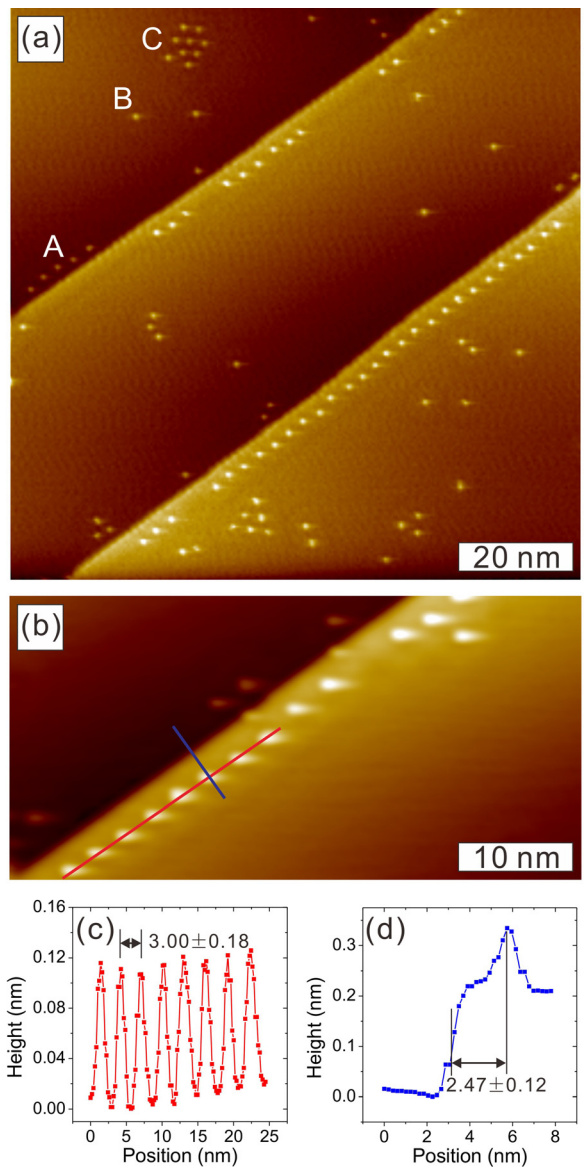

FIG. 1. (a) STM image of Gd atomic strings near the step edges of Ag(111) at 3.8 K (coverage = 1.0×10^{-3} MLE, $U = 100$ mV, and $I_t = 2$ pA). (b) A zoomed-in image of the atomic string. (c) and (d) are the line-profiles along and perpendicular to the string direction as marked in (b), respectively.

To obtain the quantitative information, line-profiles along and perpendicular to the string direction are made in a zoomed-in image, which are marked by red and blue lines, respectively [Fig. 1(b)]. The line-profile along the string direction shows that the nearest-neighbor Gd separation is 3.0 ± 0.2 nm [Fig. 1(c)]. This distance is consistent with the results of two-dimensional hexagonal superlattice and the Gd-Gd LRI discussed previously.[31] The line-profile perpendicular to the string direction shows that Gd adatoms are 2.5 ± 0.1 nm away from the step edge [Fig. 1(d)]. This indicates the interaction between Gd adatom and step edge has an attractive minimum around 2.5 nm. Understanding the spatial distribution of the attractive minimum may require more theoretical inputs, such as the first principle calculations.[13,14]

After obtaining the topographic information of Gd atomic string, we perform low-temperature STS measurements to reveal the characteristic electronic properties of this self-assembled structure. The scanning conditions are $U = 150$ mV and $I_t = 0.5$ nA. As a reference, we first take dI/dU spectra on the clean and wide Ag(111) terrace to check the tip's condition. The surface-state band that starts at about 67 meV below E_F is clearly observed (not shown), which is in good agreement with previous findings.[32] Due to the tip-induced adatom motion, the dI/dU spectra on top of Gd adatoms are not very well reproducible. Therefore, we focus our study on the dI/dU spectra obtained at the center of two neighboring adatoms in a string, shown as red triangles in the upper panel of Fig. 2(a) [Location of taking spectra is indicated by the cross in the inset]. And we find that the local density of states (LDOS) shows a peak at approximately 65 meV above E_F. We note that unoccupied electronic states were also observed in previous STS results of close-packed one-dimensional chains.[4,24–27]

To understand the experimental results, we performed TB calculations similar to previous study in Ce/Ag(111).[28] The TB Hamiltonian is described as follows:

$$H = t\sum_{n.n.} |i\rangle\langle j| + \sum_{i} (\varepsilon_0 + V_i)|i\rangle\langle i|, \qquad (1)$$

where t is the isotropic hopping integral, ε_0 is the on-site potential of the bare Ag(111) lattice, and V_i describes the correction to the on-site potential induced by Gd adatoms or steps. We take $t = -0.75$ eV and $\varepsilon_0 = 4.437$ eV to reproduce

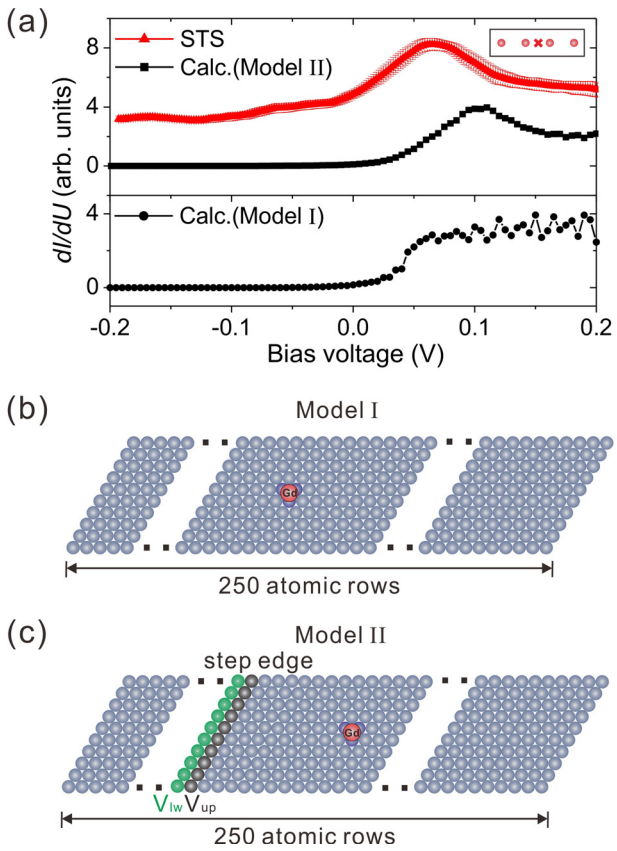

FIG. 2. (a) Upper panel shows the experimental dI/dU spectra (red triangles) and the tight-binding calculated LDOS (black rectangles) using Model II of the Gd atomic string. The dI/dU spectra are measured at the position indicated by the cross in the inset. Lower panel shows the calculated spectra of the Gd atomic string using Model I. The experimental results have been shifted vertically for clarity. (b) Model I: atomic string on a flat terrace (10×250 unit cell). (c) Model II: atomic string near a step edge (10×250 unit cell). The upper and lower step edges are modeled as two Ag atomic rows whose on-site potentials are V_{up} (black spheres) and V_{lw} (green spheres), respectively.

the onset energy and the effective mass of Ag(111) surface states.[32] The local V_i is set to be V_{nn} at the three nearest-neighbor Ag atoms supporting the Gd adatom and 0 elsewhere in each unit cell. We use a 44×44 unit cell to adjust V_{nn} to reproduce the phase shift δ_0 of Friedel oscillations [$(0.43 \pm 0.02)\pi$ for Gd[31]]. And V_{nn} is found to be -1.7 ± 0.2 eV. We further check the feasibility of the calculations by comparing the TB calculations and experimental results of Gd hexagonal superlattice on Ag(111)[31] as the method has been well demonstrated on Ce similar structure on Ag(111).[28] The calculated dI/dU spectra at the center of the triangle formed by three Gd adatoms in the well-ordered superlattice show a peak at approximately 100 meV above E_F which is similar to the peak found in Ce/Ag(111).[28] As discussed by Ternes *et al.*,[28] the STM tip may induce the hexagonal lattice constant increasing during the measurements, so we also make calculation with slightly larger lattice constant (11×11 instead of 10×10 unit cell). The results yield a peak around 65 meV, in excellent agreement with the experimental value of 70 meV.

The good agreement in hexagonal superlattice evidences that the feasibility of the calculations in this system and the parameters are properly chosen. Then we use 10×250 unit cell to describe the atomic strings [Model I in Fig. 2(b)]. The atomic strings have an interatomic separation of about 3.0 nm and are separated by more than 60 nm from each other in this model. So, they can be considered as isolated strings. Gd and Ag atoms are indicated by red and gray spheres, respectively. Due to the different on-site potentials, the three nearest-neighbor Ag atoms supporting the Gd adatom are indicated by dark blue spheres. The calculated LDOS based on Model I is plotted as black circles in the lower panel of Fig. 2(a) and it shows a curve with a step shape which is in sharp contrast with the experimental finding.

By comparing Model I with the detailed experimental geometry of Gd atomic string, we realize that the step edge may play an important role. Therefore, the step edge is introduced to make the model closer to the actual environment of the strings [Model II in Fig. 2(c)]. The upper and lower step edges are modeled as two Ag atomic rows whose on-site potentials are V_{up} and V_{lw}, respectively. This will add a phase shift to the scattered electron wave function near the steps. These two potentials are determined to be $V_{up} = +0.6$ eV and $V_{lw} = -0.6$ eV to best reproduce the dI/dU oscillation near Ag(111) step edge revealed by STS.[32] Then the TB calculations are performed and the calculated LDOS based on Model II shows a peak around 100 mV with a similar shape to the experiments [black rectangles in the upper panel of Fig. 2(a)]. This agreement verifies the important contribution of the step edges to the spectroscopy of self-assembled atomic string. The slight difference in peak position may come from the tip-induced lattice enlargement of Gd string similar to that in Gd superlattice discussed above.

To further confirm the role of the step edge, we also measure the spectroscopy of the isolated atomic string on a flat terrace experimentally to see whether it is consistent with the calculated result from Model I. Gd atoms cannot form a good atomic string naturally on a flat terrace because the hexagonal arrangement is energetically more favorable. Instead of Gd, we build an isolated atomic string with Fe atoms by atomic manipulation with the method described previously.[33] Fe atoms have higher diffusion barrier than Gd adatoms[34] and they are immobilized after positioning at 4.7 K. And we note that the calculated results for Fe string are similar to self-assembled Gd atomic string because their on-site potentials are close to each other.[31,33] Figure 3(a) shows the STM image of the Fe atomic string on a flat terrace of Ag(111). It has the same average periodicity of 3.0 nm as the self-assembled Gd atomic strings in Fig. 1. The experimental dI/dU spectra (red triangles) and TB calculated LDOS (black rectangles, based on Model I) of the isolated string are shown in Fig. 3(c). The experimental results indeed have a step-shape and agree well with the theoretical prediction except for the peak around -280 meV and surface state of Ag(111) which is not suppressed. We attribute the exception to the simplicity of the effect of adatom's potential on Ag electrons. The agreement in the isolated atomic string further confirms the feasibility of the calculations and indicates the importance of the detailed experimental geometry, i.e., the step edge near the self-assembled string in Fig. 1.

Moreover, we also built the Fe atomic string near the step edge of Ag(111) by atomic manipulation [Fig. 3(b)] to verify the step contribution in this different system. It has the

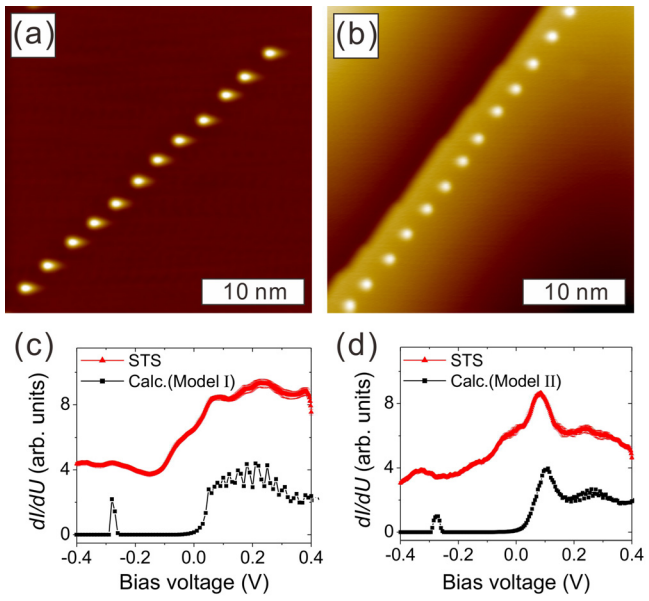

FIG. 3. STM images of the Fe atomic strings on a flat terrace (a) and near the step edges (b) of Ag(111) at 4.7 K ($U = -1$ V and $I_t = 1$ nA). They have the same average periodicity. The string near the step edges has the same separation from step edges as the self-assembled Gd atomic strings. The experimental dI/dU spectra (red triangles) of strings in (a) and (b) and their tight-binding calculated LDOS (black rectangles) using the Models I and II in (b) and (c) of Fig. 2, are presented in (c) and (d), respectively. The experimental results have been shifted vertically for clarity.

same interatomic periodicity and distance from step edge as the self-assembled Gd atomic strings. The experimental dI/dU spectra at the center of two neighboring adatoms in a string [red triangles in Fig. 3(d)] have the similar feature to Gd strings and show a slightly larger peak around 85 meV. The calculated LDOS based on Model II shows a peak around 100 mV with a similar shape to the experiments [black rectangles in Fig. 3(d)] and it agrees with the experiment with the same exception as the isolated Fe string. Comparing the Gd and Fe atomic strings near the step edge, we find that the experimentally spectroscopic peak in the Gd string has larger deviation from the calculation despite their similar calculated LDOS. This can be understood, as the diffusion barrier of Gd is a factor of 6 smaller than that of Fe on Ag(111). In such case, a larger tip-induced lattice distortion is expected. The comparison of Fe strings on the flat terrace and near the step edges further evidences that the scattering of Ag(111) surface-state electrons by both the atoms of the strings and nearby step edges should be considered for the self-assembled string system guided by the step edges.

In summary, in a joint effort of both experiments and theory, we explore the spectroscopy of the self-assembled Gd atomic strings and Fe atomic strings created by atomic manipulation on Ag(111) surface. Quantitative analysis reveals that the nearest-neighbor Gd separation is about 3.0 nm and the atomic string resides on the upper terraces with a distance of 2.5 nm away from the step edge. Scanning tunneling spectroscopy measured in this self-assembly structures shows a characteristic peak above Fermi level. By performing TB calculations and comparing the spectra of Fe strings on a flat terrace and near the step edges constructed by atomic manipulation, we find that the peak is originated from the combined electronic scattering processes by the atoms in the string and the nearby step edges. The findings demonstrate that the local environment of the low dimensional structures should be considered in their electronic property exploration.

This work is supported by the State Key Program for Basic Research of China (Grant Nos. 2010CB923401 and 2010CB923404), NSFC (Grant No. 11023002), NSF of Jiangsu (Grant No. BK2012300) and PAPD.

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