Anomalous temperature dependence of antistripe width in the annealing of submonolayer Fe on Ru(0001)

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(Received 16 December 2010; published 2 May 2011)

Utilizing scanning tunneling microscopy, we investigate the coverage- and temperature-dependent morphology evolution of submonolayer Fe on Ru(0001) near the surface alloying temperature. Submonolayer Fe deposited on Ru(0001) at room temperature grows in the three-dimensional island format. The morphology is investigated after annealing at various temperatures. With annealing around 900 K, large compact islands are divided into small pieces by triangular vacancy islands and labyrinthine antistripes. The width of the antistripes increases with increasing temperature, in sharp contrast with other systems where the opposite behavior was commonly found. The observed anomaly can be attributed to simultaneous surface alloying and amorphization during the annealing process.

DOI: 10.1103/PhysRevB.83.193402 PACS number(s): 68.37.Ef, 05.65.+b

I. INTRODUCTION

In a heteroepitaxial system, surface stress exists due to the lattice mismatch between the film and the substrate. The surface stress can have strong influence on the growth of the film. Interestingly, in some systems, it can lead to the formation of various two-dimensional patterns, including dots, antidots, stripes, and antistripes, etc.[1–8] In addition to their fundamental interest, these patterns in principle offer a way to control the structure and hence functionality of surfaces such as self-assembled templates and heterogeneous catalysis.[9] The domain patterns arise from the competition between the short-range interatomic attractive interaction, which leads to phase boundary energy, and the long-range dipolar repulsive interaction between two phases due to the different surface stress. Phase boundary energy coarsens the domain while elastic interaction refines it. The balance of the competition often leads to self-organized patterns or patterns with particular sizes. For regular domain patterns due to the surface stress effect on solid surfaces, an analytical theory for the feature size has been proposed.[10–12] For more complicated patterns, kinetic simulations were required.[5–8]

Typically, the phase boundary free energy decreases with increasing temperature and the stress has little temperature dependence. Therefore, in systems with stripe patterns, the width of the stripe generally decreases with increasing temperature. For instance, in Au on W(110), de la Figuera *et al.*[3] found that the temperature-dependent stripe width follows this trend and the experimental results are in good agreement with the theoretical calculation near the two-dimensional critical points. The authors further predicted its general validity for immiscible systems of adlayer and substrate. In Pd on W(110), Menteş *et al.*[4] found that stripes behave according to the scaling laws for the two-dimensional Ising model with increasing temperature in a wide temperature range. In some systems, the adlayer can also intermix with the substrate and form a surface alloy. Interestingly, two-dimensional patterns were also found in such surface alloy systems.[1] In the PdCu/Cu(111) system, Plass *et al.*[13] found that the temperature-dependent stripe width follows the same rule as in immiscible systems. The chemical composition of the alloy as well as the surface stress in this particular system was found to have little temperature dependence.[2,14] When there is a strong temperature-dependent surface alloying process, the surface alloy can reduce the stress and at the same time the interatomic attractive interaction. In such a case, the temperature dependence can be rather different. When Fe is deposited on the Ru(0001) substrate, there is about 8.3% tensile lattice mismatch, which gives rise to large surface stress and very likely two-dimensional patterns. It was reported that Fe can mix with the Ru(0001) substrate through random exchange when the annealing temperature is higher than 700 K.[15] So it could be a candidate to study the temperature dependence of the two-dimensional patterns formed by surface alloys.

In this work, we use scanning tunneling microscopy (STM) to study the coverage- and temperature-dependent morphology evolution of submonolayer (sub-ML) Fe on Ru (0001) near the surface alloying temperature. Sub-ML Fe deposited on Ru(0001) at room temperature grows in the three-dimensional island format. The morphology is investigated after annealing at various temperatures. With annealing around 900 K, large compact islands are divided into small pieces by triangular vacancy islands and antistripes. The orientation of the triangular vacancy islands is related to the type of underlying stacking layer. Surprisingly, we find that the width of the antistripes increases with increasing temperature, in sharp contrast with other systems where the opposite behavior was commonly found. This anomaly is found to be related to a strongly temperature-dependent surface alloying and amorphization process.

II. EXPERIMENT

The experiments are carried out in an ultrahigh-vacuum (UHV) chamber which is equipped for STM and Auger spectroscopy. The base pressure is 4×10^{-11} mbar. The single-crystal substrate Ru(0001) is cleaned by repeated cycles of Ar^+ sputtering and flash annealing to 1400 K in an atmosphere of 4×10^{-7} mbar O_2. After that, the substrate is flash annealed to above 1600 K under UHV conditions to remove the residual oxygen completely. The clean surfaces with low impurity concentration are checked by STM. Sub-ML Fe is deposited by means of electron beam evaporation onto the Ru(0001) substrates from a thoroughly outgassed Fe rod with a typical rate of deposition 0.2 ML/min. The deposited samples are annealed *in situ* for 5 min and further investigated by STM at room temperature. We do not find any apparent difference when the annealing time is extended to 15 min. Electrochemically etched tungsten tips are used for the STM measurements. The bias voltage V_s refers to the sample voltage with respect to the tip. The STM images are typically obtained on several different spots on the same sample and the measurements are repeated for each temperature.

III. RESULTS AND DISCUSSION

We first investigate the growth of sub-ML Fe on Ru(0001) deposited at room temperature. Figure 1(a) shows a typical morphology of 0.5 ML Fe on Ru(0001). The image shows mainly three-dimensional islands consisting of two layers, which agrees with the previous study by Liu and Bader.[16] The Fe islands have average size of 10 nm. To explore the strain relaxation, we further obtain high-resolution images on the first and second layers. Figure 1(b) represents the atomic image of the first layer, showing that it has (1×1) commensurate structure despite the large 8.3% lattice mismatch between Fe and Ru. This suggests that the interaction between the first Fe layer and the Ru substrate is strong. The amplified image on the second Fe layer, Fig. 1(c), shows that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction (marked by the white circle) occurs in the center of the second layer. This can be understood as the surface reconstruction releasing the stress[17] and it most likely first appears at the position with the largest stress, which is typically located at the island center.[18]

As the surface-stress-induced patterns can be different for different coverage,[1,3] we prepare samples with different coverages and image their topography after annealing at around 880 K. Figures 2(a) and 2(b) show the overview and the amplified image for the coverage of 0.3 ML. One can see that the double-layer islands are mainly transformed into a single layer and become triangular vacancy islands, and around 10-nm-wide serpentine stripes. The temperature evolution

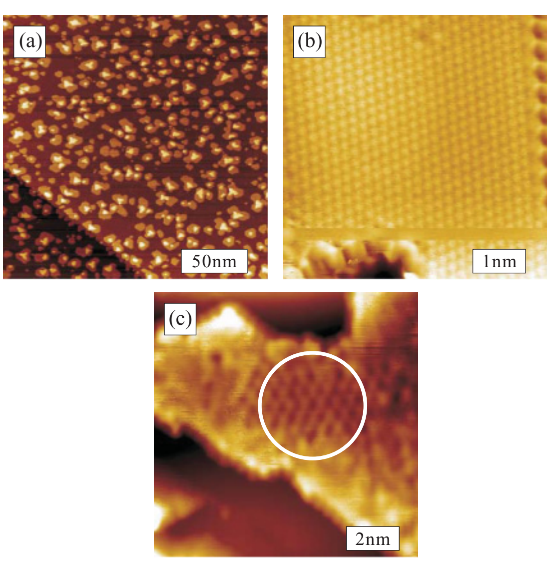

FIG. 1. (Color online) (a) STM images of 0.5 ML Fe on Ru(0001) deposited at room temperature. (b) Atomic-resolution image of the first Fe layer. (c) High-resolution image of the second Fe layer.

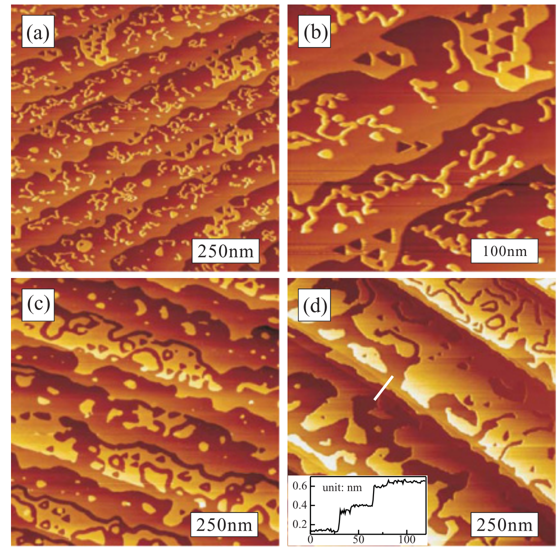

FIG. 2. (Color online) STM images of sub-ML Fe on Ru(0001) deposited at room temperature after annealing at about 880 K. The coverages in (a), (c), and (d) are 0.3, 0.5, and 0.7 ML, respectively. (b) Zoomed-in image for the coverage 0.3 ML. Inset in (d) is a line profile across a Ru step edge at the position marked by the white line.

of the double-layer to a monolayer structure has recently been discussed in the Ru/Pt(111) system.[19] We find that the triangular vacancy islands on the same terrace have the same orientation while vacancy islands at nearest-neighbor terraces always have opposite orientations. The edges of the triangular vacancy islands align along one type of the close-packing crystalline directions. This may be due to the large energy difference between the two types of close-packing edges[20,21] and the stress relaxation in the substrate and adlayer.[22] At the coverage of 0.5 ML, the morphology is different as shown in Fig. 2(c). There are only a few stripes. Instead, the patterns are mainly formed by antistripes, vacancy islands, and islands which are circled by antistripes. We also find that most of the antistripes share a similar width, indicating a kind of self-organization. The antistripes are randomly orientated forming labyrinthine structures. Figure 2(d) shows the typical morphology obtained at the coverage of 0.7 ML. One can see that the pattern mainly contains antistripes with similar widths besides a few triangular vacancy islands. The triangular vacancy islands have the same orientation in the whole image, in contrast with the alternating orientation for neighboring terraces found at 0.3 and 0.5 ML. When we take a closer look on the image, we find that almost all the steps twin together. The inserted line profile across the step edge shows that one type of the Ru hcp stacking narrows down to about 40 nm and the other expands to about 300 nm. As the vacancy islands do not show up in the the narrower terrace, the dominance of the one stacking results in the same orientation of the triangular vacancy islands in the whole image. The detailed mechanism for the step twinning is unclear at present. We find that the vacancy islands can have different orientations if we repeat the same experiments and statistically both orientations appear with almost the same probability.

To investigate the temperature dependence of the width of the antistripes, we anneal the samples at different temperatures

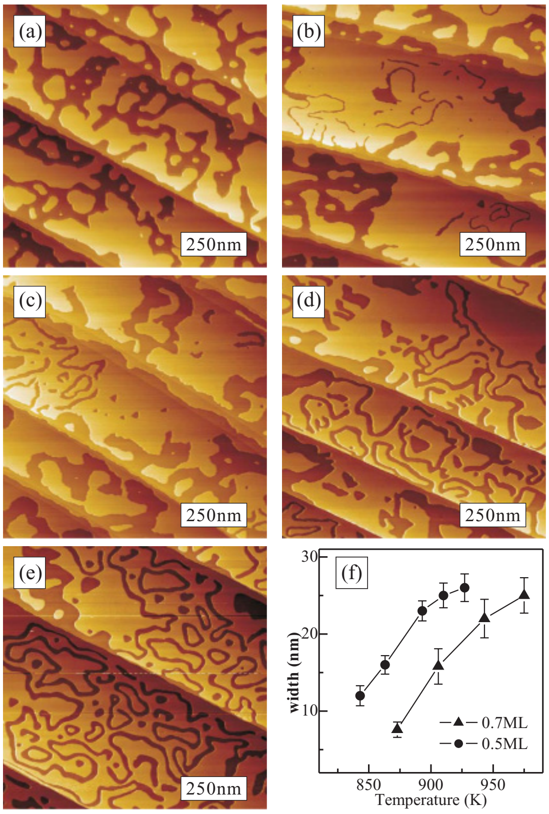

FIG. 3. (Color online) STM images of 0.7 ML Fe on Ru(0001) annealed at 837 (a), 873 (b), 910 (c), 943 (d) and 975 K (e) separately. The temperature-dependent width of the antistripes is shown in (f).

for a fixed coverage. Figures 3(a)–3(e) show the morphology evolution of about 0.7 ML Fe on Ru(0001) after annealing at gradually increasing temperature. During the annealing process, no apparent coverage change is found. Figure 3(a) shows the image of the sample annealed at 837 K. It shows large compact islands with average diameter about 200 nm, which is different from the morphology after deposition at room temperature. This change of the morphology is due to the increment of the diffusion constant and decreasing numbers of stable nucleation centers with increasing temperature. As the island expands, the stress built between the substrate and adlayer also increases. The strong stess can cause large compact islands to repel each other when they are close. At about 873 K, some thin antistripes appear as shown in Fig. 3(b). The antistripes share a common width of about 10 nm and they are winding around. With further increase in the annealing temperature step by step, Figs. 3(c)–3(e), one can see that more and more vacancy islands and antistripes appear. Some of them become ring shaped but branching and crossing of antistripes is rarely found. Surprisingly, we find that the antistripe width increases with increasing temperature, which is in sharp contrast with other systems where the opposite behavior is commonly found.[3,4,13] To quantify the temperature dependence of the antistripe width, we average the width of the antistripes and plot the results in Fig. 3(f). We find that at both coverages, 0.5 and 0.7 ML, the antistripes widen with increasing temperature, suggesting it is not the property of a special coverage but the general character of the Fe on Ru(0001) system. As in the ML region Fe starts intermixing with the Ru substrate at around 700 K,[15] we suspect that this anomaly is related to the surface alloy and amorphization; in particular, they could be temperature dependent.

From the analytical theory,[10,11] the size of the elastically stabilized stripes and antistripes can be described by $l = 2\pi a e^{C_1/C_2+1}$, where a is the microscopic cutoff length at the scale of the lattice constant, C_1 is the free energy of the stripe boundary, and C_2 is the energy gain in the elastic relaxation due to the formation of stripes. In an immiscible system, C_1 was found to decay linearly with increasing temperature due to the increase of entropy[2,23] and C_2 is almost temperature independent. This leads to a stripe width decrease with increasing temperature, which has been verified experimentally.[3,4] When the adlayer intermixes with the substrate, the surface stress can be released and C_2 is no longer a constant. Instead it decreases with the release of the surface stress. When the intermixing is temperature dependent, C_2 is also temperature dependent. The intermixing can also influence C_1 as it can change the entropy chemically and structurally. As discussed above, the feature size is determined by the ratio of C_1/C_2. When C_2 decreases faster than C_1 does, the ratio can increase with increasing temperature. In this case, widening of the width of the stripes and antistripes with increasing temperature can be found.

To elucidate the temperature-dependent surface alloying, we also scan images at small scale. Figure 4(a) is a high-resolution STM image near the step after annealing at 873 K. The inserted white dashed lines show the positions of the Ru step edges. The epitaxial adlayer can be easily distinguished from the Ru substrate due to their apparent height difference [see also the inserted line profile in Fig. 2(d)]. We find that the surfaces of the adlayers adjacent to the Ru step edges become rough, suggesting that the Fe atoms intermix with Ru atoms and form amorphous structures. We also performed atomic-resolution imaging on both the exposed Ru substrate

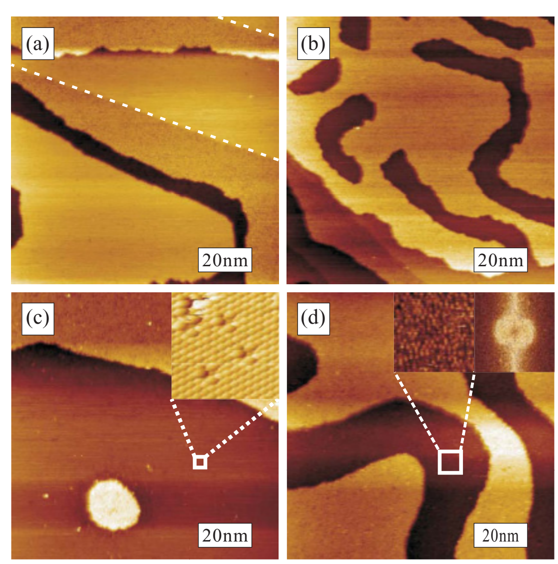

FIG. 4. (Color online) STM images of 0.7 ML Fe on Ru(0001) annealed at 873 (a), 910 (b), 943 (c), and 975 K (d). Insets in (d) show the amplified image and its corresponding Fourier transform (from center to edge is 5 nm^{-1}).

and the adlayer isolated from the Ru steps and found that the surfaces are well-ordered (1 × 1) structures. These suggest that the alloy initially only occurs near the Ru step edges. This can be understood as showing that the Fe atoms in the adlayer adjacent to the Ru step edge and the Ru atoms on the upper terrace are on the same atomic terrace; the Fe and Ru atoms do not require extra energy to jump to a different terrace for intermixing. Therefore, intermixing occurring at the Ru step edges is energetically most favorable. This observation is consistent with the results on the Ag/Pt(111) (Ref. 24) and Ni/Cu(111) (Ref. 25) systems. We also note that this process was not observed in the Pt/Ru(0001) (Ref. 26) and Pd/Ru(0001) (Ref. 27) systems. After intermixing at the Ru step edges, the maximum stress should appear at the isolated pure Fe adlayers, especially the large adlayers. These most likely could be the places for the next step in intermixing. Indeed, we find that all the adlayers become rough when the annealing temperature is increased up to 910 K, as shown in Fig. 4(b). The surface roughness of the isolated adlayer is almost the same as that of the adlayer adjacent to the Ru step edges. With increase in the annealing temperature further to 943 K, we find that the surface at the isolated island periphery becomes rough as well, suggesting that interchange mixing continues at the island periphery, as shown in Fig. 4(c). The inset figure shows the atomic-resolution image of the Ru surface about 30 nm away from the Fe-Ru alloy islands. It shows that most of the surfaces are ordered (1 × 1) structures and the intermixing only appears at a few spots. Figure 4(d) shows the image at the same scale after annealing at 975 K. We find that the surfaces on the antistripes also become rough, as shown in the inset amplified image and its corresponding Fourier transform. The missing sharp spots in the Fourier transform suggest that all the topmost layer is intermixed and becomes amorphous in order to reduce the stress. From Figs. 4(a)–4(d), we can conclude that the intermixing of Fe on Ru(0001) continues in the broad temperature range that we explored. This will lead to a continuous decrease of the surface stress and therefore a constant C_2. Due to the complex nature of the intermixing, a quantitative study of the temperature-dependent C_2 is difficult. The simultaneous observation of the anomalous temperature-dependent antistripe width and the broad temperature-dependent intermixing, however, suggests a strong link between these two phenomena; in particular, the intermixing and amorphization apparently would reduce the surface stress. We note that the temperature-dependent feature size of Fe/Ru(0001) is different from that in the PdCu/Cu(111) system.[1,13] In PbCu/Cu(111), the system consists of an alloy coexisting with pure Pb on the same atomic plane. Annealing does not change the composition of the alloy, nor does it change the fractions of clean Pb and of the alloy.[14] These facts lead to a weak temperature dependence of the surface stress, as confirmed experimentally.[2] In Fe/Ru(0001), both the composition and the surface structure change with temperature. In this case, a strong temperature dependence of the surface stress is expected.

IV. CONCLUSION

In this paper, we present a study of the coverage- and temperature-dependent morphology evolution of sub-ML Fe on Ru (0001) near the surface alloying temperature by scanning tunneling microscopy. Sub-ML Fe deposited on Ru (0001) at room temperature grows in the three-dimensional island format. The morphology is investigated after annealing at various temperatures. After annealing around 900 K, large compact islands are divided into small pieces by triangular vacancy islands and antistripes. The orientation of the triangular vacancy islands is related to the type of the underlying stacking layer. The width of the antistripes increases with increasing temperature, in sharp contrast with other systems where the opposite behavior was commonly found. We find that this anomaly is accompanied by a strong temperature-dependent surface alloying and amorphization process. As the surface alloying and amorphization can effectively reduce the surface stress, the temperature dependence of the surface stress may overcome the change of the phase boundary energy, which leads to this anomalous effect.

ACKNOWLEDGMENTS

This work is supported by NSFC (Grants No. 10834001, No. 10874076, No. 10974087 and No. 11023002), and the State Key Programme for Basic Research of China (Grants No. 2007CB925104 and No. 2010CB923401).

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