

Epitaxy controlled by self-assembled nanometer-scale structures

T. M. Parker, L. K. Wilson, and N. G. Condon

Interdisciplinary Research Centre in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom

F. M. Leiblsle*

*Interdisciplinary Research Centre in Surface Science, University of Liverpool, Liverpool L69 3BX, United Kingdom
and Department of Physics, University of Missouri-Kansas City, 1110 E. 48th Street, Kansas City, Missouri 64110*

(Received 19 May 1997)

We demonstrate how periodic arrays of islands consisting of an atomic nitrogen-induced reconstruction of the Cu(100) surface can be used to direct and control the shapes and distributions of islands of epitaxially grown Fe and Cu. This has resulted in the selective creation of either arrays of nanometer-scale stripes or two-dimensional periodic arrays of islands. [S0163-1829(97)03535-2]

The controlled fabrication of nanometer-scale structures is a tremendous challenge. Interest in such structures comes from both the desire to create and understand the properties of “quantum dots”¹ and similar scale magnetic structures.² Techniques for creating these structures are limited, those based on scanning probe microscopies are limited both by the difficulty and the time required to create structures over macroscopic distances.^{3,4} There is, therefore, a motivation to find systems where nanoscale structures self-assemble. No guarantee, however, exists that such systems will have the properties that are desired. It is therefore important to find self-assembled systems that can then be used as templates to create desirable structures.

In this paper, we demonstrate how one such self-assembled template can be used to create a family of structures. We have studied how periodic arrays of islands consisting of an atomic nitrogen-induced surface reconstruction of the Cu(100) surface can be used to channel the epitaxial growth of transition metals (Cu/Fe) to form narrow 5-nm-wide metal lines or two-dimensional periodic arrays of Cu/Fe islands depending on the initial nitrogen coverage. In itself, N on Cu(100) may not seem interesting, however, transition-metal growth, particularly Fe and Co on the Cu(100) surface, has been extensively studied because of the interest in magnetic layers and the fcc-bcc growth transition.⁵⁻⁸ Similarly there is also interest in the magnetic properties of 3d metal clusters on surfaces.⁹

These experiments were performed in a conventional ultrahigh-vacuum (UHV) chamber equipped with a commercial room-temperature Omicron Vakuumphysik scanning tunneling microscope (STM). The Cu(100) surfaces were cleaned using cycles of argon-ion bombardment followed by annealing to 720 K. Nitrogen deposition was performed by bombarding the surface with 500-eV nitrogen ions followed by annealing (for details, see Ref. 10). Cu and Fe were deposited onto the surfaces using electron-beam heated evaporators.

Atomic nitrogen interacts with Cu substrates in interesting ways. N acts to passivate Cu surfaces¹¹ in a similar fashion to As and H passivation of Si surfaces. With atomic nitrogen coverages of less than 0.5 ML on the Cu(100) surface, annealing results in self-assembled regular arrays of islands of

the $c(2 \times 2)N$ reconstruction.¹⁰ The island size ($5 \times 5 \text{ nm}^2$) is extremely regular and is believed to be due to a slight incommensuration of the $c(2 \times 2)N$ structure with the underlying substrate.¹⁰ Figure 1 shows a typical area of a Cu(100) surface with an atomic nitrogen coverage of 0.2 ML, upon annealing $5 \times 5 \text{ nm}^2$ $c(2 \times 2)N$ islands have self-assembled, these islands have aligned along $\langle 001 \rangle$ and $\langle 010 \rangle$ directions and form an additional long-range periodicity consisting of equally spaced lines of $c(2 \times 2)N$ islands separated by areas of the clean 1×1 surface. Similar effects have also been

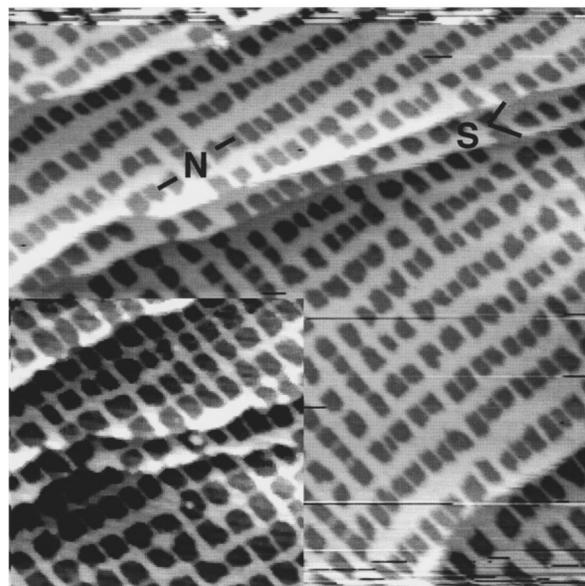


FIG. 1. STM images showing the ability of N to form self-assembled, highly regular nanometer-scale structures on Cu(100) surfaces. The main image shows a $120 \times 120 \text{ nm}^2$ area of a Cu(100) surface with an atomic nitrogen coverage of 0.2 ML. Upon annealing, the nitrogen forms small $5 \times 5 \text{ nm}^2$ islands of the $c(2 \times 2)N$ structure. The islands align forming long rows separated by areas of the clean surface. Nitrogen islands are denoted by N, step edges are denoted by S. The inset shows a STM image of a $60 \times 60 \text{ nm}^2$ region of a Cu(100) surface with an increased nitrogen coverage of 0.24 ML, the rows of islands are much more closely spaced giving the surface a “Cartesian” appearance.

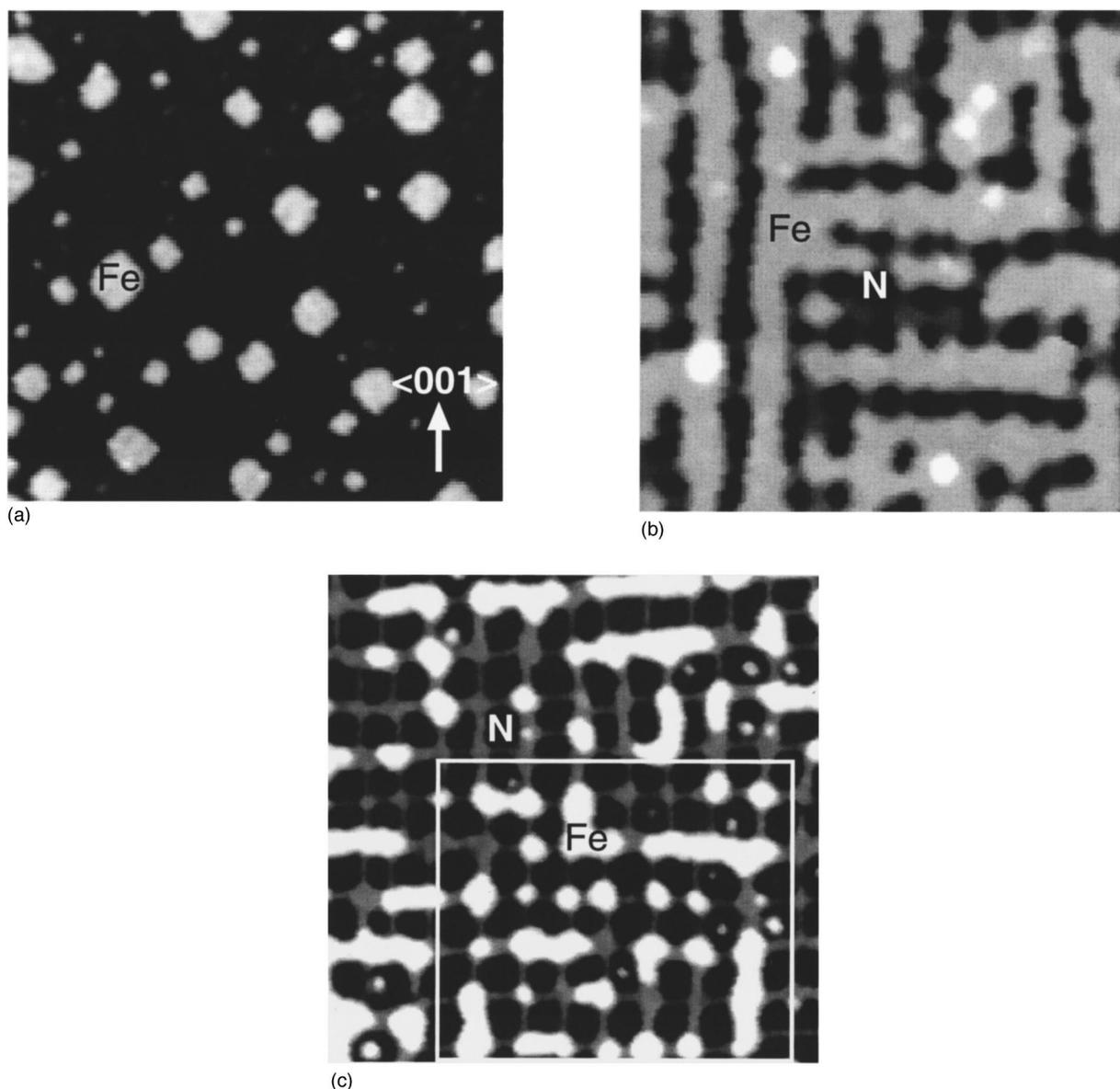
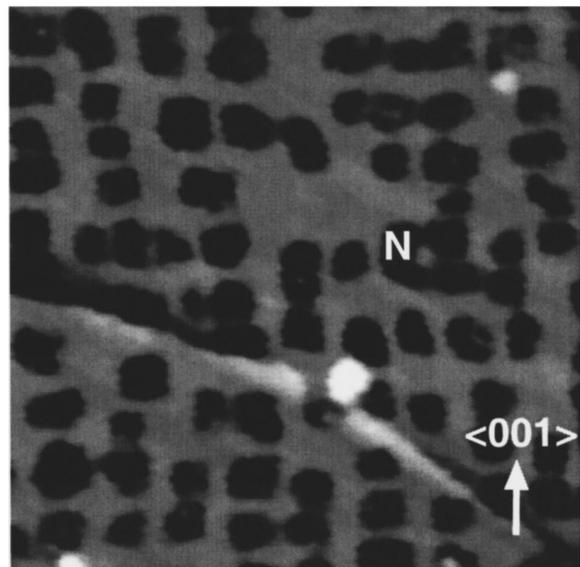


FIG. 2. A series of three $60 \times 60 \text{ nm}^2$ STM images showing how the growth of Fe onto Cu(100) surfaces can be controlled by the presence of N islands. (a) shows a clean Cu(100) surface onto which 0.13 ML of Fe was deposited at room temperature. The Fe has grown as small randomly spaced islands, with island edges running in the $\langle 011 \rangle$ directions. (b) shows a Cu(100)- $c(2 \times 2)$ N surface, similar to that shown in Fig. 1, on which 0.4 ML of Fe has been grown. The epitaxially grown Fe is channeled into the regions between the N islands forming long narrow stripes with island edges now running in the $\langle 001 \rangle$ directions. Some second-layer growth can also be observed, one area of which has been boxed. (c) shows a Cu(100)- $c(2 \times 2)$ N surface similar to that shown in the inset of Fig. 1, on which 0.2 ML of Fe has been grown. Again the epitaxially grown Fe is channeled into regions between the N islands. The region enclosed in the rectangle shows an almost perfect two-dimensional square array of Fe islands on this surface.

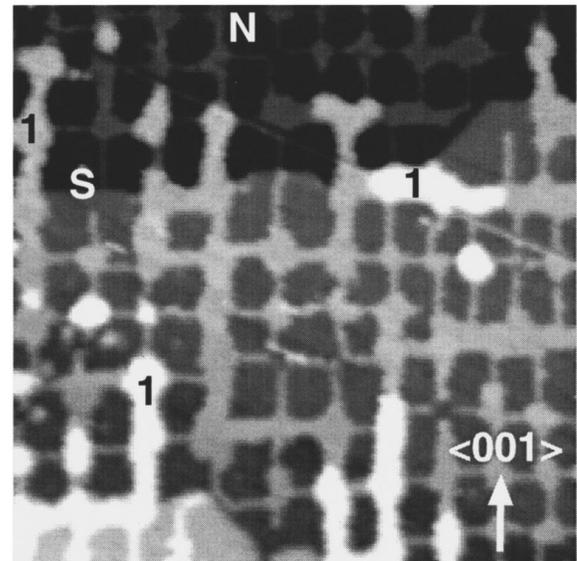
observed for the Cu(110)- (2×1) O system¹² and explanations for such periodic structures involve electrostatic interactions and surface stress effects.¹³ As the nitrogen coverage is increased, the spacing between the lines of islands is reduced to eventually form a Cartesian-like array of $c(2 \times 2)$ N islands as shown in the inset in Fig. 1. It should be noted that the methods of sample preparation, involving equipment common to virtually all UHV systems, could routinely create these nanometer-scale structures uniformly across the whole of our $5 \times 7 \text{ mm}^2$ sample.

Figure 2 shows the result of submonolayer depositions of Fe onto clean Cu(100) surfaces [Fig. 2(a)] and those that

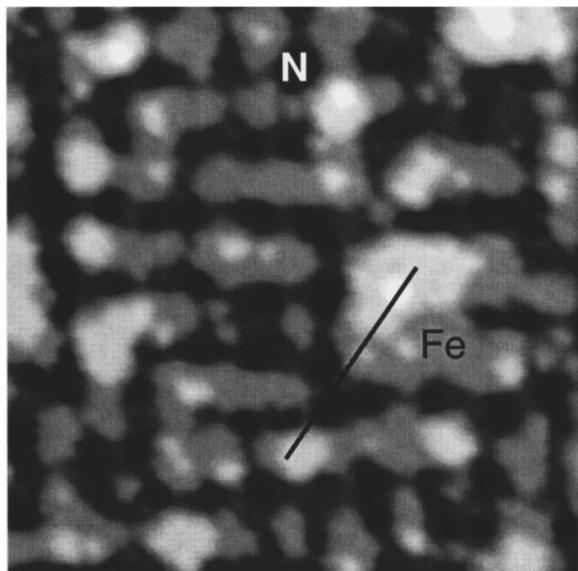
have been prepatterned with the $c(2 \times 2)$ N islands [Figs. 2(b) and 2(c)]. As can be seen in Fig. 2(a), Fe deposition onto the clean Cu(100) surface results in islands randomly spaced across the surface with island edges running along the $\langle 011 \rangle$ directions consistent with studies of other epitaxially grown transition metals on this surface.¹⁴ When Fe is grown onto surfaces like those shown in Fig. 1, the island shapes are dramatically influenced by the presence of the $c(2 \times 2)$ N islands. The Fe is channeled into the regions between the islands. In Fig. 2(b), where the substrate initially contained lines of $c(2 \times 2)$ N islands, Fe deposition results in elongated Fe islands found between the N islands, both the



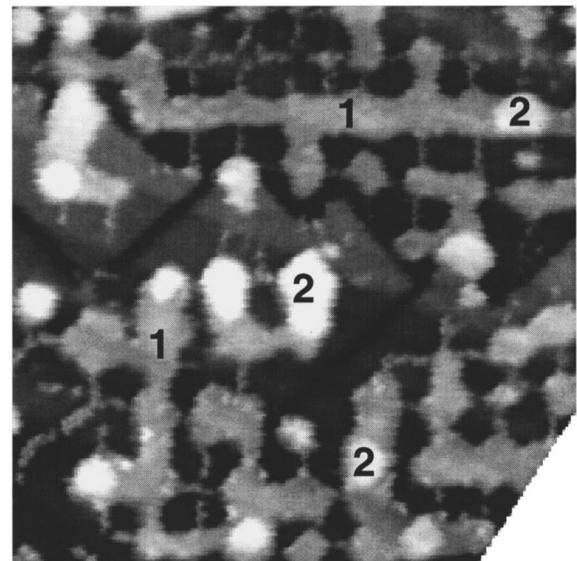
(a)



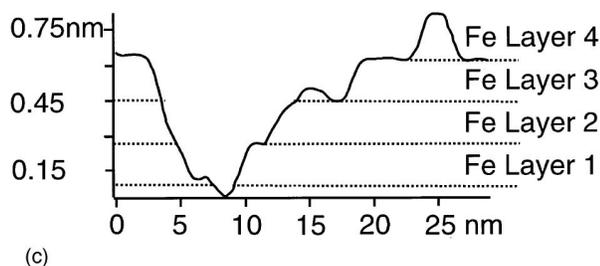
(a)



(b)



(b)



(c)

FIG. 3. STM images and linescans showing that the presence of N islands on the Cu(100) surface serve to control the growth of Fe well beyond the first Fe monolayer. (a) and (b) show two $55 \times 55 \text{ nm}^2$ STM images of a Cu(100)- $c(2 \times 2)$ N surface. The image in (a) shows the $c(2 \times 2)$ N islands on the clean Cu(100) surface; the image in (b) shows an area of the same surface as (a) after an Fe deposition of 1.5 ML. (N islands are denoted by N.) (c) shows the results of a linescan as indicated in (b). (b) shows that the nitrogen islands still govern the positions of the islands of epitaxially grown Fe. The linescan indicates that the Fe islands are 3–4 atomic layers high.

FIG. 4. Two $60 \times 60 \text{ nm}^2$ STM images demonstrating that N islands serve to direct the epitaxial growth of Cu as well as Fe (N islands denoted by N, step edges by S). (a) shows a region with a 0.2-ML N coverage with 0.11 ML of epitaxially grown Cu. Epitaxial grown Cu islands (denoted by 1) grow either out from step edges or on the terraces. In either case, the epitaxially grown Cu is channeled into the regions between the N islands. (b) shows a region after a 0.50-ML Cu deposition, showing both first- (1) and second-layer (2) growth. Note that the small islands of second-layer growth initially show edges running in the $\langle 011 \rangle$ directions indicative of layer-by-layer growth, and larger islands take the shape of the preceding layer. This demonstrates that the method creates small bi-atomic layer islands.

widths and the lengths of the Fe islands are clearly controlled by the N islands. As can be seen in Fig. 2(b), the Fe island width is limited to the 5-nm spacing between the N islands whereas island lengths up to 80 nm have been observed. Also the Fe island edges are now along the $\langle 001 \rangle$ directions of the substrate.

When Fe is deposited onto a substrate similar to that

shown in the inset in Fig. 1, the resultant surface is similarly affected [Fig. 2(c)]. Again, the Fe is channeled into the regions between the N islands. By fine tuning the preparation of the N-prepatterned surfaces and the amount of deposited Fe, it should be possible to create a near perfect two-dimensional array of Fe islands across the whole of the surface. In the field of magnetic data storage, factors such as magnetic grain size and separation are important with typical dimensions for the best materials being grain sizes of about $(10 \text{ nm})^2$ and densities of $4 \times 10^8/\text{mm}^2$.¹⁵ An optimal N-prepatterned surface could yield a grain size of $(1.5 \text{ nm})^2$ and a very tightly controlled grain density of $4 \times 10^{10}/\text{mm}^2$. Whereas recent work has studied the magnetic properties of random two-dimensional assemblies of nanometer-sized islands,² the surfaces created here are highly ordered.

There are two additional aspects of this work that must be discussed. First, the N-prepatterned surfaces serve to direct epitaxial growth beyond the first atomic layer of deposited material (Fig. 3). Figure 3(a) shows a Cu(100) surface with a nitrogen coverage of 0.21 ML; this surface was not sufficiently annealed to produce a high degree of ordering among the nitrogen islands. When 1.5 ML of Fe is deposited onto this surface [Fig. 3(b)], it is apparent from the linescans that even though the Fe islands are 3–4 atomic layers high, their positions on the surface are still influenced by the underlying N islands. Secondly, in Fig. 4, we show that our results also extend to other transition metals. Here Cu is deposited onto Cu(100) surfaces that have been prepatterned with N islands and similar results are obtained.

It should be noted that this work is similar to that of others who have shown that periodic dislocations on the Au(111) surface can serve as nucleation sites for transition-metal growth^{16–18} or that vicinal surfaces can be used as templates to create metal islands at step edges.¹⁹ There are some significant similarities and differences between our re-

sults and these previous results. Likewise, we have developed a methodology for templating the surfaces by using the N islands to direct the epitaxial growth of Fe and Cu on the Cu(100) surface to form regular arrays of islands or metal lines. Likewise, we also believe that our results will similarly hold for other transition metals and quite probably other materials such as C_{60} . Our results differ in that we have clearly demonstrated a degree of control over the initial substrate resulting in the ability to produce on the same substrate either equally spaced epitaxially growth metal lines or two-dimensional arrays of metal islands. Figures 3 and 4 demonstrate that the N islands affect the morphology of the surface well beyond the monolayer level. Other differences are as follows, if the growth of transition metals onto the Au(111) surface is layer-by-layer, then the effect of the dislocations serving as nucleation sites is lost after the first layer is complete. If, as in the case of Co growth on Au(111), clustering occurs, then the individual clusters may not have a particularly well-ordered lattice. In the results presented here (Figs. 3 and 4), it can be clearly seen that the islands of deposited metal are confined laterally by the nitrogen islands but in the vertical dimension layer-by-layer growth occurs.

In conclusion, we have demonstrated that periodic arrays of $5 \times 5 \text{ nm}^2$ islands of a $c(2 \times 2)\text{N}$ reconstruction can be used to direct the epitaxial growth of transition metals on the Cu(100) surface for coverages between 0 and 4 atomic layers. Varying the initial N coverage can lead optimally to islands of epitaxially grown material in periodic 5-nm-wide stripes, or periodic two-dimensional arrays of small islands across macroscopic distances.

The authors would like to thank F. J. Himpsel for reading preliminary drafts of this manuscript and for many helpful conversations. We acknowledge funding from the United Kingdoms Engineering and Physical Sciences Research Council. T. M. Parker would also like to gratefully acknowledge funding from Unilever Research Laboratories.

* Author to whom correspondence should be addressed.

¹J. Tersoff, C. Teichert, and M. G. Lagally, *Phys. Rev. Lett.* **76**, 1675 (1996).

²M. R. Scheinfein, K. E. Schmidt, K. R. Heim, and G. G. Hembree, *Phys. Rev. Lett.* **76**, 1541 (1996).

³E. J. Heller, M. F. Crommie, C. P. Lutz, and D. M. Eigler, *Nature (London)* **369**, 464 (1994).

⁴A. D. Kent, T. M. Shaw, S. von Molnar, and D. D. Awschalom, *Science* **262**, 1249 (1993).

⁵K. Kalki, D. D. Chambliss, K. E. Johnson, R. J. Wilson, and S. Chiang, *Phys. Rev. B* **48**, 18 344 (1993).

⁶G. L. Nyberg, M. T. Kief, and W. F. Egelhoff, *Phys. Rev. B* **48**, 14 509 (1993).

⁷J. Giergiel, J. Shen, J. Woltersdorf, A. Kirilyuk, and J. Kirschner, *Phys. Rev. B* **52**, 8528 (1995).

⁸M. Straub, R. Vollmer, and J. Kirschner, *Phys. Rev. Lett.* **77**, 743 (1996).

⁹K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, *Phys. Rev. Lett.* **75**, 509 (1995).

¹⁰F. M. Leibsle, S. S. Dhesi, S. D. Barrett, and A. W. Robinson, *Surf. Sci.* **317**, 309 (1994).

¹¹R. Spitzl, H. Niehus, and G. Comsa, *Surf. Sci. Lett.* **250**, L355 (1991).

¹²K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. George, and G. Comsa, *Phys. Rev. Lett.* **67**, 855 (1991).

¹³D. Vanderbilt, *Surf. Sci. Lett.* **268**, L300 (1992).

¹⁴J. Shen, J. Giergiel, and J. Kirschner, *Phys. Rev. B* **52**, 8454 (1995).

¹⁵Y. Miura, *J. Magn. Magn. Mater.* **134**, 209 (1994).

¹⁶D. D. Chambliss, R. J. Wilson, and S. Chiang, *Phys. Rev. Lett.* **66**, 1721 (1991).

¹⁷B. Voigtländer, G. Meyer, and N. Amer, *Phys. Rev. B* **44**, 10 354 (1991).

¹⁸B. Voigtländer, G. Meyer, and N. Amer, *Surf. Sci. Lett.* **255**, L529 (1991).

¹⁹T. Jung, R. Schlittler, J. K. Gimzewski, and F. J. Himpsel, *Appl. Phys. A* **61**, 467 (1995).