Self-assembled magnetic nanostripes by organic patterning

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Selective adsorption of Fe deposited on the organic molecule 3,4,9,10-perylene-tetracarboxylic-3, 4,9,10-dianhydride (PTCDA) is used to prepare a self assembled magnetic nanostripe structure on a vicinal Ag surface. Scanning tunneling microscopy reveals that after PTCDA deposition on the Ag(10 8 7) surface a grating-like domain pattern is formed. It consists of alternating stripes of molecule-covered facets and uncovered (111) terraces. Fe adsorption takes place selectively on the molecule-covered stripes forming disk-shaped super-paramagnetic islands with a polar easy magnetization axis. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1751228]

The preparation of nano-structures is a prerequisite for the study of fundamental physics in low-dimensional systems, since in general the reduction of dimensionality induces physical properties, which are often substantially different as compared to their bulk analogs.[1] In this context magnetic systems are under intense investigation, since due to the intimate correlation of structure with magnetism this opens the field to tailor magnetic structures which show unusual behavior not accessible in three dimensions. Consequently, many different approaches to prepare nanodots, nanowires and two-dimensional superlattices were developed.[2–9]

In general, the underlying principle for the growth of nano-structures is the preparation of a suitable template, which serves as a nucleation center for the subsequently deposited material. For instance, this procedure has been successfully applied by using periodic dislocation networks on several closely packed surfaces[2–4] or by using regularly stepped surfaces.[5–9] All these studies have in common that a regular assembly of structural units was used. This is an intrinsic property of the template, which in principle does not allow any structural flexibility.

In contrast, organic supra-molecular structures show a great variety and flexibility of structures when adsorbed on single crystal surfaces. Consequently it appears tempting to use organic molecules as a template for the preparation of a magnetic nanostructure and to take advantage of their structural flexibility to prepare a suitably designed nanostructure. The basic advantage of organic pre-patterning as compared to the methods referenced above is that the structure of the template can be varied in a systematic and controllable way just by modification of the molecular film structure. Consequently, our approach bears the potential to allow the preparation and investigation of low-dimensional magnetic structures with a good flexibility. Prerequisite for this procedure is that the metal atoms selectively adsorb on the molecular sites and that the morphology of the molecular structure is preserved upon metal adsorption.

The preparation and characterization of large organic molecules (with masses above 200 amu) deposited on single crystal surfaces has made considerable progress.[10–14] Interest has focused on several classes of archetype molecules with potential technological applications like 3,4,9,10-perylene-tetracarboxylic-3,4,9,10-dianhydride (PTCDA). It is characterized by a large π-conjugated system and forms well-ordered superstructures on low index Ag surfaces.[11–14] Figure 1(a) shows the structural formula of PTCDA. It is planar and its lateral dimensions are 14.2×9.2 Å^2. The molecule is very mobile on Ag surfaces, even at room temperature, and forms large well-ordered islands already at low coverage supported by its quadrupole moment.[12] Interest on PTCDA also originates from its properties to serve as a template for site selective adsorption. It has been shown that the anhydride groups are preferential adsorption positions for reactive metals such as In, Ti, Sn, and Al.[15,16] Bond formation between the metal and the anhydride groups is proposed in these studies. Although no detailed investigations with regard to Fe are available so far, the high affinity of Fe to oxygen justifies the assumption that Fe atoms are also preferentially adsorbed at the anhydride groups.

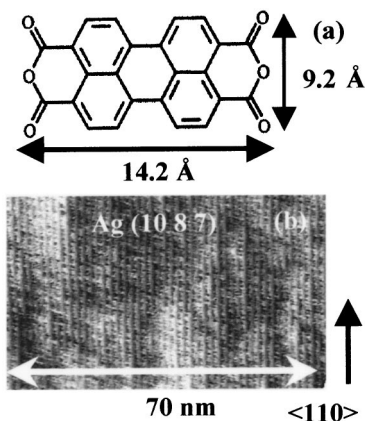Thus, its structural flexibility, its potential to reconstruct

FIG. 1. (a): Structure formula of PTCDA. (b): 70×40 nm^2 STM image of the uncovered Ag(10 8 7) surface characterized by monatomic steps separated by 1.7-nm-wide (111) terraces.

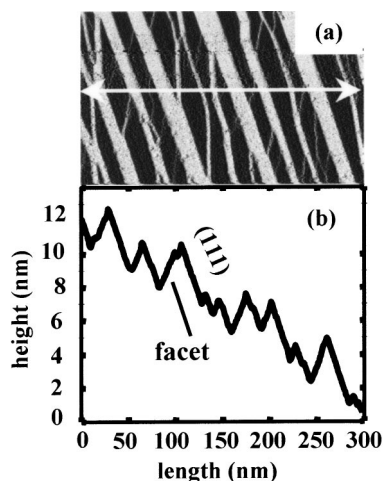[a]Author to whom correspondence should be addressed; electronic mail: hmeyerhm@mpi-halle.de

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FIG. 2. (a): A 300×130 nm^2 STM derivative image of the Ag(10 8 7) surface after deposition of 0.4 ML PTCDA. Dark and bright areas correspond to uncovered terraces and facets, respectively. (b): Line profile along the bright arrow in (a).

FIG. 3. A 300×220 nm^2 STM image after deposition of 1.1 ML Fe on the Ag surface with PTCDA covered steps. The inset shows the zoom-in line profile along two Fe islands (see circle).

the surface on large scales[17] (see below), and its affinity to reactive metals make PTCDA an interesting candidate to serve as a template for the preparation of suitably designed metallic nano-structures. We have carried out scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and magneto-optic Kerr effect (MOKE) experiments to investigate the structure and magnetic properties of Fe grown on PTCDA deposited on a Ag surface. Our results clearly show that Fe solely adsorbs on the PTCDA covered areas of the substrate in this way forming a magnetic nanostripe structure.

First we discuss the preparation of a nano-stripe structure using a PTCDA covered substrate surface. Nucleation of PTCDA on Ag(111) first occurs at steps.[12] Moreover, upon annealing step bunching is observed on Ag(111) which is initiated by the stronger PTCDA bonding at steps as compared to the (111) terraces and which leads to PTCDA covered step bunches and uncovered (111) terraces at low coverage.[17] This scenario can be extended using a high index Ag surface such as the (10 8 7) surface. It is vicinal to (111) and forms a well-defined nanostripe structure upon adsorption of PTCDA as described in more detail elsewhere[17] and as briefly discussed in the following.

The Ag(10 8 7) surface was prepared by cutting a crystal with an inclination angle of 8.5° relative to the (111) surface. The sample surface was prepared by several cycles of 1 keV Ar$^+$-ion sputtering and annealing up to 700 K. Figure 1(b) shows a 70×40 nm^2 topographic STM image of the clean Ag surface. It is characterized by an ordered array of monatomic steps separated by 1.7-nm-wide (111) terraces. PTCDA was deposited by sublimation from a Knudsen cell operated at 600 K. During deposition the substrate temperature was kept at 500 K in order to improve the mobility of the steps. Figure 2(a) shows a 300×130 nm^2 derivative STM image illustrating the surface morphology after PTCDA deposition. Bright and dark regions correspond to facets and flat (111) terraces, respectively. STM images with molecular resolution (not shown) indicate that PTCDA exclusively adsorbs at steps and bunches them to facets (bright stripes), until all of them are covered. The facet edges run
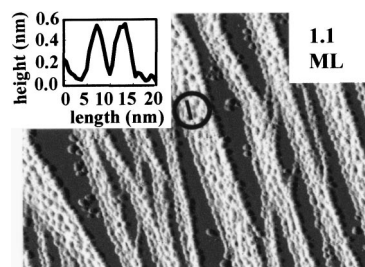
closely parallel to the [11$\bar{2}$] direction. At a coverage of 40% of a complete monolayer (ML) all steps are covered by PTCDA as shown in Fig. 2(a). Between the stripes there are flat (111) terraces [dark regions in Fig. 2(a)], which are not covered by PTCDA. The line profile [Fig. 2(b)] reveals that the surface is characterized by an "up-hill" and "down-hill" morphology corresponding to the stepped and terrace regions, respectively.

After preparation of the stripe structure Fe was deposited by electron beam evaporation from an Fe rod while keeping the substrate at 450 K. The amount of Fe deposited is given in ML, where 1 ML corresponds here to 1.53×10^{15} atoms/cm^2 using the Fe/Cu(001) interface as reference. Figure 3 shows a STM image recorded after deposition of about 1.1 ML Fe. The Fe film is grown by preserving the stripe morphology. Fe is agglomerated in small disk-shaped islands with a diameter of 4–6 nm and 0.5 nm height (see the zoom-in line profile in the inset). The Fe atoms are almost exclusively adsorbed on the PTCDA covered facets only, a minor fraction is found on the terraces. The latter is estimated to be about a few percent of the total Fe coverage ≈ 0.05 ML and is attributed to Fe overdosing. Continued Fe deposition (up to about 3.5 ML) also leads to the adsorption of Fe on the terraces beginning at local defects and steps. Based on the STM image in Fig. 3 showing Fe clusters of about 0.5 nm thickness corresponding to an Fe-layer thickness of 2–3 ML, we can conclude that it is the very stable chemical (covalent) bonding of the Fe atoms next to the PTCDA molecules which is the decisive factor for the preferential adsorption in the coverage regime up to about 1 ML coverage. This is in agreement with studies on the metal adsorption on PTCDA carried out so far.[15,16]

LEED patterns (not shown) confirm the STM results. While upon Fe adsorption superstructure spots originating from the molecules adsorbed at the facets are no longer observable, the specular reflections related to the facet structure are still observed, although attenuated. Furthermore, the (1 $\times$ 1) spots from the (111) terraces are unchanged. These observations are only compatible with Fe atoms adsorbed on the molecule-covered facets.

The magnetic characterization of the nanostripe structure was carried out by *in situ* MOKE. Figure 4 shows hysteresis loops recorded for 1.1 ML Fe in polar geometry measured at temperatures between 60 and 118 K. When the magnetic signal is plotted versus $\mu_0 H/T$ the curves are nearly identical, which in addition to the absence of any remanence is a signature for superparamagnetism.[18] Fitting the data to the Langevin function by using the saturation magnetization
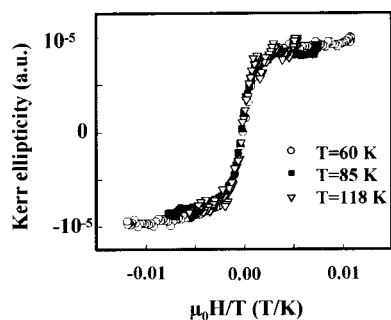
FIG. 4. Temperature normalized magnetization curves by MOKE for 1.1 ML Fe in polar geometry measured at 60, 85 and 118 K.

of fcc-Fe ($\mu_0 M_s = 0.75$ T)[19] yields a cluster volume of about 17 nm^3 corresponding to a disk of 6.6 nm in diameter and 0.5 nm in height in good agreement with the STM analysis. In the polar direction an applied field in the order of 0.15 T is sufficient to saturate the magnetization. In contrast, for a magnetic field applied in the surface plane up to 0.8 T, no saturation could occur. Thus, the easy magnetization axis is perpendicular to the surface. On the basis of the phenomenological description using anisotropy energies, this is because in the low thickness limit the effective anisotropy is dominated by the (positive) surface anisotropy constant (K_S) favoring perpendicular magnetization.[6,8]

In summary, we have shown that a magnetic nanostructure can be prepared by using a regular pattern of large organic molecules as a template for subsequent metal adsorption. This procedure takes advantage of the site selective Fe adsorption on previously deposited PTCDA molecules. Due to the great variety of molecular ad-layer structures on metal surfaces and their known tunability as a function of the preparation conditions, our results have wide implications for the study of low-dimensional systems in general.

[1] C. M. Schneider and J. Kirschner, in *Handbook of Surface Science*, edited by K. Horn and M. Scheffler (Elsevier, Amsterdam, 2000), p. 511.

[2] H. Röder, E. Hahn, H. Brune, J.-P. Bucher, and K. Kern, Nature (London) **366**, 141 (1993).

[3] H. Brune, M. Giovannini, K. Bromann, and K. Kern, Nature (London) **394**, 451 (1998).

[4] O. Fruchart, M. Klaua, J. Barthel, and J. Kirschner, Phys. Rev. Lett. **83**, 2769 (1999).

[5] J. Shen, R. Skomski, M. Klaua, H. Jenniches, S. S. Manoharan, and J. Kirschner, Phys. Rev. B **56**, 2340 (1997).

[6] J. Shen, M. Klaua, P. Ohresser, H. Jenniches, J. Barthel, Ch. V. Mohan, and J. Kirschner, Phys. Rev. B **56**, 11134 (1997).

[7] F. K. Men, L. Feng, P. J. Wang, C. H. Chen, D. L. Cheng, J. L. Lin, and F. J. Himpsel, Phys. Rev. Lett. **88**, 096105 (2002).

[8] P. Gambardella, A. Dallmeyer, K. Maiti, M. C. Malagoli, W. Eberhard, K. Kern, and C. Carbone, Nature (London) **416**, 301 (2002).

[9] C. Yu, D. Li, J. Pearson, and S. D. Bader, Appl. Phys. Lett. **79**, 3848 (2001).

[10] E. Umbach, Prog. Surf. Sci. **35**, 113 (1991).

[11] E. Umbach, M. Sokolowski, and R. Fink, Appl. Phys. A: Mater. Sci. Process. **63**, 565 (1996).

[12] K. Glöckler, C. Seidel, A. Soukopp, M. Sokolowski, E. Umbach, M. Böhringer, R. Berndt, and W.-D. Schneider, Surf. Sci. **405**, 1 (1998).

[13] F. S. Tautz, S. Sloboshanin, V. Shklover, R. Scholz, M. Sokolowski, J. A. Schaefer, and E. Umbach, Appl. Surf. Sci. **166**, 36 (2000).

[14] C. Seidel, J. Poppensieker, and H. Fuchs, Surf. Sci. **408**, 223 (1998).

[15] Y. Hirose, A. Kahn, V. Aristov, P. Soukiassian, V. Bulovic, and S. R. Forrest, Phys. Rev. B **54**, 13748 (1996).

[16] A. Palma, A. Pasquarello, and R. Car, Phys. Rev. B **65**, 155314 (2002).

[17] S. Schmitt, C. Seidel, M. Sokolowski, and E. Umbach (unpublished)

[18] C. P. Bean and J. D. Livingston, J. Appl. Phys. **30**, 120 (1959).

[19] U. Gradmann, W. Kümmerle, and P. Tilmanns, Thin Solid Films **34**, 249 (1976).