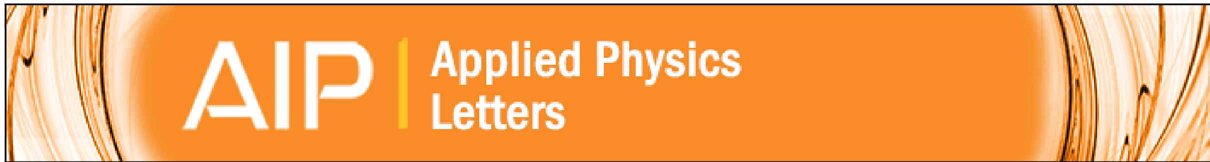

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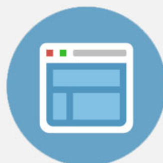

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Molecular scale alignment strategies: An investigation of Ag adsorption on patterned fullerene layers

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We have developed a procedure for atomic scale alignment with respect to macroscopic objects. Metallic and etched registration marks on clean reconstructed Si surfaces are used to guide the tip of a scanning tunnelling microscope. The metallic marks are formed from Ta and can withstand thermal cycling up to 1500 K. These procedures have been used to investigate the interaction of Ag with a patterned fullerene multilayer deposited on Si(111)-7×7. © *1997 American Institute of Physics.* [S0003-6951(97)00646-3]

In recent years there have been many demonstrations of atomic and molecular scale modification of semiconductor surfaces using a scanning tunnelling microscope (STM).[1–7] There are two broad objectives of much of this work:

(i) the fabrication of experimental atomic scale nanostructures;
(ii) local surface science experiments.

To achieve these goals it is necessary to align individual atoms and molecules with respect to macroscopic features. Such a technology is a requirement for the formation of contact tracks to a modified region and would also permit novel surface science experiments. Notable progress has recently been reported[8–10] showing that it is possible to re-visit a region which has been modified on an atomic scale on an otherwise *homogeneous* surface by careful design and machining of mechanical components. To align on the atomic scale with respect to the macroscopic world an *inhomogeneous* surface on which registration marks are formed must be used. The combination of registration marks and STM has been demonstrated[11–14] but only on surfaces which are not clean or well defined on the atomic scale. To extend these studies to atomic and molecular scale alignment it is necessary to address the compatibility of conventional semiconductor processing and the cleanliness and thermal cycling required to produce clean reconstructed surfaces. This remains an unexplored area.

In this letter we show that metallic and etched registration marks may be used to identify and relocate individual molecules in positions which are determined with respect to macroscopic features. The metallization process may ultimately be used for both registration marks and the formation of contact tracks. We demonstrate its use by investigating the deposition of Ag on a patterned C_{60} multilayer.

Our experiments were performed on Si substrates. Electron beam lithography was used to form a sub-micron pattern in a poly methyl methacrylate (PMMA) resist. This pattern is transferred into the substrate either by the evaporation of Ta followed by lift-off or by etching. For the etched marks we used a (100) p-type wafer ($\rho \sim 1\ \Omega$ cm) and chose as an etchant KOH:H_2O:propanol 2:6:1. For the metallic marks Ta was deposited on a (111) p-type wafer ($\rho \sim 1\ \Omega$ cm). Ta was chosen since it is used widely as a mechanical connection when heating Si up to 1500 K without giving rise to a gross modification of the surface reconstruction. Following the removal of the PMMA in acetone both the etched and metallized samples were cleaned in Micro Ten resist stripper.

Figure 1 shows an image of an etched sample taken in ambient conditions using contact mode atomic force microscopy (Topometrix Explorer). The registration marks (L shapes) are oriented towards a central 1 μm square region highlighted in Fig. 1. The pitch of the array of L's is 2 μm so that at least one feature appears in each frame of our STM.[15] A number of etched trenches run into the central region which for the equivalent metallized sample could ultimately play the role of contact tracks. The array of L's covers a total area of 400×400 μm and is surrounded by large squares which are visible through binoculars and permit coarse alignment of the STM tip to within ~100 μm of the center of the pattern.

The etched and metallized samples were loaded into an ultrahigh vacuum (UHV) system, outgassed at ~900 K and annealed at temperatures in the range 1100–1500 K for ~60 s. For a clean unpatterned sample annealing at 1500 K

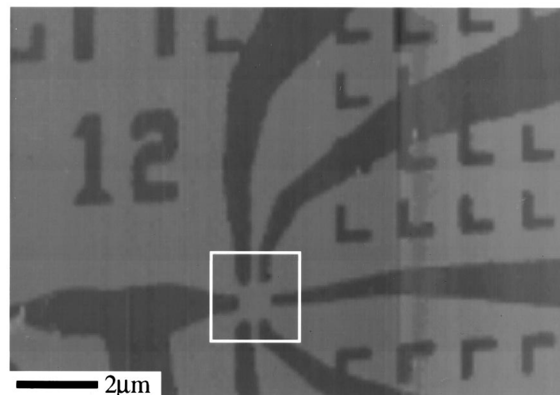

FIG. 1. Image of Si(100) etched registration marks taken using an atomic force microscope. The white square highlights the central region of the pattern.

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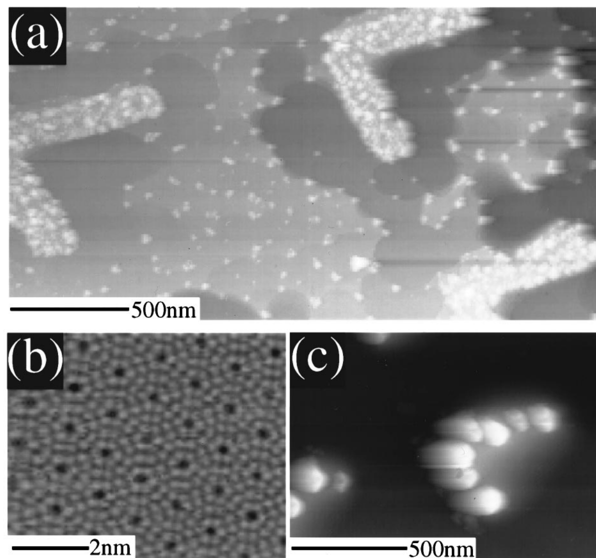

FIG. 2. (a) STM image of Ta marks on Si(111) after annealing at 1280 K. Scan parameters −3.5 V, 0.2 nA (sample biased). (b) High resolution scan of an area of the surface shown in (a) illustrating clean (7×7) reconstruction. Scan parameters +3.0 V, 0.3 nA. (c) Image of sample annealed at 1500 K showing highly raised marks. Scan parameters +3.5 V, 0.1 nA.

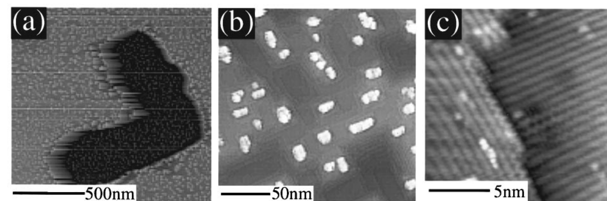

FIG. 3. STM image of Si(100) etched registration marks annealed at 1200 K, taken with scan parameters −3.5 V and 0.1 nA. (b) Zoom of (a) taken outside the etch pits. Scan parameters +3.0 V and 0.2 nA. (c) High resolution scan showing 2×1 surface reconstruction. Scan parameters +3.0 V, 0.1 nA.

results in a (2×1) reconstruction for the (100) surface and a (7×7) reconstruction for the (111) surface.

Figure 2(a) shows STM images of a Si(111) surface with Ta marks (height 20 nm) following annealing at 1280 K. Si(111) terraces (typical width 200 nm) run between bunches of steps which are pinned due to the presence of C. A similar surface morphology is observed for a clean unpatterned sample when annealed at the same temperature. The terraces are terminated by a (7×7) reconstruction with a very low defect density [Fig. 2(b)]. The step bunching is eliminated by a higher temperature anneal. Figure 2(c) shows a registration mark following annealing at 1500 K. In between the marks the Si surface is essentially identical to that observed for a clean unpatterned (111) surface. However, the marks have a more globular appearance and are much higher, typically ~100 nm with pronounced step bunches around their edges. We believe that this is due to the accumulation within the marks of Si atoms which are diffusing during the high temperature anneal.

Away from the marks the Ta has a negligible effect on the ordering of the Si surface and we find that the (7×7) reconstruction continues to within a few nm of the Ta. The registration marks therefore fulfill the objectives identified above. However, the marks with a high aspect ratio can lead to tip crashes and artifacts such as image doubling. These problems are more severe for marks which have been annealed to a high temperature [Fig. 2(c)]. There is therefore a compromise in the selection of annealing temperature between surface quality and ease of imaging. In the work described below we use a surface as shown in Figs. 2(a) and 2(b) for which ~97% of the surface (excluding the Ta marks) is terminated by the (7×7) reconstruction with terrace widths up to 200 nm.

We have conducted a similar series of experiments with the etched (100) samples. Figure 3(a) shows the registration marks after a 1200 K anneal. C is also present on this sample and gives rise to rectangular SiC defects [Fig. 3(b)].[16] Coexisting with the defects are rows of Si dimers which form a (2×1) reconstruction [Fig. 3(c)]. Apart from the SiC there is a low density of surface defects such as missing dimers. The etched marks have a depth of 25 nm and while Fig. 3(c) shows an area on the unetched surface, an image of the bottom of the etch pit is essentially identical. For a higher temperature anneal (1400 K) C is partially removed from the surface and no longer pins the step bunches, however the resolution of the etched marks is much poorer. As for the metallized (111) surface there is therefore a compromise between the ease of use of the alignment marks and surface cleanliness.

Our approach permits the identification of individual molecules and atoms at positions which are fixed with respect to macroscopic objects. We illustrate the use of these procedures through an investigation of the interaction of Ag with a patterned fullerene layer.

Two monolayers (ML) of C_{60} are deposited on a Si(111) sample with metallized marks which has previously been annealed at 1360 K. We then use the STM tip to pattern the fullerene layers using a method which we have recently reported.[17] Figure 4(a) shows a large scale image of the surface including two alignment marks. Figure 4(b) shows the area highlighted in Fig. 4(a). The darkest level is the lowest C_{60} layer which is strongly bound to the Si(111)-7×7.[18] The lighter levels are the second and third layers which interact with each other and the lowest C_{60} layer via van der Waals forces. Due to this weak interaction the second and higher layers may be easily modified by the STM tip.[17] The dark line ~10 nm wide which runs up Fig. 4(b) slightly to the left of center is such a modified area where the STM tip has displaced the second and higher layers to the right hand edge of the line.

To investigate potential applications of this process we have deposited a noble metal, Ag, on the patterned fullerene multilayer. Figures 4(d) and 4(e) show images of the patterned region following deposition (performed in a separate chamber) of 0.14 ML and 0.37 ML of Ag, respectively (1 ML corresponds to a hexagonal close packed arrangement with an atomic separation equal to that of bulk Ag). Comparison of Figs. 4(c) and 4(d) reveal that following Ag deposition several additional topographic features are observed on the lowest C_{60} layer of the modified region. Comparison of this area with parts of the surface in which the lowest C_{60} monolayer is exposed [see area A in Fig. 4(b)] reveals that the distribution of adsorbed features is the same on patterned

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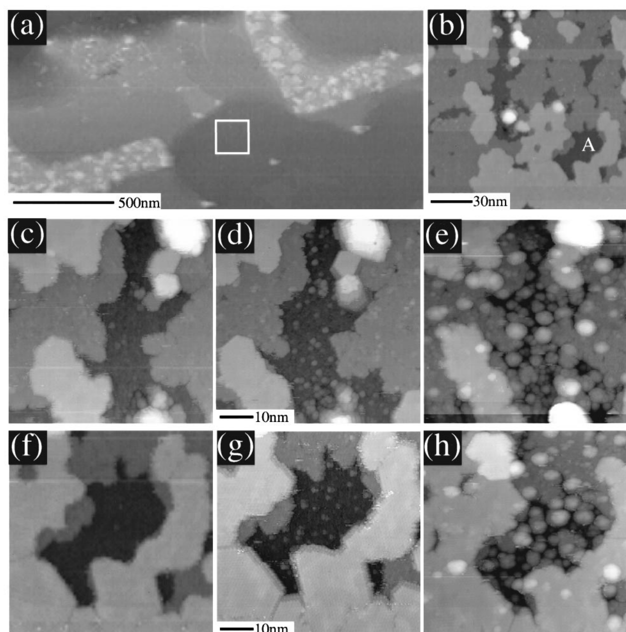

FIG. 4. (a) Image of Ta marks following C_{60} multilayer deposition. STM tip modification has been applied within the area indicated by the white box in between two alignment marks. Scan parameters −3.5 V, 0.2 nA. (b) Zoom of (a) showing tip modified area. Scan parameters +3.5 V, 0.2 nA. (c)–(e) STM images of modified region and (f)–(h) unmodified part of the surface marked A in (b). The sample is exposed to 0.14 [(d) and (g)] and 0.37 [(e) and (h)] monolayers of Ag in a separate chamber.

and unpatterned areas [Figs. 4(f)–4(h) show the area A following Ag deposition]. This implies that, as expected,[17] the lowest C_{60} layer has not been modified by the patterning process. No adsorbed material is observed on the higher layers of C_{60}. One possible reason for this is that Ag has diffused across the higher layers and onto the lowest C_{60} layer. However this hypothesis is in conflict with a comparison between the cluster distribution in Figs. 4(d) and 4(e) and that on a control sample.

The control is a C_{60} monolayer formed on Si(111)-7 $\times 7$[18] on which Ag is deposited. Similar features to those in Fig. 4(d) are observed on the control sample and have been identified as Ag clusters. The cluster density ($0.04\ \text{nm}^{-2}$), average apparent width (1.5 nm), and height (0.46 nm) are close to the values observed for Fig. 4(d). The features observed in Fig. 4(d) are therefore clusters formed from Ag which has directly impinged on the lowest C_{60} layer.

The absence of Ag on the second layer C_{60} implies either an extremely low sticking coefficient on the upper layers, or diffusion into a site between the first and second C_{60} layers. The latter possibility is more likely since Fig. 4(e) shows that after deposition of 0.33 ML of Ag the higher C_{60} layers undergo some disruption. If Ag was simply desorbed we would expect no modification regardless of the total coverage. Note also in Fig. 4(e) the higher density of Ag clusters adsorbed on the lowest C_{60} layer.

Metal atoms/ions incorporated in bulk C_{60} occupy interstitial sites. In a bilayer for each C_{60} bonded to the Si(111) there is one interstitial site of radius 0.20 nm and two of radius 0.11 nm which can accommodate a Ag ion (radius 0.126 nm—an ion can occupy an interstitial site which is smaller than its ionic radius[19]). 1 ML of Ag corresponds to 12.2 atoms for each C_{60} in a close packed layer and the coverage in Figs. 4(d) and 4(e) corresponds to 1.7 and 4.5 atoms for each C_{60} bonded to the Si(111). The interstitial sites below the second C_{60} layer therefore become saturated after the adsorption of 3 atoms per C_{60}. We argue that after the first deposition Ag diffuses into interstitial sites but after the second deposition all such sites are filled and the excess Ag causes disruption of the fullerene bilayer. Note that areas of the surface terminated by three rather than two C_{60} layers undergo much less disruption [for example see Fig. 4(g)] due to the greater number of interstitial sites (six per surface C_{60}) available in the three-layer regions. This is consistent with related work on diffusion of noble metals in C_{60}.[20,21]

Registration marks have been used to re-locate atomic and molecular scale features in positions which are determined with respect to the macroscopic world. This technique is used to show that adsorbed Ag exhibits different behavior on monolayer and multilayer C_{60} and that the adsorption of Ag may be controlled by prepatterning a fullerene layer.

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[1] P. Avouris, Acc. Chem. Res. **28**, 95 (1995).
[2] R. S. Becker, G. S. Higashi, Y. J. Chabal, and A. J. Becker, Phys. Rev. Lett. **65**, 1917 (1990).
[3] I-W Lyo and P. Avouris, Science **253**, 173 (1991).
[4] H. Uchida, D. Huang, F. Grey, and M. Aono, Phys. Rev. Lett. **70**, 2040 (1993).
[5] T-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, P. Avouris, and R. E. Walkup, Science **268**, 1590 (1995).
[6] P. H. Beton, A. W. Dunn, and P. Moriarty, Appl. Phys. Lett. **67**, 1075 (1995).
[7] A. W. Dunn, P. H. Beton, and P. Moriarty, J. Vac. Sci. Technol. B **14**, 1596 (1996).
[8] J. W. Lyding, T-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, Appl. Phys. Lett. **64**, 2010 (1994).
[9] T-C. Shen, C. Wang, and J. R. Tucker, Phys. Rev. Lett. **78**, 1271 (1997).
[10] Ch. Witt, U. Mick, M. Bode, and R. Wiesendanger, Rev. Sci. Instrum. **68**, 1455 (1997).
[11] G. C. Rosolen, A. C. F. Hoole, M. E. Welland, and A. N. Broers, Appl. Phys. Lett. **64**, 1932 (1994).
[12] J. W. G. Wildoer, A. J. A. van Roy, H. van Kempen, and C. J. P. M. Harmans, Rev. Sci. Instrum. **65**, 2849 (1994).
[13] P. M. Campbell, E. S. Snow, and P. J. McMarr, Appl. Phys. Lett. **66**, 1388 (1995).
[14] S. Rubel, M. Trochet, E. E. Ehrichs, W. F. Smith, and A. L. de Lozanne, J. Vac. Sci. Technol. B **12**, 1894 (1994).
[15] Oxford Instruments (formerly WA Technology) STM with a frame size of 2.5 μm.
[16] S. M. Gray, M. K-J. Johansson, and L. S. O. Johansson, J. Vac. Sci. Technol. B **12**, 1043 (1996).
[17] A. W. Dunn, P. Moriarty, and P. H. Beton, J. Vac. Sci. Technol. A **15**, 1478 (1997).
[18] A. W. Dunn, P. Moriarty, M. D. Upward, and P. H. Beton, Appl. Phys. Lett. **69**, 506 (1996).
[19] See D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbagh, J. C. Tully, and R. E. Walstedt, *The Fullerenes*, edited by H. W. Kroto, J. E. Fischer, and D. E. Cox (Pergamon, Oxford, 1993), p. 152.
[20] D. Sarkar and N. J. Halas, Appl. Phys. Lett. **63**, 2438 (1993).
[21] Z. Y. Rong and L. Rokhinson, Phys. Rev. B **49**, 7749 (1994).

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