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STM investigation and manipulation of C₆₀ molecules adsorbed on an Si(111) surface

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Abstract. We have used an ultra-high-vacuum (UHV) scanning tunnelling microscope (STM) to image C₆₀ molecules adsorbed on a Si(111) 7 × 7 surface. At low coverage (~ 0.01 monolayers) molecules are adsorbed at random sites. For coverages close to a monolayer they are partially ordered in a hexagonal arrangement. Second- and higher-layer islands, in which the C₆₀ molecules are clearly resolved, are observed at higher coverage. These islands may be desorbed by annealing in the range 200–300 °C, leaving an Si surface terminated by a C₆₀ monolayer. This surface is stable to exposure to air and immersion in water. In addition, recent work on manipulation of C₆₀ molecules at various coverages is reviewed and results relating to tip alignment in UHV are discussed.

The use of scanning probe microscopes as tools for patterning surfaces offers a means of fabricating experimental device structures which have an active region comparable with single atoms or molecules. There are several different ways of using the tip of a scanning tunnelling microscope (STM) to pattern a surface. In the first demonstration of atomic-scale modification by Becker *et al* [1] an atom was transferred from tip to substrate by applying a voltage pulse. The most celebrated example of atomic manipulation was achieved by exploiting the attractive force between an STM tip and an Xe atom to drag an atom across a metal surface [2]. In this and subsequent work [3] low-temperature operation and a metal substrate were used. Another notable example of STM modification is H desorption from the hydrogen-passivated Si surfaces. This desorption results in local chemical changes such as a change in surface reconstruction [4, 5] for UHV operation or oxide formation for ambient operation [6, 7].

We have recently conducted a series of experiments with the objective of extending the atomic and molecular manipulation techniques described in [2] and [3] to room-temperature operation and the use of semiconductor substrates. At the outset of this work it was not clear that there would be a suitable combination of adsorbate and substrate which would have a sufficiently strong interaction that the arrangement of molecules would remain stable at room temperature, but would be sufficiently weak for the molecules to be moved by the STM tip. C₆₀ on Si(111) 7 × 7 was identified as a promising combination by Li *et al* [8] on the basis of STM results, and also by a number of theoretical groups [9, 10]. In fact, we have found that C₆₀ adsorbed on Si(111) 7 × 7 fulfils these requirements. However, we believe that in our

experiments the interaction between tip and molecule is repulsive, in contrast to the attractive forces which control low-temperature STM manipulation of inert gas atoms [2]. We also draw attention to more recent work by Jung *et al* on manipulation of porphyrin derivatives on a metallic substrate [11].

The Si samples for our experiments were cut from a p-type Si(111) wafer (resistivity > 1 Ω cm). After loading into a UHV system (base pressure 10⁻¹⁰ Torr), the samples were outgassed overnight and flash annealed at 1200 °C for 1–2 min to form a 7 × 7 reconstruction on the sample surface. C₆₀ is deposited from a Knudsen cell at a rate of ~ 2 monolayers per hour. The Si is held at room temperature for the deposition, and also for STM [12] imaging and manipulation. We use W tips which are electrochemically etched from polycrystalline wire and heated in UHV by electron bombardment.

C₆₀ manipulation may be achieved simply by scanning at an appropriate voltage, V , applied to the sample and tunnel current, I , while maintaining feedback control of the current, i.e. in the normal imaging mode. This is illustrated in figure 1, which shows two 40 nm × 40 nm images of C₆₀ adsorbed on Si(111) 7 × 7 taken with $V = -2.5$ V and $I = -0.1$ nA. The C₆₀ molecules are the bright topographic features in the image. The Si atoms of the 7 × 7 reconstruction are also clearly resolved. Between the acquisition of these images a 20 nm × 20 nm STM image was acquired (scan direction parallel to the horizontal axis of the image) with $V = -1.5$ V and $I = 0.1$ nA. A reduction in the potential difference between tip and sample will result in a reduction in the tip-sample separation. The area covered by this intermediate scan is identified by the white square in figure 1. It is clear that the C₆₀ molecules

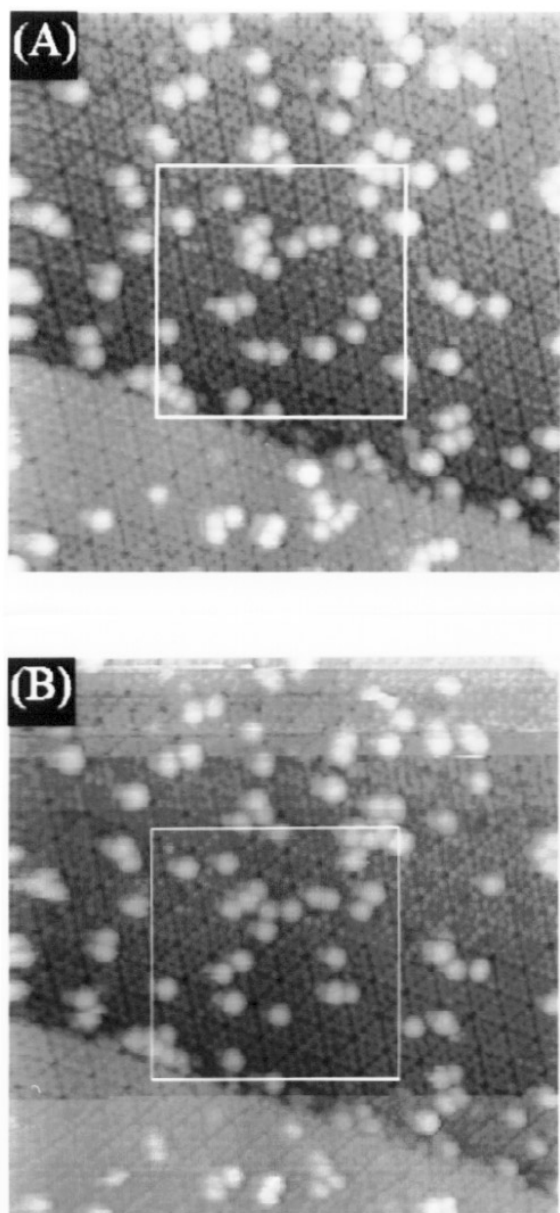


Figure 1. (a) 40 nm^2 scan showing initial arrangement of molecules prior to reduced bias (sample voltage -1.5 V , 0.1 nA , 20 nm^2 scan in centre of image—denoted by the white square. The scan parameters (sample voltage, current) were (a) -2.5 V and 0.1 nA . (b) 40 nm^2 , -2.5 V and 0.1 nA scan showing reordering of molecules in central region as a result of a single 20 nm^2 scan at -1.5 V and 0.1 nA .

outside this white square are unaffected by the intermediate scan but many of those within the square have been moved. This type of manipulation, which we have found difficult to reproduce, results in re-randomization of the arrangement of C_{60} molecules and was first reported by Maruno *et al* [13]. We have not observed a dependence of the rearrangement on scan direction.

In order to manipulate molecules in a more controlled manner we have used the cycle of tip movements shown

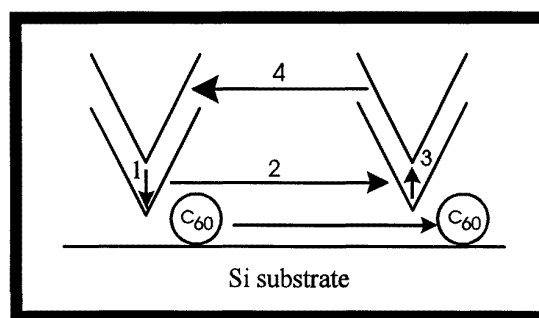


Figure 2. A schematic diagram showing the manipulation procedure used in positioning individual C_{60} molecules on the $\text{Si}(111) 7 \times 7$ surface.

schematically in figure 2. The tip is first positioned close to a C_{60} molecule which is to be moved. The tip-sample separation is reduced by adjusting I and V while maintaining feedback control. The tip is moved parallel to the surface and then retracted by readjusting the values of I and V . It is then returned to its initial position. For our experimental arrangement it is difficult to position the tip directly behind the molecule and therefore we typically sweep out a number of parallel lines separated by 0.6 nm . This procedure results in movement of the C_{60} molecule with a success rate which varies from 10–50%. An example of such movement is shown in figures 3(a)–(c). The tip is first positioned at the cross in figure 3(a) and the sweeping procedure is applied. This results in movement of the uppermost C_{60} molecule as is clear from a comparison with figure 3(b). The sweeping procedure is then applied again, resulting in further movement of the molecule (see figure 3(c)). Each of the displacements between figures 3(a), (b) and (c) occurred after a single application of the manipulation procedure, although there were also several (typically two to five) unsuccessful applications of the procedure. Typically we find that the molecule does not move through the full extent of the tip excursion during the manipulation procedure. For the movements between figure 3(a)–(c), the tip is moved by 6 nm but the resulting displacements of the C_{60} are $2\text{--}3 \text{ nm}$. The C_{60} is often displaced at an angle (typically $\sim 30^\circ$) to the tip displacement. This, together with the observation that there are few instances of C_{60} adhesion to the tip, is suggestive of a repulsive interaction between tip and molecule. We have also attempted to move molecules with a positive sample bias, but have found that this produces a significant degree of damage in the substrate surface due to the removal of Si adatoms.

We have used sequences of this procedure to move molecules along two orthogonal directions to create simple patterns [14]. However, this is rather time consuming and we have investigated using this sweeping technique to create patterns in a different way. For this experiment we use a higher coverage of C_{60} (~ 0.1 monolayer) and rather than attempt to position individual molecules at special sites we try to remove C_{60} from a particular area. A typical result is shown in figures 4(a)–(c). This is achieved by

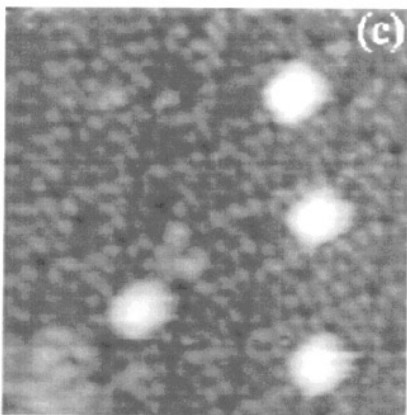
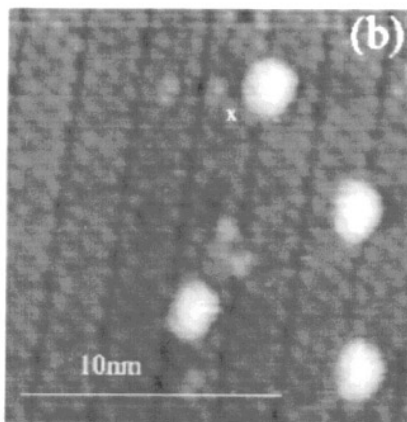
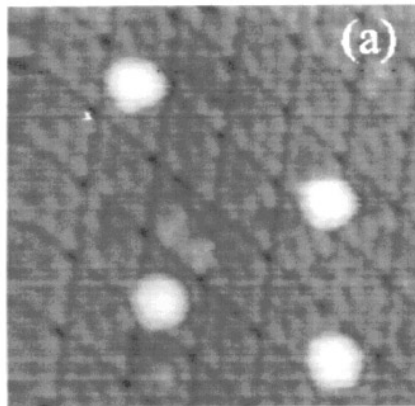


Figure 3. Controlled movement of a single C₆₀ molecule on the Si(111) (7 × 7) surface. The figures are STM topographic images with sample voltage −2.0 V and tunnel current −1 nA. The sweeping parameters were −0.4 V and −4 nA. The molecule in the upper right section of (a) is induced to move approximately 4 nm in the positive x direction, as shown in (b), and subsequently a further 3 nm, resulting in the arrangement of molecules shown in (c). The letter x marks the bottom left corner of the 6 nm × 6 nm area swept out by the tip in repositioning the C₆₀ molecule.

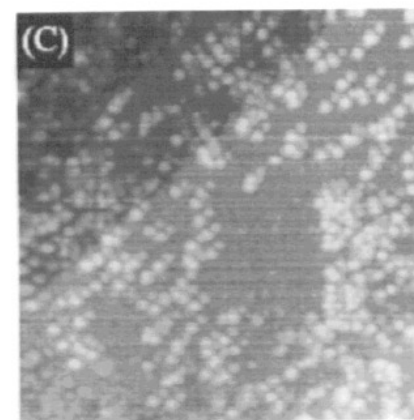
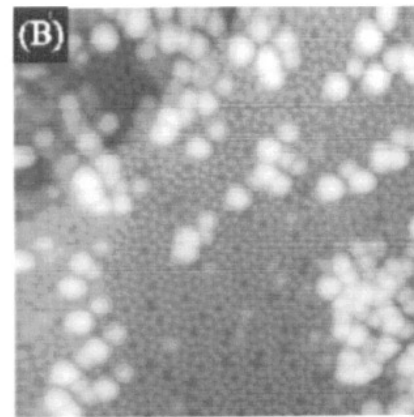
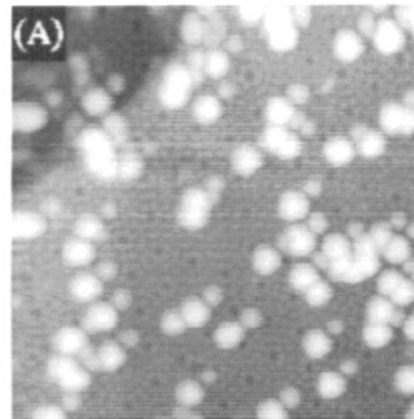


Figure 4. (a) 30 nm² scan showing arrangement of molecules after six applications of the sweeping procedure in the lower left of the image. (b) 30 nm² scan showing arrangement of molecules after a further 14 applications of the sweeping procedure. (c) 60 nm² scan showing a 16 nm² region cleared of C₆₀ molecules after a total of 31 applications of the sweeping procedure. Sweeping parameters (sample voltage, current): −0.4 V and 4 nA. Scan parameters (sample voltage, current): +2.0 V, 0.1 nA.

repeated application of our manipulation procedure. A comparison of figure 4(a) and (b) shows that the molecules in the upper half of figure 4(a) remain unchanged when the manipulation procedure is applied in the lower half of the image. In contrast, the molecules in the bottom half of the image have been moved towards the right-hand side where they form a cluster. Figure 4(c) shows a lower-magnification image in which the area cleared of C_{60} is shown clearly. The local density per unit area of C_{60} molecules is much greater at the right-hand side of the cleared region. The 7×7 reconstruction of the Si surface is resolved in figures 4(a)–(c), and damage to the surface during manipulation is minimal. We have recently repeated this work using a higher coverage of C_{60} (~ 0.25 monolayers). For this coverage, a continuous linear cluster of C_{60} with a width of order 2–3 nm and length 40 nm is formed [15]. An attraction of this approach as compared with positioning individual molecules is that it takes a few minutes rather than a few hours. It is conceivable that by using this technique nanostructures could be fabricated using molecular manipulation which could have dimensions ranging from 1 nm up to several 100 nm, which is comparable with features formed using conventional lithographic techniques.

Figures 5(a) and (b) show STM images after a total coverage of ~ 2 monolayers of C_{60} has been deposited. We find that a complete partially ordered monolayer of C_{60} is formed and then islands of second and third layers are formed with a high degree of hexagonal order. In figure 5(a) the terrace steps of the underlying Si may be resolved. The darkest contrast level is the monolayer coverage, the small bright areas are third-layer islands and the intermediate contrast level regions are second-layer islands. A higher-magnification image shown in figure 5(b) reveals that two domains of hexagonal ordering with principal axes $\pm 11^\circ$ with respect to those of the Si. Such double domain ordering was proposed for thick C_{60} layers by Xu *et al* [16] who proposed that the first monolayer was absorbed at random sites and was therefore disordered. They further proposed that an order–disorder transition took place during the growth of subsequent layers. Chen *et al* [17] showed that there was some short-range order, even in the first layer, but our experiments show that the order can extend over domains of width several tens of nanometres. Note that the nearest-neighbour C_{60} separation in the double domain structure corresponds closely to that observed in bulk C_{60} and so higher layers of C_{60} may be incorporated in well ordered hexagonal layers.

After annealing a sample with the surface structure shown in figure 5(b) in the range 200–300 °C for 1–30 min, we find that the second- and third-layer islands are desorbed, leaving a monolayer termination which retains the double domain ordering. This presumably means that second and subsequent C_{60} layers are bonded rather weakly to the first monolayer. However, the first monolayer is bonded much more strongly to the underlying Si. The C_{60} monolayer therefore provides a surface coating which interacts rather weakly with subsequent adsorbate layers.

To investigate the stability of the C_{60} monolayer-terminated Si(111) 7×7 we have exposed samples to

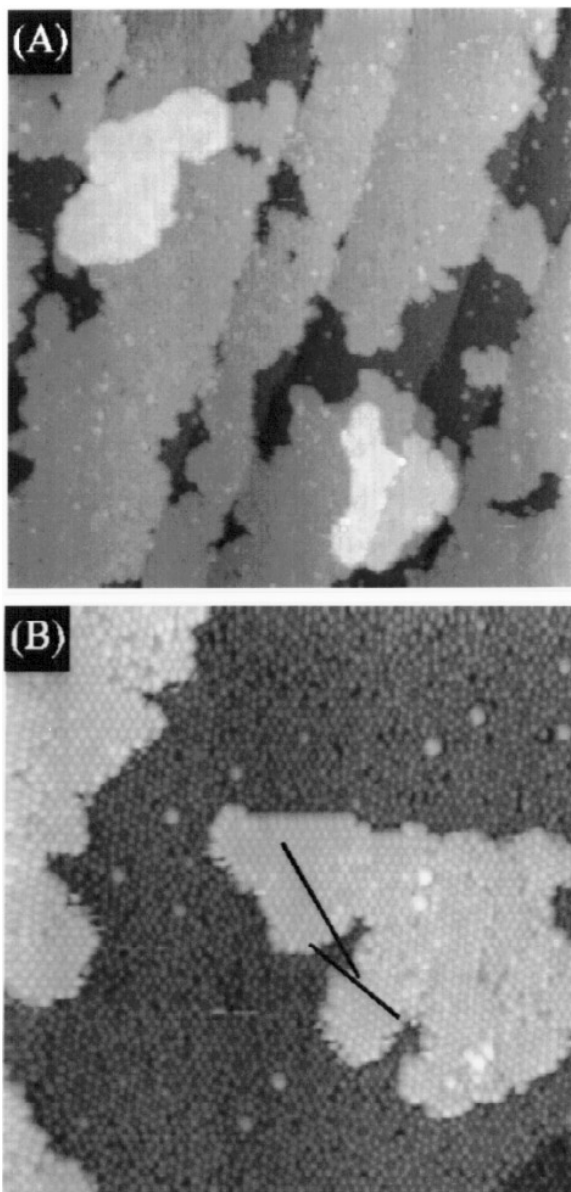


Figure 5. (a) 150 nm^2 scan of multilayer coverage of C_{60} on the Si(111) 7×7 surface. Dark regions correspond to the complete first monolayer, mid-tone, to patches of second layer, and the brightest contrast regions are third-layer islands. Detail of Si steps can be seen running from the upper right of the image to the lower left region. (b) 60 nm^2 scan of the surface shown in (a) showing a second-layer island on top of the first monolayer. The thick dark lines show a principal axis for each domain. Scan parameters (sample voltage, current): +3.5 V and 0.1 nA.

atmosphere for up to 30 min and immersed them in water for up to 1 min. This treatment would result in complete corruption of the Si(111) 7×7 surface. In contrast, the C_{60} monolayer appears to completely inhibit chemical attack of Si(111) 7×7 and thus acts to passivate the Si surface. Note that thick C_{60} layers have previously been shown to passivate Si [18] and Al [19] surfaces. Typical results are shown in figure 6. Figures 6(a) and 6(b) show large- and small-area STM scans of a sample which has been exposed

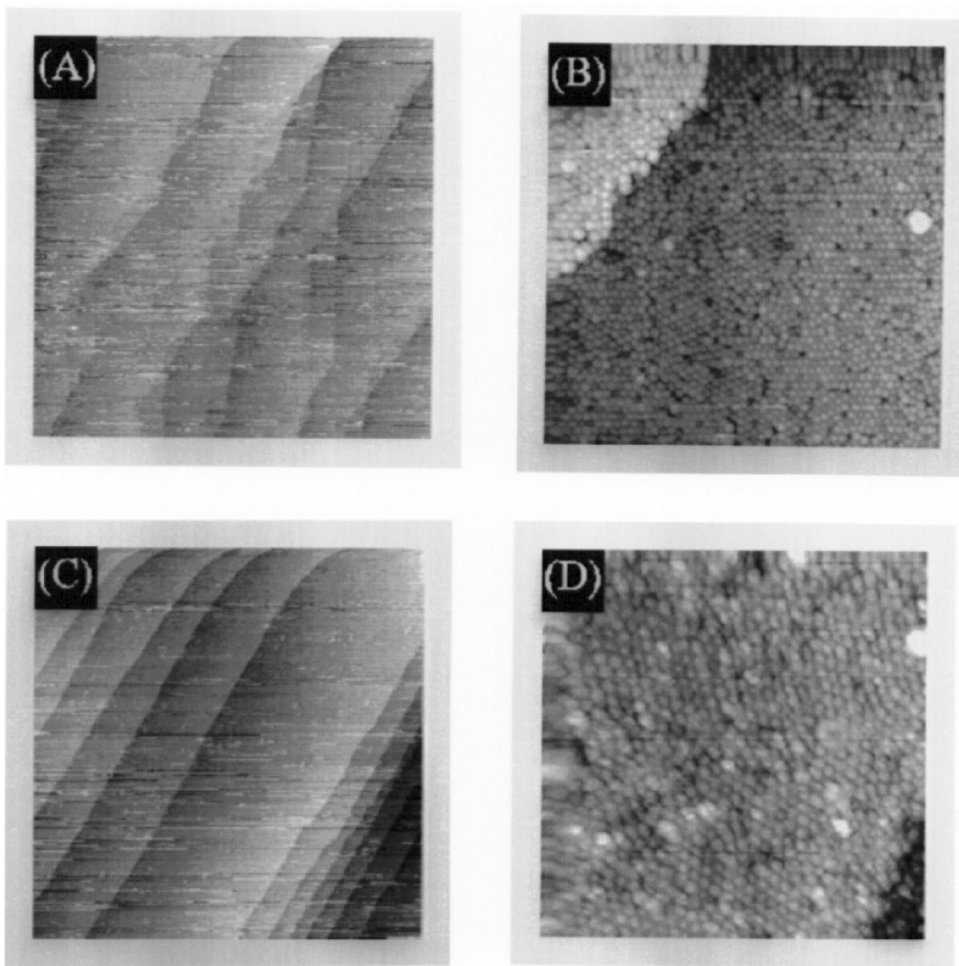


Figure 6. (a) 500 nm² scan of a single monolayer adsorbed on the Si(111) 7 × 7 surface which has been exposed to atmosphere for 1 min. Scan parameters (sample voltage, current): +3.5 V and 0.1 nA. (b) 50 nm² scan of a single monolayer adsorbed on the Si(111) 7 × 7 surface which has been exposed to atmosphere for 30 min, and then annealed at 260 °C for 60 min. Double domain ordering of the C₆₀ molecules is observed. Scan parameters (sample voltage, current): –3.5 V and 0.1 nA. (c) 400 nm² scan of a single monolayer on the Si(111) surface following a 30 s dip in deionized water. Scan parameters (sample voltage, current): +3.5 V and 0.1 nA. (d) 30 nm² scan of the surface shown in (c) following a 260 °C anneal for 15 min. Again, double domain ordering of the first monolayer can be seen indicating that the (7 × 7) reconstruction of the Si is maintained. Scan parameters (sample voltage, current): +3.0 V and 0.2 nA.

to atmosphere for 1 min. This sample has been annealed in UHV at ~ 200 °C for 15 min prior to imaging.

In the large-area image Si terraces are clearly resolved, while in figure 6(b) individual C₆₀ molecules are resolved which are ordered in the double domain structure discussed above. Note that the double domain ordering of the C₆₀ molecules is directly related to the position of the Si adatoms of the underlying 7 × 7 reconstruction. Observation of double domain ordering therefore shows that the underlying 7 × 7 reconstruction of the Si surface remains intact. Note that STM images acquired without annealing also show this hexagonal ordering but image quality is rather poor due, we believe, to physisorbed material on the surface. Similarly, figures 6(c) and (d) show that the C₆₀ molecules and Si terraces can be resolved even after immersion in deionized water for 1 min at room temperature. Thus the C₆₀ monolayer inhibits chemical attack by both water and atmospheric oxygen.

Finally, we address a point which is sometimes neglected in discussions on UHV/STM modification. This relates to the problem of locating specific sites on a surface. This is generally rather difficult since access for optical microscopy is usually limited. One solution is to incorporate the STM in a scanning electron microscope (SEM) [20], although this also has drawbacks in terms of ease of construction and possible corruption of surfaces. As an alternative, we have developed an alignment strategy based on the use of registration marks formed using electron beam and optical lithography. These registration marks may be etched or formed by lift-off of metal overlayers. Figure 7(a) shows an SEM image of some etched marks while figure 7(b) shows STM images of the same area. Note that this central 4 μm × 4 μm square has been located on a 5 mm × 5 mm Si sample. The Si in this case is a (100) wafer, offcut by 4° towards (001). It is interesting to note that after flash annealing we observe Si

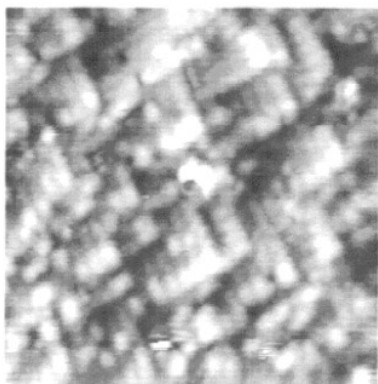
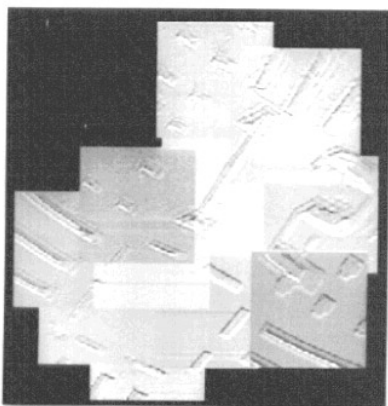
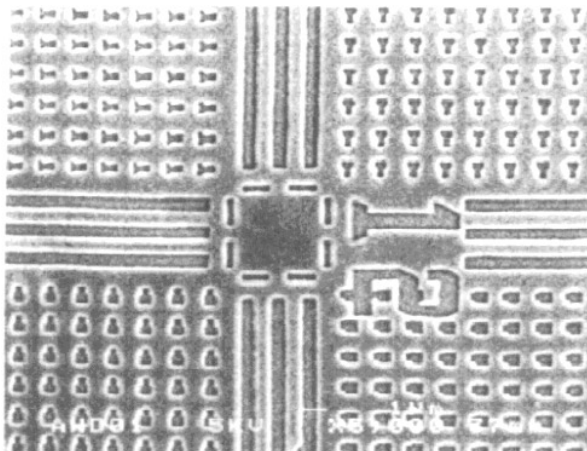


Figure 7. A series of images to demonstrate the formation and use of alignment marks. The top figure shows an SEM micrograph of a series of alignment marks wet etched in a Si(100) (misaligned by 4° towards the (001) direction) surface. These marks were formed using electron beam lithography. The central region is a square of side $4\ \mu\text{m}$. The middle image is a montage of several STM images, each of which covers an area $2.5 \times 2.5\ \mu\text{m}^2$. In addition each of the images has been differentiated to highlight the etched marks. Scan parameters are sample voltage $-4\ \text{V}$, $0.1\ \text{nA}$. The lowest image is taken using the STM (sample voltage $2\ \text{V}$, $0.23\ \text{nA}$, $20\ \text{nm} \times 20\ \text{nm}$) and shows the Si(100) surface following flash annealing at 1200°C . Dimer rows are clearly resolved in this image.

dimer rows forming a 2×1 reconstruction and terrace steps zig-zagging across the surface (the preferred terrace step is oriented along [110]). An STM image of this surface is shown in figure 7(c). This means that the formation of registration marks which requires coating the sample with resist is compatible with the formation of clean Si surfaces.

Our results have shown that it is possible to manipulate C_{60} molecules on Si(111) 7×7 and form nanometre scale clusters. In addition we have shown that C_{60} can act to chemically passivate Si(111) 7×7 . We are optimistic that these results, in conjunction with our alignment techniques, will be developed further to fabricate experimental structures with an active region on an atomic or molecular scale.

Acknowledgments

This work was supported by the UK EPSRC. We are grateful to Dr S Thoms (University of Glasgow) for help with electron beam lithography.

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