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# Passivation of Si(111)-7×7 by a C$_{60}$ monolayer

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*Department of Physics, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

C$_{60}$ monolayers are formed on a Si(111)-7×7 surface under ultrahigh vacuum (UHV) conditions. The effects of exposure to atmosphere (for 30 min) and water (for 30 s) are assessed by comparing images of the surface acquired using an UHV scanning tunneling microscope. Following exposure and/or immersion we are able to resolve the C$_{60}$ molecules exhibiting hexagonal order in an arrangement which is essentially identical to that formed prior to withdrawal from the UHV system. Our results clearly show that deposition of one monolayer of C$_{60}$ on a Si surface can inhibit chemical attack by water and atmospheric oxygen. © *1996 American Institute of Physics.* [S0003-6951(96)00130-1]

The surfaces of semiconductors are generally chemically reactive and oxidize on exposure to the atmosphere. Following work by Yablonovich,[1] there has been an intensive research effort devoted to the preparation of semiconductor surfaces which are passivated, that is chemically treated to reduce their reactivity. The most widely studied examples of passivation are Si surfaces treated with hydrofluoric acid and/or ammonium fluoride for which the dangling bonds formed on the free surface are passivated by H termination resulting in Si–H bonds.[2,3] This surface may be also formed in ultrahigh vacuum (UHV) by exposure to atomic H.[4,5] In addition to its chemical stability the Si:H is electronically passivated since there are no midgap surface states. It is also possible to passivate GaAs surfaces using aqueous sulphide compounds,[6,7] however there are few other examples of passivation.

In this letter, we describe a passivation treatment which results in a chemically unreactive Si(111) surface. An important difference between our work and previous studies is that the passivated Si surface retains the atomic configuration of the 7×7 reconstruction rather than forming the bulk terminated (1×1) surface structure which results from H passivation. A partially ordered monolayer of C$_{60}$ molecules forms the passivating layer. The passivation is inferred from a comparison of scanning tunneling microscopy (STM) images taken in UHV immediately after the surface preparation, and subsequent images taken after the surface has been exposed to the atmosphere and/or immersed in water.

Previous studies have shown that thick (20 nm) C$_{60}$ films could protect Si(111)-7×7 (Ref. 8) and Al (Ref. 9) surfaces from the atmosphere. It was assumed in the work on Si(111)-7×7 that the interaction between C$_{60}$ and Si was weak and that the thick layer prevented diffusion of atmospheric gases to the C$_{60}$/Si interface.[8] However, we argue below that the C$_{60}$/Si interaction is in fact relatively strong and show that only a single monolayer is required for passivation.

A piece of Si(111)($\sim$7×5 mm$^2$) cut from a B doped wafer (resistivity $\rho > 1$ $\Omega$ cm) is loaded into an UHV chamber (pressure $\sim 10^{-10}$ Torr). After outgassing overnight (temperature $T \sim 700$ °C) the sample temperature is raised to $\sim 1200$ °C for 1 min to create a 7×7 reconstruction. STM[10] images are taken at room temperature using electrochemically etched W tips which are cleaned by heating in UHV. C$_{60}$ is deposited from a Knudsen cell heated to 320°, with the sample held at room temperature. The total coverage is in the range 1–3 monolayers. At this stage STM images of the surface reveal a full monolayer coverage together with islands of second and, for higher total coverage, third layers. The sample is then annealed at a temperature in the range 200–300 °C. The resulting surface is covered uniformly by a single monolayer of C$_{60}$.

C$_{60}$ on Si(111)$-$7×7 has been studied at submonolayer coverage,[11,12] monolayer coverage[13] and multilayer coverage,[14] and has been used for experiments on molecular manipulation.[15,16] Close to a monolayer coverage C$_{60}$ molecules are hexagonally ordered with one molecule above each corner hole of the 7×7 reconstruction and the remainder absorbed midway between Si adatom pairs.[17] This leads to two possible domains which are oriented at ±11° to the principal axes of the Si.[13,14] Figure 1 shows a STM image of C$_{60}$ terminated Si in which an area corresponding to each domain is identified. Note that the configuration of C$_{60}$ molecules in the double domain structure[14] is determined by adsorption at particular sites on the 7×7 surface. Observation of this structure therefore implies that the atomic configuration of the underlying Si corresponds to that of the 7×7 surface.

C$_{60}$ terminated Si was then extracted from UHV and exposed to air for times between 1 and 30 min. Exposure to
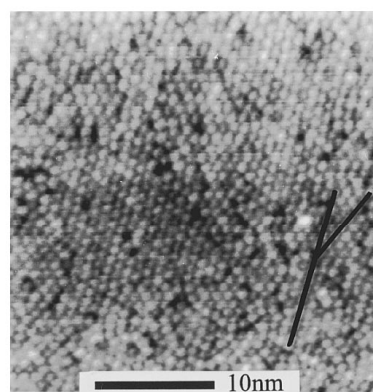


FIG. 1. Constant current STM image (sample bias 3.5 V, tunnel current 0.1 nA) of monolayer coverage of C$_{60}$ on the Si(111) surface after annealing at 290 °C for 10 min. The angle between the principal axes of the two domains is 22°.
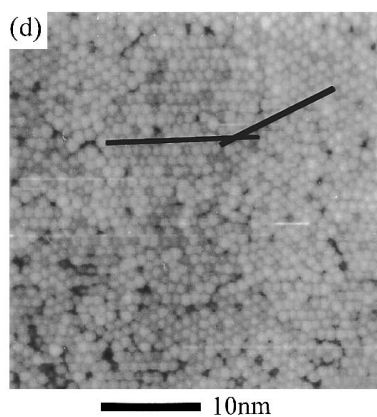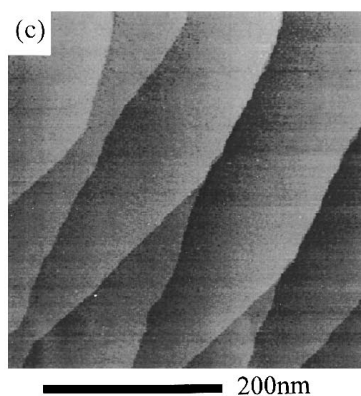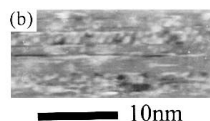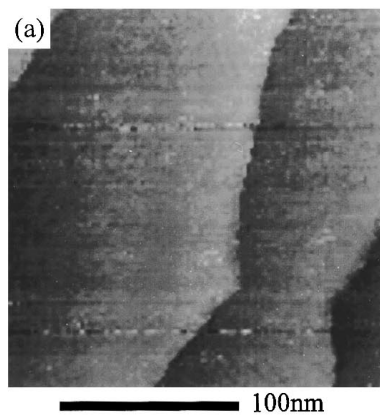
(a)

100nm

(b)

10nm

(c)

200nm

(d)

10nm

FIG. 2. Constant current STM images of $C_{60}$ monolayer on Si(111)-7×7 after exposure to atmosphere: (a) large area scan (2.0 V, 0.4 nA) showing terraces preserved after exposure for 1 min; (b) small area scan (2.5 V, 0.1 nA) of (a) showing several tip changes. Although image quality is generally poor there are a few scan lines with molecular resolution; (c) large area scan (−3.5 V, 0.1 nA) of sample exposed to atmosphere for 30 min and then annealed at 260 °C for 60 min prior to STM imaging; (d) small area scan (−3.5 V, 0.1 nA) of (c) showing double domain ordering of $C_{60}$ monolayer. This image should be compared with Fig. 1.
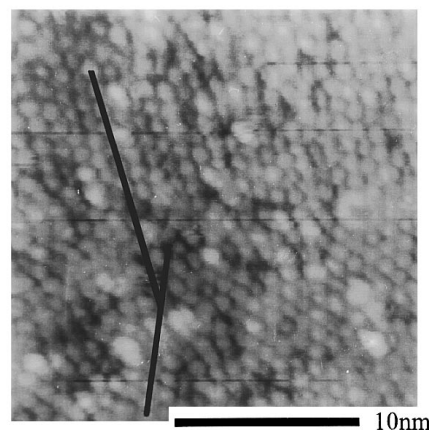


10nm

FIG. 3. Small area STM image (3.0 V, 0.2 nA) of a $C_{60}$ monolayer on Si(111)-7×7 which has been taken out to atmosphere, immersed in deionized water for 30 s, blown dry with $N_2$, returned to UHV and then annealed at 260 °C for 15 min. The double domain structure indicative of the underlying 7×7 reconstruction is clearly resolved.

with Fig. 1. Figures 2(a) and 2(b) show, respectively, a large and small area scan of a surface taken immediately after reloading the sample into UHV after an exposure time of 1 min. In Fig. 2(a) atomic terraces and bilayer steps (height 0.31 nm) may be resolved. In Fig. 2(b) it is possible to resolve the individual $C_{60}$ molecules. However, the image quality in Figs. 2(a) and 2(b) is poor and this surface is difficult to image, due we believe, to physisorbed material on the surface. This material induces many tip changes and in general results in poor resolution as shown in Fig. 2(b) where a small number of scan lines have good resolution while the rest of the image is of poor quality.

Figures 2(c) and 2(d) show STM images of a surface which has been exposed to atmosphere for 30 min and then annealed at 260 °C for 60 min, a cycle similar to that undergone by the sample prior to extraction from UHV. Following annealing, the stability of the tip is markedly improved and the quality of STM images is acceptable, due, we believe, to the desorption of physisorbed material from the surface. The surface prior to exposure to atmosphere and that following annealing are very similar [compare Figs. 1 and 2(d)]. In particular the double domain hexagonal ordering is clearly resolved in Fig. 2(d) indicating that the adatom configuration of the 7×7 reconstruction remains in tact beneath the $C_{60}$ monolayer. This shows that an adsorbed $C_{60}$ monolayer inhibits chemical attack of Si(111) by atmospheric gases.

We have also investigated the effects of immersion of Si(111)-7×7/$C_{60}$ in water. For this experiment the sample is prepared as described above and then immersed in deionized water (resistivity 18 MΩ) for 0.5 min. The sample is then returned to the UHV chamber and annealed at 260 °C for 15 min. As discussed above STM imaging is difficult without annealing. Figure 3 shows a STM image acquired following sample annealing. The hexagonal double domain ordering is clearly resolved in Fig. 3. This implies that the $C_{60}$ monolayer has inhibited the chemical interaction of the Si with the water.

The interaction of $C_{60}$ and Si(111)-7×7 is not fully understood but there is a consensus that electrons are transferred from Si dangling bonds to the $C_{60}$ molecules.[18–20] Suto *et al.* have investigated $C_{60}$/Si(111)-7×7 using

atmosphere of clean Si(111)-7×7 leads to oxidation and the complete corruption of the 7×7 reconstruction. In contrast the $C_{60}$ terminated Si(111) withstands exposure to atmosphere. This is clear from a comparison of Figs. 2(a)–2(d)

HREELS (high resolution electron energy loss spectroscopy) and show that there are 2 electrons per $C_{60}$ for a coverage close to one monolayer, although there is a large quoted error ($\pm 1$ electron). In a recent theoretical study of the energy levels and charge density of isolated $C_{60}$ molecules Yamaguchi[20] has argued that 3.35 electrons are transferred to $C_{60}$ from Si dangling bonds. This charge is localized around 9 C atoms close to the point of contact between the $C_{60}$ and the Si surface.

Our results indicate that $C_{60}$ forms a strong bond with the Si surface and that it both inhibits chemical attack of the Si by the reactive constituents of the atmosphere, and also remains stable itself. There are two possible mechanisms for the protection of the Si surface. The first is that the 19 electrons per $7\times7$ unit cell in Si dangling bonds are either transferred to or involved in bonding to the $7C_{60}$ molecules per unit cell and therefore are not available for bonding with other species. This corresponds to $\sim 2.7$ electrons per $C_{60}$, a number which is consistent with the theoretical and experimental evidence cited above. The second possibility is that the presence of the $C_{60}$ molecules on the surface restricts the access of other molecules, for example $O_2$, $H_2O$, to the underlying Si. To assess the second possibility we take the hard sphere diameter, $d_0$, of $C_{60}$ as 1.0 nm.[11] This gives a maximum diameter, $d_m = 0.15$ nm $[=(1/\sin 60° - 1)d_0]$ for a molecule to pass through the close packed $C_{60}$ monolayer. This is much smaller than the van der Waal's diameter of O (0.28 nm).

While we are not able to draw a strong conclusion as to which of these effects, if either, dominate, we note that there are many domain boundaries and packing faults where steric protection alone might not be expected to be effective. These packing faults have a similar appearance in images before and after exposure to atmosphere/water [compare Figs. 1 and 2(d)] implying that the inhibition of atmospheric attack by the formation of the $C_{60}$/Si bond must play some role.

There are several potential applications for the $C_{60}$ terminated Si(111)-$7\times7$ surface which fall predominantly into two classes. The first is as a protective resist with a thickness of order 1 nm. Typically the smallest lateral feature formed in a resist will have a width comparable with the resist thickness, so that this protective layer may be suitable for the definition of nanometer scale features. The second class of application would be as a passivated silicon substrate for STM manipulation of additional adsorbed molecular species. This is based on our observation that the $C_{60}$ is unreactive and so should be bonded fairly weakly to subsequent adsorbed molecules.

In conclusion we have shown that the $C_{60}$ monolayer/ Si(111)-$7\times7$ surface is chemically stable with respect to exposure to atmosphere and immersion in water.

*Note added in proof.* We have recently conducted a series of photoemission experiments on $C_{60}$/Si(111). Our results confirm that the $C_{60}$ inhibits atmospheric oxidation although some oxidation is observed for samples exposed to atmosphere for over 1 h.

[1] E. Yablonovich, D. L. Allara, L. C. Chang, T. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57**, 249 (1986).

[2] R. S. Becker, Y. J. Chabal, G. S. Higashi, and A. J. Becker, Phys. Rev. Lett. **65**, 1917 (1990).

[3] G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker, Appl. Phys. Lett. **58**, 1656 (1991).

[4] F. Owman and P. Martensson, Surf. Sci. **303**, L367 (1994).

[5] J. W. Lyding, T.-C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abeln, Appl. Phys. Lett. **64**, 2010 (1994).

[6] E. Yablonovich, C. J. Sandroff, R. Bhat, and T. Gmitter, Appl. Phys. Lett. **51**, 439 (1987).

[7] C. J. Sandroff, R. N. Nottenburg, J.-C. Bischoff, and R. Bhat, Appl. Phys. Lett. **51**, 33 (1987).

[8] H. Hong, W. E. McMahon, P. Zschack, D.-S. Lin, R. D. Aburano, H. Chen, and T.-C. Chiang, Appl. Phys. Lett. **61**, 3127 (1992).

[9] A. V. Hamza, J. Dykes, W. D. Moseley, L. Dinh, and M. Balooch, Surf. Sci. **318**, 368 (1994).

[10] The STM, electronics and software were provided commercially by Oxford Instruments SPM Group, formerly WA Technology, Cambridge, UK.

[11] Y. Z. Li, M. Chander, J. C. Patrin, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **45**, 13837 (1992).

[12] X.-D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, Jpn. J. Appl. Phys. **31**, L983 (1992).

[13] D. M. Chen, J. Chen, and D. Sarid, Phys. Rev. B **50**, 10 905 (1994).

[14] H. Xu, D. M. Chen, and W. N. Creager, Phys. Rev. Lett. **70**, 1850 (1993).

[15] S. Maruno, K. Ianaga, and T. Isu, Appl. Phys. Lett. **63**, 1339 (1993).

[16] P. H. Beton, A. W. Dunn, and P. Moriarty, Appl. Phys. Lett. **67**, 1075 (1995).

[17] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1988).

[18] D. Chen and D. Sarid, Phys. Rev. B **49**, 7612 (1994).

[19] S. Suto, A. Kasuya, O. Ikeno, C.-W. Hu, A. Wawro, R. Nishitani, T. Goto, and Y. Nishina, Jpn. J. Appl. Phys. **33**, L1489 (1994).

[20] T. Yamaguchi, J. Phys. Soc. Jpn. **64**, 1258 (1995).