



## Room temperature manipulation of the heterofullerene C 59 N on Si(100)-2×1

M. J. Butcher, F. H. Jones, P. Moriarty, P. H. Beton, K. Prassides, K. Kordatos, and N. Tagmatarchis

Citation: [Applied Physics Letters](#) **75**, 1074 (1999); doi: 10.1063/1.124601

View online: <http://dx.doi.org/10.1063/1.124601>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/75/8?ver=pdfcov>

Published by the [AIP Publishing](#)

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



# Room temperature manipulation of the heterofullerene C<sub>59</sub>N on Si(100)-2×1

M. J. Butcher, F. H. Jones, P. Moriarty, and P. H. Beton

*School of Physics and Astronomy, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom*

K. Prassides, K. Kordatos, and N. Tagmatarchis

*School of Chemistry, Physics and Environmental Sciences, University of Sussex, Brighton, East Sussex BN1 9QJ, United Kingdom*

(Received 23 February 1999; accepted for publication 30 June 1999)

The adsorption of the heterofullerene C<sub>59</sub>N on the Si(100)-2×1 surface has been investigated using scanning tunneling microscopy (STM) under ultrahigh vacuum conditions. The molecules are adsorbed in monomer form in the troughs between silicon dimer rows. It is possible to use the tip of the STM to manipulate the molecules parallel and perpendicular to the dimer rows in a controlled fashion at room temperature. To determine the stability of the C<sub>59</sub>N monomer we have examined the response of pairs of molecules to STM manipulation and found that the Si(100)-2×1 surface inhibits conversion to (C<sub>59</sub>N)<sub>2</sub> dimers. © 1999 American Institute of Physics. [S0003-6951(99)04034-6]

Over recent years there has been a growing interest in experimental devices which have active regions formed from a small number of atoms or molecules. Fullerene based materials have been of particular importance in these developments. In recent work phase coherent electron transport has been observed in single walled carbon nanotubes.<sup>1</sup> In addition individual C<sub>60</sub> molecules have been positioned on semiconductor and metallic surfaces using the tip of a scanning tunneling microscope (STM)<sup>2-4</sup> constituting one of the few demonstrations (see also Ref. 5) that the mode of manipulation developed by Eigler and Schweizer<sup>6</sup> can be realized at room temperature. Wires<sup>7</sup> and arrays of fullerene molecules may be formed on Si and in the light of recent progress towards alignment and contacting<sup>8</sup> on the nanometer scale there are excellent prospects for the connection of fullerene based nanostructures to macroscopic contact pads.

One reason that fullerenes are particularly susceptible to STM manipulation relates to their near spherical shape. This results in a relatively small area of contact with an underlying substrate, but a large cross section available for interaction with the STM tip. Another important aspect of fullerenes is the wide range of derivatives which are available, for example endohedral fullerenes<sup>9-11</sup> in which an atom is encapsulated by the carbon cage, and also the “doped” azafullerene, C<sub>59</sub>N, in which a single carbon atom is replaced by a group V nitrogen atom.<sup>12</sup> The possibility of combining such derivatives with STM manipulation gives rise to exciting and diverse possibilities for the formation of molecular nanostructures. However at this stage it is not clear how the modification of a fullerene cage will affect the response of the resulting molecule to STM manipulation.

In this letter we address this question by examining the adsorption and manipulation of C<sub>59</sub>N on Si(100)-2×1. C<sub>59</sub>N is a reactive free radical and in its bulk form dimerizes to form (C<sub>59</sub>N)<sub>2</sub>.<sup>13-15</sup> However in recent work it has been shown that C<sub>59</sub>N sublimes in monomer form. Following adsorption on a Si(111)-7×7 surface [and, as we show below, the Si(100)-2×1 surface] C<sub>59</sub>N is unable to diffuse and redimerize, at least for submonolayer coverages.<sup>16</sup> Despite the

reactive nature of the free radical monomer we find that STM manipulation is possible on this surface with a response that is very similar to that of C<sub>60</sub>.<sup>3</sup> This result demonstrates that STM manipulation is possible even for a modified fullerene cage and that fabrication of complex molecular nanostructures should be possible using this approach.

Experiments were carried out in a commercially available STM system. Si(100) samples were loaded into a UHV system (base pressure 1×10<sup>-10</sup> Torr) and outgassed at approximately 700 °C for 12 h. Samples were then heated to 1200 °C for 60 s, annealed at 800 °C for 5 min, and allowed to cool. This procedure results in a 2×1 reconstruction with a low defect density. C<sub>59</sub>N was loaded into a Knudsen cell and after thorough outgassing was heated to 550 °C and sublimed with a typical deposition rate of 1 monolayer/h. The sample, which was held at room temperature during deposition, was then transferred to the STM. For imaging and manipulation electrochemically etched W tips were used which were cleaned in UHV by electron beam heating. Both imaging and manipulation experiments were undertaken at room temperature.

The schematic in Fig. 1 shows the atomic configuration of the Si(100)-2×1 surface. Filled circles represent highest layer atoms which dimerize by forming a  $\sigma$  bond with a neighboring atom.<sup>17</sup> Rows of Si dimers run along [011] and [011] on alternate terraces, resulting in a higher anisotropic surface. Also shown in Fig. 1 is a STM image of C<sub>59</sub>N (bright circular features) adsorbed on the Si(100)-2×1 surface (the bright lines in the background correspond to Si dimer rows<sup>17</sup>). The molecules appear as bright circular features and have the same height (~0.7 nm) and apparent width (~2.1 nm) as observed in STM images of C<sub>60</sub> on this surface.<sup>18,19</sup> Stable STM images of the molecules require bias voltages with magnitude >3 V.

C<sub>59</sub>N is adsorbed at sites centered in the troughs between dimer rows. There are two possible adsorption sites (denoted A and B in Fig. 1) corresponding, respectively, to the molecular center lying midway between four sets of dimers and two sets of dimers. Analysis on 150 molecules show that

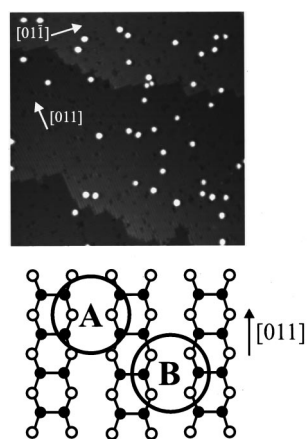


FIG. 1. STM image of a low coverage of  $C_{59}N$  on  $Si(100)-2\times 1$  ( $60\times 60\text{ nm}^2$  +3 V, 0.2 nA). Schematic diagram shows the  $2\times 1$  reconstruction and the two possible adsorption sites for  $C_{59}N$ : (A) four-dimer site; (B) two-dimer site.

$\sim 75\%$  of molecules reside on A sites and the remaining 25% sit on B sites. In higher resolution images the  $C_{59}N$  shows internal structure which differs from molecule to molecule. This implies that molecules are not rotating, and do not all adopt the same orientation on the surface. There is no evidence for dimerized molecules or clustering.

The monomers may be manipulated using a technique used previously for  $C_{60}$  manipulation on  $Si$ .<sup>2,3</sup> Controlled manipulation is achieved by first moving the tip towards the surface (by increasing the tunnel current and decreasing the bias voltage) close to a target molecule. The tip is then moved across the surface through a predetermined displacement which passes through the initial position of the adsorbed molecule. A successful application of this procedure results in a displacement of the target molecule to the final position of the STM tip. Typically the tip moves through a distance of 2.4 nm in steps of 0.6 nm. The tunnel current is updated through feedback control at the end of each step. The tip is then retracted from the surface and returned to its original position.

Figures 2(a)–2(c) show the lateral translation of a  $C_{59}N$  molecule. Between the acquisition of Figs. 2(a) and 2(b) the manipulation procedure is applied with parameters of  $-1.0$  V and  $-1.0$  nA. The initial and final positions of the tip are identified on Figs. 2(a) and 2(b). Note that the tip trajectory during manipulation is parallel to the horizontal edge of the image and at a slight angle to the dimer rows. Figure 2(c) shows an image taken after a further application of this procedure.

For the parameters used in Fig. 2 the molecule is moved through the full extent of the tip displacement, and a success rate (percentage of attempts at manipulation which resulted in displacement of molecules) of  $\sim 90\%$  is achieved. It was also possible to manipulate molecules using a positive bias voltage of +1 V, 1 nA with a comparable success rate. Manipulation could be achieved with all tips which were used. In many cases the tip would suffer some degradation after, typically, a few hours although the tip condition could be recovered by the application of a voltage pulse.

Manipulation of a molecule across dimer rows is more difficult [Figs. 2(d)–2(f)]. A lower success rate for manipulation is observed ( $\sim 30\%$ ) and there is less control of the

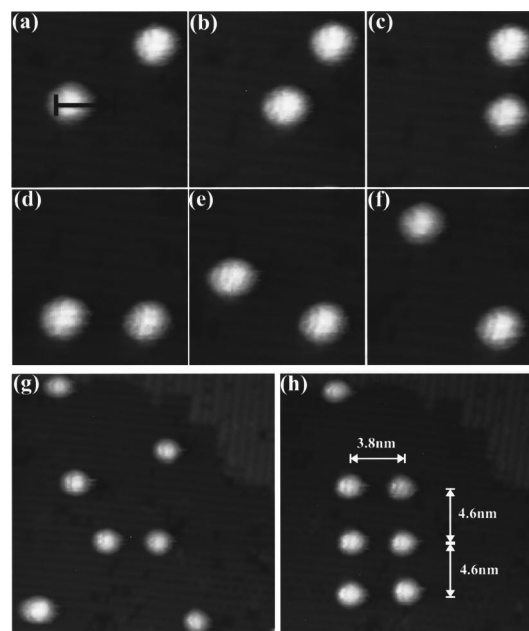


FIG. 2. Demonstration of  $C_{59}N$  manipulation: (a)–(c) parallel to the  $Si(100)-2\times 1$  dimer rows. (d)–(f) perpendicular to the dimer rows. (Scan areas of  $8\times 8\text{ nm}^2$ , manipulation parameters:  $-1.0$  V, 1.0 nA, scanning parameters:  $-3.5$  V, 0.2 nA); (g) six molecules before manipulation; (h) the same six molecules after manipulation to precise positions.

molecule, often with a displacement parallel to the rows. The  $C_{59}N$  molecule therefore exhibits an anisotropic response to manipulation due to its interaction with the underlying surface. Note that for Figs. 2(a)–2(c) (manipulation parallel to rows), the dimer rows are at a slight angle to the tip displacement, but the molecule remains in the same trough and is not displaced across a row. Thus the troughs effectively act to guide the molecule.

To demonstrate the control of manipulation that can be achieved a simple pattern has been formed. One such example is shown in Figs. 2(g) and 2(h), where six molecules have been manipulated to precise positions. The accuracy of positioning is determined by the underlying  $2\times 1$  surface periodicity. The manipulation procedure does not induce any additional defects in the underlying surface. As well as arrays “wire” like structures can also be fabricated consisting of many molecules.

We have attempted to manipulate molecules with a range of tunneling currents and negative bias voltages. The results are summarized in Fig. 3 in which the success rate for

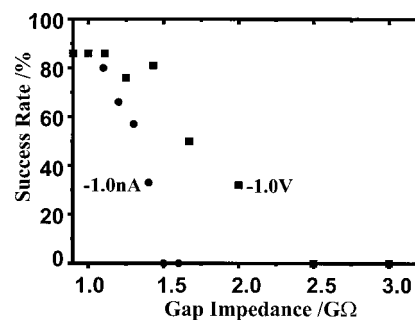


FIG. 3. Graph showing manipulation success rate parallel to the dimer rows as a function of tip-sample gap impedance by: (a) keeping the bias voltage constant at  $-1.0$  V and varying the tunnel current and (b) keeping the tunnel current constant at  $-1.0$  nA and varying the bias voltage.

manipulation parallel to the dimer rows is plotted versus the gap impedance. Two sets of data are presented in which either the bias voltage or tunnel current is held constant. The threshold gap impedance for manipulation is in the range 1.5–2.5 G $\Omega$ . A test is used to determine the nature of the interaction between the tip and the molecule using a modified manipulation procedure in which the tip is not retracted away from the surface before returning to its original position. It was found that after each attempt the molecule remains at the maximum excursion of the tip and was not dragged back to the starting position. This indicates that a repulsive interaction between the tip and molecule gives rise to manipulation, as was also found for C<sub>60</sub>.<sup>3</sup>

We have also used the manipulation technique to probe the interactions between the molecules. C<sub>59</sub>N monomers are radical species in the gas phase and are predicted to be highly reactive.<sup>12–15</sup> An experiment was therefore undertaken to attempt to redimerize the adsorbed monomers by pushing one molecule towards another molecule adsorbed in the same trough. However, over many attempts it proved impossible to push two molecules closer together than 1.15 nm in the same trough. The resulting configuration of the molecules always involves a translation of one of the molecules into a neighboring trough as observed for C<sub>60</sub>.<sup>3</sup> The positions of the C<sub>59</sub>N molecules are therefore determined by molecule–substrate interactions rather than intermolecular bonding.

The presence of a N atom within the cage leads to pronounced differences in the chemistry and reactivity of C<sub>59</sub>N as compared with C<sub>60</sub>. However the response of the C<sub>59</sub>N monomer to manipulation is not greatly affected by the incorporation of N. This implies that the mechanical properties of fullerenes and heterofullerenes are rather similar even though their electronic properties may be quite different. Our results therefore imply that fullerenes and their derivatives constitute a set of building blocks which may be used to form nanostructures in which both the position and electronic properties of each component may be precisely specified.

The authors thank the U.K. Engineering and Physical Research Council for financial support. N.T. acknowledges support from the E.U. in the form of a Marie Curie Fellowship. The authors also are very grateful to Professor F. Wudl, at the University of California Los Angeles, for assistance with the synthesis of the C<sub>59</sub>N source.

- <sup>1</sup>S. J. Tans, M. H. Devoret, H. J. Dai, A. Thess, R. E. Smalley, L. J. Giergigs, and C. Dekker, *Nature (London)* **386**, 474 (1997).
- <sup>2</sup>P. H. Beton, A. W. Dunn, and P. Moriarty, *Appl. Phys. Lett.* **67**, 1075 (1995).
- <sup>3</sup>P. Moriarty, Y.-R. Ma, M. D. Upward, and P. H. Beton, *Surf. Sci.* **407**, 27 (1998).
- <sup>4</sup>M. T. Cuberes, R. R. Schlitter, and J. K. Gimzewski, *Appl. Phys. Lett.* **69**, 3016 (1996).
- <sup>5</sup>T. A. Jung, R. R. Schlitter, J. K. Gimzewski, H. Tang, and C. Joachim, *Science* **271**, 181 (1996).
- <sup>6</sup>D. M. Eigler and E. K. Schweizer, *Nature (London)* **344**, 524 (1990).
- <sup>7</sup>A. W. Dunn, P. H. Beton, and P. Moriarty, *J. Vac. Sci. Technol. B* **14**, 1596 (1996).
- <sup>8</sup>A. W. Dunn, B. N. Cotier, A. Nogaret, P. Moriarty, P. H. Beton, and S. P. Beaumont, *Appl. Phys. Lett.* **71**, 2937 (1997).
- <sup>9</sup>Y. Chai, T. Guo, C. M. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. H. Wang, J. M. Alford, and R. E. Smalley, *J. Phys. Chem.* **95**, 7564 (1991).
- <sup>10</sup>D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. DeVries, and C. S. Yannoni, *Nature (London)* **366**, 123 (1993).
- <sup>11</sup>R. D. Johnson, M. S. DeVries, J. Salem, D. S. Bethune, and C. S. Yannoni, *Nature (London)* **355**, 239 (1992).
- <sup>12</sup>J. C. Hummelen, B. Knight, J. Pavlovich, R. Gonzalez, and F. Wudl, *Science* **269**, 1554 (1995).
- <sup>13</sup>W. Andreoni, A. Curioni, K. Holczer, K. Prassides, M. Keshavarz, K. J.-C. Hummelen, and F. Wudl, *J. Am. Chem. Soc.* **118**, 11335 (1996).
- <sup>14</sup>C. M. Brown, L. Cristofolini, K. Kordatos, K. Prassides, C. Bellevia, R. Gonzalez, M. Keshavarz-K., F. Wudl, A. K. Cheetham, J. P. Zhang, W. Andreoni, A. Curioni, A. N. Fitch, and P. Pattison, *Chem. Mater.* **8**, 2548 (1996).
- <sup>15</sup>T. Pichler, M. Knupfer, M. S. Golden, S. Haffner, R. Friedlein, J. Fink, W. Andreoni, A. Cuirioni, M. Keshavarz-K., C. Bellavia-Lund, A. Sastre, J.-C. Hummelen, and F. Wudl, *Phys. Rev. Lett.* **78**, 4249 (1997).
- <sup>16</sup>M. J. Butcher, F. H. Jones, P. H. Beton, P. Moriarty, B. N. Cotier, M. D. Upward, K. Prassides, K. Kordatos, N. Tagmatarchis, F. Wudl, V. Dhana, T. K. Johal, C. Crotti, C. Comicoli, and C. Ottaviani (unpublished).
- <sup>17</sup>R. M. Tromp, R. J. Hamers, and J. E. Demuth, *Phys. Rev. Lett.* **55**, 1303 (1985).
- <sup>18</sup>D. Chen and D. Sarid, *Surf. Sci.* **318**, 74 (1994).
- <sup>19</sup>X.-D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina, and T. Sakurai, *Phys. Rev. B* **47**, 15923 (1993).