

Nanoscale Templating of One-Dimensional Surface Molecular Structures

P. W. Murray, I. M. Brookes, S. A. Haycock, and G. Thornton

Interdisciplinary Research Centre in Surface Science and Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom

(Received 11 August 1997)

Scanning tunneling microscopy has been used to demonstrate the formation of self-assembled one-dimensional rows of C_{60} on Au/Ni(110), which is of interest in relation to molecular wire growth. This made use of the [001] direction chain structures formed at Au coverages greater than 0.4 monolayers to act as adsorption templates, the interchain separation being dictated by the coverage. C_{60} molecules adsorb on the Au chain structures forming single molecular rows aligned along the direction of the Au chains. The separation of C_{60} molecules along [001] is approximately 10 Å, the same as the bulk intermolecular spacing. [S0031-9007(97)05177-6]

PACS numbers: 61.16.Ch, 68.35.Bs, 81.15.Ef

The search for viable methods of nanostructure mass fabrication is being pursued with some vigor because of the unique potential of their physiochemical properties. Current industrial methods cannot achieve the length scales required [1], which are on the order of 10 nm, requiring new strategies to be evaluated. Two avenues are being examined in which structures are built up from the surface using surface science techniques. In one, specific structures have been created by manipulating individual atoms or molecules with a scanning tunneling microscope (STM) tip [2–4]. This was initially demonstrated for substrates at 4 K, although it has now been shown that atoms and molecules can be manipulated at room temperature [5,6].

The nanostructures formed by tip manipulation are created over a very small area of the sample (i.e., the area that the tip scans). An alternative method is to use templates to pattern subsequent overlayer growth. This self-assembly approach has been demonstrated for two dimensions using a template based on misfit dislocations. These were used to create ordered Ge islands on $Si_{(1-x)}Ge_x/Si$ [7]. Here we demonstrate that templating can be used for one-dimensional molecular structures, which are of importance in nanowire growth and the emerging field of molecular electronics [8,9]. Specifically, we describe the formation of one-dimensional C_{60} structures by adsorption on Au chains preformed on Ni(110) [10]. C_{60} was chosen to demonstrate this method because of the interest in its novel physical, chemical, and electronic properties [11].

In general, C_{60} adopts a close-packed hexagonal structure on metal surfaces, which arises from intermolecular van der Waals attraction [12]. In some cases, however, the natural morphology of the substrate has been shown to induce a more complicated structure. For example, adsorption on Au(110)-(1 × 2) results in a corrugated fullerene overlayer [13], while an fcc(110) termination is formed on $TiO_2(100)$ -(1 × 3) [14] due to the massive microfacet reconstruction. On Ni(110), the substrate of interest here, C_{60} adsorption induces a significant restructuring to form corrugated hexagonal C_{60} islands [15]. The modification of this behavior by preformed Au chain structures illus-

trates how heteroepitaxial metal growth can be used to engineer surfaces with specific physiochemical properties.

The experiments were performed using a commercial Omicron ultrahigh vacuum STM operated at room temperature. The base pressure of the instrument during this work was $\leq 10^{-10}$ mbar. The Ni(110) crystal (Metal Crystals & Oxides, Cambridge, UK) was prepared by repeated cycles of Ar ion bombardment and annealing to 900 K until judged clean and ordered by low-energy electron diffraction and Auger-electron spectroscopy as well as STM. Au deposition onto the substrate at 700 K was carried out by resistively heating a conical W filament which contained Au wire (Goodfellow, 99.99%). An elevated substrate temperature ensured a greater coherence of the Au chains. C_{60} evaporation involved heating a ceramic crucible containing C_{60} (Strem Chemicals, Newburyport, USA, 99.5%) to 500 K. C_{60} adsorption was also carried out with a sample temperature of 700 K to increase the degree of order. The same degree of order was achieved by 700 K postannealing an overlayer formed by room temperature adsorption. The pressure during evaporation of Au and C_{60} remained below 1×10^{-9} mbar. Coverages of both Au and C_{60} were estimated from the STM images. STM imaging was carried out using the constant current mode with typical tunneling parameters of $V_s = 0.5$ V, $I_t = 1$ nA. Variations in polarity and tunneling conditions had little effect on the images. Calibration of the STM employed images of Cu(110)-(2 × 1)-O, for which the dimensions are well known.

Figure 1(a) shows a model of the Au structures formed on Ni(110) for $\theta_{Au} > 0.4$ ML (monolayer). These have been previously investigated in detail using STM and effective-medium theory calculations, which have shown that the chain structure is more complicated than a simple Au overlayer [10]. The structures consist of alternating Au dimers and trimers, which are located above Ni vacancies. Furthermore, the chains are also stabilized by two rows of substituted Au atoms on either side. There is considerable deviation of the Au atomic separations compared to bulk Au and thus a considerable amount of strain. The spacing

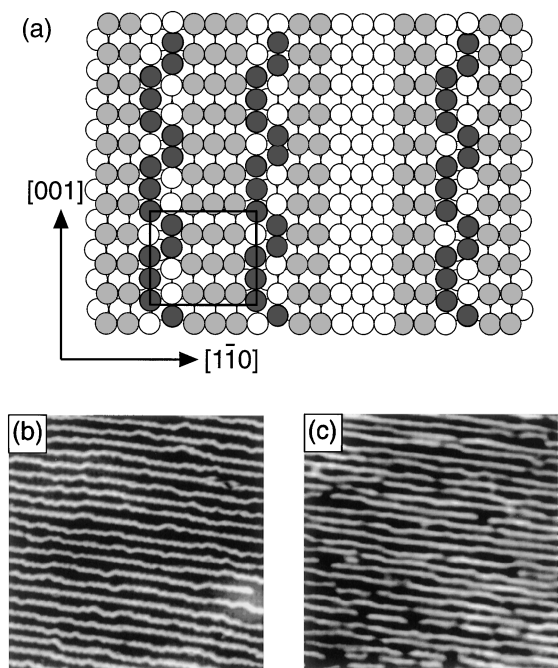


FIG. 1. (a) Schematic model of the Au structures formed on Ni(110) for $\theta_{\text{Au}} > 0.4$ ML. Ni atoms are represented by open circles, the Au chains by dark circles, and the substituted Au by shaded circles [10]. As the coverage increases the chains converge until the saturation (5×3) structure, indicated in the diagram, is reached. (b) An STM image ($300 \times 300 \text{ \AA}^2$) of the Au chain structure on Ni(110) depicted in (a), with the chains separated by 17 Å along $[1\bar{1}0]$. This corresponds to an Au coverage of 0.67 ± 0.05 ML. (c) An image ($300 \times 300 \text{ \AA}^2$) recorded following a higher Au deposition (0.95 ± 0.05 ML) in which the chain separation is reduced to 12 Å.

between the chains can be controlled as a function of coverage (i.e., the higher the Au coverage the closer the chains). This continues until a saturation structure with a 5×3 periodicity is reached. STM images corresponding to such structures are shown in Figs. 1(b) and 1(c). Figure 1(b) shows an image recorded at an Au coverage of 0.67 ± 0.05 ML in which the average spacing of the chains is on the order of 17 Å apart, while Fig. 1(c) is a higher Au coverage (0.95 ± 0.05 ML) in which the saturation (5×3) structure is formed where the chain spacing is reduced to 12 Å.

When the separation of the Au chains is close to the bulk C_{60} spacing (i.e., 12 Å in the 5×3 structure), C_{60} adsorption results in the formation of small hexagonal islands, as seen in Fig. 2. It is important to note that this structure differs from the corrugated hexagonal islands observed following adsorption onto clean Ni(110) [15]. This indicates that the reactivity of the Ni substrate has been considerably modified by the deposition of submonolayer Au, as does the lack of preferential adsorption at step edges which is observed on clean Ni(110) [15].

A dramatic change in the C_{60} structures occurs when the Au interchain separation is increased. Instead of forming hexagonal islands, the fullerenes form one-dimensional rows orientated along the $[001]$ direction, as seen in

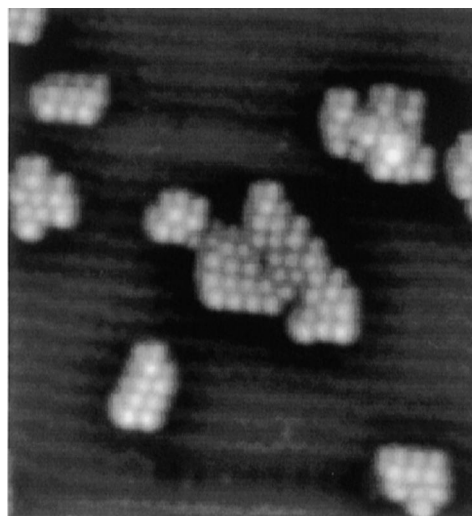


FIG. 2. An STM image ($220 \times 220 \text{ \AA}^2$) of C_{60} structures formed on Au/Ni(110) for an Au coverage of 0.95 ± 0.05 ML, in which the row spacing is 12 Å. Small hexagonal islands can be seen, and there is no evidence for the restructuring which was observed following C_{60} deposition on clean Ni(110) [15].

Fig. 3(a). The separation of molecules within the rows is close to the bulk spacing of 10 Å, while the separation of the rows along $[1\bar{1}0]$ is the same as the spacing of the Au chains (i.e., 15 Å). Increasing the C_{60} coverage leads to larger C_{60} chain lengths, as shown in Fig. 3(b). In places, rows of up to 150–200 Å can be seen [labeled A in Fig. 3(b)]. Higher resolution images, such as that shown in Fig. 3(c), reveal that the C_{60} molecules are located on sites above the Au chains. No change in Au chain separation is seen within experimental uncertainty (6%), ruling out the possibility that Au is squeezed out by C_{60} in order to create adsorption sites on the underlying Ni vacancies. The fact that two-dimensional islands of C_{60} are absent clearly indicates that adsorbate–Au atom bonding is stronger than the intermolecular interaction.

In a few areas the separation of the Au chains is closer, and the molecules within adjacent rows can be seen to line up. This can be explained simply by the fact that, at such reduced separations, intermolecular forces begin to take effect. By lining up, the separation of the molecules between adjacent rows is minimized. For the molecules imaged in Fig. 3(c), the intermolecular distance is 12 Å. Similar effects have been observed on Si(100) for C_{60} molecules adsorbed on the (2×1) reconstructed dimer rows [16]. As the row separation increases, the intermolecular attraction is so weak that the effect is negligible.

Given the known interaction of C_{60} molecules with Au and Ni surfaces it is, at first sight, surprising that the Au chains act as preferential adsorption sites. From previous electron energy loss spectroscopy data [17], a much stronger interaction is seen between the fullerenes and Ni(110) than it is for Au(110), as evidenced by a greater degree of charge transfer into the C_{60} lowest unoccupied molecular orbital (LUMO). Charge transfer was not correlated with the work function, indicating that transfer

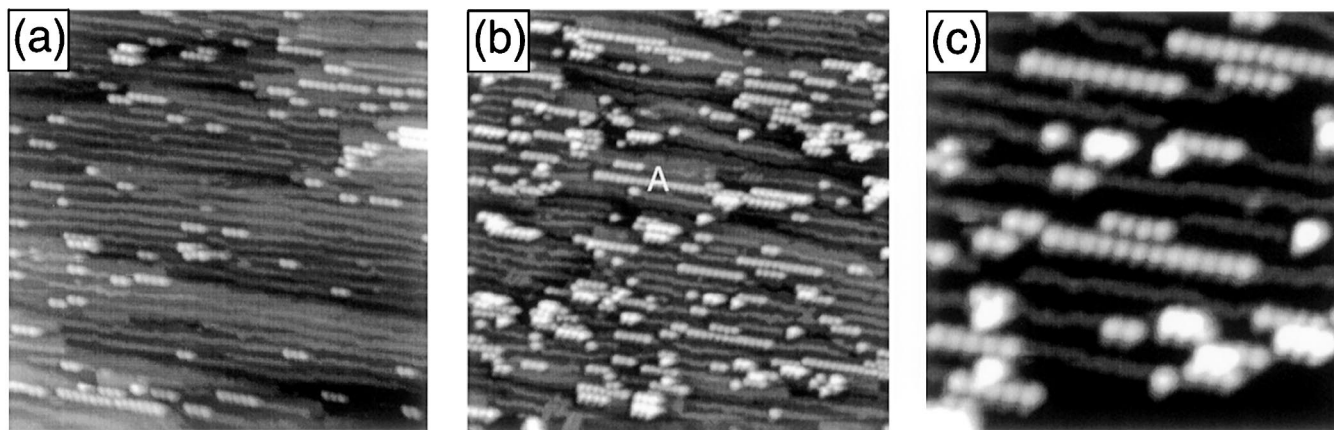


FIG. 3. (a) STM image ($500 \times 500 \text{ \AA}^2$) following deposition of 0.05 ± 0.01 ML of C_{60} on a Ni(110) surface with 0.65 ± 0.05 ML of predosed Au. The fullerene molecules can be seen to form short chains along the [001] direction. (b) An STM image ($500 \times 500 \text{ \AA}^2$) recorded following further C_{60} deposition up to 0.20 ± 0.01 ML on the same Au precovered Ni substrate, which shows an increased length of the molecular chains. In places the chains are on the order of 200 \AA in. long as indicated by the label A. No evidence is seen for any islands of C_{60} molecules. (c) High resolution image ($150 \times 150 \text{ \AA}^2$) of the C_{60} chain structures revealing that the adsorption site is on top of the Au chain structures.

occurred via the formation of chemical bonds. In the case of Ni the d band is close in energy to the C_{60} LUMO, resulting in a strong hybridization [15]. On this basis, and in a situation where Au chains are separated by clean Ni(110) terraces, adsorption might be expected on the Ni terraces. However, the Au structures formed on Ni(110) are alloyed and under considerable strain, and the reactivity of these low coordinated structures is likely to differ considerably from an Au(110) surface. Indeed, the electronic structure of Au on bimetallic surfaces can differ considerably from that of bulk Au [18]. For Au deposition on transition metals a shift is seen in the Au d band, which is accompanied by d band narrowing. If the d band shift is large enough to bring it close to the C_{60} LUMO this would explain the enhanced reactivity of the Au chains, allowing Au to compete successfully with Ni for C_{60} adsorption without the need for restructuring of the Ni(110) substrate.

In summary, we have demonstrated the use of a template to pattern subsequent overlayer growth, with Au chains on Ni(110) serving as a template to grow one-dimensional [001] direction rows of C_{60} molecules. Although a detailed mechanism has yet to be evaluated, the results demonstrate that the growth of one metal on another (or the formation of surface alloys) can dramatically affect the chemical properties. Our work illustrates a potential application of this surface modification in the field of self-assembled nanostructures.

Useful discussions with L. Pleth Nielsen, M. Ø. Pedersen, F. Besenbacher, and I. Stensgaard are gratefully acknowledged. This work was funded by the United Kingdom Engineering and Physical Sciences Research Council.

[1] W. M. Tolles, in *Ultimate Limits of Fabrication and Measurement*, edited by M. E. Welland and J. K. Gimzewski,

- NATO ASI, Ser. E, Vol. 292, (Kluwer, Dordrecht, 1995).
- [2] D. M. Eigler and E. K. Scheizer, *Nature (London)* **262**, 524 (1990).
- [3] M. F. Crommie, C. P. Lutz, and D. M. Eigler, *Science* **262**, 218 (1993).
- [4] G. Meyer, B. Neu, and K. H. Rieder, *Europhys. News* **26**, 7 (1995).
- [5] T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang, and C. Joachim, *Science* **271**, 181 (1996).
- [6] P. H. Beton, A. W. Dunn, and P. Moriarty, *Appl. Phys. Lett.* **67**, 1075 (1995).
- [7] S. Yu. Shiryayev, F. Jensen, J. Lundsgaard Hansen, J. Wulff Petersen, and A. Nylandsted Larsen, *Phys. Rev. Lett.* **78**, 503 (1997).
- [8] F. L. Carter, *Molecular Electronics* (Dekker, New York, 1987).
- [9] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour, and P. S. Weiss, *Science* **271**, 1705 (1996).
- [10] L. Pleth Nielsen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, C. Engdahl, P. Stoltze, and J. K. Nørskov, *Phys. Rev. Lett.* **74**, 1159 (1995).
- [11] *The Fullerenes*, edited by H. W. Kroto, J. E. Fisher, and D. Cox (Pergamon, Oxford, 1993).
- [12] T. Sakurai, X.-D. Wang, Q. K. Xue, Y. Hasegawa, T. Hashizume, and H. Shinohara, *Rep. Prog. Surf. Sci.* **51**, 263 (1996).
- [13] J. K. Gimzewski, S. Modesti, and R. R. Schlitter, *Phys. Rev. Lett.* **72**, 1036 (1994).
- [14] P. W. Murray, J. K. Gimzewski, R. R. Schlittler, and G. Thornton, *Surf. Sci. Lett.* **367**, L79 (1996).
- [15] P. W. Murray, M. Ø. Pedersen, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, *Phys. Rev. B* **55**, 9360 (1997).
- [16] D. Klyachko and D. M. Chen, *Phys. Rev. Lett.* **75**, 3693 (1995).
- [17] M. R. C. Hunt, S. Modesti, P. Rudolf, and R. E. Palmer, *Phys. Rev. B* **51**, 10039 (1995).
- [18] J. A. Rodriguez, *Surf. Sci. Rep.* **24**, 223 (1996).