INSTRUMENTS AND METHODS OF INVESTIGATION

## Scanning tunneling microscopy of fullerenes on metal and semiconductor surfaces

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<u>Abstract.</u> The current state of the ultra-high vacuum scanning tunneling microscopy (STM) of fullerene molecules is reviewed with the use of the authors' work. We focus our work on absorption and reaction of the C<sub>60</sub> and C<sub>70</sub> fullerenes, separately or in mixture, with semiconductor [Si(111)-7×7 and Si(100)-2×1] and metal [Cu(111)-1×1 and Ag(111)-1×1] surfaces. By using the STM, the adsorption geometry and the corresponding reconstruction are directly observed on these surfaces, and the intramolecular structures are revealed in high resolution STM images which are analyzed theoretically within the local charge distribution model. Results on the ordered growth of fullerene films on metal and semiconductor surfaces are presented and discussed.

## 1. Introduction

Fullerenes [1], a novel allotropic form of carbon in which carbon atoms form closed-cage molecules, have received considerable attention since the recent breakthrough in their synthesis made their macroscopical amounts available [2].

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The first report of this phenomenon — specifically of the highly symmetric  $C_{60}$  molecule, which is the most stable among the fullerenes — was made in Ref. [3], where also the soccer-ball structure of this particular fullerene was proposed. C<sub>60</sub> is the third form into which, in addition to the well-known planar graphite and tetrahedral diamond, pure carbon may crystallize. Let us note some of its properties here. Solid  $C_{60}$ (fullerite) is a molecular crystal bound by van der Waals forces, with a consequence that it has low coupling energy and hence can and does readily exhibit relatively low-temperature phase transitions. Thus, at  $T \ge 260$  K C<sub>60</sub> forms a facecentered cubic (FCC) lattice of free-to-rotate spherical molecules [4], whereas below 260 K this rotation is partially hampered and the structure transforms into a simple cubic one with four molecules per unit cell [5]. At  $T \leq 90$  K, the molecular motion stops completely. Both crystals and films of C<sub>60</sub> show semiconducting properties [6], and their doping with alkali atoms gives rise to metal conductivity [7] and may even cause a superconducting transition at relatively high temperatures of 18 to 33 K [8, 9]. And finally, the large internal space within the C<sub>60</sub> and C<sub>60</sub> molecules should be noted.

 $C_{70}$ , the second most important fullerene, has lower symmetry, its structure being reminiscent of the rugby ball [10].  $C_{70}$  forms a hexagonal close-packed (HCP) lattice when in the solid phase. Because the  $C_{70}$  molecule is a spheroid, its phase diagram turns out to be more complex than that for  $C_{60}$ [11].

The advanced techniques for synthesis and purification of  $C_{60}$  proposed in 1990, as well as the discovery of higher fullerenes ( $C_{70}$ ,  $C_{76}$ ,  $C_{84}$ ,  $C_{90}$ ,  $C_{96}$ ,...) [2, 12–15] and metalcontaining fullerenes (metalfullerenes or fullerides, of which those with Gd [16], Sc [17], La [18, 19], and Y [20–22] are currently known) have spurred research in the physics and chemistry of these materials and stimulated considerably their application in the design of new materials, new types of lubrication, nonlinear optical devices, etc. — as witnessed by a sharp growth of publications on this topic [23–27]. Since most of the existing and, even more so, of potential fullerene applications depend on surface interactions or the use of thin films, and because fullerene electrochemistry is directly related to metal surface processes, the crystalline and electronic structure of fullerene coatings as well as fullerene film properties and film growth mechanisms become a problem of great topical interest. To solve it, the most powerful tools are of course the scanning tunneling microscopy/spectroscopy (STM/STS) [28, 29] and related (e.g., scanning probe microscopy) techniques which have proved very useful in the atomic resolution study of the morphology and electronic structure of real-space solid surfaces.

In the present study, the STM and STS techniques have been employed to investigate fullerenes (C<sub>60</sub>, C<sub>70</sub>, C<sub>84</sub>), metallofullerenes (ScC<sub>74</sub>, Sc<sub>2</sub>C<sub>74</sub>, Sc<sub>2</sub>C<sub>84</sub>, YC<sub>82</sub>, GdC<sub>82</sub>), and their interaction with typical semiconductor [Si(111), Si(100)] and metal [Cu(111), Ag(111), Pt(111)] surfaces. The aim of the present review is to describe the state of the art of the subject and to demonstrate and analyse the most typical results. For consistency purposes, our original results on C<sub>60</sub> and  $C_{70}$  adsorption on the Si(111)-7×7, Si(100)-2×1, Cu(111)-1×1, and Ag(111)-1×1 surfaces are primarily presented. While the first two of these surfaces were chosen as the most interesting and practically important ones, the last two are typical for the noble metals, and their surface lattice parameters are close to those of the  $C_{60}$  and  $C_{70}$  bulk phase lattices: an important point as far as regular fullerene film growth is concerned. While our primary interest was the adsorption properties of surfaces with respect to the fullerenes, some features of thin fullerene film growth in these systems were also investigated.

### 2. Fullerene preparation and the experimental procedure

Comprehensive description of the synthesis and purification of the C<sub>60</sub>, C<sub>70</sub>, and C<sub>84</sub> fullerenes and ScC<sub>84</sub>, ScC<sub>74</sub>, and  $Sc_2C_{74}$  metalfullerenes can be found elsewhere [16, 30-32]. The fullerenes were formed by thermal decomposition of graphite in an arc discharge [30] between two graphite electrodes in 200-100 torr of buffer helium using a d.c. current of 200-250 A. The fullerene-enriched soot so obtained was first rinsed with a non-polar solvent (specifically benzene, which dissolves fullerenes very effectively) after which the mixture is very thoroughly filtered and vapored. The resulting highly dispersive (polycrystalline) black powder, a mixture of various fullerene species, was washed with hexane, methanol, and high-purity benzene to be employed for the extraction of fullerenes. The final isolation of the fullerenes was performed using the two-stage liquid-chromatographic techniques of Shinohara and coworkers [16, 33]. The so-called endohedrals — i. e., fullerenes with a metal atom in the unit cage — were obtained by the burning in arc flame of a composite rod containing — assuming the metal to be Sc — a high-purity  $S_2O_3$  — graphite powder and a filler (resin). Such scandium-graphite rods were cured and carbonized at T = 1000 °C for several hours in vacuum of  $10^{-5}$  torr and then used as positive electrodes in a d.c. current spark mode under static helium pressures of 50 to 100 torr. The resulting soot, which also contained endohedral complexes, was extracted with carbon disulphide, after which scandium endohedrals were isolated from pure fullerenes by the same liquid-chromatography technique [33] and so could be

accumulated in sufficient amounts. The formation of the fullerenes and endohedrals was confirmed directly by laser desorption with a subsequent time-of-flight spectroscopy measurements analysis of the desorption products. The resulting purity of the C<sub>60</sub>, C<sub>70</sub>, and C<sub>84</sub> samples are 99.5%, 99%, and 98%, respectively. To obtain the desired ratios of C<sub>60</sub> and C<sub>70</sub> in the mixture, original pure powders of these fullerenes were used.

In order to deposit the fullerene onto the surface under study, the fullerene powder so obtained was loaded into a Ta foil dozer preliminary outgassed in a ultra-high vacuum chamber. The dosator was then placed near the clean surface of the sample and heated until the desired temperature was achieved. The evaporation temperature for  $C_{60}$  and  $C_{70}$  was about 300–330 °C, and for  $C_{84}$ , about 400 °C. For the Sc fullerenes, it ranged between 500 and 700 °C owing to the higher coupling energy.

Most of the experiments were carried out in the ultra-high vacuum STM at Tohoku University which is equipped with a field ion microscope to characterize and modify the scanning tip performance [34, 35], and also provided with an additional sample preparation chamber with a built-in ULS-020 unit composed of an electron Auger spectrometer and a low energy electron diffraction (LEED) system. To secure the stability and reproducibility of data, (111) oriented singlecrystal tungsten tips were used. Tungsten was chosen because of the isotropic s/p component which it has in the conduction electron density of states at the Fermi level and which gives the main contribution to the tunneling current for the electrode configuration used, and the  $\langle 111 \rangle$  orientation was intended to secure a long-term stability of the tip shape. The final scanning tip shape, with a few or even single atoms on the tip apex (as shown [34] crucial for true atomic resolution STM) was obtained by room temperature field evaporation under continuous field ion microscope monitoring. The main ultra-high vacuum chamber was continuously being evacuated by a custom design ion pump 'Riber' at a rate of 1200 lb/ s, the base pressure is below  $3 \times 10^{-11}$  torr. The final annealing of the Si samples was conducted at chamber pressures not exceeding  $1 \times 10^{-10}$  torr. Further details of STM are described elsewhere [34, 36, 37].

Si(111)-7×7 and Si(100)-2×1 surfaces were cleaned by annealing the Si surface following a number of ion bombardment cycles; or, alternatively, by subjecting the sample to a series of high-temperature (up to 1230 °C) heat treatments. It was through such treatments followed by smooth cooling at 10 K/s [38, 39] that a defect density below 0.1%  $(1.5 \times 10^{13} \text{ cm}^{-2})$  could be achieved at these surfaces. The samples themselves were cut from silicon wafers and measured 5 × 20 × 0.5 mm in size.

The surfaces of the Cu(111) and Ag(111) single crystals were cleaned by several 500-eV Ar<sup>+</sup> ion bombardment cycles followed by annealing at 500 °C (Cu) or 420 °C (Ag) until the clean  $1 \times 1$  surfaces were ultimately observed with LEED or STM.

### 3. C<sub>60</sub> and C<sub>70</sub> adsorption on a silicon surface

# 3.1 Structure of the $C_{60}$ and $C_{70}$ fullerenes and of the Si(100) and Si(111) surfaces

As is known [3], the fullerene molecule  $C_{60}$  is modeled well by a highly symmetrical, truncated closed-surface icosahedron which is hollow unlike the corresponding carbon cluster. The surface of the molecule is formed by hexagons and pentagons at whose vertices there are located, in equivalent positions, carbon atoms [30, 40], each shared by two hexagons and one pentagon: an arrangement facilitated also by the structure of the  $s^2p^2$  shell of the carbon atom. In this framework, the radius of the  $C_{60}$  is  $\approx 0.35$  nm in agreement with X-ray results [40], and there are two types of bonding, a single one and a double one, to form this structure.

The structure of the  $C_{70}$  molecule is modeled fairly well by a spheroidal surface, also made of pentagons (in particular, in the polar regions) and hexagons [10] whose vertices, with the carbon atoms located at them, are linked by three bonding groups [41]. The height of the spheroid, i.e., the distance between the two pentagons at the opposite poles, is, in absence of rotation, 0.78 nm, and the equatorial diameter of the spheroid does not exceed 0.67 nm.

Since the Si(100)-2×1 and Si(111)-7×7 surfaces play an extremely important role in both fundamental surface physics study and the electronic device industry, an understanding of all aspects of their interaction with fullerenes is essentially important. The structures of these surfaces have recently been extensively studied and are now well established. The corresponding atomic models, namely the dimer model for Si(100)-2×1 [42] and Takayanagi's DAS model for Si(111)- $7 \times 7$  are now commonly accepted. According to these models, for Si(100)-2×1 each surface silicon atom involved in dimer formation has one dangling bond, whereas for Si(111)-7 $\times$ 7 surface each corner hole atom, adatom and rest atom has one dangling bond. STM images of these two surfaces, with clearly visible Si dimers and adatoms, may be found in every modern monograph on semiconductor surface physics [44]. Thus, due to the high density of dangling bonds, a strong interaction of silicon surface with fullerenes could be expressed. Also, it may be conjectured that such a strong interaction will hamper or even stop completely the rotation of C<sub>60</sub> molecules, which is a well-known effect in bulk C<sub>60</sub> [45, 46], and will enable a direct STM observation of the fullerene internal structure.

# 3.2 Adsorption of $C_{60}$ on Si(100)-2×1 and comparison with computer simulation results

We have study the C<sub>60</sub> adsorption geometry, thin film growth, and the electronic structure of the  $C_{60}$  molecules. Figure 1 shows a typical STM image of the initial stage of absorption of  $C_{60}$  on Si(100)-2×1, the bright spherical protrusions in the figure reflecting the arrangement of individual C<sub>60</sub> molecules. At this stage, it is seen that most  $C_{60}$  molecules are adsorbed in a random but steady way and that they occupy troughs between dimer rows without any preference to the for either step edges or nucleation into or island growth at the defected areas and along the troughs, where they are also distributed randomly. This indicates that the interaction of  $C_{60}$  molecules with the substrate is strong enough to make their migration along the Si surface highly unlikely after their deposition. During the surface scanning at bias voltages in the range -1.6 $V \leq +1.6$  V, however, the C<sub>60</sub> molecules were seen to be repeatedly trapped by the scanning tip as indicated by arrows in Fig. 1. From the same STM image the lateral diameter of the  $C_{60}$  is readily estimated to be 20 A, compared to its actual size of 0.7 A [26]. This may be explained by the tip-C<sub>60</sub> molecule convolution effect [47], which develops even for socalled 'monatomic' tips.

When the coverage is further increased to one monolayer (ML), second layer islands do not start to form until the first



**Figure 1.** STM image of the initial stage of  $C_{60}$  adsorption on the Si(100)-2×1 surface at ~0.01 ML coverage (tip bias voltage  $V_s = -2.0$  V, tunneling current  $I_t = 2.0 \times 10^{-11}$  A = 20 pA).

layer is complete (further evidence for the strong  $C_{60}$  substrate interaction), whereas the second layer  $C_{60}$  molecules are remain mobile enough before they find the area where the Si bare surface is exposed. The first layer  $C_{60}$  molecules demonstrate local ordering, a process which, as shown in Fig. 2, can actually proceed in two ways, with molecules either arranging themselves into a square type of local ordering at



50 A

**Figure 2.** STM image of about one monolayer of C<sub>60</sub> on Si(100). Top: an ordered c(4×4) arrangement; lower right: close-packed hexagonal c(4×3) layer. Dark areas: bare Si without C<sub>60</sub> coverage ( $V_s = -4.0 \text{ V}$ ,  $I_t = 20 \text{ pA}$ ). Arrow indicates the dimer row direction on the Si substrate.

the top of the image or into a hexagonal-like arrangement at the bottom. In this image, the dimer rows on the Si substrate run in the direction (011) marked by an arrow. The dark areas represent defects having no C60 molecules. A careful examination of this and similar STM images suggests a geometrical adsorption model for this system which is shown in Fig. 3 where the most favorable locations of the adsorbed particles (the so-called adsorption sites) and their local ordering may be seen. The dashed and solid circles in Fig. 3 are the buckled Si dimers, namely: the dashed circles are silicon atoms at the lower position; solid circles, those at the upper position; and large open circles represent  $C_{60}$ . It was also observed that, because of the adsorption of C<sub>60</sub>, the bending of the Si dimers becomes fixed, similar to what occurs with the alkali metals on Si(100)- $2 \times 1$  [34, 35]. At the very beginning of the adsorption process  $C_{60}$  resides the site (A), that is, the geometrical center of the four nearest-neighbor Si dimers which are, in their turn, surrounded by eight Si atoms. At slightly higher coverages, sites (B) (Fig. 3a) or (B') (Fig. 3b) become available for another C<sub>60</sub> molecule. Based on this model, both local ordering types seen with STM may be obtained in a natural way. Analysis of STM results shows that



**Figure 3.** Geometrical model of  $C_{60}$  adsorption on Si(100)-2×1. Solid and dashed circles show the buckled dimers, where the solid circles are Si atoms in the upper position.  $C_{60}$  molecules initially adsorb at A, B, and B' sites. At the monolayer coverages they form local ordered structures c(4×4) (a) and c(4×3) (b).

at the initial adsorption stage the nearest-neighbor distance is 12 A, which is much greater than the 10.9 A for position B and 9.6 A for (B') obtained from Fig. 3, suggesting repulsion between neighboring  $C_{60}$  molecules. Taking the spacing of FCC  $C_{60}$  at room temperature to be 10.0 A [2, 26], the higher value cited above points to charge transfer from the Si substrate to the  $C_{60}$  molecule.

The local ordering shown in Fig. 3a is a square-type molecular arrangement, i.e., a  $c(4\times4)$  adsorption layer, with nearest-neighbor distance of 10.9 A. In Fig. 3b, the local arrangement of adsorbed molecules shows a  $c(4\times3)$  quasi-hexagonal structure, and the (A)-(A) and (A)-(B') spacings are 11.5 A and 9.6 A, respectively. The surface concentrations of adsorbed molecules are  $1.13\times10^{14}$  cm<sup>-2</sup> for the  $c(4\times3)$  phase and  $8.42\times10^{13}$  cm<sup>-2</sup> for  $c(4\times4)$ . These are, respectively, 98% and 73% of the surface molecular density for the close-packed face (111) of the FCC C<sub>60</sub> crystal ( $1.15\times10^{14}$  cm<sup>-2</sup>): a clear indication that the first layer of C<sub>60</sub> is highly contracted. The formation of such stressed structures in the first layer on Si(100) suggests that the bonding between C<sub>60</sub> and Si substrate is stronger than among the C<sub>60</sub>.

Whereas the first  $C_{60}$  layer turns out to be strongly bound to the Si substrate, on the layer itself — and this even at room temperature — a second and subsequent (multiple) ordered layers may form indicating that the dangling bonds at the surface are passivated because of the first layer as seen from Fig. 4a. It was found that the second  $C_{60}$  layer was formed as islands which showed the Stransky-Krastanov† mode growth at room temperature. At close inspection, the islands show pronounced, ordered close-packed hexagonal structures reminiscent of the (111) surface of the FCC  $C_{60}$  crystal, with both the first and second layers showing only local ordering similar to the multilayered coverage of Fig. 2. Ordered hexagonal structures start to form above the third, fourth etc. layers, as shown clearly in Fig. 4b. The nearestneighbor distance in this case is 10.4 A, somewhat larger than in the FCC  $C_{60}$  fullerite at room temperature (10.0 A). So, even the fifth (marked in the figure) C<sub>60</sub> layer on this island is also slightly stretched as compared with the bulk crystal. A detailed analysis of the third, fourth, and fifth layers showed that they are oriented somewhat differently and are at an angle of about  $5^{\circ}$  to one another. As noted previously, the first and second layers are somewhat more stretched than the third indicating a gradual relaxation from the first layer to the bulk, of the atomic structure of the multilayered  $C_{60}$  film grown on Si(100)- $2 \times 1$ . Note that the molecules on the STM image of this surface (Fig. 4b) are equal in brightness, suggesting a high degree of order and symmetry in their arrangement. In some cases, certain types of defects, such as missing molecular defects and screw dislocations, were observed and their mobile nature was noted, the latter fact showing in turn that the surface of the  $C_{60}$  crystal film is itself quite mobile [47, 48].

To analyse the electronic structure of the  $C_{60}$  film on the Si(100) surface, the scanning tunneling spectroscopy (STS) technique was used. In previous calculations of density-of-states curves by Kawazoe and coworkers [49, 50], the position of the Fermi level had to be shifted downward by 0.4 eV to fit the experimental data. A good agreement between the calculated and experimental peaks on the STS curves is

<sup>†</sup> Kern R, Le Lay G, Metois J J "Basic mechanism in the early stages of epitaxy", in *Current Topics in Materials Science* Vol. 3 (Ed. H Kaldis) (Amsterdam: North-Holland, 1979) Ch. 3



Figure 4. STM images of the C<sub>60</sub> multilayers on Si(100)-2×1 ( $V_s = -3.5$  V,  $I_t = 20$  pA, scanning area 1600 A × 1600 A (a). Zoomed in image of the close-packed FCC(111) top layer of a C<sub>60</sub> island (140 A × 140 A,  $V_s = -3.0$  V,  $I_t = 20$  pA) (b).

achieved by incorporating a 0.1-0.3-electron per molecule charge transfer into the calculation [48, 47].

Thus the C<sub>60</sub>-Si(100) interaction takes place via dangling bonds leading ultimately to a charge transfer from the Si substrate to the adsorbed C<sub>60</sub> molecules. It is well known that molecules in bulk FCC C<sub>60</sub> rotate at 10<sup>9</sup> rp s<sup>-1</sup> at room temperature [4, 45, 46]. It would therefore be logical to expect that this strong interaction will substantially suppress or even stop the rotation of the first-layer C<sub>60</sub> molecules. Indeed, the images of the monolayer C<sub>60</sub> film adsorbed on Si(100) repeatedly exhibited internal structures in the form of three of four stripes for each C<sub>60</sub> as shown in Fig. 5a. Such structures reflect the structure of electronic states in real space and therefore differ considerably from the atomic structure of C<sub>60</sub>. Images of this kind were visible only with high- resolution STM.

An important feature of these intramolecular structures is their two-fold symmetry. In order to reveal the two-fold symmetry of the  $C_{60}$  molecule, however, one of the double carbon bonds between two closed hexagons on the spherical surface of  $C_{60}$  should face down on the Si(100) surface. If one of the closed pentagons on this surface faces the substrate, the molecule must exhibit five-fold rather than the observed twofold symmetry. If one of the closed hexagons on the surface faced down on the surface, the molecule would reveal a threefold symmetry. Based on the analysis above, we proposed [47] a geometrical model which adequately accounts for the two possible orientations of  $C_{60}$  on Si(100). Note that the internal structure in the form of 3 or 4 parallel stripes for each C<sub>60</sub> was discovered by us for the first time and could only be seen for the first-layer C<sub>60</sub> molecules [47, 48]. Reports [51, 52] of six- or five-membered ring structures have not been confirmed experimentally.

As is well known, STM actually images the spatial distribution of the local electronic density of states near the Fermi level. To calculate and simulate the intermolecular structures observed we took the theoretical STM interpreta-



Figure 5. STM image of the first C<sub>60</sub> layer on the Si(100)-2×1 (90 A × 90 A,  $V_s = -1.6$  V,  $I_t = 20$  pA).

tion due to Kawazoe et al. [49, 50] with adsorption geometry of the system being taken from experiment. Fig. 6 shows the results of the theoretical calculation of local density of states for two bands of the  $c(4\times3)$  single crystal layer of  $C_{60}$  on Si(100) as calculated from the formalism of Ref. [49] assuming the above adsorption model (Fig. 3) using the arguments of Refs [47, 48] for the orientation of molecular adsorbates on the substrate. Shown in the figure are the total density of states and the position of two closed hexagonal rings and two



**Figure 6.** Computer simulated images as the spatial distribution of the electronic density of states near the Fermi level within a  $C_{60}$  molecule adsorbed on Si(100)-2×1, (a) for the total charge, (b) and (c) for contributions from the levels 180 and 184, respectively.

closed pentagonal rings (a); and also the charge density distributions for the LUMO (lowest unoccupied molecular orbital) and the HOMO (highest occupied molecular orbital) bands (c), both distributions showing striped structures analogous to that imaged by STM. The level 180 is the original HOMO located 0.9 eV below the Fermi level on the energy scale. Given the scanning conditions leading to Fig. 5 ( $V_s = -1.6$  V), it is clearly this level which must control the STM imaging. The charge density distribution from level 180 in Fig. 6b exhibits four- stripe peaks and shows a good agreement with the STM image in Fig. 5.

### 3.3 Adsorption of C<sub>60</sub> on the Si(111)-7×7 surface

The Si(111) surface also shows a very strong interaction with  $C_{60}$  molecules. The early STM studies of the initial stage of  $C_{60}$  adsorption on Si(111) showed a random surface distribution of  $C_{60}$  molecules thus confirming their being strongly bound to the substrate [53]. Surprisingly, however, the images of individual  $C_{60}$  were found to differ in height, and STS showed different densities of states thus reflecting the local differences in substrate properties and in the nature of bonding [53, 54]. Accordingly, an attempt was made in

this study to determine more accurately the geometrical arrangement of the adsorbed C<sub>60</sub> [55]. Fig. 7 shows an STM image of the Si(111)-7×7 surface coated by an  $\sim$ 0.01 ML of C<sub>60</sub> molecules which appear as large bright spherical protrusions 3.6 A to 6.0 A high; the protrusion height could be measured to within 0.2 A because it is determined by local tunneling between the most protruding atoms of the scanning tip and the C<sub>60</sub> molecule and because, further, the environment of the tip is of minor importance in this context. From Fig. 7, the transverse dimensions of the protrusions are easily found to be between 20 and 30 A and to be dependent on the shape of the scanning tip (the convolution effect [47, 56]). When the sizes of the probing tip and of the object are comparable (as is the case here), so are their contributions to imaging, which gives further justification for our using a field ion microscope for scanning tip characterization [34]. From this and higher-coverage images, preferred areas of adsorption were located within the unit cell  $7 \times 7$  [55]. The Si(111)-7×7 surface is well described by Takayanagi's DAS model [43, 44], and each half of the unit cell has four almost equivalent sites for the C<sub>60</sub> adsorption, each of which is surrounded by three Si atoms. Specifically, among those four possible sites  $C_{60}$ molecules most frequently (in 80% of cases) choose the one which has the highest (in this case, three-fold) symmetry and does not contain the rest-site Si atom in its center. All these observations can be understood based on the highly symmetric characteristics of the C<sub>60</sub> molecule. Because of its large (7.1 A) diameter, only one  $C_{60}$  molecule can be adsorbed per one half of the unit cell, implying that at most two such molecules can be accommodated in a unit  $7 \times 7$  cell. A statistical analysis of our data showed  $C_{60}$  to prefer that half of the unit cell having a stacking defect (56% of cases) over the unfaulted half (30%). In some cases (7%) C<sub>60</sub> molecules occupy corner vacancies, but these were observed only rarely on dimer lines. These findings were later confirmed by Maruni et al. [57]. The fact that C<sub>60</sub> molecules prefer the faulted halves proves that there is a considerable



Figure 7. STM image of the initial adsorption of C<sub>60</sub> on Si(111)-7×7 (500 A × 1000 A,  $V_s = -2.0$  V,  $I_t = 20$  pA).

charge transfer from the substrate to the adsorbate since earlier STM work on Si(111)-7×7 showed these halves to be energetically more favorable and to have a greater density of states near the Fermi level [43, 58]. The charge transfer effect can also be seen directly on STM images provided the bias  $V_s$  is properly chosen. Thus, a decrease in the local density of states near the Fermi level has been convincing demonstrated [55] in the vicinity of a single C<sub>60</sub> adsorbed at the corner hole site on Si(111)-7×7.

As in the case of Si(100)-1×2 (Section 3.1), the adsorption of C<sub>60</sub> on Si(111)-7×7 also led to the elimination of their rotation at room temperature. Fig. 8a shows a single C<sub>60</sub> molecule positioned on an area of three-fold symmetry, and in Fig. 8b, where the molecule's structural details are shown, one clearly distinguishes four slightly curved rows running in the  $\langle \bar{1}10 \rangle$  direction with respect to the Si substrate, each row having an internal structure of its own. As noted previously, the process of STM imaging of an individual C<sub>60</sub> fullerene



**Figure 8.** (a) Single  $C_{60}$  molecule sitting at a three-fold symmetric site of the Si(111)-7×7 surface. (b) some details of the molecule's internal structure.

large scale convolution between the tip and the molecule [47, 56], so that under such conditions no atomic-resolution image can be expected. On the contrary, the image must be washedout nature due to averaging, over the lateral direction, by  $(r_t + r_m + d)$ , where  $r_t$  and  $r_m$  are the radii of the tip and of the C<sub>60</sub> molecule, respectively, and *d* is the distance between the tip and the sample surface. Even such STM image, however, provides valuable information on the adsorption geometry of C<sub>60</sub> on Si(111)-7×7.

One may speculate that the formation of a surface bond crucially depends on the orientation of the adsorbed molecule i.e., on which part of it faces the substrate — because it is precisely this orientation which determines the anisotropy of the interaction potential. If the C<sub>60</sub> molecule is oriented such that one of its pentagons faces the Si(111) surface, then its STM image must be five-fold symmetric with respect to the zaxis (normal to the Si substrate); if a hexagonal portion, then the symmetry must be three-fold. Neither case has been observed experimentally, though, and as seen in Fig. 8b, only two-fold symmetry showed up in individual molecular images. The only possible explanation is that one of the carbons in C<sub>60</sub> must occupy the center of a three-foldsymmetric site with three Si adatoms, and each of the carbon atoms must have as its neighbors three C atoms at 120° or 108° for the hexagon and pentagon, respectively. As far as the internal nature of the rows of Fig. 8b themselves is concerned, it may be due to the enhanced electron tunneling around the sites with a  $\pi$ -like double carbon bond.

In Ref. [59] a well-ordered crystalline  $C_{60}$  film is reported to have been successfully grown on Si(111)-7×7 whose STM images showed the crystalline  $C_{60}$  islands to be predominantly oriented in two directions independent of height and size. The phenomenon was explained as the pinning of the first layer  $C_{60}$  molecules by the 7×7 structure of Si(111) surface related to the order-disorder phase transition. It has also been found that with increasing temperature  $C_{60}$  molecules on Si(111) become chemically active. By using STM and Auger spectroscopy the fullerene cage breaking was observed at 1020 K [60] accompanied by the increasing Si–C bond Auger signal. A similar observation in our work on the adsorption of  $C_{70}$  on Si(100)-2×1 [61] should be noted.

# 4. Adsorption of $C_{60}$ and $C_{70}$ molecules of the $Cu(111)-1\times 1$ and $Ag(111)-1\times 1$ surfaces

#### 4.1 Fullerene films on metal surfaces

Since noble metal surfaces are rather inert, they have been favorably chosen to be well suited for the study of the incipient growth of fullerene films. So far, the adsorption of C<sub>60</sub> and other higher fullerenes on Au(111) [15, 62-66], Au(110) [51, 67], Au(100) [68], Cu(111) [69-72), and Ag(111) [66, 64, 73-74] have been studied with STM. Early STM observations of the C60 molecules showed them to form ordered close-packed structures on the Au(111) [62, 63] and Ag(111) [64, 66, 73-74] surfaces. Also, a C<sub>70</sub> monolayer on Au(111) observed with STM in air showed [65] an ordered rhombohedral arrangement (reflecting the HCP bulk structure [75]). For Au(110), ordered arrangements of C<sub>60</sub> molecules and carbon ring structures of C<sub>60</sub> and C<sub>70</sub> molecules were even seen in aqueous solutions [68]. The intramolecular structures of  $C_{60}$  on Au(111) first seen by Chen et al. [65] were explained as tunneling through electronic states with a characteristic  $\pi$  bonding.

On the other hand, on some metal surfaces a very strong chemical bonding with a fullerene have been found to occur. One example is the work of Kuk and coworkers [68] on the adsorption of  $C_{60}$  on Au(100). The choice of this particular surface is interesting in that, due to its  $5 \times 20$ ' reconstruction (in which every fifth row of atoms is buckled outwardly by about 1.0 A along the  $\langle 110 \rangle$  direction, and which has a dislocation at every 18 to 20 spacings along  $\langle \overline{1}10 \rangle$ ), it was anticipated that the C<sub>60</sub> molecules must stop the free rotation. Indeed, it was shown that the  $C_{60}$  molecules prefer the dislocation sites and ridge sites, and that a C<sub>60</sub> monolayer forms commensurate  $n \times 14.4$  A (*n* is an integer) reconstructions. The C<sub>60</sub> molecules in these reconstructed areas turn out to be highly stressed along the <110> direction, so that the nearest-neighbor distance reduces to 8A, 2A less than the bulk C<sub>60</sub> spacing of 10.0 A. Because of this stress one expects that the charge density distribution around a C<sub>60</sub> molecule will be distorted, and this was indeed observed in ultraviolet photoelectron spectroscopy (UVES) and STS studies [76, 77] which revealed charge transfer to energetically more favorable LUMO derived states to occur.

Altman and Colton investigated [64, 66, 73] C<sub>60</sub> film growth on Au(111) and Ag(111) surfaces bearing in mind that the structure of these surfaces i.e.,  $2\sqrt{3} \times 2\sqrt{3}$  has a lattice constant equal to the nearest distance between  $C_{60}$ molecules in the bulk phase (10.0 A). A detailed study of the initial stage of adsorption shows that fullerene molecules prefer step edge absorption and may form a well ordered monolayer. As a result, two ordered superstructures predominate on the Au(111) surface: one is in-phase  $2\sqrt{3} \times 2\sqrt{3}$ - $R30^{\circ}$  and the other one is out-phase  $38 \times 38$  and the same orientation as the Au(111)-1 $\times$ 1. The nearest-neighbor distance is 10A in both phases. The 38×38 structure was believed to result from the growth of a  $C_{60}$  film out from a step edge with a subsequent alignment of the film owing to the effect of the  $\langle 110 \rangle$  step edge. A similar interaction with C<sub>60</sub> molecules was exhibited by the Ag(111) surface, but in this case the interaction was stronger than for the  $C_{60}/Au(111)-1\times 1$ 

system. In some cases, also intramolecular structures correlating with adsorption geometry were observed, but neither details of reconstruction formation nor the stability and arrangement of  $C_{60}$  in the reconstructions were examined.

Compared with Au and AG, the surface of Cu is more active chemically and is therefore more suitable for the study of catalytic reactions and surface structures. Moreover, Cu(111) is an almost ideal substrate to grow C<sub>60</sub> films because its structure is close to that of C<sub>60</sub> and because there is only a slight (~ 2%) mismatch between their lattices: the spacing of bulk C<sub>60</sub>, 10.0 A, is close to four times the Cu spacing, 10.2 A. Recent studies of C<sub>60</sub> adsorption on Cu(111), Cu(110), and Cu(100) using x-ray photoelectron spectroscopy (XPS), LEED, and high-resolution electron energy loss spectroscopy [76, 77] showed that:

(1) the Cu substrate donates charge to the  $C_{60}\ LUMO$  band, and

(2) on Cu(111), single-domain ( $4 \times 4$ )-superlattice epitaxy and a layer-by-layer growth of a C<sub>60</sub> film may be achieved.

In the C70 fullerene, the nearest-neighbor distance as measured in its bulk (both FCC and HCP) phases was found to be 10.6 A [75], 4% more than four times the Cu-Cu distance, 10.2 A, on the Cu(111) surface. Therefore pure C70 molecules are also very likely to form a 4×4 superstructure on Cu(111), by taking the upright position with one of the pentagon rings facing the Cu(111) surface whereas the long axes of the spheroids are oriented perpendicular to the surface. Under this configuration the molecule-molecule distance is 10.2 A, i.e., the same observed for the adsorption of pure C<sub>60</sub>. When C<sub>60</sub> and C<sub>70</sub> molecules are absorbed simultaneously on the Cu(111) surface, a situation may arise in which some of the  $C_{70}$  molecules take lying down position with the long axis parallel to the surface, two reasons for this being a different surface stress and the adsorbate – adsorbate interaction effect. These speculations have prompted us to image the intramolecular structures of various C60-C70 compositions on the Cu(111) and Ag(111) surfaces. We also investigated the initial stage adsorption and the adsorption



Figure 9. (a) STM image of the Cu(111)-1×1 surface covered with 0.05 C<sub>60</sub> ML ( $V_s = -3.5$  V,  $I_t = 20$  pA, 480 A × 480 A) exhibiting the step-edge segregation of C<sub>60</sub> molecules. (b) STM image of the first layer of the C<sub>60</sub> molecules on the Cu(111) surface, together with a second layer at room temperature ( $V_s = -2.0$  V,  $I_t = 20$  pA, 320 A × 320 A).

geometry of the molecules and showed that  $C_{60}(x)C_{70}(1-x)/Cu(111)-4\times4$  could serve as a good model for a dimer-alloy-type system for studying phase enrichment [69, 70, 72, 74].

## 4.2 Adsorption of $C_{60}$ on the Cu(111)-1×1 surface

The initial stage of adsorption of C<sub>60</sub> on Cu(111) at room temperature has showed that  $C_{60}$  is quite mobile on flat terraces and stabilized only at step edges (Fig. 9a). As coverage increases C<sub>60</sub> molecules start to form two-dimensional islands growing from the step edge towards the next edge of the lifting step thus producing a monolayer film (Fig. 9b). In Fig. 9a, which is the STM image of the Cu(111) surface with a 0.05 ML  $C_{60}$ , one can see the nucleation of  $C_{60}$  islands on step edges but no linear C<sub>60</sub> chains along terrace edges emerge. This is a far cry from the low-mobile non-segregating  $C_{60}$  molecules on the Si(111)-7×7 and Si(100)-2×1 surfaces (Sections 3.2 and 3.3). In Fig. 9b, where the first layer and islands of the second layer of the adsorbed C<sub>60</sub> molecules are shown, the second layer exhibits a distinct, ordered  $4 \times 4$ structure with a high density of domain boundaries, and it is seen that the steps that form in the monolayer  $C_{60}$  film are replicas of those in the Cu(111) substrate. Slight annealing at  $T \approx 290 \,^{\circ}\text{C}$  for 1 min leaves, aside from point defects and domain boundaries, only the first C<sub>60</sub> layer with a well ordered  $4 \times 4$  structure as shown in Fig. 10. This STM empty states image shows clearly that, except at domain boundaries and lower symmetry areas, each C<sub>60</sub> molecule is of three-leaf clover shape with its three blades oriented strictly in the same direction; note that the steps are aligned in the (011) direction, i.e., along the atomic rows of the substrate, although in the case of a monolayer  $C_{60}$  film the steps themselves do not form straight lines (Fig. 9b). From this, the stability of  $\langle 011 \rangle C_{60}$ chains and a substantial surface mass transport of Cu atoms while the surface is being annealed at 290 °C can be inferred.

To determine the charge distribution and the adsorption geometry, dependences of STM images and of the corresponding internal structures on the bias  $V_s$  and thus on scanning tip properties and the tunneling gap were obtained, typical examples of which are shown in Fig. 11. Although the general shape and symmetry of the images remained unchanged, at  $V_s = -2.0$  V (filled states image) each C<sub>60</sub> was round-shaped and contained a hole at its center (Fig. 11a); at biases close to zero (i.e., to the Fermi level), triangle internal structures were observed (Fig. 11b); and at  $V_s = +2.0$  V the clover-leaf image which had a distinct three-fold symmetry and represented empty states, was seen (Fig. 11c). This sharp bias dependence of the STM image is well explained by the variation in the



**Figure 10.** The empty state STM image of the monolayer of C<sub>60</sub> adsorbed on Cu(111) at room temperature and annealed at 290 °C for 5 min ( $V_s = +2.0 \text{ V}$ ,  $I_t = 20 \text{ pA}$ , 230 A × 320 A).

spatial charge density distribution around the molecules (see Section 4.4). Since  $C_{60}$  molecules may rotate both in the bulk of a fullerene crystal and at various types of surfaces, the three-fold symmetry mentioned above have until now evaded observation. Clearly, one of the hexagonal rings of  $C_{60}$  must face down on the Cu(111) surface in order for the three-fold symmetry to show up.

Turning now to the geometrical arrangement of  $C_{60}$ molecules and to the exact location of the adsorption sites leading to the  $C_{60}/Cu(111)$ -(4×4) structure, one can think of only two adsorption geometries compatible with the observed symmetry of the STM images, namely the atop sites, and three-fold hollow sites. Since the size of the hexagonal carbon ring is almost identical to the interatomic Cu–Cu distance and because each carbon atom takes up the position of hollow site around the central Cu atom, it follows that the six-fold symmetry of an atop site may indeed accommodate well to the position of the C<sub>60</sub> molecule. On the other hand, if a C<sub>60</sub> molecule occupies the three-fold hollow site, there are two kinds of adsorption sites, namely, HCP site and FCC site, to exist. Presumably, STM images with domain boundaries



Figure 11. Bias-dependent intramolecular structure of  $C_{60}$  molecules adsorbed on Cu(111):  $V_s$ : (a)  $V_s = -2.0$  V; (b)  $V_s = -0.1$  V; (c)  $V_s = +2.0$  V ( $I_t = 20$  pA). All STM images are obtained in the 'linear scale' regime.

reflect this difference. If  $C_{60}$  molecules adsorb at the threefold hollow sites, one domain may be expected to displace with respect to the next by 1/3 of the Cu–Cu interatomic distance in the  $\langle 0\bar{1}1 \rangle$  direction. For 'atop' site adsorption, no such displacement is to be expected. The experiments above did indeed reveal a shift by 1/3 of the unit Cu-Cu distance on the  $\langle 0\bar{1}1 \rangle$  direction. Based on these considerations, we suggested a two-dimensional lattice model for C<sub>60</sub> adsorption on Cu(111) which assumes the existence of FCC and HCP sites such that their adsorbed C<sub>60</sub> molecules may be oriented differently (so that the sites themselves may be at ±30° with respect to one another), but the lattice constant of the 4×4 phase is always (10.1 ± 0.2) A, which is very close to that of bulk C<sub>60</sub>, 10.0 A [47, 70, 74].

# 4.3 Behavior of $C_{70}$ and the $C_{60}(x)C_{70}(1-x)$ binary system on the Cu(111)-1×1 surface

The initial stage of adsorption of  $C_{70}$  molecules on Cu(111)-1×1 is similar to that of  $C_{60}$  molecules in that they also occupy step edges thus exhibiting high mobility even at room temperature. As coverage is increased,  $C_{70}$  islands start to grow on both the upper and lower sides of the steps, the brightness contrast between the molecular images being readily explained by different orientations of the adsorbed  $C_{70}$  molecules. However, the fact that, unlike  $C_{60}$ , the second layer of  $C_{70}$  starts growing on islands even before the first monolayer is complete indicates that interaction between the adsorbed molecules is stronger than that between the adsorbate and the substrate.

The formation of a well ordered 4×4 structure after the  $T \approx 320$  °C annealing of the adsorbed layer has also been observed on Cu(111) (see Fig. 12), but the STM images of individual C<sub>70</sub> molecules in a pure C<sub>70</sub> layer do not here reveal any evidence of intramolecul structure at  $V_s$  in the range from + 2.5 to -2.5 V [72]. This suggests that, having as they do an elongated shape, the C<sub>70</sub> molecules take a upright position and, this done, continue their rotation along their long axes. Since the short-axis size of C<sub>70</sub>, 7.0 A, is close to the size of the C<sub>60</sub> cage whereas the long-axis size is 7.9 A and because the



20 A

**Figure 12.** STM images of  $C_{70}$  molecules adsorbed on the Cu(111) and annealed at  $\approx 320 \,^{\circ}\text{C}$  ( $V_{s} = +1.1 \text{ V}$ ,  $I_{t} = 30 \text{ pA}$ ). The surface shows a well ordered  $C_{70}$  layer with the 4×4 reconstruction

nearest neighbor distance in the  $4 \times 4$  phase (10.2 A) is only slightly less than that in bulk C70 (10.6A), the upright position must act to reduce the surface stress, especially for low concentrations of C<sub>60</sub>. Calculations of Gao and coworkers [78] indicate that the upright position is optimal because it is energetically most favorable for C<sub>70</sub> molecules to align their long axes strictly parallel. On the other hand, it has been shown [75] that while at  $T \ge 340$  K C<sub>70</sub> molecules are completely disordered orientationally in the bulk phase, in the intermediate temperature range 280-340 K they align their long axes parallel and persist in rotating about these axes. Given the mismatch between the three-fold symmetry of the substrate and the five-fold symmetry of the C<sub>70</sub> molecules and bearing in mind the smaller adsorbate – substrate interaction in this particular case, one readily sees that the long-axis rotation of a vertically oriented C70 is rather difficult to decelerate. The above seems to be the most likely reason for our failure to observe intramolecular C<sub>70</sub> structures at the upright position of the molecules.

On the other hand, since the spacing of bulk  $C_{60}$  (10.0 A) is less than the  $4 \times 4$  lattice constant (10.2 A), the presence of a C<sub>60</sub>-C<sub>70</sub> mixture could readjust the surface stress thus changing molecular orientation. When 30% of  $C_{60}$  molecules on Cu(111) were mixed with the remaining  $C_{70}$  molecules, these latter were found to exhibit a new type of adsorption geometry. In Fig. 13, the STM images of a C<sub>70</sub>-C<sub>60</sub> mixture are obtained in the so-called 'dual mode' by alternately switching on positive [(a): empty states image,  $V_s = +2.0$  V] and negative [(b): filled states image,  $V_s = -2.0$  V] voltage. The  $C_{60}$  molecules are easily distinguished by their peculiar three-leaf clover-shaped empty state images [69, 70]. For the  $C_{70}$  molecules, in addition to the ordinary, uniform circular image like that in Fig. 12, two-fold  $C_{70}$  images appeared. In some of these latter, the bifurcation of each semi-segment was also seen. Taking into account the molecular symmetry of  $C_{70}$ , one realizes that the two-fold symmetry can be obtained only if a C<sub>70</sub> molecule takes the lying down position with its long axis parallel to the surface. Also, STM images showed that the long axes of the C70 molecules in this position are always oriented parallel to the close-packed  $\langle \bar{1}10 \rangle$  rows.

In Fig. 14, the adsorption structures suggested by the twofold symmetric behavior of C70 are shown. These are: a structure that bonds four hexagons with faces down (Fig. 14a); an equator-centered hexagon with face down [basically the same as the adsorption geometry observed for  $C_{60}$  on Cu(111), see Section 3.2] (Fig. 14b); and a structure with one carbon atom located on the equator and oriented downward (Fig. 14c). In the configurations 14a and 14c there are two pentagonal rings on the protruding part of the molecule surface, compared to four in the 14b case. The configuration (c) can hardly be considered as favorable because of its relatively low symmetry and because it does no agree well with the observed STM image. Assuming (as in the case of  $C_{60}$  on Cu(111) [69, 70]) that the LUMO-induced states (localized at the pentagonal rings) predominantly contribute to the formation of empty state images, it is the 14a configuration which would produce the two round protrusions for each individual C70 images; and the 14b configuration would lead to four round (or two elongated) protrusions. It is therefore appropriate that the STM image in Fig. 13a be related to the 14b configuration which predicts two elongated protrusions in the  $C_{60}$  images; note that in higher- resolution experiments this image might appear as a four-protrusion one.



 $\langle \bar{1}10 \rangle$ 





Figure 13. A dual mode STM image showing the two-fold symmetry of  $C_{70}$ molecules in the  $C_{60}$  –  $C_{70}$  mixture for (a)  $V_s = +2.0$  V and (b)  $V_s = -2.0$  V  $(I_{\rm t} = 30 \, {\rm pA}).$ 



Figure 14. Possible arrangements of adsorbed C70 molecules with long axes along the  $\langle \bar{1}10 \rangle$  direction of the Cu(111) surface: (a) with a bond linking four hexagons facing down; (b) with a hexagon centered on the equator; (c) with one carbon atom located at the equator. The dark pentagon rings show bright features observed on the STM image.

### 4.4 Computer simulation of STM images and the behavior of the fullerenes at domain boundaries

Kawazoe and coworkers [49, 50] performed two-dimensional band structure and charge density distribution calculations for the  $C_{60}{-}4{\times}4$  structure by combining the local density approximation and density functional theory in the same manner used in the work on C<sub>60</sub> molecules on the Si(100) surface. The two-dimensional energy band shown in Fig. 15 readily yields the local charge density distribution and thus enables the computer simulation of the STM images to be performed. The results of the simulation are shown in Fig. 16. The charge density distribution for the levels 177, 178 and 179 were found to have a characteristic HOMO state shape, a circle with a hole in the center (Fig. 16a) very similar to the STM image of Fig. 13a. For the level 180 one obtains a circle without a central hole (Fig. 16b), and for 181, 182, and 183 a characteristic three-fold symmetry representing of three pentagonal carbon rings in the LUMO-derived states (Fig. 16c). Since the charge transfer from the Cu substrate to the  $C_{60}$  monolayer is difficult to calculate accurately, the absolute position of the energy level cannot be determined unambiguously. In this case, the theoretical result was shifted to lower energies by 0.5 eV to fit the experimental data, and the Fermi level (denoted by a dash-dot line) lies in the vicinity of the molecular level 181 (Fig. 15). The corresponding level shift may, in charge transfer terms, reach one electron per C<sub>60</sub> molecule, in good agreement



**Figure 15.** Energy band structure of the C<sub>60</sub> monolayer [47]. Conventional notation  $\Gamma = (0,0)$  (centre) and  $\mathbf{M} = (\pi/a, \pi/a)$  is used for the special points of the Brillouin zone.

with the XPS and energy loss spectroscopy results of Rowe et al. [77]. For the STM scheme under study the image at  $V_{\rm s} = -2.0$  V (Fig. 11a) should be the mixed charge density resulted from the levels 177, 178, 179, 180, and (to a lesser extent) 181; the  $V_s = -0.1$  V image (Fig. 11b), due to the level 181; and that at  $V_s = +2.0$  V (Fig. 11c), should be from sum of levels 181, 182, and 183. Thus, the computer simulated STM images of Fig. 16 result from combined contributions from the levels 178, 179, 180, and 181 (a) or from 182 an 183 (c) and agree well with what we observed experimentally in both the 'linear scale' regime (Fig. 11) and the conventional representation (Figs 16d and 16e). Note that individual  $C_{60}$  molecules were seen at biases in the range  $-3.0 \text{ V}_{s} \leq +3.0 \text{ V}$  (which was impossible for the Si substrate at low  $V_s!$  [53, 55]) even within the HOMO-LUMO gap owing to the gap states formed by the electron charge transfer from the substrate to the  $C_{60}$  monolayer. This last circumstance gives confirmation of the strong interaction between the Cu(111) substrate and the  $C_{60}$ fullerene molecules.

Later, Kawazoe and coworkers performed a theoretical calculation of the configuration of Fig. 14b using the same computational scheme previously used for the  $C_{60}/Cu(111)$ - $4\times4$  system [47, 50, 51], and simulated the unit-cell charge density distribution for LUMO- and HOMO-induced states [49, 79]. Because the resulting images agree quite satisfactorily

with their real counterparts in Figs 12 and 13, it can be argued that  $C_{70}$  molecules in a mixture of  $C_{70}-C_{60}$  domains are in sites (b) shown in Fig. 14. Another interesting observation is that the  $C_{70}$  layer displays not metallic but rather semiconducting properties. As noted previously,  $C_{60}$  molecules can be imaged at  $V_s \approx 0.001$  eV indicating the metallic properties of the coating (large charge transfer from the Cu substrate to the adsorbed layer [76, 77]), whereas the molecules on the surface and those aligned vertically could not be imaged at voltages below  $|\pm 0.3 \text{ V}|$  and  $|\pm 0.3 \text{ V}|$ , respectively, implying somewhat insulating features.

We next turn our discussion to the behavior of the fullerenes on domain boundaries. Although the two-dimensional phase diagram of the system  $C_{60}(x)C_{70}(1-x)$  is not yet known, it seems to have dilute alloy phase near pure  $C_{60}$ ,  $C_{70}$  films and a miscibility gap. In dilute  $C_{60}(x)C_{70}(1-x)$ phases with  $0 < x \le 0.1$ , the C<sub>60</sub> molecules were found to segregate on the domain boundary, the  $C_{60}-C_{70}$  interaction potentials being of van der Waals attraction type [23-25, 80]. In Fig. 17, which shows the STM image of the Cu(111) surface coated with a  $C_{60}(x)C_{70}(1-x)$  ( $x \approx 0.08$ ) monolayer and then annealed at 320 °C, one clearly distinguishes two kinds of molecule image, namely darker and brighter ones. That the dark circles correspond to C60 follows from the fact that their measured concentration ( $\sim 8\%$ ) is close to that in the powder used as a fullerene source and that the height difference as determined from the scanning profile is approximately equal to the difference ( $\sim 8 \,\mathrm{A}$ ) between the long axis diameters of  $C_{60}$  and  $C_{70}$ . Fig. 17 also shows that well ordered  $C_{70}$ -4×4 domains are divided into several domain boundaries, some of the walls exhibiting the segregation of  $C_{60}$  molecules. Another interesting experimental observation is that C<sub>60</sub> segregation in trimer or monomer forms is presumably more stable as can be concluded from their more frequent occurrence.

It was also found that C<sub>60</sub> domain boundary segregation is determined by the nearest-neighbor distance between the molecules, as is shown in Fig. 17. It was found by a careful analysis of scores of STM images that C60 molecules mainly segregate on domain boundaries separated by a wider gap compared to that between two close-packed rows within  $4 \times 4$ domains. In Fig. 18a, which is a STM image of such a surface after annealing for 5 min at 330 ° C, one sees a zigzag domain boundary stable owing to the presence, on the surface, of a novel bright spot feature presumably due to a residual largerthan-C<sub>70</sub> molecule. Fig. 18b shows a structural model for the zoomed area of the domain boundary shown by dash-dot lines in Fig. 18a. The C<sub>60</sub> molecules, which are imaged darker than Cu atoms, segregate at the upper part of the domain boundary, whereas in the lower part no segregation is observed. For the section AB of the domain boundary, the nearest-neighbor distance  $d_{AB}$  as expressed in terms of the Cu spacing in the substrate, a, was found to be 4.6a compared to 3.6*a* for BC ( $d_{BC}$ ).

The driving force of the segregation to the domain boundary is undoubtedly the fact that the system tends to minimize its free energy [81]. A simple broken-bond model of surface segregation assumes that for the total surface energy to be minimized, a component with a lower sublimation energy must appear. Since our measurement showed that the sublimation energy of C<sub>60</sub> is ~40 kcal× mole<sup>-1</sup>, i.e., less than that for C<sub>70</sub> (~43 kcal mole<sup>-1</sup> [82]), it is precisely the C<sub>60</sub> molecules which may be expected to appear on the surface, a conclusion which agrees well with the results quoted above.



**Figure 16.** Computer simulated C<sub>60</sub> images [47]: (a)  $V_s = -2.0$  V; (b)  $V_s = -0.1$  V; (c)  $V_s = +2.0$  V; (d) experimental high-resolution STM image of C<sub>60</sub> molecules on Cu(111) for  $V_s = -2.0$  V (close-up); (d) the same for  $V_s = +2.0$  V ( $I_t = 20$  pA).



Figure 17. STM image showing the segregation of C<sub>60</sub> molecules on domain boundaries 10-min  $T \approx 320$  °C annealing ( $V_s = +2.0$  V,  $I_t = 20$  pA).

# 4.5 $C_{60}$ fullerenes on Ag(111)-1×1: domain boundaries and defect areas

The Ag(111) surface was also believed to be optimal for the growth of thin C<sub>60</sub> films because its  $(2\sqrt{3}) \times (2\sqrt{3})R30^{\circ}$  structure is found to have almost the same lattice constant as FCC C<sub>60</sub> (for Ag,  $a_0 = 2.89$  A and the nearest-neighbor distance  $2\sqrt{3}a_0 = 10.0$  A) and it was therefore reasonable to expect the reconstruction of  $(2\sqrt{3}) \times (2\sqrt{3})R30^{\circ}$  to be a stable surface phase. Indeed early studies by Altman and Colton indicated that the  $(2\sqrt{3}) \times (2\sqrt{3})R30^{\circ}$  phase is predominant on the as-deposited first layer of C<sub>60</sub> and that small step edge areas display two domains rotated at 10° and 15°; the authors, however, did not report any details on the stability and adsorption geometry of these phases [66, 73].

In spite of its stable and closed structure,  $C_{60}$  can interact rather strongly with the silicon surface because this latter has a large number of dangling bonds, but the interaction of the molecule with noble metal surfaces is weak. It is, however, steps on noble metal surfaces which are known to be highly active [68, 73] — unlike terrace edges on superconductor surfaces, where a large number of various types of reconstructions reduce the free energy of the surface by reducing the number of dangling bonds in it [44, 83]. As is the case for the  $C_{60}/Cu(111)$  system, at low coverage the  $C_{60}$  molecules are very mobile on the Ag(111) terraces even at room temperature and tend to sediment and nucleate preferably at the step



**Figure 18.** (a) STM image of a monolayer  $C_{60}(x)C_{70}(1-x)$  film showing the domain boundary segregation of  $C_{60}$  molecules ( $V_s = +2.0$  V,  $V_s = 20$  pA, 160 A × 160 A) (b) structural model of the domain boundary observed in the centre of Fig. 18(a) (magnified).

edges, where the island growth is towards the terraces. It is noteworthy that close-packed hexagonal C<sub>60</sub> lattices are here observed in both the first and subsequent layers. Careful examination of the STM images showed that over most of the substrate C<sub>60</sub> molecules form the  $(2\sqrt{3}) \times (2\sqrt{3}) R30^{\circ}$  reconstructions with a nearest-neighbor distance of 10.0 A. However, a number of other reconstructions were frequently observed, which also demonstrated close-packed hexagonal layers. For these phases we found the nearest-neighbor distance to be  $10.0 \pm 0.1$  A, i.e., almost the same as that for  $(2\sqrt{3}) \times (2\sqrt{3})$ R30°. A typical STM image of such a surface with one C<sub>60</sub> monolayer coverage (Fig. 19) indicates the presence of three reconstructions and agrees well with Ref. [66]. The upper part of the image is a  $(2\sqrt{3}) \times (2\sqrt{3}) R30^{\circ}$ structure, and the domains in its lower left and lower right parts are rotated by respectively 12° and 46° with respect to  $\langle \bar{1}10 \rangle$ . The same type of analysis was applied to other phases,



**Figure 19.** STM image of the first C<sub>60</sub> layer as- deposited on Ag(111). The domains in the upper part of the image is the  $(2\sqrt{3}) \times (2\sqrt{3})$ R30° structure; the domain at the lower left part is rotated 12° from the (110) direction, and the domain at lower right part is rotated 46° from the (110) direction. Note the equal brightness of C<sub>60</sub> images in the  $(2\sqrt{3}) \times (2\sqrt{3})$ R30° phase.

which also were found to be at various (but fixed) angles with respect to the  $\langle 110 \rangle$  Ag(111) direction. In most cases, these angles can be grouped into two types between 11.5° and 13.5° or between  $45^{\circ}$  and  $47^{\circ}$ . It is important to note that  $C_{60}$ molecules yielded images of nearly the same brightness in the as-deposited  $(2\sqrt{3}) \times (2\sqrt{3})$ R30° phase as well as in all other phases. This suggested that the observed phase stabilities were due to a certain adsorption geometry of the coverage with respect to the substrate periodicity pattern, i.e., the structure of the fullerene film was expected to be coherent under these conditions. It was also found that the reconstructions under study undergo changes depending on the duration of (lowtemperature) surface anneal. Similar to what happens to the  $C_{60}$  film on Cu(111) [69], the Ag(111) surface with a multilayered adsorbed C<sub>60</sub> film was found to retain only the first layer after being subject to a brief annealing at 300 °C. Although in phases other than  $(2\sqrt{3}) \times (2\sqrt{3}) R30^{\circ}$  all C<sub>60</sub> molecules were still imaged equally bright, within  $(2\sqrt{3}) \times (2\sqrt{3}) R30^\circ$  their brightness varied considerably so that both dim and bright molecules could be seen [74]. From the image contrast, the effective difference in the site heights of these two molecule types was readily found to be within 0.6 A for a bias voltage  $V_s = -1.2$  V. We also note that most of the surface shown in Fig. 19 is covered by a mixture of dim and bright  $C_{60}$  molecules and that their concentration ratio remained unchanged even after a long-term (to 36 hours) anneal, whereas at a discontinuous scanning of the same region under the same conditions, a switching of brightness between the dim and bright molecules was observed. Since the initial fullerene powder was extremely pure, one can rule out the possibility that the observed brightness variations are due to the presence of other - higher - fullerenes such as C70 or C<sub>84</sub>. Assuming that even in  $(2\sqrt{3}) \times (2\sqrt{3}) R30^{\circ}$  all C<sub>60</sub> molecules are in equivalent positions, one expects their STM images to be identical — but this proves to be at odd with the fact that they show two levels of brightness depending on the annealing duration. This behavior may be thought to be due to the relaxation of the stress that forms in the  $C_{60}$  layer because of the adsorbate-substrate interaction. Although the nearest- neighbor distance in the  $(2\sqrt{3}) \times (2\sqrt{3}) R30^{\circ} C_{60}$ film is nearly the same as in the bulk FCC crystal, the Ag substrate-film charge transfer, whose existence is shown by STM [66] and photoemission [21 83, 84] studies, should cause in the C<sub>60</sub> layer an electrostatic repulsion which must lead to a considerable displacement of some of the C60 molecules from their equilibrium positions in order to compensate the resulting stress. Because the dim and bright C<sub>60</sub> molecules switched brightness frequently enough, these brightness variation of the C<sub>60</sub> images was naturally attributed to the variation in molecular orientations, this latter corresponding to differences in charge distributions rather than to real differences in the height distribution of the C<sub>60</sub> molecules. Orientation variations due to this stress were also often seen on domain boundaries (where the nearest-neighbor distance changes) as well as in certain defect-containing regions.

A long-term (to 36 hours) annealing led, in addition, to the disappearance of all the other phases except for  $(2\sqrt{3}) \times (2\sqrt{3})$ R30°, suggesting that this latter is the most stable one energetically. It was also established that, as is the case for the C<sub>60</sub>/Cu(111)-4×4 system, the adsorption centers on the  $(2\sqrt{3}) \times (2\sqrt{3})$ R30° Ag(111) are unoccupied threefold symmetric areas. Finally, based on data on nearestneighbor distances and rotation angles, structural models for C<sub>60</sub>-Ag(111) phases were developed [74].

Thus, compared to fullerene adsorption on Cu(111), the interaction between fullerene molecules and Ag(111) turns out to be relatively weak thus leaving the molecule-molecule interaction to dominate. Monolayer hexagonal close-packed films form owing to the van der Waals interaction between the fullerene molecules, the molecules in the films retaining their freedom to rotate relative the substrate. The stability of the phases themselves is closely related to those molecules in the unit cell occupying the most stable three-fold hollow sites.

On the Ag(111) surface, the intramolecular structures for the three phases shown in Fig. 19 were observed only after a short annealing at  $\sim 300$  °C. The structures imaged by dim C<sub>60</sub> molecules had a rather symmetric shape with a three-fold symmetry axis and looked like a clover leaf with its lobes aligned along the close-packed C<sub>60</sub> chains, whereas for the bright C<sub>60</sub> molecules only weak contrast variations were seen. Importantly, three-fold images were observable for dim C<sub>60</sub> molecules at biases in the range  $\pm 2.5$  V even in the absence of contrast and brightness variations. Fig. 20 shows the intramolecular C<sub>60</sub> structures in a phase other than  $(2\sqrt{3}) \times (2\sqrt{3})$ R30°, which also resulted from a short-term annealing of the surface at ~ 300 °C. Although three-fold intramolecular structures could again be resolved in most C<sub>60</sub> images, variation of orientation with time was not seen explicitly in this case. The fact that all phases could be imaged at bias voltages  $V_s \leq \pm 0.1$  V is an indication of the metallic properties of the surface.

### 5. Conclusions

That STM has a great potential for the study of fullerenes is clear even at the present stage of its development. However, it is only now that reliable explanations of the vast body of data gathered for the last five years are beginning to appear, and indeed for many phenomena in this field even qualitative explanations are still lacking. We have presented ultra-high vacuum STM results, mostly obtained by ourselves, on the adsorption of the  $C_{60}$  and  $C_{70}$  fullerenes on metal [Ag(111) and Cu(111)] and semiconductor [Si(111) and Si(100)] surfaces. Particular attention has been given to the adsorbatesubstrate interaction which we consider essential for the understanding of the growth mechanism and other physical and chemical properties of fullerene films. It should be noted that ours is to some extent preliminary work and that further research, both experimental — in particular on the interaction between the higher fullerenes and surfaces of various geometry and reactivity — and theoretical — to find new interpretations for the extremely complicated phenomena involved — are needed in order to secure progress in this extremely exciting and promising field.

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**Figure 20.** STM images showing intramolecular C<sub>60</sub> structures: (a) in phase ' $\alpha$ ', with close-packed rows at about 12.5° with respect to the substrate  $\langle \bar{1}10 \rangle$  direction ( $V_s = -0.5$  V,  $I_t = 30$  pA); (b) in phase ' $\beta$ ', with close-packed rows aligned at about 47° ( $V_s = +2.0$  V,  $I_t = 30$  pA).

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