$C_{59}N$ Monomers: Stabilization through Immobilization

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$C_{59}N$ is found to sublime in monomer free radical form rather than the more stable dimers which are normally observed. Using a scanning tunneling microscope operating in ultrahigh vacuum we have found that the monomer form may be immobilized and therefore stabilized on clean Si surfaces. On the less reactive H-terminated Si(100) surface $C_{59}N$ diffuses and forms disordered islands, and a lower limit for the interaction energy between two monomers may be estimated at 0.8 eV. Synchrotron based photoemission experiments have also been performed and show diffusion and redimerization occur for multilayer deposition of $C_{59}N$.

The azafullerene, $C_{59}N$, represents an exciting addition to the family of fullerene derivatives. In this molecule a single carbon atom of the C_{60} fullerene cage is replaced by a group V nitrogen atom [1]. The direct substitution of nitrogen for carbon together with the presence of an extra electron on the N atom invites comparison with dopant impurities in a semiconductor [2]. However this analogy may be drawn only loosely, since $C_{59}N$ is a reactive molecular free radical and has so far been observed only in the form of dimers in which a weak C-C bond connects two cages [3–5]. In this form all molecular orbitals are fully occupied, and the possibilities for novel properties are rather limited.

In this Letter we show that it is possible for $C_{59}N$ to exist in *monomer* form. Stabilization of the monomer is achieved through adsorption on a clean silicon surface. The monomers are immobilized and therefore unable to diffuse and re-form dimers. In contrast, on surfaces for which diffusion is possible $C_{59}N$ diffuses, and strong intermolecular interactions result in the formation of disordered islands. Furthermore synchrotron based photoemission experiments show that redimerization occurs for multilayer deposition of $C_{59}N$.

The azafullerene sample used in the present study was prepared, purified, and characterized as described before [1,3]. Our experiments are conducted under ultrahigh vacuum (UHV) conditions. Pieces (3×7 mm^2) of p-type Si (resistivity 1 Ω cm) were cut from a (111) wafer, loaded into a UHV system (base pressure 5×10^{-11} Torr), outgassed overnight at 600 °C, and flash annealed at 1200 °C for 60 s resulting in the formation of a (7×7) reconstruction [6]. $C_{59}N$ was loaded into a Knudsen cell and after thorough outgassing was sublimed with a typical deposition rate of 1 monolayer (ML) per hour at a temperature of 550 °C. The surface was then examined using an STM operating at room temperature in constant current mode. Electrochemically etched W tips were used throughout. Samples for use in photoemission experiments were prepared in a similar way and valence band and core level photoemission spectra were acquired at both beam line 4.1 of the U.K. synchrotron radiation source (SRS) and at the VUV beam line ELETTRA, Italy.

Figure 1(a) shows an STM image following deposition of 0.01 ML of $C_{59}N$ on Si(111)-(7×7). The $C_{59}N$ molecules appear as isolated bright topographic features with a near-circular shape. They have an apparent width
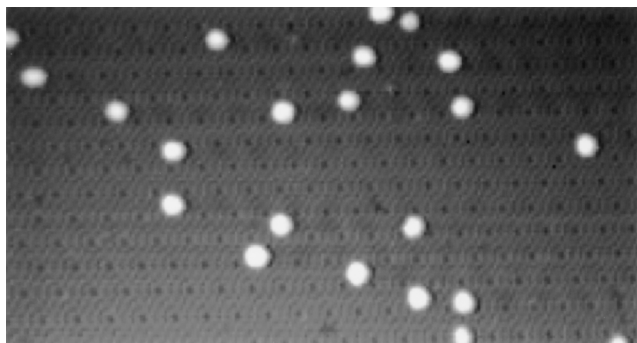
FIG. 1. STM image of $C_{59}N$ monomers adsorbed on Si(111)-(7 × 7). Image size 60 nm × 30 nm, scanning parameters 3.0 V/0.2 nA (sample voltage/tunnel current).

2.1 ± 0.1 nm and height 0.71 ± 0.01 nm. These values are very close to those observed for C_{60} on this surface [7–9]. The apparent width is larger than the fullerene cage (hard sphere diameter ~1 nm) due to the finite radius of the curvature of the STM tip. In the background the hexagonal arrangement of the corner holes and adatoms of the (7 × 7) reconstruction is clearly resolved. Note that a small fraction (~4%) of monomers is adsorbed at corner hole sites and appears smaller in our images (see, for example, the second molecule from the top of Fig. 1), as also observed for C_{60}. We see no evidence of $(C_{59}N)_2$ dimers in our images. Statistical analysis has revealed that the nearest neighbor $C_{59}N$ separation is governed by Poisson statistics with no evidence of clustering. This shows that $C_{59}N$ impinges on the surface in monomer form and following adsorption at room temperature is unable to diffuse. Sublimation in monomer rather than dimer form is a consequence of the weak nature of the C-C intercage dimer bond.

Our observations of $C_{59}N$ monomers are apparently at odds with published data which have provided evidence for $(C_{59}N)_2$ dimers [1,3,4]. To verify that the adsorbed species is $C_{59}N$ we have undertaken photoemission experiments [1 ML of $C_{59}N$ on Si(111)-(7 × 7)] in which a N 1s core level peak is clearly resolved, and the observed ratio of C 1s and N 1s peak areas is found to be consistent with the presence of $C_{59}N$ on the surface. Furthermore our results may be reconciled with previous work since the immobilization and stabilization of the $C_{59}N$ monomer are consequences of the direct interaction between $C_{59}N$ and the silicon surface. For thicker films (as used in previous experiments) the incident $C_{59}N$ impinges on layers of adsorbed $C_{59}N$ rather than silicon and it is likely that the molecules making up the higher layers of a thick film will be able to diffuse and redimerize following adsorption.

This hypothesis is confirmed by valence band photoelectron spectra of a $C_{59}N$ thick film (18.5 ML; see inset of Fig. 2). Two well-defined peaks are observed at binding energies of 2.3 and 3.5 eV (these peaks are also observed for C_{60} and originate from the highest and next highest occupied molecular orbitals (HOMO and HOMO-1) [10]).
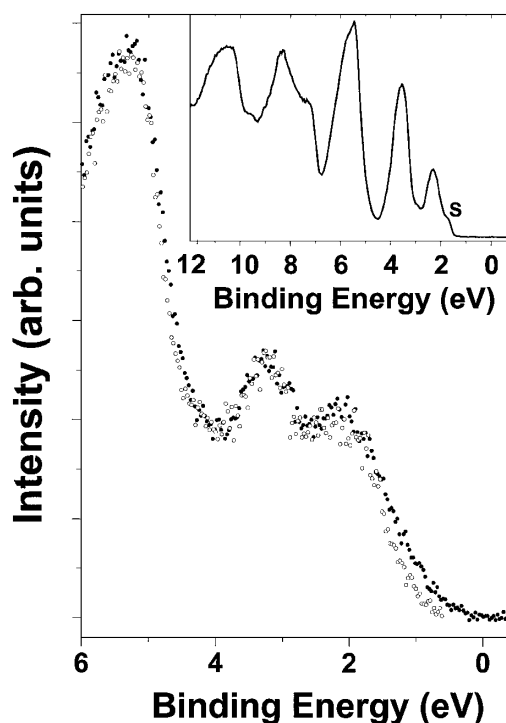

FIG. 2. Valence band photoemission spectra for $C_{59}N$ and C_{60} films adsorbed on Si(111)-(7 × 7). Measurements for 1 ML of $C_{59}N$ (filled circles) and 1 ML of C_{60} (open circles) are shown in the main figure. The inset shows the spectrum for a thick film with a coverage of 18.5 ML. Incident photon energy 30 eV.

A clear shoulder, labeled S, is observed at approximately 1.6 eV. This feature is due to the formation of a C-C intercage bond in a $(C_{59}N)_2$ dimer [4]. The very close similarity between the thick film spectrum shown in Fig. 2 and previous valence band spectra of $(C_{59}N)_2$ [4] conclusively demonstrates that, at sufficiently high coverages, redimerization of monomers occurs.

Valence band photoelectron spectra for a C_{60} and a $C_{59}N$ monolayer on Si(111) are also shown in Fig. 2. The positions of the HOMO and HOMO-1 derived peaks are identical for the C_{60} and the $C_{59}N$ monolayers, although they are broadened compared to those of bulk C_{60} and $(C_{59}N)_2$ [4,11]. An additional tail at low binding energy is observed for $C_{59}N$, although we observe no emission at the Fermi level.

The energy levels for free $C_{59}N$ monomers have been calculated previously [12,13] and it is predicted that a state lying 0.3–0.4 eV below the lowest unoccupied molecular orbital (LUMO) is partially occupied. For a simple model in which electron-electron correlation effects are neglected, the occupation of a state with this energy would lead to a nonzero density of states at the Fermi level together with a rigid shift of the energies of the valence band peaks as compared with C_{60}. This behavior is not consistent with our measurements implying that the energies and occupation of the states associated with $C_{59}N$ monomers are strongly influenced by the

surface. One possible mechanism for this interaction is the formation of a Si-N bond resulting in the occupation of a lower energy state. However Si $2p$ core level spectra reveal no significant differences between C_{60} and $C_{59}N$ adsorption. Therefore there is no clear evidence for the formation of Si-N bonds.

An alternative explanation is that a Si-C bond is formed between the monomer and the surface resulting in the transfer, or partial transfer, of an electron to a state localized close to the N atom. The energy of the resulting state would vary depending on the orientation of the $C_{59}N$, i.e., the separation of the N atom and the point of contact between the cage and the surface. Note that the resolution of intramolecular features, similar to those observed for C_{60} [9], in our STM images provides evidence for a random molecular orientation. Emission of electrons from these states, for which the energy varies from molecule to molecule, would account for the tail in the valence band photoelectron spectrum of $C_{59}N$.

Our results have shown that there is little difference between C_{60} and $C_{59}N$ following adsorption on substrates for which diffusion is *not* possible. In contrast there are pronounced differences between C_{60} and $C_{59}N$ for adsorption on H:Si(100)-(2 × 1), on which diffusion *does* occur. This surface is prepared using standard techniques [14]. Si(100)-(2 × 1) is heated to 350 °C and exposed to atomic H forming a monohydride surface on which all dangling bonds are terminated by a H atom. The absence of dangling bonds results in an unreactive surface on which many adsorbates diffuse readily [14]. Figures 3(a) and 3(b) show the H:Si(100)-(2 × 1) surface following the deposition of 1 ML of $C_{59}N$ and C_{60}, respectively. Figure 3(b) shows islands of C_{60} which are highly faceted and have a smooth top surface. These islands have a height of 2 or 3 ML, and higher resolution images reveal that they are composed of hexagonally ordered arrays of C_{60} molecules. Between the large islands there are many bright features in the STM image. These are individual molecules adsorbed on residual Si dangling bonds which correspond to defects of the H termination.

STM images acquired following deposition of $C_{59}N$ are quite different [Fig. 3(a)]. The islands are not obviously faceted, have a much rougher top surface, and a much higher areal density. Higher resolution scans reveal only very limited short range ordering of molecules. We do not observe an increase in defects in the H termination following $C_{59}N$ deposition which, together with the observation that $C_{59}N$ can diffuse over lengths ≥10 nm, implies that there is no direct chemical interaction between $C_{59}N$ and the H-terminated Si (for example, reaction with chemisorbed H). Most importantly we observe that there are much smaller number of isolated single $C_{59}N$ monomers adsorbed at defects between the larger islands as compared with C_{60}.

The results for $C_{59}N$ and C_{60} adsorption on H:Si(100)-(2 × 1) show that the intermolecular in-
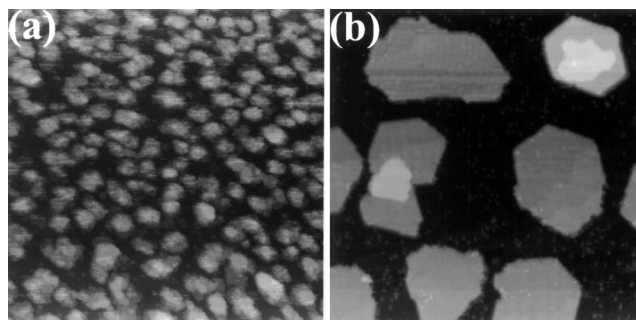

FIG. 3. STM images of (a) $C_{59}N$ and (b) C_{60} adsorbed on H:Si(100)-(2 × 1). The coverage for each figure is 1 ML. Image sizes 200 nm × 200 nm and scanning parameters (a) 3 V/0.1 nA, (b) −6 V/0.02 nA.

teractions between adsorbed $C_{59}N$ are stronger than those between adsorbed C_{60}. The differences may be understood in terms of the nucleation of fullerene islands. On exposure of the surface to sublimed molecules both C_{60} and $C_{59}N$ molecules initially diffuse and become trapped at the most reactive sites on the surface (residual dangling bonds where the H termination has not been effective—this is confirmed by experiments at lower coverage). Further molecules which impinge on the surface diffuse until they encounter a trapped molecule. Because of intermolecular interactions characterized by an energy E_B, the diffusing molecules become temporarily bound at such states for a time $\tau_B = \tau_0 \exp(E_B/kT)$, where τ_0 ($\sim 10^{-12}$ s) is a constant related to the vibrational frequency of the molecular pair. If $\tau_B > \tau_A$, where τ_A is the average arrival time of diffusing molecules at a particular site, then each trapped molecule acts as a nucleation site for island growth. This limit corresponds to the case of $C_{59}N$ adsorption for which 85% of isolated molecules nucleate island growth (this figure is determined from our STM images and is the ratio of the areal density of $C_{59}N$ islands observed at high coverage to that of isolated trapped $C_{59}N$ monomers at low coverage). If $\tau_B < \tau_A$, that is the intermolecular interactions are weaker, the diffusing molecules do not remain in contact with the trapped molecule. The density of diffusing molecules thus increases until a nucleation site is formed from a random collision of a larger (>2) number of molecules. Thus, for $\tau_B < \tau_A$, corresponding to C_{60}, only a small fraction of trapped molecules is expected to act as nucleation sites for island growth. This accounts for the isolated trapped C_{60} molecules between larger islands in Fig. 3(b). Note that only 5% (determined as above from STM images) of isolated C_{60} monomers act as nucleation sites, a much lower fraction than observed for $C_{59}N$.

Our results therefore show that $E_B(C_{59}N) > E_B(C_{60})$ as expected for a more reactive species. It is possible to estimate a lower limit for $E_B(C_{59}N)$ as follows: $\tau_A(C_{59}N) \sim n_d/D$, where n_d ($\sim 5 \times 10^{-3}$ nm^{-2}) is the number of nucleated $C_{59}N$ islands per unit area (evaluated for a lower coverage, 0.17 ML, for which island overlap

is negligible), and D ($\sim 3 \times 10^{-4}$ molecules $nm^{-2}\,s^{-1}$) is the number of incident molecules per unit time per unit area. This gives a lower limit for $E_B(C_{59}N) > kT \ln(\tau_A(C_{59}N)/\tau_0) \sim 0.8$ eV. The calculated energy of the $(C_{59}N)_2$ dimer bond, $E_d \sim 0.78$ eV [5], is close to this value. Note that internal intramolecular detail of $C_{59}N$ monomers adsorbed at residual dangling bond sites may be resolved in STM implying [9] that these molecules have a fixed orientation. Consequently the orientation of the dimer bond will not necessarily be parallel to the surface and some molecules may adopt a configuration which completely inhibits the formation of such a bond. This may account for: (i) the roughness of $C_{59}N$ islands; (ii) the failure of $\sim 15\%$ of $C_{59}N$ monomers to act as nucleation sites. Furthermore the quantity $E_B(C_{59}N)$ is relevant only for the addition of a second $C_{59}N$ monomer at a nucleation site. The behavior of a nucleated island with three or more monomers will be much more complex and the exact configuration will involve a competition between van der Waals interactions, the formation of dimer bonds, and related interactions between $C_{59}N$ monomers and dimers.

In conclusion we have shown that $C_{59}N$ exists in monomer form as a molecular free radical in the vapor phase and that the monomer may be stabilized through immobilization by direct adsorption on a Si surface. This is a new way of stabilizing a reactive species and could be exploited for new routes to chemical synthesis, for example, through exposure of adsorbed monomers to further reagents. In addition it may be possible to form new molecular nanostructures based on $C_{59}N$ monomers with novel electronic properties. $C_{59}N$ molecules deposited on either H:Si(100)-(2×1) or layers of $C_{59}N$ are not immobilized and a strong interaction between monomers controls the morphology and properties of the resulting films.

Note added.—An AFM study of $C_{59}N$ deposition has recently been published by Sommerhalter *et al.,* Surf. Sci. **433**, 486 (1999).

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