PHYSICAL REVIEW B VOLUME 59, NUMBER 15 15 APRIL 1999-I

# Direct evidence of $C_{60}$ chemical bonding on Si(100)

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(Received 5 October 1998)

The deposition of $C_{60}$ on Si(100):H2×1 surface was investigated as a function of substrate temperature in the range RT-800 °C by means of photoemission spectroscopies. In this range, the interaction of $C_{60}$ molecules with both the hydrogenated and the bare Si(100)2×1 surface could be studied and followed until the temperature was high enough to cause the fragmentation of $C_{60}$ cage and the formation of SiC layers. It is found that the fullerene molecules physisorb on the hydrogenated surface but form a covalent bond on the clean surface. The transition from physisorption to chemisorption entails the appearance of a new peak in the ultraviolet photoemission spectroscopy spectra intermediate between that of the HOMO (highest occupied molecular orbital) and HOMO-1 bands. [S0163-1829(99)03216-6]

The formation of monolayer and multilayer fullerene films on various kinds of surfaces is a topic of great interest and was recently investigated extensively. In particular, the interaction of the $C_{60}$ molecules with silicon surfaces has been studied by several groups, due to the fundamental science involved in this interaction and the potential industrial applications. However, the nature of bonding on the Si(100) surface is still a matter of debate. From the theoretical point of view, calculations[1–3] were performed for the configuration where the $C_{60}$ molecules are adsorbed on four Si dimers. It was found that strong covalent bonds should be formed between the surface Si atoms and the adjacent C atoms of the $C_{60}$ molecules. However, conflicting conclusions were obtained on the amount of ionic contribution to the bonds and on the total electronic charge transferred to the $C_{60}$ molecule, which varied from a value as high as 4 electronic charges,[1] to an intermediate one[2] of 2.44 e and a lower one[3] of 0.66 e. Furthermore, it was found that the system should be metallic.[3]

From the experimental point of view, several works have investigated the $C_{60}$ bonding on Si, mostly by using scanning tunnel microscopy (STM). Wang *et al.*[4] combining STM and scanning tunnel spectroscopy (STS) data concluded that even at room temperature the $C_{60}$ molecules are chemisorbed on Si(100), resulting in an electronic structure of the first fullerene monolayer appreciably different from that of bulk $C_{60}$. Furthermore, they found a small charge transfer from Si to $C_{60}$, equal to 0.1–0.3 e and a metallic character for the system. Quite to the contrary, Yao *et al.*[5] denied chemisorption at room temperature and pointed out that the physisorption bond that $C_{60}$ molecules form at RT is so weak that it is not possible to perform STS measurements. In Ref. 6 the formation of a chemical bond is reported to occur upon annealing at 600 °C. Investigations with different experimental techniques gave similarly conflicting results.[7–11]

Concerning the interaction between $C_{60}$ and the hydrogenated Si(100) surface Schmidt *et al.*[12] suggest a Van der Waals-like interaction between the $C_{60}$ adsorbate and the substrate which is stronger than the $C_{60}$-$C_{60}$ interaction.

In the present work the electronic structure of the interface layer has been studied by means of ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS), the morphology of the films by means of reflection high-energy electron diffraction (RHEED) and atomic force microscopy (AFM) measurements.

UPS measurements were recorded with a double-pass cylindrical mirror analyzer. The resolution was 70 meV. The Fermi level position was determined measuring the UPS spectrum of a freshly evaporated gold layer. XPS measurements were performed with a monochromatized ($h\nu = 1486.6$ eV) electron spectroscopy for chemical analysis system equipped with hemispherical electron analyzer. The resolution of the system was 0.35 eV.

We have prepared a series of samples by evaporating in situ a fixed amount of $C_{60}$, i.e., 4 monolayers (ML), on the Si(100):H substrates heated at different temperatures. The Si substrate were previously cleaned in UHV preparation chamber. A silicon buffer layer has been grown by low-pressure CVD (chemical vapor deposition) at 850 °C using high-purity silane. By cooling the substrate in hydrogen atmosphere we obtained the monohydride Si(100):H surface with the 2×1 surface recontruction. The contamination of the surface was beyond the XPS detection limit. The 2×1 reconstructed surface was checked *in situ* by means of RHEED measurements. The amount of evaporated $C_{60}$ was determined during deposition with a quartz-crystal thickness monitor. The amount adsorbed on the silicon substrate was instead determined from the intensity ratio of the C1*s* and Si 2*p* core levels, as measured by XPS.

In Fig. 1, we report the $C_{60}$ coverage as a function of the substrate temperature $T_s$ during the deposition. The curve exhibits a minimum at ~280 °C corresponding to a coverage of about 1/4 ML. For temperature higher than 450 °C the curve saturates to a value of 1 ML ($1\ \mathrm{ML} \simeq 8.5 \times 10^{13}\ \mathrm{mol/cm^2}$). The behavior of Fig. 1 can be explained in the following way. In the region between room temperature and 280 °C the Si surface is hydrogenated. The bonding between $C_{60}$ and the hydrogenated substrate is weak and comparable to that between $C_{60}$ molecules. As a result, the amount of $C_{60}$ molecules remaining on the surface is the smaller the higher the temperature. For $T_s \geqslant 280\,°\mathrm{C}$ the hydrogen starts to desorb so that $C_{60}$ molecules can bond directly to the bare Si surface. In this case the interaction is

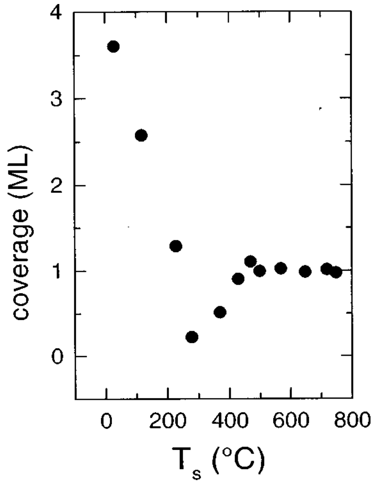

FIG. 1. $C_{60}$ coverage as a function of substrate temperature.

stronger and the $C_{60}$ molecules are retained at high temperatures also. The increase of the coverage is then related to the amount of desorbed hydrogen. At 450 °C the surface is completely dehydrogenated and is saturated by 1 ML of $C_{60}$. Since the temperature is higher than the $C_{60}$ sublimation temperature, sticking beyond 1 ML is not possible and, consequently, the coverage remains constant up to 750 °C. Beyond this value, a further increase of temperature determines the opening of the $C_{60}$ cages and the formation of silicon carbide.[7,13,14] The fact that in our experiment less than 1 ML is retained on the hydrogenated surface around 280 °C indicates that the interaction of $C_{60}$ with the hydrogenated silicon surface is of the same order of magnitude or even smaller than that between $C_{60}$ molecules. This is reasonable due to the inertness of the Si(100):H2×1 surface and has been confirmed by AFM results showing clusterlike growth.[13]

In conclusion, the data of Fig. 1 can be interpreted by assuming that the substrate temperature $T_{s,min}$, corresponding to the coverage minimum, signals the transition from physisorption on hydrogenated surface sites to chemisorption on bare silicon sites. This interpretation is strongly supported by the evolution of the UPS spectra, as shown in the following, and further confirmed by the core level analysis. As for the latter, a shift of 0.40 eV toward lower binding energies of the $C_{60}$ $C1s$ core level has been observed for $T_s > T_{s,min}$ pointing to a variation of the charge and/or the polarizability of the molecule surroundings.

Representative UPS data for different $T_s$ are reported in Figs. 2 and 3. In Fig. 2 the lower binding energy region of a typical UPS spectrum of a submonolayer thick $C_{60}$ sample deposited on $c$-Si:H at room temperature is compared to that of bulk fullerene. Also shown is the $c$-Si:H valence band spectrum and the difference spectrum. It is apparent that the $C_{60}/c$-Si:H spectrum is a superposition of contributions from $C_{60}$ molecules and Si substrate and that, furthermore, the difference spectrum is practically identical to that of bulk $C_{60}$. This situation remains unchanged for $T_s$ increasing in the range $T_s < T_{s,min}$ as shown in Fig. 3, where the UPS spectra of samples grown at different $T_s$ are reported. It is apparent that the valence band of the $T_s = 200$ °C sample[15] is unchanged as compared to the RT sample. We conclude, therefore, that the valence states of fullerene molecules are not perturbed by the presence of the hydrogenated Si surface, a strong evidence against the formation of a chemical bond.

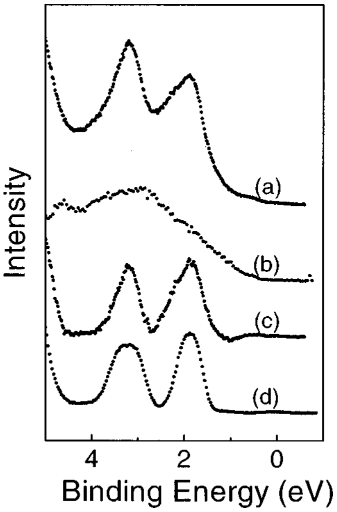

FIG. 2. (a) UPS spectrum of a submonolayer thick $C_{60}$ sample on Si(100):H2×1 surface; (b) UPS spectrum of the hydrogenated Si(100) 2×1 surface; (c) difference between curve (a) and (b); (d) UPS spectrum of bulk $C_{60}$. The bulk-$C_{60}$ spectrum has been shifted by 0.2 eV in order to account for the different screening.

We see in Fig. 3 that for $T_s > T_{s,min}$ a new peak appears between the highest occupied molecular orbital (HOMO) and HOMO-1 bands. The higher binding energy peaks are only slightly affected, the main variation being a broadening related to the increase of the deposition temperature. An overall shift of 0.1 eV is present in the spectrum of the sample grown at $T_s = 280$ °C probably related to a slightly different screening effect in submonolayer-thick samples. Concerning the new peak intermediate between the HOMO and HOMO-1 bands, we note that its position relative to the HOMO-1 and HOMO band does not change as a function of

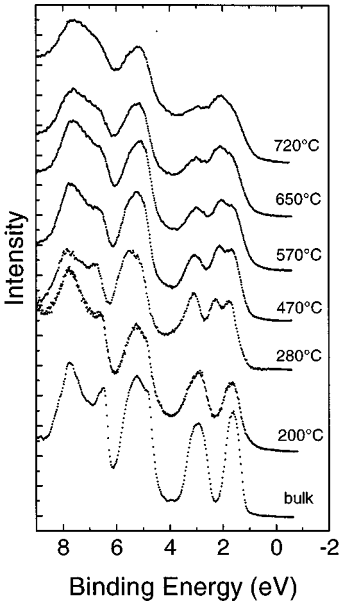

FIG. 3. UPS spectra of samples grown at different substrate temperatures $T_s$. The 200 °C and bulk-C60 spectra have been shifted by 0.3 and 0.5 eV, respectively.

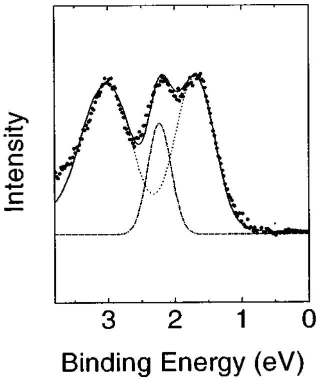

FIG. 4. UPS spectrum of the $T_s = 280\,^\circ\text{C}$ sample (circle) after the subtraction of the Si(100):H contribution and its decomposition: the dot line represents the bulk $C_{60}$ contribution, the dot-dashed line the new peak contribution, and the heavy continuous line represents their sum. For details see text.

$T_s$, the energy separation from the HOMO-1 band being 0.8 eV. The energy position of the new peak in the UPS spectra is in good agreement with the STS data of Chen *et al.*[5] showing the appearance of a single broader band intermediate between the HOMO and HOMO-1 bands for $C_{60}$ molecules adsorbed on defects or surrounded by Si, i.e., in the case of $C_{60}$ molecules located in a way to form many bonds with silicon.

An interpretation for the new peak is that it is due to the formation of a direct bond between the $p_z$ orbital of the C atoms and the Si dangling bonds. The finding that the energy positions of both the new valence band peak and the C1*s* core level do not change as a function of $T_s$ proves that the same kind of bonding is present from 280 °C up to 750 °C.

For $T_s \leqslant 470\,^\circ\text{C}$ the HOMO and HOMO-1 bands are still very well defined and the new peak is narrower than the HOMO and HOMO- 1 bands themselves. This situation is compatible with the formation of few localized bonds between the single $C_{60}$ molecule and the Si surface. In this temperature range all the structures are narrow enough to allow an accurate determination of the relative intensities. We have therefore analyzed the data as a superposition of the spectrum of bulk $C_{60}$, progressively broadened in order to simulate the effect of deposition temperature, plus a Gaussian peak. For samples with a $C_{60}$ concentration lower than one monolayer the contribution due to the uncovered Si regions was also taken into account. The result of this fitting procedure for the $T_s = 280\,^\circ\text{C}$ sample is shown in Fig. 4. This analysis is based on the assumption that the electronic structure of $C_{60}$ is not greatly perturbed by the interaction with the silicon surface if only few $p_z$ orbitals out of sixty are used by the molecule to form bonds with silicon. STM results[4,6] support this hypotesis by showing that the preferential sites for the adsorbed $C_{60}$ molecules on Si(100) are either the four dimer in the troughs between dimer rows or the two dimer between dimer rows or the site on the top of a dimer and that, therefore, the bonds formed by each molecule are four at the maximum.

The analysis provided two interesting results. First of all, it was found that, the total intensity of the three peaks practically equals that of the bulk HOMO and HOMO-1 bands, suggesting that the new peak is mostly made out of $p_z$ states. Second, the intensity of the new peak accounts for ~15% of the total area of the three peak structure. Assuming the mean value of the HOMO and HOMO-1 cross sections as the cross section for the electrons photoemitted from the new structure, the weight of the new structure gives a total of ~4 electrons in the new bonds. Because at this photon energy the cross section of silicon is quite lower than the cross section of carbon, the value suggests the formation of 4 bonds for $C_{60}$ molecule as expected in the case of $C_{60}$ adsorbed on the four-dimer site in the troughs between dimer rows. However, due to the uncertainty of the cross sections, the estimated value is not accurate enough to rule out the possibility that two bonds are formed, as expected in the case of $C_{60}$ adsorbed on the top of a dimer site.

As clearly apparent in Fig. 3, upon increasing the deposition temperature above 500 °C the HOMO and HOMO-1 bands broaden resulting in a rounding off of the peaks and the spectra exhibit a maximum at the energy of the new peak. We believe that this behavior is due to the deformation of the $C_{60}$ molecules and the increase of the number of C atoms interacting with the silicon substrate. This process terminates with the opening of the $C_{60}$ cage and the formation of crystalline SiC for $T_s > 750\,^\circ\text{C}$.

Finally, it is worth remarking that the spectral density at the Fermi level is low for the whole deposition temperature range, so that our data rule out the possibility of a metallic behavior, as suggested by several authors[3,4] for this system.

In conclusion, we have investigated the deposition of fullerene on Si(100):H2×1 surface as a function of substrate temperature from room temperature up to 800 °C. The interaction of $C_{60}$ molecules with both the hydrogenated and the clean Si(100) surface could be studied. It is found that the transition from physisorption to chemisorption entails the appearance of a new peak in the UPS spectra intermediate between that of the HOMO and that of the HOMO-1 bands. As a consequence the UPS technique appears the technique of choice for investigating the nature of the $C_{60}$ bonding on semiconductor surfaces.

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[15] In order to avoid the formation of clusterlike islands and to be sure that the UPS signals comes only from $C_{60}$ molecules adjacent to Si, a submonolayer-thick sample was used for $T_s = 200\,^\circ\mathrm{C}$ measurements.