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Interaction of C_{60} with clean and hydrogenated SiC-(3 × 3) probed through the unoccupied electronic states

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The effect of hydrogenation on the conduction bands of the Si-rich $6H$-SiC(0001)-(3 × 3) reconstruction is studied using inverse photoemission spectroscopy in order to distinguish surface from bulk states. These results are exploited for the comparative study of the interaction of C_{60} adsorbed on (3 × 3) and on hydrogen-terminated (3 × 3). For the latter, as in the case of hydrogen-terminated Si, C_{60} is electronically decoupled from the substrate. Upon annealing a C_{60} thick film deposited on hydrogenated (3 × 3) up to 670 K, there is a hint for a possible hydrogen transfer to the C_{60} molecules. The initially physisorbed molecules then adopt covalent bonding with Si, forming the contact layer. Part of the substrate is already found uncovered at this temperature. By further annealing up to 860 K all H atoms have desorbed. Finally, at 1100 K the remaining covalently bound C_{60} have desorbed. Unexpectedly, the structural damages caused by H and C_{60} deposition and by the successive annealing steps do not prevent a final restoration of the initial (3 × 3) reconstruction at about 1100 K.

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I. INTRODUCTION

The growth of organic molecular layers on various surfaces is currently widely exploited to tune the electronic properties of a substrate[1] or to obtain functional nanomaterials.[2] In particular, the fascinating and rich field dealing with C_{60} adsorption on semiconducting surfaces has been the subject of a large number of studies, recently exhaustively reviewed by P. J. Moriarty.[3] A large part of the studies quoted in this work are dealing with Si semiconducting surfaces, mainly represented by the well-known Si(111)-(7 × 7) and Si(100)-(2 × 1) reconstructions. The overwhelming consensus is that the bonding of C_{60} with Si(111)-(7 × 7) and Si(100)-(2 × 1) is strong and predominantly covalent according to the terminology used by Maxwell *et al.*.[4] The possibility that a fraction of physisorbed molecules may also be present at the surface before any anneal still seems a matter of debate.[3] Moreover, conflicting results regarding C_{60} adsorption on Si surfaces may be the consequence of one monolayer (ML) coverage indetermination.[3] There is thus not yet a clear unified picture describing the interaction of C_{60} with the various existing Si-rich surfaces.

Only a very small number of publications were devoted to C_{60} interaction with the (3 × 3) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructions of $6H$-SiC(0001), two Si-rich semiconducting reconstructions. Based on scanning tunneling microscopy (STM) experiments, Li *et al.*[5] suggested that deposited C_{60} are not mobile over these two surfaces. They found that a strong bonding drives C_{60} decomposition at high temperature, resulting in SiC island formation as happens for both Si(111)-(7 × 7) and Si(100)-(2 × 1) surfaces.

However, in contrast to SiC-$(\sqrt{3} \times \sqrt{3})R30^\circ$ and Si reconstructions, we have recently shown, using inverse photoemission spectroscopy (IPES),[6] that, upon annealing above 1100 K, C_{60} desorbs out of the (3 × 3) reconstruction, probably without dissociation. This unexpected result was attributed to the low density of Si reactive centers available on the (3 × 3) surface. The IPES study revealed that the (3 × 3) is singular against C_{60} adsorption compared to other Si-rich semiconducting substrates. Moreover, it suggests that the bonding of C_{60} with the (3 × 3) has both soft and strong character: soft because the molecules desorb upon annealing, leaving a recovered substrate as happens with noble metals,[4] and strong because a high-temperature annealing is necessary to break the covalent bonding. Further experimental and theoretical work is needed to understand the peculiar nature of the interaction of C_{60} with the (3 × 3) reconstruction.[7]

Since C_{60} orbitals will primarily hybridize with the surface states, it is important as a first step to identify these states. For the (3 × 3), angle-resolved ultraviolet photoemission spectroscopy experiments already provided some information about valence states[8] but, to our knowledge, only a limited amount of data involving the (3 × 3) conduction bands has been published so far.[8,9] One possibility to distinguish the surface from the unoccupied bulk states is to use hydrogen passivation. Hydrogenation of semiconductor surfaces, in particular Si, has been widely used to study their reactivity, the adsorption-desorption mechanisms, and many other aspects of their physical properties.[10–13] Indeed, in the present work, the exposure of reactive sites to activated hydrogen is expected to remove the unoccupied surface states.[8] We are able here to distinguish several surface states or resonances of the (3 × 3) from the SiC bulk states. This distinction, combined with a surface-sensitive technique like IPES, allows us to identify the completion or near completion of the first C_{60} layer, whatever the actual growth mode. This is exploited here to investigate the peculiarities of C_{60} adsorbed on hydrogenated SiC-(3 × 3), noted (3 × 3)-H hereafter. Differences and similarities with C_{60}

deposited on H-terminated Si are also explored by annealing the film up to 1100 K.

II. EXPERIMENTS

The (3×3) reconstruction was prepared by annealing under ultra-high vacuum a $6H$-SiC(0001) sample cut in an n-doped wafer (Sterling Semiconductors), simultaneously exposing its Si-terminated polar surface to a Si flux. The quality of the reconstruction is assessed from low-energy electron diffraction (LEED) [see Fig. 1(a)] and its characteristic IPE spectrum with six prominent features.[9,14] The sample was radiatively heated using a W filament approached at ∼2 mm of its backside. For the study of molecular desorption, we used 10-min duration annealings as in the previous study.[6] Passivation of the (3×3) reconstruction is obtained using activated hydrogen produced by a hot W filament placed 5 cm away from the sample in a high-purity H_2 atmosphere (10^{-6} mbar). Carefully outgassed C_{60} was sublimated at 670 K and deposited on (3×3)-H held at room temperature (RT). Several molecular films corresponding to an evaporation duration of 10, 20, 30, 40, 60, and 120 min have been prepared. The spectra of only two characteristic molecular films are shown for brevity. As will be shown, the thinner ones, designated hereafter "10min," are representative of C_{60} films having their first layer nearly but incompletely filled. The thicker ones are about 50 Å thick as measured with a quartz microbalance. They are characteristic of a typical thick film (TF) and are labeled "120 min" in this manuscript. LEED and IPES experiments were performed with the sample held at RT.

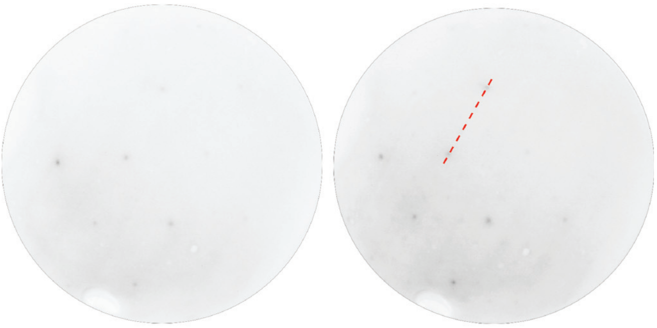
The IPE spectrometer is based on a I_2/He Geiger-Müller type detector fitted with a CaF_2 window. It works in the isochromat mode, detecting photons around a fixed energy of 9.7 eV.[15] The absorbed current of the order of 1 μA is used to normalize the photon counts. The kinetic energy of the incident electrons is varied in 0.1-eV steps to give a spectrum, typically obtained by accumulation over ten scans. All the spectra presented here have been obtained at normal incidence. Calibration of the Fermi level (E_F) was made using a cleaned Ta sample.

III. STRUCTURE OF THE (3 x 3) RECONSTRUCTION

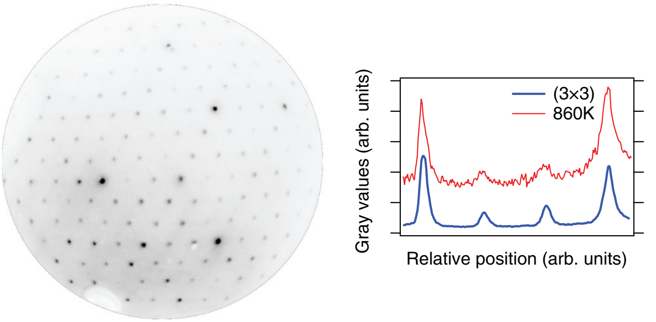
The (3×3) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ Si-rich reconstructions of SiC(0001), which have markedly different structures, both belong to the class of surface Mott-Hubbard insulators.[16,17] On $6H$-SiC(0001)-(3×3) the outer C-Si bilayer is terminated by a compact Si adlayer capped by Si tetramers arranged in a (3×3) periodicity.[18] There are, in this structure, not less than four different types of Si atoms: the outer Si adatom of the tetramers, the basal Si adatoms of the tetramers, the Si atoms belonging to the adlayer, and the Si forming the outer C-Si bilayer. Therefore we can expect several types of surface states or resonances which should manifest at distinct energies in the IPE spectra.[8]

By contrast, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction is much simpler. It is solely constituted of Si adatoms in T_4 positions[19] on top of the outer C-Si bilayer. As such, the incident low-energy electrons in IPES should be more sensitive to bulk SiC with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ sample.

(a) Clean (3×3) (b) 1200 L H*



(c) 10 min C_{60} (d) 860 K



(e) 1100 K (f) Comparison of the intensity profiles of (a) and (d)

FIG. 1. (Color online) (a)–(e) Characteristic LEED patterns corresponding to the IPE spectra shown in Figs. 2 and 3. All LEED patterns were acquired with an incident-beam energy of 180 eV. (a) Pristine (3×3), (b) after exposure to 1200 L of activated hydrogen, (c) after deposition of a C_{60} thin film on the hydrogenated surface, (d) after annealing the C_{60} film at 860 K, (e) after further annealing at 1100 K, (f) comparing the intensity profiles along the dashed line displayed in (a) and (d). The heights of the (1×1) peaks have been normalized. H* stands for activated hydrogen.

IV. IDENTIFICATION OF SURFACE AND BULK STATES OF 6*H*-SiC(0001)-(3 x 3) RECONSTRUCTION

Figure 2 shows the IPE spectra of a clean (3×3) reconstruction (thin black curve) and after exposure to 1200 L of activated hydrogen (thick red curve). From a clean (3×3) reconstruction to (3×3)-H, the LEED pattern changes from a (3×3) to a (1×1) pattern [Figs. 1(a) and 1(b)]. Further exposition does not lead to any change, neither in the LEED pattern nor in the IPE spectrum. The loss of the (3×3) periodicity indicates that exposure to atomic H substantially modifies the Si tetramers of the initial reconstruction. However, the (3×3) reconstruction can be fully recovered upon annealing at 860 K as shown by the dotted spectrum in Fig. 2. The similarity of the LEED patterns obtained before and after annealing at 860 K (not shown) supports the statement that all H atoms desorb and the disordered surface reconstructs to a fully recovered (3×3). We note that this desorption temperature is similar to what has been observed on hydrogenated silicon surfaces.[20–22] Moreover the recovery at 860 K of a well-reconstructed (3×3) is striking because the (3×3) is usually prepared under Si-rich conditions at much higher temperatures, typically in a narrow temperature interval between 1070 and 1140 K.[8,9,14,18,23]

Figure 2 shows that the spectrum of the hydrogenated surface is markedly affected between E_F and $E_F + 5$ eV. Indeed, it can be seen that the intensities of peaks a, b, and c are strongly reduced by the hydrogenation process, while peaks e and f remain barely affected. This result calls for a surface origin of the three bands associated to a, b, and c peaks while e and f peaks are most probably associated to genuine bulk bands. The assignment of the first unoccupied state at (0.6 ± 0.1) eV above E_F (peak a) was already discussed in the literature. Since it lies within the bulk band gap and dispersion measurements[8] show that this state remains far away from the Fermi level, it was attributed to the upper band of a Mott-Hubbard surface state. The corresponding density of states is mostly localized at the apex of the outer silicon atom of the Si adcluster (see Sec. III). The origin of the weakly dispersive b and c peaks[9] has not been discussed up to now, neither on a theoretical nor on an experimental ground. The present spectroscopic result indicates that peaks b and c at, respectively, (1.8 ± 0.1) and (2.8 ± 0.1) eV also correspond to resonances or higher-lying surface states.

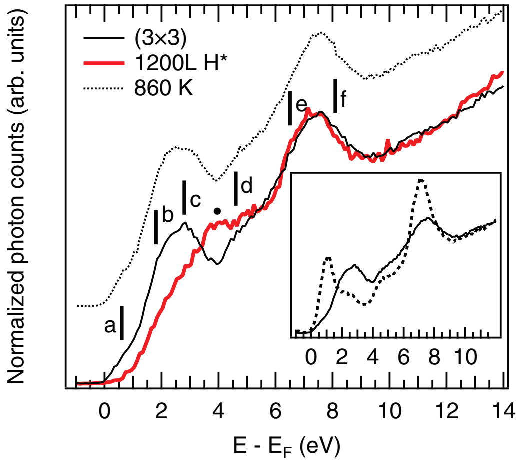


FIG. 2. (Color online) Comparison of normal-incidence IPE spectra of a (3×3) surface before (thin black curve) and after a 1200-L exposure to activated hydrogen (thick red curve) at RT. Vertical bars labeled a–f show the position of the unoccupied bands as reported in Ref. 9 for a pristine (3×3). Also shown is a typical spectrum obtained after annealing the (3×3)-H (dotted line) at 860 K. Inset: Comparison of (3×3) (continuous line) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ (dashed line) normal-incidence IPE spectra. In both panels, the spectra are normalized to the high-energy background. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ spectrum is reproduced from.[6]

The inset of Fig. 2 is also in favor of a bulk-like origin for e and f bands. In this panel, the IPE spectra of clean (3×3) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructions are compared. Considering their respective crystal structure briefly presented in Sec. III, it can be understood that the incident low-energy electrons should be more sensitive to bulk SiC with a $(\sqrt{3} \times \sqrt{3})R30^\circ$ sample. More IPE intensity in the energy range of the common bulk states, in particular around 7 eV above E_F, is therefore expected for $(\sqrt{3} \times \sqrt{3})R30^\circ$ relative to (3×3), as can be seen in the inset of Fig. 2. The aging behavior of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction[9] also supports a bulk origin for the high-energy states. Our result indicates that the broad feature at 7 eV in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ IPE spectrum actually comprises at least two peaks corresponding to e and f features in the (3×3) spectrum, which possibly could not be resolved in anterior work.[9]

The surface or bulk origin of the IPE peak d at (4.6 ± 0.1) eV[9] cannot be identified solely on the basis of this experiment. Its energy is very close to the position of the IPE peak of the (3×3)-H labeled (•) at ≈4 eV. The latter appears at an energy close to the 4.0 eV dip between peaks c and d in the IPE spectrum of the clean (3×3) reconstruction. Therefore it is attributed to a density of states specifically originating from the (3×3)-H corresponding to the antibonding counterpart of covalent Si-H bonds.

Finally, by looking at the (3×3) IPE spectra already published, one can notice some variations in the relative intensities of peaks b and c although the reported LEED patterns were of good quality. For instance, in 9 and 14, peak c is more developed than peak b after a background subtraction, while in 8 it is the reverse. These variations can be qualitatively explained by considering the high sensitivity of IPES to the reconstruction quality, the numerous defects commonly observed by STM,[25–29] and the surface origin of peaks b and c.

V. INTERACTION OF C_{60} WITH HYDROGENATED 6H-SiC(0001)-(3 × 3)

A. Film growth

Figure 3 shows various representative IPE spectra corresponding to full hydrogen passivation of the (3×3), C_{60} deposition on (3×3)-H, and annealing of a TF at various temperatures. The observed LEED pattern is also indicated at the bottom of each IPE spectrum. These LEED patterns can also be seen in Figs. 1(a)–1(e).

On the C_{60} TF spectrum five major structures can be seen, labeled hereafter 1–5. The origin of the three low-lying peaks was discussed, e.g., in Refs. 24 and 30. Among their peculiarities, it was noticed that part of the wave function contributing to peak 3 is localized in the center of the C_{60} molecule[24] while peak 2 shows more dispersion than the two adjacent ones. The intensity of peak 2 appears strongly reduced for different C_{60} thin films deposited on some metallic[31] and semiconducting surfaces.[32,33] At about 10 eV above E_F, where the IPE spectrum of the clean (3×3) reconstruction is featureless, there is a much weaker feature characteristic

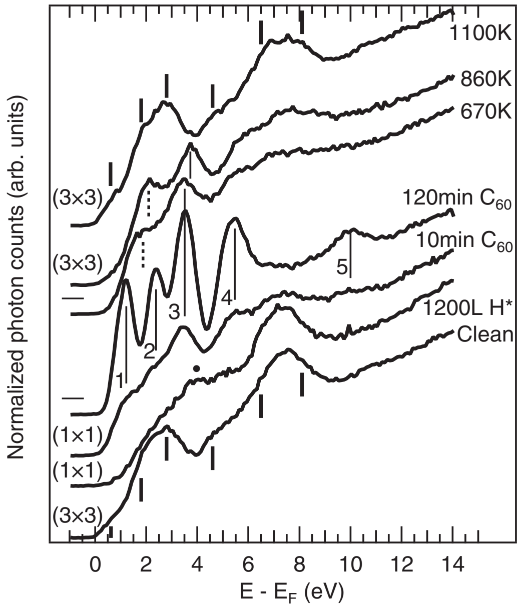


FIG. 3. From bottom to top, the normal-incidence IPE spectra of a pristine (3 × 3) surface and the spectra of the same surface successively exposed to atomic H, then to 10- and 120-min C_{60} flux, and the latter surface annealed at various temperatures up to 1100 K (vertical thick bars, see Fig. 2). Vertical thin bars allow us to compare the positions of the main C_{60} IPE peaks for the two film thicknesses studied, and vertical dashed bars show the temperature evolution of C_{60} LUMO.[24] For each surface, the obtained LEED pattern, if any, is also indicated on the left side. H* stands for activated hydrogen.

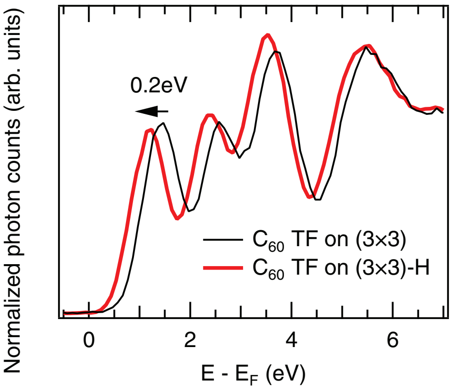


FIG. 4. (Color online) Comparison of the normal-incidence IPE spectra of a C_{60} TF deposited on a clean and hydrogenated (3 × 3) reconstruction. The spectrum shown by the thin (black) line is reproduced from.[6]

of a TF, peak 5. The center of this more dispersive peak 5[24] is located more than 4 eV above the center of the closest feature, peak 4. When comparing many C_{60} IPE spectra of various thicknesses, it is observed that peak 5 is actually well developed only for the thicker ones. To our knowledge, the modification of peak 5 consecutive to the interaction of C_{60} with a surface has not been reported before.

It can be seen in Fig. 3 that after a 10-min deposition some IPE intensity corresponding to peaks *e* and *f* from bulk SiC remains visible and a faint (1 × 1) LEED is still measured [Fig. 1(c)]. Since one single close-packed layer of C_{60} is able to quench the IPE signal from the underlying substrate to a hardly detectable value,[34] we deduce that for the 10 min spectrum the first layer[35] is not yet fully completed. Part of the substrate remains indeed uncovered. Since all the IPE peaks characteristic of the C_{60} TF spectrum are located at their respective TF energies, although with a much weaker intensity (the peak 5 amplitude is at the spectrometer limit of detectability), we deduce that, prior to any heat treatment, the bonding of C_{60} to the (3 × 3)-H is weak (i.e., of van der Waals type). This argumentation remains valid even if a few molecules grow on the first layer before its full completion.

As can be seen in Fig. 4, it is also interesting to notice that the IPE spectra of C_{60} TF (the 120 min spectrum) deposited on (3 × 3)-H and on a clean (3 × 3) reconstruction are slightly different. Although the overall spectral shape looks identical, the former is rigidly shifted with respect to the second one by an amount of about 0.2 eV toward E_F. The fullerene energy bands keep these rigidly shifted positions whatever the amount of extra deposited molecules from sub- to multilayer coverage. This effect can therefore not be attributed to any charge-transfer phenomena. In this case, the molecules in direct contact with the substrate would be electronically perturbed but not the outermost one in the case of a TF layer.[36] This result confirms the previous deduction stating that the interaction between as-deposited C_{60} and (3 × 3)-H must be very weak. On (3 × 3)-H, as-deposited C_{60} are therefore electronically decoupled from the hydrogenated substrate. On the other hand, the molecular level positions also depend on the initial band bending of the semiconducting substrate. For example, it is well known that atomic hydrogen adsorption on 6*H*-SiC(0001)-(3 × 3) reduces the band bending of around 0.5 eV following the elimination of acceptor-like surface states related to Si tetramers[37] and downward band bending (on *n*-type samples) toward flat-band conditions. In the case of 1-ML C_{60}/SiC(0001)-(3 × 3), it was recently shown that C_{60} is covalently bound,[6,7] and we have also observed a similar band bending reduction, although with a limited value around 0.25 eV.[38] This smaller value is related to the near-spherical shape of the fullerene and to the strongly corrugated character of the (3 × 3) reconstruction, which preclude any molecular binding with more than one Si tetramer[7,38] while leaving a significant fraction of the Si tetramers uncovered. Therefore, the residual band bending of the C_{60}-covered SiC(0001)-(3 × 3) should be larger (about 0.25 eV) than the H-covered (3 × 3). Therefore, the observed shift of the molecular levels toward the Fermi level is attributed to the reduced surface potential of the hydrogenated SiC substrate.

B. Annealing effects

After the annealing at 670 K of a C_{60} TF deposited on (3 × 3)-H, peaks *e* and *f* characteristic of bulk SiC gradually emerge as the annealing temperature further increases (see Figs. 3 and 5). This means that at 670 K part of the substrate is already uncovered because some of the physisorbed C_{60} molecules have desorbed. At the same time, one notices that peaks 2 and 5 of the TF are no longer visible on the 670-K spectrum. Also visible at 670 K is the reduction of the C_{60} peak 1 to peak 3 splitting caused in large part by the strong 0.5-eV upward shift of peak 1 and an overall broadening. This

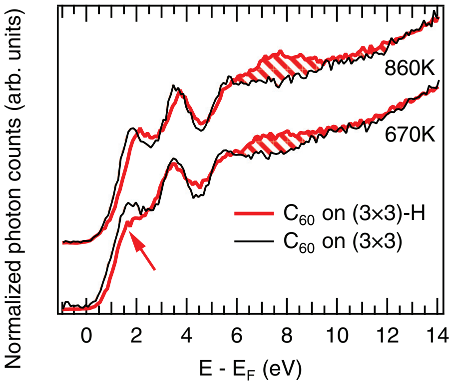


FIG. 5. (Color online) Effect of a 10-min annealing, at 670 and 860 K, of a C_{60} TF deposited on a clean and on a hydrogen-terminated (3 × 3) reconstruction. The dashed region above 6 eV shows the evolution of the IPE intensity from the SiC bulk states upon annealing from 670 up to 860 K. The spectra at 670 and 860 K are normalized to the high-energy background. (The arrow is discussed in the text.) The 860-K spectrum shown by the thin (black) line is reproduced from.[6]

shows that the remaining molecular layer is now covalently bound[33] to the substrate as in the case of Si, where it was also shown that upon annealing some of the hydrogen atoms first escape and transfer to the adsorbate forming C-H bonds.[39] Indeed, on H-terminated Si(100)-(2 × 1), at about 800 K, C_{60} adsorption configuration changes from physisorption to chemisorption after H atoms forming C-H and Si-H bonds have desorbed. Comparison of the 670- and 860-K spectra in Figs. 3 and 5 allows us to suggest that for (3 × 3)-H, too, a C_{60} hydrogenation takes place. Figure 5 compares the IPE results for annealed C_{60} thick films deposited on a (3 × 3)-H (thick red curves) and on a hydrogen-free (3 × 3) reconstruction (thin black curves). The 670- and 860-K spectra for C_{60}/(3 × 3)-H appreciably differ from their counterparts on clean (3 × 3). At 670 K, peak 1 intensity is clearly reduced (arrow), peak 3 remaining the sole well-developed molecular feature. By further annealing at 860 K, the intensity of peak 1 looks increased compared to the 670-K spectrum. The relative intensities of peak 1 and 3 are now similar to the ones obtained at 860 K after annealing a C_{60} TF deposited on a clean (3 × 3)[6] (Fig. 5). Since the energy band corresponding to peak 1 derives from the C_{60} lowest-unoccupied molecular orbital (LUMO)[24] we argue that the marked reduction of peak 1 intensity at 670 K is caused by some hydrogen transfer from the substrate to the molecules. The recovery at 860 K of some IPE intensity within peak 1 is attributed to the final hydrogen desorption from the C_{60} while a large fraction of the first C_{60} layer still remains bound to the substrate. To give more credit to this interpretation, we have performed a series of successive hydrogenation and annealing cycles on a C_{60} film chemisorbed on a few-nm-thick amorphous Si layer.[40] Similar effects on the IPE spectra are observed: strong peak 1 reduction after a hydrogenation and peak 1 recovery after annealing at 860 K. Therefore it is reasonable to assume that with C_{60} on (3 × 3)-H hydrogen atoms have been displaced upon annealing from the hydrogenated substrate toward the molecules and that, for some H atoms, the desorption is indeed a two-step process.

In parallel, it can be seen in Fig. 5 that the SiC bulk states e and f whose intensities grow with the temperature increase are visible with the previously hydrogenated surface but not with clean (3 × 3). This result shows that the preliminary hydrogenation eases subsequent C_{60} desorption. At 860 K, the simultaneous presence of spectral features relative to molecular and SiC bulk states together with the recovery of a faint (3 × 3) LEED pattern [see Figs. 1(d) and 1(f)] indicate that some C_{60} desorbed with the remaining hydrogen atoms. By contrast, this is not the case with the (3 × 3), where no LEED pattern appears at 860 K.[6] Since bulk transitions are detected as early as 670 K (Fig. 5) after hydrogenation, we deduce that C_{60} desorption occurs over a wide temperature range which spreads over more than 250 K. Obviously, the hydrogenation process introduces some heterogeneity at the surface, while C_{60} desorption happens in a narrow temperature interval with no prior hydrogenation of the (3 × 3).[6]

One can also notice at 860 K and not at 670 K (see Fig. 5) that on the (3 × 3)-H spectrum the fullerene spectral components are rigidly shifted to the high-energy side with respect to their counterparts on the (3 × 3) spectrum. This rigid-band shift can be understood by considering the restoration of the initial band bending of the (3 × 3) or a part of its initial value, though a screening effect may also contribute.[41]

Further annealing at 1100 K allows us to recover a (3 × 3) reconstruction as revealed by the full recovery of the LEED pattern presented in Fig. 1(e) and of an IPE spectrum characteristic of a clean (3 × 3) (Fig. 3). The presence of the three a, b, and c surface states strongly supports the absence of extra molecular fragments remaining anchored at the reactive centers of the ideal reconstruction. This result is qualitatively very similar to what happens with the high-temperature desorption of C_{60} deposited on clean (3 × 3).[6]

As a last remark, Takami *et al.*[21] showed using STM that a much lower hydrogen dose than that used in this study is sufficient to induce the loss of the (3 × 3) periodicity following structural damages. In this context, it is interesting to note that such damages resulting from the present (3 × 3) hydrogenation at 1200-L exposure do not prevent C_{60} desorption nor do they prevent the recovery of a perfectly reconstructed (3 × 3) final state after strongly bound C_{60} have desorbed. However, a particularity of the (3 × 3)-H is that covalently bound C_{60} desorption begins at much lower temperatures, i.e., between 670 and 860 K from our spectroscopic measurements.

VI. SUMMARY

We have used activated hydrogen exposure to distinguish the unoccupied surface states or resonances of the 6H-SiC(0001)-(3 × 3) reconstruction from the bulk states via IPES. These results are useful for the understanding of the intrinsic electronic properties of the (3 × 3) surface. They also allow us to follow the desorption process after successive annealing steps of a C_{60} thick film deposited on (3 × 3)-H.

Our results confirm the surface origin of the first unoccupied state, the closest peak to E_F at (0.6 ± 0.1) eV. We identify in the present study two other surface states or resonances corresponding to peaks b and c at (1.8 ± 0.1) and (2.8 ± 0.1) eV above E_F, respectively. A total of six surface states or resonances have been now identified, three occupied and three unoccupied. By contrast, the two high-energy peaks *e* and *f* are associated to bulk transitions.

After C_{60} deposition on (3×3)-H and upon film annealing, it is found that H atoms desorb first while some of the initially physisorbed C_{60} adopt covalent bonding with Si and/or H. Finally, at ≈1100 K a (3×3) reconstruction is fully recovered, supporting the desorption of covalently bound C_{60}. In contrast to what is observed with C_{60} deposited on (3×3), we show that for (3×3)-H the desorption of covalently bound C_{60} already begins between 670 and 860 K. Finally, as for Si(100)-(2×1)-H, the (3×3)-H provides a possibility to obtain an electronically decoupled C_{60} layer which may be of interest for molecular manipulation at surfaces.

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