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Non-adiabatic *ab initio* molecular dynamics of supersonic beam epitaxy of silicon carbide at room temperature

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In this work, we investigate the processes leading to the room-temperature growth of silicon carbide thin films by supersonic molecular beam epitaxy technique. We present experimental data showing that the collision of fullerene on a silicon surface induces strong chemical-physical perturbations and, for sufficient velocity, disruption of molecular bonds, and cage breaking with formation of nanostructures with different stoichiometric character. We show that in these out-of-equilibrium conditions, it is necessary to go beyond the standard implementations of density functional theory, as *ab initio* methods based on the Born-Oppenheimer approximation fail to capture the excited-state dynamics. In particular, we analyse the Si-C_{60} collision within the non-adiabatic nuclear dynamics framework, where stochastic hops occur between adiabatic surfaces calculated with time-dependent density functional theory. This theoretical description of the C_{60} impact on the Si surface is in good agreement with our experimental findings. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4774376]

I. INTRODUCTION

A fundamental problem in materials science is the understanding and control of epitaxy mechanisms for the production of high-quality crystals. In particular, thin film crystal growth of silicon carbide (SiC), a semiconductor synthesized to replace silicon in harsh working conditions, in opto- and micro-electronics, and in biomedical and biosensing applications,[1] is affected by many factors, notably the temperature. In the usual thin film growth processes, a deposition temperature in excess of 1000 K is used to synthesize this material and speed up growth and nucleation. However, a higher growth temperature results in a larger number of crystallographic defects, such as voids, stacking faults, and dislocations. The presence of these defects represents a substantial drawback as it strongly influences the electronic and optical properties of SiC in a uncontrollable way. Furthermore, the temperature issue is emphasized in SiC growth, as one has to deal with the different thermal expansion (8% larger in SiC) of lattice-mismatched substrates (20% larger in Si) inducing stress and strain in the grains. Therefore, a reduction of the growth temperature of SiC thin films represents an undisputed advantage.

To achieve this reduction down to room temperature conditions, we present in this work a technique[2] based on supersonic molecular beams of fullerene (C_{60}) impinging on a Si surface (SuMBE). By seeding a carrier gas, such as H_2, He, and Ar, within an injection chamber with the material to deposit (in our case carbon), and by using aerodynamical acceleration to reach supersonic velocities out of the injection cell, high fluence, and directionality of the particles towards the Si surface can be obtained with a substantial freezing of the internal degrees of freedom to typical temperatures of a few kelvins.[2] In this way, different processes, such as cage disruption, Si-C covalent bond formation, and, finally, SiC growth can be activated.

After presenting experimental evidence of SiC formation at room temperature by electron spectroscopy of core (XPS) and valence bands (UPS)[3] for a 35 eV C_{60} beam impinging

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on a Si(111) reconstructed (7×7) surface, our analysis will be mainly focused on the theoretical modeling of the C_{60} cage rupture, which triggers all further chemical-physical processes. Furthermore, this investigation will enable us to envisage the role of the C_{60} kinetic energy in initiating the SiC growth and driving the chemical reactions.

The study of high-energy cluster beam impact on solid surfaces is an old topic,[4] both from a theoretical and experimental point of view, with many applications ranging from materials science, for sputtering[5] or thin film deposition,[6] to chemistry, for initiating reactions,[7,8] and even nuclear fusion experiments.[9] In particular, the studies of C_{60} impact on semiconductor surfaces are important in materials science for the growth of carbon-based nanostructures. Several reasons make C_{60} a very good precursor for SiC epitaxy. First, C_{60} is the most abundant among fullerenes, and can be inexpensively obtained either by a discharge between two nearby graphite electrodes in an inert atmosphere, or by other self-assembly mechanisms that have been recently proposed.[10] Second, this molecule has a large total mass and thus can be accelerated in the SuMBE experiment by exploiting the aerodynamical acceleration mechanism.[11,12] Finally, hydrogen is not present in pristine fullerene, avoiding the presence of an undesired chemical element into a SiC growing film.

On the other hand, state-of-the-art experimental and theoretical investigations in high-energy cluster beam impacts are far from being conclusive on the nature of the chemical and physical processes occurring at the surface. While SiC epitaxy has been already achieved in experiments,[11,12] the right stoichiometric ratio was obtained only above 800 K and for a beam kinetic energy of 5 eV. However, available computer simulations based on classical molecular dynamics (MD)[13] or tight-binding approach[14] are in complete disagreement with these experiments. In these studies Si structural order is maintained, with simple superficial permeation and no evidence of C_{60} cage breaking up to an energy per atom three times the experimental value obtained by SuMBE. In this paper, we show that the reason of the failure in explaining the C_{60} cage rupture at the observed kinetic energy is the neglect of the coupling between the electronic and nuclear degrees of freedom within the widely used Born-Oppenheimer (BO) approximation. To overcome this limitation, we decided to describe the coupled electronic-nuclear dynamics via a non-adiabatic approach.[15] In fact, recent modeling efforts point out the importance of non-adiabatic effects in describing various physical and chemical phenomena occurring at surfaces.[16–18]

This paper is structured in the following way. In Sec. II, we briefly outline the experimental apparatus and techniques used to obtain the SiC growth. Experimental evidence of the SiC growth at room temperature by electron spectroscopy is provided in Sec. III. The ensuing calculation of the fullerene cage impact on the Si(111)-(7×7) surface by different methods within BO approximation is then described in Sec. IV. Section V illustrates the results obtained by switching-on non-adiabatic surface hopping method to describe the C_{60} rupture for the problem of SiC epitaxy.

II. EXPERIMENTAL TECHNIQUES

The study has been performed at the IMEM-CNR laboratory where an experimental setup, devoted to ultrahigh vacuum (UHV) thin film growth by SuMBE and *in situ* analysis, has been developed. A detailed description of this technique is provided by Ref. 2. The supersonic beam is formed in a separate "source chamber" (base pressure of 1×10^{-7} mbar) while film deposition and characterization is performed in the main μ-metal chamber at a pressure of 3×10^{-11} mbar. Auger (AES), X-ray (XPS), and ultraviolet (UPS) photoemission electron spectroscopies can be performed. XPS spectra have been taken using Mg Kα photons at 1253.6 eV, while the valence band structure was probed using the HeI 21.2 eV of a Helium discharge lamp. The electron energy analyzer, a VG hemispherical device (CLAM2), allows a total energy resolution of 0.95 eV for XPS and about 0.1 eV for UPS. The C_{60} source is essentially made of two coaxial quartz capillary tubes, resistively heated by a tantalum foil. The experiments were carried out using free-jet expansions of H_2 in which the seeded fullerene particles, using appropriate low percentages, reach a kinetic energy of about 35 eV, with an average growth rate of about 0.1 Å/min in the direction perpendicular to the substrate. The substrates used were obtained from a Si(111) wafer (resistivity 1.20×10^{-4} Ωm) cleaned by a modified Shiraki procedure.[12] The silicon oxide film was then removed in vacuum by several annealing cycles, until a Si(111)-(7×7) surface reconstruction was obtained, as checked by the well-known sharp LEED pattern. The core level analysis has been performed by Voigt lineshape deconvolution after background subtraction by a Shirley function. The typical precision for peak energy positioning is ±0.05 eV, uncertainty for full width at half maximum (FWHM) is less than 5% and for area evaluation is about 2.5%.

III. EXPERIMENTAL FINDINGS

C_{60} supersonic molecular beams by SuMBE technique have been used to grow high quality crystalline SiC thin films. In this method, the formation and cleavage of bonds and the activation of surface processes are kinetically driven. Epitaxy experiments at room temperature have been carried out aiming to estimate the effects of the initial kinetic energy on the growth without thermal contributions. Fig. 1 shows the C1s core level of a 0.7 monolayer (ML) fullerene film deposited at room temperature by SuMBE. The peak lineshape is quite complex and four components have been introduced to achieve the best curve fit, showing the same FWHM of 1.00 eV. The features are located at binding energies (BE) of 283.03, 283.73, 284.46, and 285.10 eV and are characterized by a percentage over the whole C1s signal of 12.0%, 42.7%, 23.4%, and 21.9%, respectively. The peak at higher BE is typical of physisorbed C_{60} at room temperature deposition, possibly showing covalent interaction between a few fullerene carbon atoms and the silicon surface.[19–21] The structure at 284.46 eV has been observed only in MBE experiments where the substrate temperature was at least 700 K; it is considered representative of the formation of several covalent

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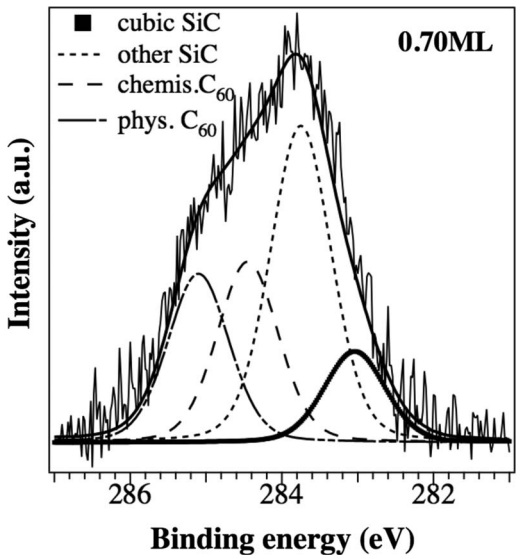

FIG. 1. C1s core level photoemission for a film of C_{60} on Si(111)-(7×7) surface at room temperature deposited by SuMBE, at a coverage of 0.7 ML. The curve has been fitted using four components, corresponding to different carbon chemical species as shown in the legend.

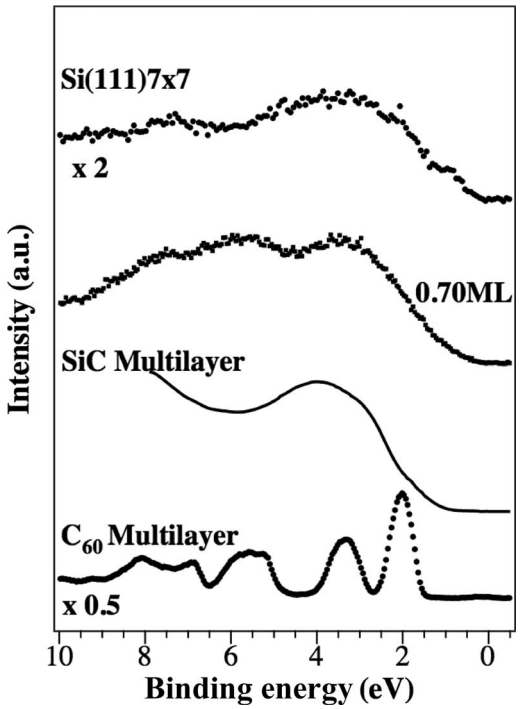

FIG. 2. From top to bottom: Valence band spectra (HeI source, photon energy of 21.2 eV) from the Si(111)-(7×7) bare surface, from the 0.7 ML film of C_{60} on Si(111)-(7×7) surface at room temperature deposited by SuMBE, from the 3C-SiC film synthesized on Si(111)-(7×7) surface at 1070 K by SuMBE approach, and finally, from a C_{60} multilayer. The different intensities are evidenced by the labels.

Si-C bonds that will lead to cage opening and fragmentation at higher temperatures. The two peaks in the 283–284 eV range are representative of carbides showing different properties, in particular the component at 283.03 arise from amorphous and stoichiometric SiC[20,22] or from the cubic polytype,[23] while the one at 283.73 can be associated to non-stoichiometric SiC compounds[24,25] or to hexagonal polytype SiC.[26] Noteworthy, the presence of these two carbide-related peaks is a clear evidence that the SiC synthesis has been achieved at 300 K, while in MBE experiments this occurs at temperatures of 1000 K or higher. Moreover, they represent the 54.7% of the whole C1s photoemission, thus showing that the carbide has been synthesized by the SuMBE approach at room temperature.

Figure 2 shows the valence band (VB) photoemission spectrum of the 0.7 ML film of C_{60}, deposited at room temperature by SuMBE. For comparison, the VB from a C_{60} multilayer, from a thick SiC film (synthesized by SuMBE, with Si(111)-(7×7) surface at 1070 K) and from the bare reconstructed Si surface are also reported. The 0.7 ML spectrum is characterized by a main broad band around 4 eV, with features in the 5–10 eV range that somewhat resemble those of fullerene. The Si(111)-(7×7) surface states are absent, and the overall intensity is higher than that of bare Si. This suggests that the observed lineshape is by no means that of the Si substrate, but is in fair agreement with that of a 3C-SiC, possibly with some molecular orbitals broadening the lineshape in the 5–10 eV and HOMO region. Very similar VBs have been observed in MBE experiment only for annealed C_{60} film at a substrate temperature of 1070 K or higher,[19–21] i.e., when the carbide is definitely synthesized. Noteworthy, the rupture of the fullerene cages at about 1070 K is characterized by a VB with broadened but still distinguishable MOs, apart from the HOMO band that is highly deformed.[19–21] The physical/chemical properties of the fullerene 0.7 ML film from XPS and UPS clearly put in evidence the presence of SiC, probably in the forms of islands, with more than 50% of the deposited organic precursor leading to the synthesis of carbides. The rest of the deposited fullerene cages experience a strong chemical interaction with the Si surface, with fingerprints in both C1s and VB that have been found only in MBE experiment after annealing at 1070 K or higher temperature. This means that the high KE of the organic precursor is able to induce the formation of covalent bonds, activate chemical processes that are hindered at room temperature in experiments occurring in conditions of thermodynamic equilibrium, i.e., in MBE deposition. Moreover, being negligible the C_{60} surface mobility on Si(111)-(7×7) up to 870 K,[27] one supposes that part of the fullerene kinetic energy is used also to improve its surface mobility or that of Si atoms, in order to achieve the formation of SiC islands and not only cages covalently bonded to the inorganic surface.

IV. BO-DFT SIMULATION OF THE C_{60}-Si(111)-(7×7) COLLISION

While our experiments of deposition at the kinetic energy of ∼35 eV on Si provide evidence of the C_{60} cage breaking at room temperature, available theoretical results are in complete disagreement with this finding.

A first attempt at modeling was made by Averback[13] using the Tersoff potential[28] in the framework of classical molecular dynamics simulations. Cage disruption was found occurring only for an impinging kinetic energy larger than 100 eV. Similar results have been obtained by Galli and coworkers,[14] in a more refined model using a tight-binding

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approach. In this case, the minimum impact kinetic energy to obtain heavy damage of the diamond surface and fragmentation of the C_{60} cage is predicted to be above 200 eV.

Both of these predictions are many times higher than our experimental value. In the light of these results, it is clear that a theoretical explanation of the fragmentation mechanism is missing and a number of open questions remain unsolved. In the following, we will address these issues by progressively increasing the level of accuracy of the computational modeling, in order to understand the cage breaking mechanism, which initiates all the physical-chemical processes of the SiC growth.

We ran a first set of simulations looking for a possible mechanical explanation of the cage fragmentation, namely a mechanism based on highly-excited vibrational states, bringing about the breaking of the bonds on a timescale of picoseconds, within the reach of *ab initio* molecular dynamics.

As a first step, we chose the density-functional tight-binding (DFTB) method,[29–31] which is a systematically improvable approximation of the full density-functional theory (DFT) approach based on a second-order expansion of the electronic density. The computational cost of this approach to electronic structure is at least two orders of magnitude cheaper than the corresponding full DFT calculation, with generally only modest compromises on the accuracy. As a result of this substantial speed gain, DFTB may be used to investigate much larger systems than those accessible by DFT, thus following their evolution for much longer timescales.

We performed simulations on a series of initial kinetic energies in the range 35 eV to 450 eV. The Si(111) surface reconstructed (7×7) was simulated by means of a slab containing 494 atoms, passivated by 49 hydrogen atoms, as shown in Fig. 3.

We found that for energies less than 300 eV, the C_{60} molecule undergoes large distortion upon impact onto the surface, but does not fragment. The cage breaking occurs only from 300 eV upwards. A movie of the full trajectory for 50 eV and 450 eV initial kinetic energy can be found in the supplementary material (files 50.mpg and 450.mpg).[32]

This conclusion is strongly inconsistent with our experimental data. In order to check whether a possible reason for this failure was due to the limited accuracy of the forces calculated in the DFTB framework, we performed a number of trials using full DFT using the *ab initio* total-energy and molecular dynamics program Vienna *Ab-initio* Simulation Package (VASP).[33–36] The ion-electron interaction is described using the projector augmented (PAW) technique[37] with single-particle orbitals expanded in plane waves with a cutoff of 400 eV, which ensures convergence of the electronic structure (band gap) and of the total energy within chemical accuracy (0.01 eV).

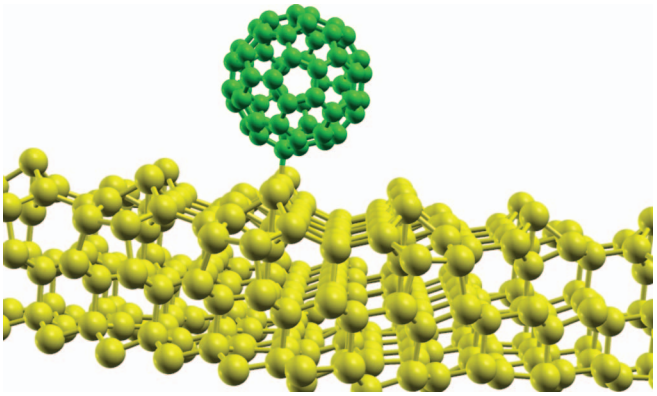

FIG. 3. Layout of the experiment. Silicon surface cleaved along the (111) direction and reconstructed (7×7), highlighting the 12 adatoms protruding from the surface plane. At some distance from the surface, we depict the impinging C_{60} molecule.

DFT-based simulations have been used successfully to investigate a wide spectrum of phenomena, ranging from the response to macroscopic electric fields,[38,39] melting,[40] and adsorption,[41,42] although several known failures exist, such as underestimation of the band-gap in insulators and semiconductors.[43,44]

The unit cell we used in the calculation measures 26.9 Å along the short diagonal, while the spacing between the adatoms is 7.68 Å within the triangular subunit, 6.65 Å across the boundary of the triangle, and the diameter of the corner hole is 13.3 Å. The dimension of the cell along the collision direction, orthogonal to the surface plane, depends on the number of Si layers in the simulation cell, ranging from 30 to 50 Å for 5 and 8 layers, respectively.

Only the Γ-point has been used to sample the Brillouin zone, due to the large number of atoms in the unitary cell (several hundreds). We tested different exchange-correlation functionals, notably based on the local density approximation (LDA)[45] and generalized-gradient correction (GGA-PBE),[46] and we found that the dynamics of the system is independent on the choice of the functional. Molecular dynamics simulations were performed in the micro-canonical ensemble, using a time step of 1 fs. The simulations used an efficient charge density extrapolation, which speeds up the simulations by approximately a factor of two.[47]

However, we found that even this more accurate level of theory does not modify the previous picture, although we tested various impact angles, different surface impact sites, several orientations of the impinging molecule, and defects on the fullerene cage enhancing the reactivity, such as found in $C_{57,\,58,\,59}$ (Ref. 48) without finding appreciable changes in the energy required for breaking the cage.

Furthermore, we ran a simulation with a negatively charged cell to take into account possible charge transfer due to clustering between fullerenes or scattering with the carrier gas. The charge transfer from Si to fullerene is then facilitated by the lowering of the HOMO-LUMO gap, decreasing from 1.65 eV to 0.8 eV at the penetration stage. Nevertheless, cage rupture is still observed at energies much higher than the experimental one.

Finally, we tried to increase the fullerene flux by simulating a collision of two C_{60} impinging one on top of the other on the Si(111) surface, as shown in Fig. 4.

Even in this case, the minimum kinetic energy needed to obtain the cage rupture was around 300 eV. While a mechanical disruption of the C_{60} cage can be safely ruled out based on our previous analysis for the kinetic energies, BO-MD simulations reported in the literature[49,50] show that a break may occur some time after a collision if the total internal energy of

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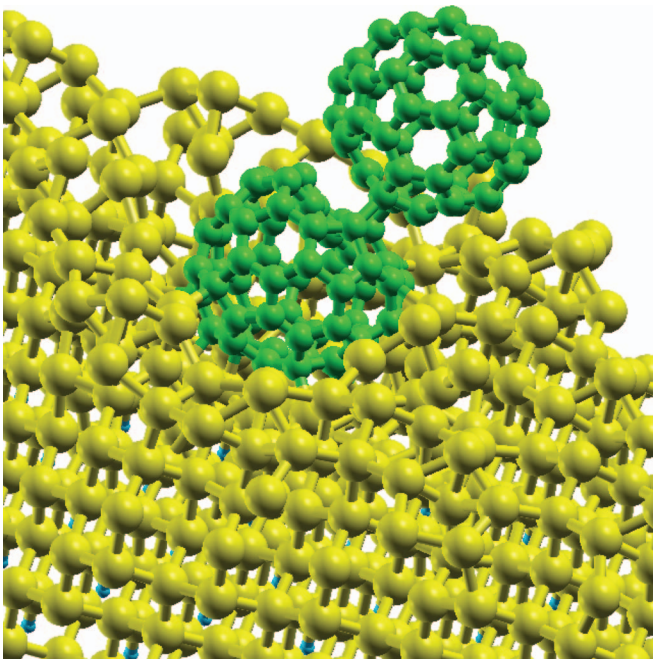

FIG. 4. Two C_{60} molecules impinging on the Si surface one on top of the other.

C_{60} (defined as the difference between the kinetic energy of the bouncing fullerene and the center of mass kinetic energy) is between 30 and 40 eV. This is a further clear indication that this approach must be missing some crucial physical process: the experimental evidence of the breaking of C_{60} at 35 eV of initial translational kinetic energy cannot obviously be consistent with a final internal kinetic energy of the molecule of 30–40 eV. However, we performed an investigation of the dependence of the final internal kinetic energy of fullerene as a function of impinging kinetic energy. The results are reported in Fig. 5, and show that for the impinging kinetic energies under investigation (35 to 300 eV), the fullerene internal energy after the collision ranges from 3 to 17.5 eV, as shown by the circles in Fig. 5. An enhancement of the substrate temperature to 1300 K increases the internal kinetic energy (downward triangles, blue in the on-line version in Fig. 5) but not so much as to cause a rupture in a short time.

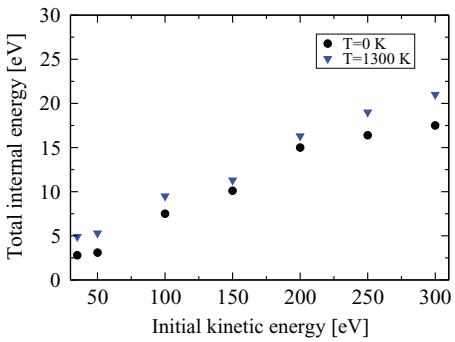

FIG. 5. Internal kinetic energies of fullerene after bouncing back from the surface for room temperature (300 K, circles) and 1300 K (downward triangles, blue in the on-line version) from BO-DFT calculations. Temperature is the same for both surface and C_{60}.

We also hypothesized that cage breaking could happen on a longer timescale than that one simulated by *ab initio* MD. To investigate this possibility, long ($\simeq$50 ns) classical MD simulations were performed by employing the Brenner-Tersoff empirical potential.[28] For the impinging kinetic energies under investigation (35 to 300 eV), we did not observe any fragmentation, whereas we did observe the fullerene chemisorption. Of course, the absence of fragmentation within a time-scale which is still relatively short does not prove that the process might be kinetically hindered, but it provides further indications that some important feature is missing in BO-MD.

V. NON-ADIABATIC MOLECULAR DYNAMICS

The results reported so far exclude a simple mechanical picture for the fragmentation of the cage at the kinetic energy experimentally measured. Therefore, this failure must be due to physical processes than are not considered in the BO-DFT description of the collision. The first hint that electronic excitations may be important to break the C_{60} cage comes from the observation that strong radiation fields lead to charge photo-excitation, ionization and plasmon excitation inducing the fragmentation of buckminsterfullerene.[51,52] In particular, upon high-intensity femtosecond laser excitation, C_{60} undergoes a "giant" plasmon resonance at 20 eV. This collective charge excitation leads to an efficient energy transfer to the vibrational modes of the molecule and to a possible rupture of the cage via two-plasmon excitation.[53] In our case, the role of the external electromagnetic field is played by the intense dipole moment created by the impact on the metallic surface of Si. Due to the short duration of the impact, electrons cannot instantaneously follow the nuclear positions, and therefore "lag behind" the nuclei during the collision. In order to explore this alternative route to cage breaking, it is necessary to take into account electronic excitations and their coupling to nuclear motion. Consequently, our computational modeling should go beyond BO-DFT and therefore adopt a method capable of treating excited electronic states.

The BO approximation relies on the assumption that ionic and electronic motions proceed on decoupled timescales. In C_{60}, the 1.6 eV band-gap corresponds to emission in the frequency region of 10^{15} Hz, and the collisional time scale in our case is of the order of few tens of femtoseconds, $\simeq 10^{14}$ Hz. The Massey parameter, defined as the ratio between nuclear (τ_p) and electronic characteristic times (τ_e), is of the order of $\xi = \tau_p/\tau_e \simeq 1$–10. In this range the BO cannot expected to be valid (ξ should be much greater than one for the BO approximation to hold).

An accurate model of the C_{60}-silicon surface impact must take into account that the nuclear and electronic timescales are comparable, and the electrons cannot relax fast enough to the ground state relative to the instantaneous configuration of the nuclei. Therefore, the potential energy surface on which the nuclear motion evolves changes significantly, possibly allowing for cage breaking at lower kinetic energy. These considerations, along with the results described so far, led us to conclude that the BO-DFT approximation is not sufficiently accurate to describe this high-energy collision. In order to

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have a first indication of the importance of the electronic excitations, we first used the Car-Parrinello approach to MD, as implemented in the CPMD code suite.[54,55] In this method, the electronic wave function is not optimized at each MD step but is propagated in time by means of a fictitious classical Lagrangian,[56] where the electronic degrees of freedom are given a fictitious mass. This does not guarantee that the wave function is exactly on the BO surface, but it stays reasonably close. For higher fictitious electronic mass, the wavefunction responds less promptly to the change in the nuclei configuration. We exploited this feature, intentionally increasing the fictitious electronic mass, in order to allow for a sizeable deviation from the BO surface, thus effectively including excited components in the wave function. Within this approach, the minimum kinetic energy required to break the cage dropped to 120 eV. A movie showing the full trajectory of the impact up to final break of the C_{60} cage is provided in the supplementary material (file mdcp.mpg).[32] This result gave us a strong hint that electronic excitation effects may play an important role in breaking the cage at lower energies than those required by classical MD.

However, a full quantum treatment of electrons and nuclei is unfeasible for the size of our problem. Therefore, we decided to use a non-adiabatic MD method. In this approach, the non-adiabatic dynamics is approximated by performing stochastic hops between adiabatic surfaces constructed with the excited states of the system, which have been calculated by using time-dependent density functional theory (TDDFT) in the Tamm–Dancoff approximation.[57]

The nuclei are propagated using Newton's equation of motion on the current adiabatic electronic state and the probability of surface hopping is evaluated by means of the Landau-Zener theory.[58,59] Forces used in the MD simulation are calculated on the adiabatic surfaces populated at the present MD step and constructed with the excited states of the system.[60]

The TDDFT surface-hopping simulations were carried out using the CPMD code.[54,55] We verified that the TDDFT approach was able to reproduce the experimental electronic excitation spectrum of fullerenes.

Unfortunately, we estimated that the computational cost for simulating the excited-state dynamics of C_{60} impinging on Si(111)-(7×7) surface would have been too high to obtain a result in a reasonable time. Therefore, we considered a smaller yet realistic system. We used a three-layer Si(100)-(2×1) slab composed of 48 silicon atoms, passivated with hydrogen atoms. The six lowest lying singlets were included in the calculation of the adiabatic surfaces. All of them were found to be visited during the dynamical evolution of the system.

From the result of our BO-DFT simulations, this crystallographic surface is equivalent, with regards to the impact of the fullerene molecule, to the Si(111)-(7×7) surface. The two bottom layers were held fixed during the MD run. Due to the smaller transversal size of the slab, we chose to simulate the impact of a C_{20} molecule, in order to avoid unphysical interactions with periodic images. The main differences between C_{20} and C_{60} consist in the HOMO-LUMO energy difference (0.54 eV vs. 1.64 eV) and the cohesive energy per carbon atom (6.26 eV/atom vs. 7.15 eV/atom). Classical MD simulations of the impact of C_{20} on graphite, with empirical potentials, are reported in the literature[61] and the kinetic energy needed for the fragmentation of the C_{20} molecule exceeds 25 eV (at least 1.25 eV/per atom). Our BO-DFT calculations agree with this value of the kinetic energy for the cage breaking upon impact with the Si surface. We performed four simulations of C_{20}, with initial kinetic energies of 35, 22.6, 11.5, and 5.0 eV (corresponding to 105, 67.8, 34.5, and 16.5 eV for C_{60} having the same initial velocity) to find the kinetic energy threshold. Each simulation lasted 0.2 ps with a time-step of 0.5 fs. The fragmentation of the cage happened in all of the first three cases, while it was not obtained in the last one. A graphical representation of the fullerene trajectory all the way from the initial condition to breaking is reported in in the supplementary material (file c20namd.mpg).[32]

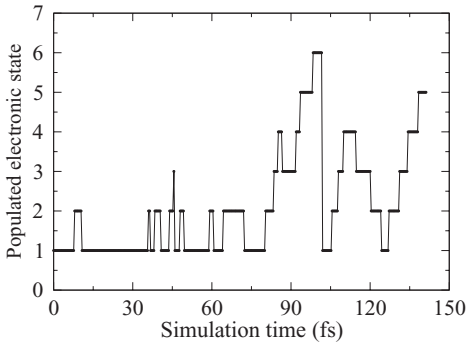

FIG. 6. Surface-hopping evolution on the first six excited states during the non-adiabatic MD simulation.

In this simulation, we clearly observe fragmentation of C_{20} impinging with a kinetic energy of 11.5 eV on the Si(111)-(7×7) surface on a timescale spanning ∼150 fs. This very short timescale confirms that a non-adiabatic description is needed for a proper modeling of the phenomena resulting from fullerene impacts.

We report in Fig. 6 the visited electronic state as a function of the simulation time. The impact between C_{20} and the surface, defined as the instant when the distance between the fullerene and the surface is at a minimum, occurs at $t = 36$ fs. It is clearly seen that from this moment on, the system visits excited surfaces. At $t = 56$ fs another carbon atom impacts with the surface and at $t = 80$ fs a considerable distortion of the C_{20} cage occurs. From this moment onwards, the energy transfer between the carbon atoms and the surface is particularly intense, as evidenced by the fact the excited states of progressively higher energy are visited along the trajectory. Interestingly, the cage rupture occurs via the ejection of a C–C dimer, which we observe in the last part of our trajectory beyond 130 fs, when hopping occurs between many excited energy surfaces. This finding is compatible with experimental evidence on fragmentation due to high-energy impacts of fullerenes.[62]

All of these processes can be observed in the movie c20namd.mpg of the supplementary material.[32]

As a check, we also performed a BO-DFT simulation of C_{20} impact at an initial kinetic energy of 11.3 eV and we did not observe the fragmentation, enforcing once more the role of the electronic excitations on the cage breaking.

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Following the epitaxy of SiC thin films is computationally not feasible due to the time-scale out of reach of MD simulations, but in principle could be tackled by methods such as dominant reaction pathways.[63] However, based on the much higher solubility of carbon at the surface with respect to the bulk and the stability of SiC, it could be argued that the system, after the cage breaking, will evolve into the state corresponding to the crystal phase without steep energy barriers.

VI. CONCLUSIONS

In this paper, experiments on the epitaxy of SiC by SuMBE technique and a first-principle model of the collision of C_{60} with Si(111)-(7×7) surface have been described. SuMBE has been used to grow high quality crystalline SiC thin films. In this experimental method, the formation and disruption of bonds and the activation of surface processes are kinetically driven. Experiments of deposition at high kinetic energy (∼30–35 eV) on Si gave evidence of SiC ordered domain formation at room temperature. *In situ* electron spectroscopy measurements confirm the epitaxy of SiC nano-islands.

Simulations using DFT based on the Born-Oppenheimer and Car-Parrinello approximations are not able to capture the dynamics of the impact, predicting a minimum kinetic energy for the cage breaking of one order of magnitude higher than the experimental value. This failure is due to the neglect in BO-DFT of the excited electronic states, populated upon the high-energy collision with the Si surface. In order to properly capture the dynamics of the system, it is mandatory to explicitly include the excited electronic states in the calculation.

Therefore, non-adiabatic MD has been used with the inclusion of several electronic excited states, so as to reproduce the coupling between the electron and nuclear dynamics through the surface hopping in the calculation of the forces. From our results, we may infer that the mechanism which makes it possible to break the fullerene cage at energies as low as 0.6 eV per atom is the change in the force field felt by the nuclei, due to the spawning of excited electronic states of the molecule upon impact with the surface.

While our theoretical approach and the calculations have been performed specifically in the case of SiC growth, we believe that the underlying model and computational tools are rather general, and can be applied to other cases of material epitaxy or organic molecule interaction by SuMBE with inorganic surfaces.

Finally, we would like to comment on the computational cost of performing these *ab initio* simulations. All of the BO-DFT calculations presented above required roughly 10^5 central processing unit (CPU) hours on modern 2.3 GHz processors of a high-end computing terascale resource. All of the non-adiabatic simulations required twice as much. The considerable computational requirements of non-adiabatic simulations allowed us to follow only the initial stage of the processes leading to SiC formation. Nevertheless, this model agrees with the experimental finding of an energy threshold for C_{60} fragmentation close to 35 eV.

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