Computational modeling of SiC formation by C_{60} epitaxy on Si(1,1,1)-7x7 surface

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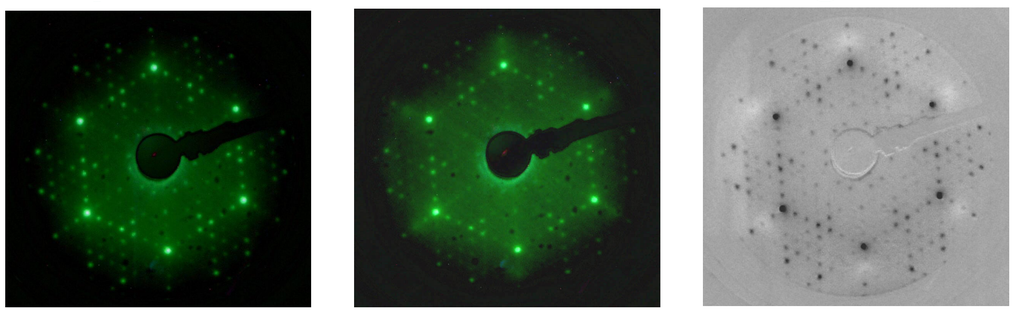
Why SiC?

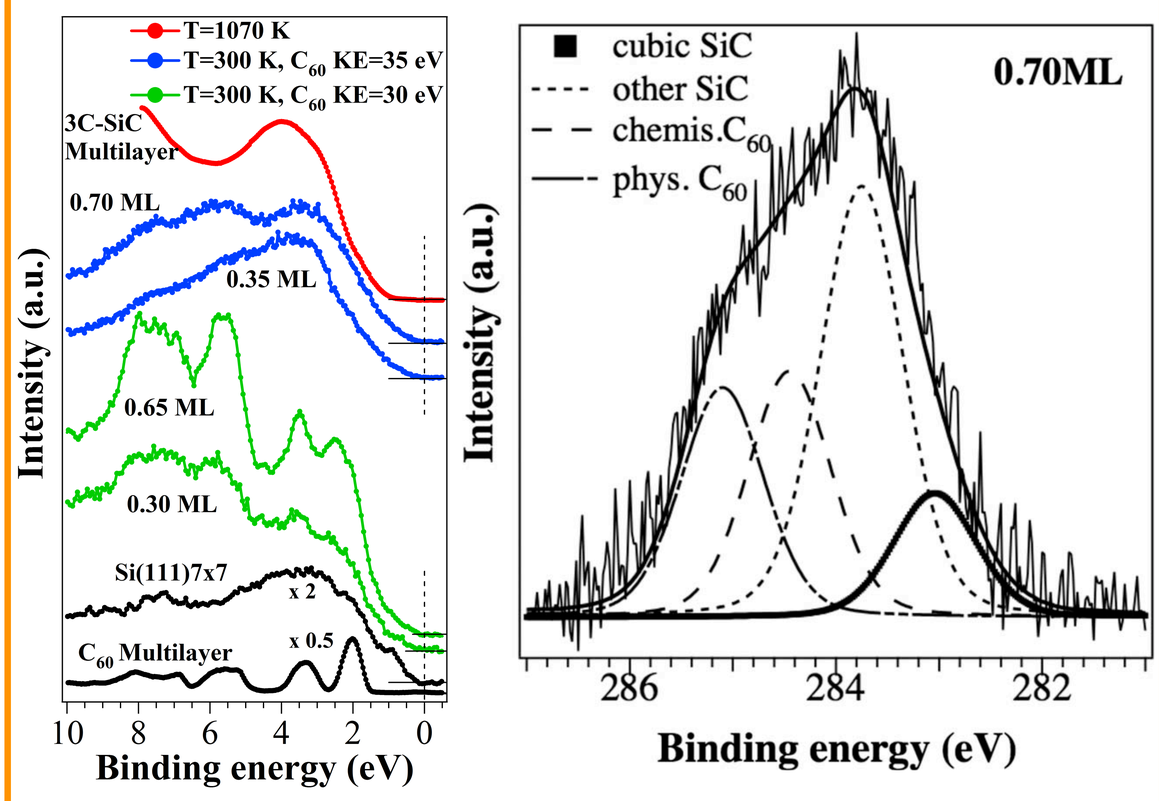
- SiC is used to replace Si in harsh working environments. More than 200 polytypes, wide band gap from 2.4 eV (3C) to 4.1 eV (2H).
- SiC is very rarely found in nature.
- The synthesis procedures are very expensive (high T, > 1300 K, lot of impurities).
- **We seek for an inexpensive way of producing SiC at room temperature.**

Experimental evidence of SiC growth



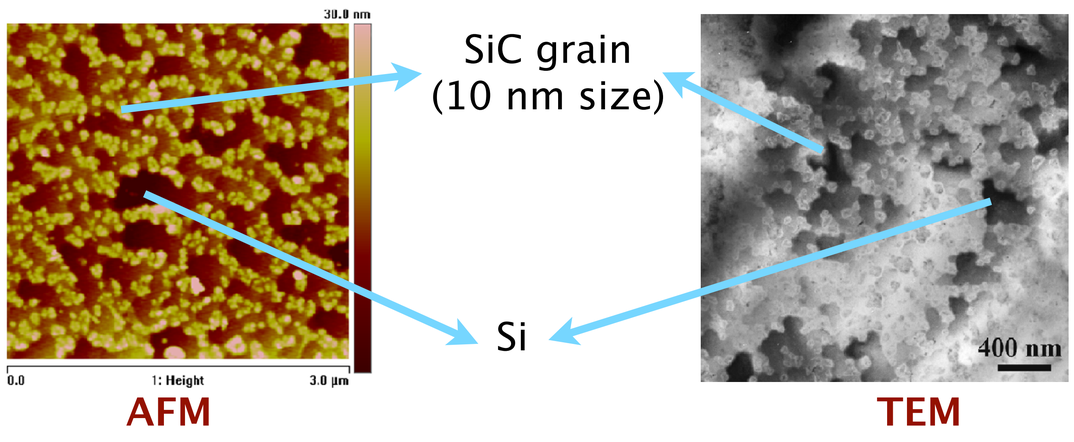
(a) (b) (c)

50 eV **LEED patterns**. (a) Si(111)7×7. C_{60}/Si(111)7×7 film, (b) 0.70 ML, 35 eV KE, showing 3C-SiC 1×1 extraspots. (c) Subtraction of image (a) to image (b): dark areas belong to the 7×7 pattern, white spots to the new 3CSiC 1×1.



Valence and core photoelectron spectra

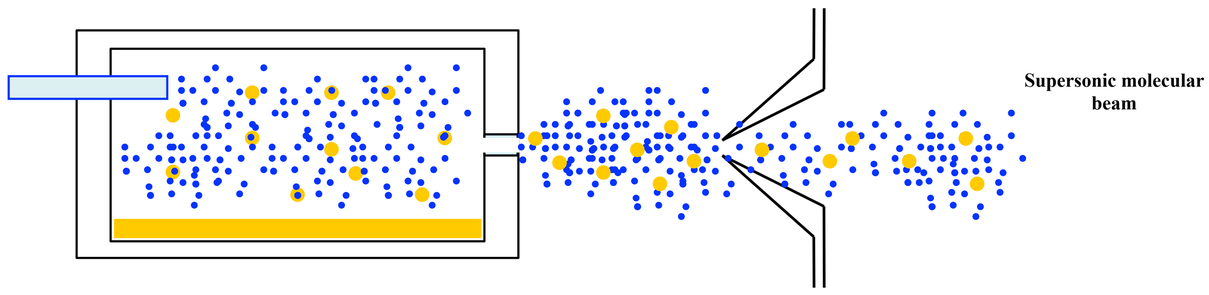
(left) Valence Bands of films grown at C_{60} KEs of 35 eV and 30 eV, and of substrate, C60 multilayer and 3C-SiC film (right) C1s core level photoemission for a film of C_{60} on Si(111)-(7x7) surface at room temperature deposited by SuMBE, at a coverage of 0.7 ML. The curve has been fitted using four components, corresponding to different carbon chemical species as shown in the legend.



AFM **TEM**

References
[Experiment] R. Verucchi et al. J. Am. Chem. Soc. **134** (2012) 17400
[Theory] S. Taioli et al. J. Chem. Phys. (in press). doi:10.1063/1.4774376

Production by SuMBE

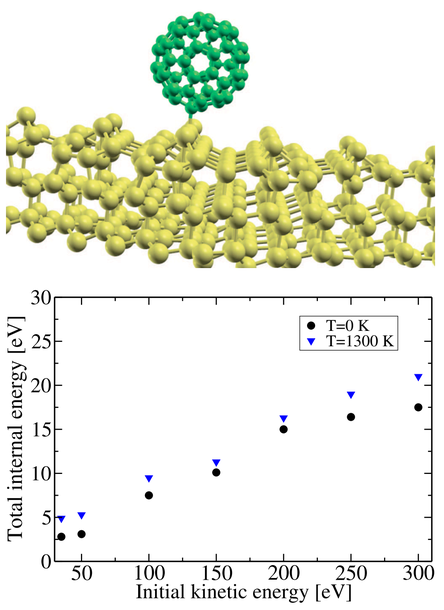


Supersonic beam produced by seeding a gas carrier (H_2, He, Ar, ...) with C_{60} out of the injection cell due to aerodynamic acceleration. Kinetic energy proportional to mass (up to tens of eV per C_{60} molecule).

High directionality and flux, low divergence.

Experiments were performed by SuMBE deposition of C_{60} at 30 and 35 eV onto the cleaned Si(111)-7x7 surface, successfully obtaining heteroepitaxial thin-film SiC growth at room temperature.

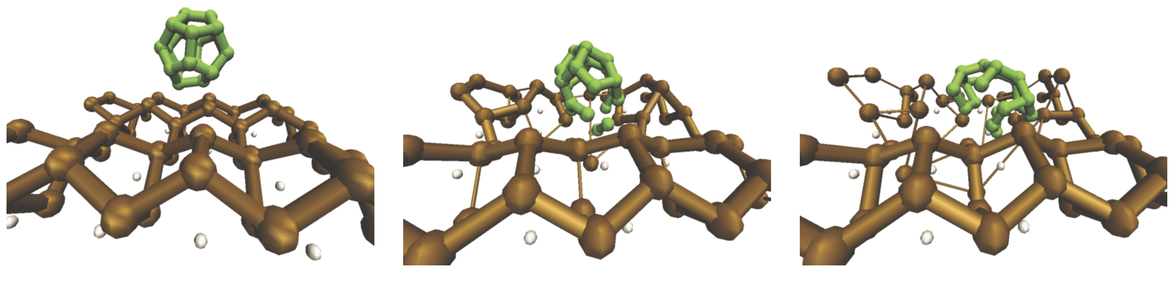
DFT-BO simulations



Born-Oppenheimer simulations at the level of Density Functional theory **cannot** reproduce C_{60} cage breaking at the experimentally observed value of ~35 eV / molecule, although we tried: 1) increase the temperature of the substrate, 2) charge the C_{60}, 3) use C_{57}, C_{58} or C_{59}, 4) smash two fullerenes on top of each other.

These models predict cage breaking with KE > 300 eV.

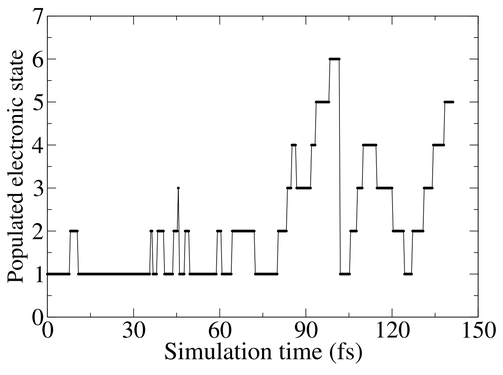
Non-adiabatic MD



Car-Parrinello MD lowers the C_{60} cage breaking energy down to ~100 eV ⇒ non-adiabatic effects can be important.

Massey parameter (~10) indicates that nuclear and electron timescales are not completely disentangled

Fully non-adiabatic simulation using TD-DFT and 6 excited states. Due to the highly intensive CPU requirements, we downscaled to C_{20}. **Cage break observed at 11 eV ✌.**



Forces used in the MD simulation are calculated on the adiabatic surfaces populated at the present time step.

Landau-Zener theory used to jump among the electronic surfaces.