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C_{60} encapsulation of the Si(111)-(7×7) surface

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The structure of a Si(111)-(7×7) surface capped by a 200 Å film of C_{60} was studied by grazing-incidence x-ray diffraction. The Si(111)-(7×7) reconstruction prepared in vacuum, including the loosely bonded "adatoms" on the surface, is preserved under the C_{60} overlayer. This result illustrates that C_{60} can be used as an inert cap for surfaces and suggests potentially interesting applications in surface science research and electronic device engineering.

The recent discovery of C_{60} has caused considerable excitement and interest in the physical properties and possible applications of this unique form of carbon.[1] Being a fairly inert van der Waals molecular solid,[2] C_{60} is a good candidate as a material for the encapsulation of delicate surface atomic structures that can be generated and otherwise kept clean only in an ultrahigh-vacuum (UHV) environment. Even in UHV, clean surfaces usually deteriorate by residual gas contamination in a matter of a few hours because of the presence of chemically active dangling bonds on the surface. This contamination problem and the need for a bulky UHV chamber can lead to severe constraints in carrying out many types of surface science experiments, such as surface x-ray diffraction. Therefore, it is highly desirable to find an inert capping material suitable for preserving the clean surface structure. The development of an inert cap (or insulating layer) is also relevant to electronic device applications. The structural and chemical integrity of the substrate under the cap is a highly desirable feature. Furthermore, the preserved periodic crystal potential at the interface can give rise to two-dimensional Bloch electronic states that might have interesting effects on the electrical performance of, for example, metal-insulator-semiconductor devices.

This experiment is a demonstration of C_{60} as an inert capping material. The surface chosen for this study is Si(111)-(7×7); its structure can be described by the dimer-adatom-stacking–fault (DAS) model.[3] In this model, the top atomic layer shows a stacking fault over one half of the (7×7) unit cell and the atoms at the boundary between the faulted and unfaulted halves of the unit cell are rebonded to form dimers. On top of this partially faulted layer are 12 "adatoms" within each unit cell. Each adatom is attached to the surface via only three back bonds (compared with four bonds for a bulk atom), and therefore, the bonding is quite weak. The Si(111)-(7×7) surface is highly reactive. Most elemental materials deposited on this surface react or alloy with the substrate, resulting in drastic structural and chemical modifications. The issue here is whether or not a layer of C_{60} deposited on this surface in vacuum can preserve the DAS structure, including the loosely bonded adatoms. All previous attempts in capping this surface have failed to preserve the adatom feature, and only in a few cases[4–6] is the stacking fault feature preserved.

In our experiment, we prepared clean Si(111)-(7×7) in UHV by heating to 1250 °C.[4] A sharp (7×7) electron diffraction pattern was observed. Commercial grade C_{60}, containing 2%–12% C_{70}, was evaporated onto the sample at room temperature by sublimation at a rate of 0.55 Å/min as determined by a thickness monitor. The total thickness was 200 Å (24 molecular layers), which was later verified by an x-ray reflectivity measurement. After the evaporation, the sample was removed from the vacuum chamber and shipped to the National Synchrotron Light Source, where we performed diffraction studies on the Oak Ridge National Laboratory beam line (X-14). An x-ray wavelength of 1.117 Å was used.

We measured intensities of the Si(111)-(7×7) fractional-order reflections within a triangle in reciprocal space spanned by (2,0) and (0,2), as shown in Fig. 1. Here, we use a hexagonal coordinate system where (1,0) corresponds to $(2/3)(2\bar{1}\bar{1})$ in the bulk. The area of each circle in Fig. 1(a) represents the relative intensity averaged for the mirror symmetry along the (1,1) direction. Shown in Fig. 1(b), for comparison, are results reported for clean Si(111)-(7×7) in UHV.[7,8] Clearly, the surface of Si(111) under the C_{60} film retains the (7×7) symmetry, as evidenced by the presence of many (7×7) reflections. Furthermore, the intensity variations from one fractional reflection to the next are similar for Figs. 1(a) and 1(b). For example, looking at the diffraction intensities from (0,0) to (2,0), one sees that the first intense peak is located at (3/7,0), followed by intense peaks at (6/7,0), (8/7,0), and (13/7,0). The locations of these intense peaks are characteristically associated with the DAS structure, and

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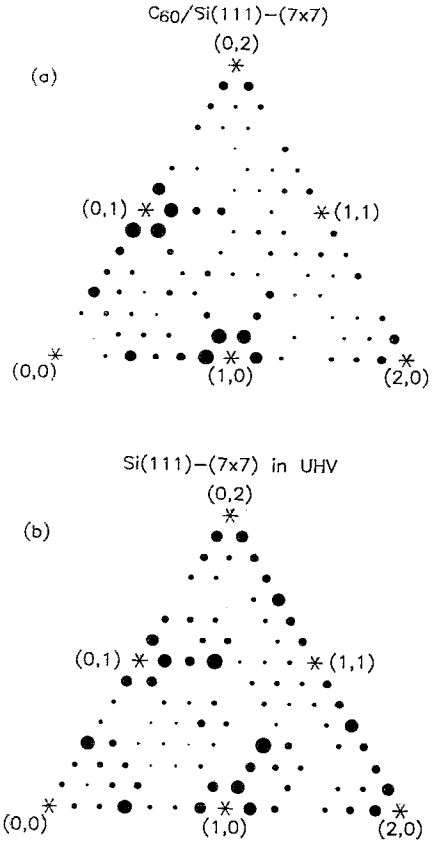

FIG. 1. Integrated intensities of (7×7) reflections for (a) Si(111)-(7×7) encapsulated by a C_{60} film and (b) clean Si(111)-(7×7) in UHV. The area of a circle is proportional to the integrated intensity.

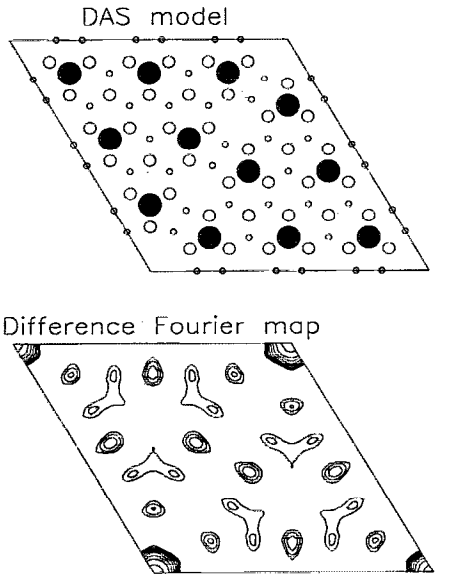

FIG. 2. The difference Fourier map of the (7×7) unit cell for C_{60}/Si(111) and a top view of the DAS structural model for clean Si(111)-(7×7). In the structural model, atoms at decreasing heights are indicated by circles of decreasing sizes. The large filled circles represent the adatoms.

therefore, this result suggests that the C_{60} overlayer does not alter the basic surface structure.[4,5] The main difference between the two intensity patterns in Fig. 1 is an overall intensity reduction for the C_{60}-covered surface for increasing momentum transfer. For instance, the linear array of peaks between (2,0) and (0,2) for C_{60}/Si(111) are noticeably weaker than the corresponding peaks for clean Si(111)-(7×7). This intensity reduction can be attributed to a static perturbation in atomic positions induced by the C_{60} overlayer (similar to the Debye–Waller effect); this point will be discussed further below.

We have carried out a Patterson analysis of the C_{60}/Si(111) structure,[9] which yields the in-plane electron-density correlation function. Our results (not shown) are nearly indentical to those reported for the clean Si(111)-(7×7) surface.[3] This confirms that the C_{60} film does not appreciably affect the underlying DAS structure of Si. An even more stringent analysis is carried out using the "difference Fourier map" method, which highlights excess electron densities on the surface that can be associated with the adatoms.[10] As mentioned earlier, the adatoms are the outermost atoms on the surface and are only loosely attached. The weakness of the interaction between the Si surface and the C_{60} overlayer can be attested by the existence of the adatoms at the correct locations under the C_{60} film. The difference Fourier map for C_{60}/Si(111) is shown in Fig. 2 as a contour plot over a (7×7) unit cell. Also shown in the figure, for comparison, is the DAS structural model in which the adatoms are indicated by large filled circles.[3] Clearly, for each adatom in the structural model, there is a corresponding positive peak in the difference map. This is direct evidence for the adatoms under the C_{60} film.[10]

Comparing the present system to the few other systems (Ag and amorphous Si and Ge on Si) for which the (7×7) reconstruction is partially preserved under the overlayer, we find that the diffraction patterns from those other systems have a very different intensity distribution; the most notable difference is the absence of an intense (3/7,0) peak. The remnant of the (7×7) diffraction pattern in those other systems has been attributed to the persistence of the surface stacking fault.[4–6] To remove the stacking fault, a large number of atoms will have to be rearranged, and thus, the kinetic barrier is relatively high.

Our C_{60} film has the face-centered-cubic structure,[11] and is oriented with its [111] direction along the surface normal. The in-plane orientation of the film was determined by scanning the ϕ angle of the four-circle diffractometer at the C_{60} (220) reflection angle using a specular reflection geometry. The result is shown in Fig. 3. Here $\phi=0$ corresponds to the (0,1) direction of Si(111). The C_{60} (220) reflection peaks at $\pm 19.1°$ and $\pm 40.9°$. Note that $40.9° + 19.1° = 60°$, which is compatible with the (111) geometry. The angle 19.1° equals the angle between (1,0) and (2,1). With this orientation, the C_{60} lattice and the Si(111)-(7×7) surface is matched to better than 1%. The full width at half maximum of the peaks in Fig. 3 is 6.5°, implying a mosaic spread of this order. This mosaic spread is likely due to the imperfect lattice match, distortions induced by the small mixture of C_{70} in the film, and other

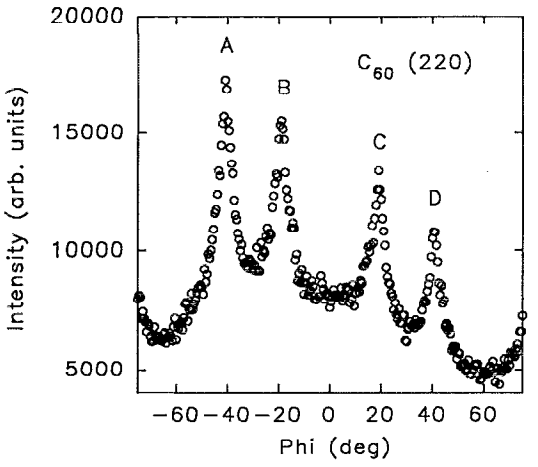

FIG. 3. Rocking curve (ϕ-scan) for the C_{60} (220) reflection. $\phi=0$ is chosen to be along the (0,1) direction of Si(111). Four peaks labeled A–D are observed at −40.9°, −19.1°, +19.1°, and +40.9°, respectively.

defect structures. Because of the mosaic spread, the registry between the C_{60} film and the substrate is imperfect. This can impose a random static perturbation on the positions of the Si surface atoms, leading to a Debye–Waller-like intensity reduction, as mentioned above.

The main reason for the successful preservation of the surface structure in this experiment is the weakness of the interaction between the C_{60} film and the Si substrate. Another requirement for preserving a surface is the absence of gas diffusion through the film to attack the substrate surface. If we model solid C_{60} as a collection of close packed spheres, the minimum diameter for an open channel threading through the film is 1.55 Å, which is apparently too small for the passage of air molecules. This finding has some impact on the idea of using C_{60} as a molecular sieve material. In a separate study, we have found that the (2×1) reconstruction of the Si(100) surface can also be preserved under C_{60}.[6] Whether or not C_{60} can be used for the preservation of other surfaces remains an interesting subject for further research. Also, methods and procedures for removing the C_{60} film without causing damage to the substrate surface need to be developed. For C_{60} on Si(111)-(7×7), we have not been able to regenerate the clean Si surface in vacuum by heating the sample to high temperatures, presumably due to the thermal decomposition of C_{60} resulting in the formation of SiC.

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