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Epitaxial growth of single-crystal C_{60} on mica by helium-atom scattering

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We report on a helium-atom-scattering study of the growth, structure, and surface dynamics of a very thin film of C_{60} sublimed in ultrahigh vacuum onto a freshly cleaved mica substrate. The resulting diffraction pattern showed that the C_{60} forms a hexagonal crystal layer that is in registry with the mica substrate and at a spacing of 10.4 Å. The dispersion results showed two Einstein modes.

The recent investigations of the fullerene forms of carbon have sparked an intense interest directed toward both an understanding of the basic characteristics of the materials as well as the view that they could lead to new directions in technology.[1,2] Considerable progress has been prompted by the recent ability to easily produce sufficient quantities for research purposes.[2] This has led to much recent experimental work,[2-7] with some directed toward the preparation and characterization of the crystalline forms of C_{60} and C_{70}, the topic of this paper. We report the use of He-atom scattering[8] (HAS) to study the growth, structure, and dynamics of very thin films of C_{60} produced in ultrahigh vacuum by sublimation from a Knudsen cell onto a freshly cleaved mica substrate held at 300 K.

Helium-atom scattering as a surface probe is nonpenetrating, inert, and extremely sensitive to surface structure and dynamics.[8] Growth of a deposited layer of C_{60} on a freshly cleaved mica substrate was monitored by measuring the decrease in the scattered specular He-atom intensity during deposition.[9] The Knudsen cell used to produce the deposited layers contained a combination of 85% C_{60} and 15% C_{70}. However, as Pan *et al.*[10] have shown, the sublimation rates are different for the two forms and at 667 K, the C_{60} is favored by a factor of approximately 20 over the C_{70}. We used this to estimate the purity of the C_{60} on the surface to be nearly 99% when we sublimed at an oven temperature of 700 K. The substrate was fixed at 300 K and the vacuum was $< 10^{-10}$ mbar. With the Knudsen cell at 700 K, several independent thickness monitor checks were made to determine that a 0.5 monolayer (ML) C_{60} film was deposited in 21 min on

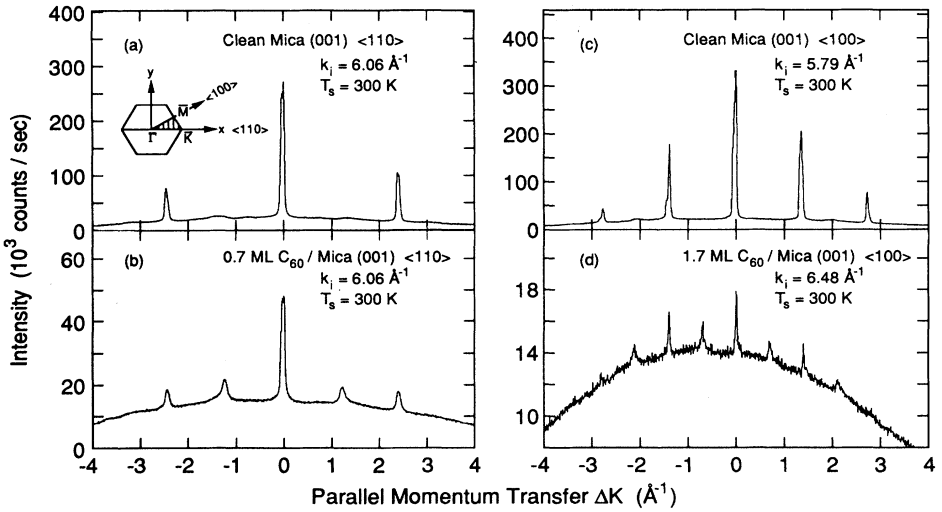

FIG. 1. He-atom intensity as a function of parallel momentum transfer (Ref. 8) for the clean mica (001) surface at 300 K (a) in the ⟨110⟩ direction, (c) in the ⟨100⟩ direction, (b) after deposition of a 0.7 monolayer of C_{60}, and (d) after deposition 1.7 monolayers of C_{60}, with both depositions at mica substrate temperatures of 300 K. The extra diffraction peaks are caused by the hexagonal crystal structure of the deposited C_{60}. The k_i values are for the incident wave vectors of the He atomic beam.

the mica substrate located 33 cm from the Knudsen effusive source with an aperture of 1.6 mm^2. This corresponds to a pressure in the Knudsen cell of 2.5×10^{-4} torr at $T=700$ K.[11] At several intervals the deposition was interrupted and diffraction patterns were obtained. Figure 1(b) shows the ⟨110⟩ diffraction result taken immediately after the deposition of 0.7 ML, while the ⟨100⟩ direction diffraction result, Fig. 1(d), was taken after annealing a 1.7 ML at 330 K for 1 h. A comparison between the diffraction patterns with C_{60} as in Figs. 1(b) and 1(d) and those from the freshly cleaved mica substrate peaks shown in Figs. 1(a) and 1(c) indicate additional peaks occurring in the C_{60} results. The spacing is used to find the nearest-neighbor distance between two C_{60} molecules (10.4 Å) which is twice that of the mica (5.2 Å).[12] The observations are that the C_{60} layer is hexagonal, aligned with the mica and at double the mica spacing; this indicates the mica acts as a template at these low coverages.[12] Figure 2 shows in real space an assumed 1-ML coverage of C_{60} molecules on the mica substrate.

Only a slight improvement of the diffraction signal occurred with the annealing process. However, a longer anneal at 450 K for 30 h effectively removed the C_{60} from the surface with only the diffraction pattern of the mica remaining.

During the initial stages of growth, we measured the surface scattering cross section (defined as Σ) for small amounts of C_{60} on the surface and found it was very large ($\Sigma\approx900$ Å^2).[13] This value is considerably larger than previously reported cross sections; however, the C_{60} molecule is also a much larger molecule than any previously studied; this clearly represents an area for further study.

We measured the surface dynamics of the 1.7-ML film in the ⟨100⟩ direction using a chopped He beam with time-of-flight analysis and determined the vibrational properties of the surface.[8] An example of a spectrum is shown in Fig. 3. An analysis of a series of spectra gave the dispersion curves for the ⟨100⟩ direction of C_{60} on mica, Fig. 4, and the results show two Einstein-type dispersionless modes.[14–16] The lowest-energy mode corresponds most likely to a vibration perpendicular to the surface of individual C_{60} molecules, while the higher-energy mode can be explained as an overtone mode. Similar behavior for the rare gases adsorbed on Ag(111) and for Xe/Pt(111) have been observed before for similar thin adsorbate layers.[15,16] No modes with the expected dispersion characteristics of Rayleigh waves were observed in these measurements and this behavior is similar to the other adsorbate studies for very thin films.[15,16] With suitable HAS and surface conditions, it is expected that the surface dynamics of the C_{60}-molecular vibrational and rotational behavior can be determined as a function of thickness and substrate temperature. Additional studies are currently underway to further explore this possibility.

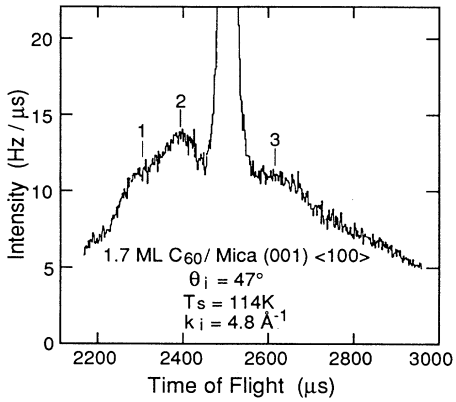

FIG. 3. A time-of-flight spectrum for He scattering from a 1.7 ML of C_{60} on a mica (001) substrate. The large peak, only partially shown, is a diffuse elastic peak caused by defects on the surface, while the two peaks at shorter times are from single phonon annihilation events and the small peak at a longer time corresponds to a single phonon creation event. The incident scattering angle and wave vector are also given.

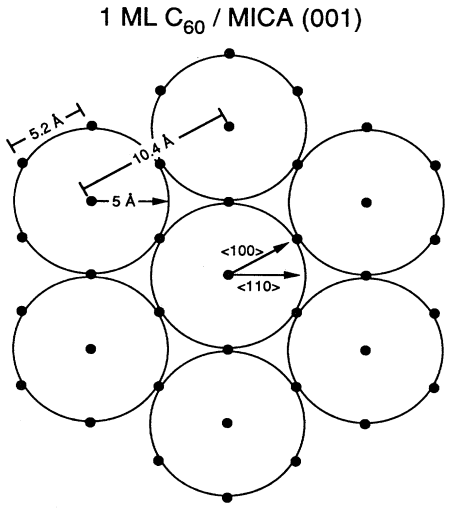

FIG. 2. A schematic view of the hexagonal lattice of mica as shown by the solid circles spaced at 5.2 Å and a 1-ML film of C_{60} with twice the mica spacing, the latter shown as circles.

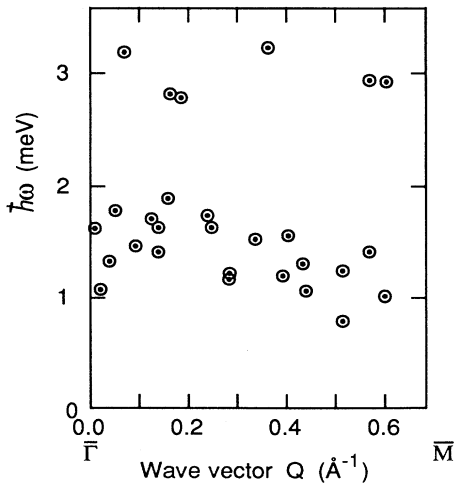

FIG. 4. Surface dispersion curves for the phonon energy vs wave vector for a 1.7 ML of C_{60} on mica (001) for the ⟨100⟩ direction. Two dispersionless Einstein-type modes are seen.

In another set of experiments, we measured the intensity of the specularly scattered beam as a function of incident wave vector and from this we determined the step height between layers for a nominal 0.7-ML film to be 9.4 ± 0.5 Å.[17] The step height derived from the bulk structure (fcc with a nearest-neighbor distance of 10.02 Å) is 8.5 Å, somewhat smaller than our result. We attribute our larger value at this 0.7-ML coverage as being caused by the mica-C_{60} steps of $\sim$10-Å height.

These experiments demonstrate that it is possible to produce epitaxial films of C_{60} of defined monolayer thickness on a crystalline insulating substrate and to measure the structural and low-energy dynamical properties. This opens up the possibility of comparisons to calculations on theoretical dynamical models.

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