Epitaxial growth and electronic structure of a C_{60} derivative prepared by using a solution spray technique

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We demonstrate and analyze the epitaxial film formation of a molecular material that cannot be evaporated in vacuum due to thermal decomposition. A solution of the material is sprayed onto single crystalline van der Waals surfaces using a pulse valve under controlled vapor pressure of the solvent. Monolayer epitaxial films are obtained and we propose that the growth is mediated by liquid ultrathin films formed on the surface. Molecular arrangement and electronic structure of $C_{60}(CH_3)_5H$ films are studied by reflection high energy electron diffraction and ultraviolet photoelectron spectroscopy, respectively. The present technique will be useful to study the electronic structure of recently synthesized molecular materials. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1379052]

I. INTRODUCTION

With the recent advance of synthetic chemistry, it is now possible to finely tune the electronic structure of molecular species to obtain materials with various electronic or optical functions which cannot be achieved using conventional semiconductor devices. This trend is now opening another stage in the field of molecular electronics or photonics and the measurement of the electronic structure of recently synthesized molecular materials has become crucially important. The best way to achieve this is to measure single crystalline samples by means of electron spectroscopy techniques such as photoelectron spectroscopy, inverse photoemission, and electron energy loss spectroscopy. Conventionally, the preparation of thin epitaxial films by vacuum deposition is necessary since those electron spectroscopy techniques require a clean surface with a large area because of the surface sensitivity and low yield of the signals. The film grown on conductive substrates must be as thin as possible while guaranteeing uniform coverage to avoid the charging up phenomenon during electron spectroscopy. The problem is that most of the molecular materials are not compatible with vacuum sublimation because they undergo thermal decomposition. Here we present controlled epitaxial growth of one such thermally weak molecule—$C_{60}(CH_3)_5H$ (Fig. 1)[1]—on surfaces without dangling bonds. We have ''sprayed'' a solution of the molecule using a pulse valve under controlled pressure of the solvent in a clean environment directly connected with ultrahigh-vacuum analysis chambers.

II. EXPERIMENT

The apparatus used in the present experiment is shown in Fig. 1. The turbomolecular-pumped vacuum system was equipped with a pulse valve (General Valve Corp. Series 9). The open time of the valve was changed from 5 to 200 ms. The solution was flushed from the outlet of the valve that had an aperture with a diameter of 0.5 mm. $C_{60}(CH_3)_5H$ was synthesized as described in Ref. 1. The saturated solution of $C_{60}(CH_3)_5H$ in toluene ($\sim 2 \times 10^{-3}$ mol/l) was filled in a glass tube with Ar gas and connected upside down to the pulse valve. As substrates, a piece of MoS_2 mineral was cleaved in air to bare its (0001) surface, while hydrogen-terminated Si(111) (H–Si(111)) was prepared by a standard procedure using buffered HF.[2] After the introduction of the substrate, the vacuum chamber was pumped to achieve a vacuum better than 1×10^{-5} Pa. The sample was transferred to face the pulse valve at a distance of 60 mm, and the valve was operated in the one shot mode or the multiple pulse mode. The turbomolecular pump (TMP; venting speed 55 l/s) was left on during the pulse valve operation when the atmosphere was not controlled intentionally. The pressure in the vessel was monitored with a Pirani gauge. We also examined the effect of introducing toluene vapor into the environment using a mass flow controller with or without venting by TMP. After spraying, the chamber was pumped by TMP for several hours and the sample was transferred to each chamber for structural and spectroscopic analyses without breaking the vacuum.

Reflection high energy electron diffraction (RHEED) images became dim in a few seconds when they were detected using a conventional phosphor screen. In order to avoid the electron bombardment effect, RHEED images were detected with dual microchannel plates that multiplied the beam intensity approximately by 10^6. Using an incident sample current of the order of 10 pA, it was possible to observe and record the detailed RHEED images of the films. The sample was also transferred to the analysis chamber for ultraviolet photoelectron spectroscopy (UPS). An angle resolved spec-

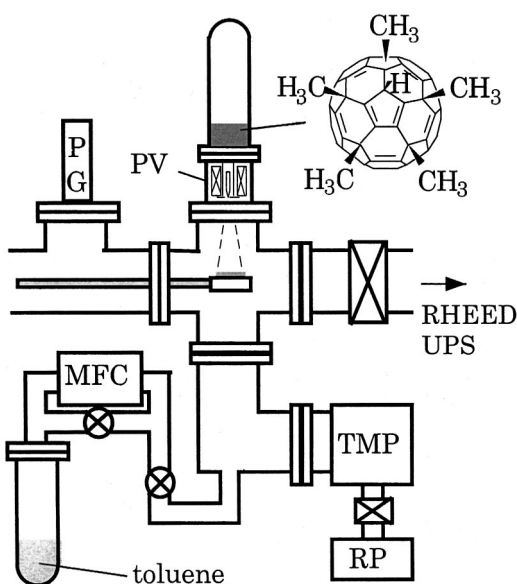[a)]Electronic mail: shimada@chem.s.u-tokyo.ac.jp

FIG. 1. $C_{60}(CH_3)_5H$ and experimental configuration. Abbreviations in the figures are: PG—Pirani gauge, PV—pulse valve, MFC—mass flow controller, TMP—turbomolecular pump, and RP—rotary pump.

FIG. 3. RHEED images of $C_{60}(CH_3)_5H$ films grown on (a)(b) MoS_2 (0001) and (c)(d) H–Si(111). The acceleration voltage was 20 kV. The incident azimuth of electrons is (a) $\langle 11\bar{2}0 \rangle$, (b) $\langle 10\bar{1}0 \rangle$, (c) $\langle \bar{2}3\bar{1} \rangle$, and (d) $\langle 41\bar{5} \rangle$. S and F indicate streaks from the films and the substrates, respectively.

trometer (Vacuum Generators ADES-500) was used with a He discharge lamp (He-II, $h\nu = 40.8$ eV). Noncontact-mode atomic force microscopy (AFM; SEIKO SPI-3800) was used in air to determine the best conditions for uniform coverage.

III. RESULTS AND DISCUSSIONS

Figure 2 shows AFM images of $C_{60}(CH_3)_5H$ films formed under various growth conditions on MoS_2 (0001) surfaces. After one 5 ms pulse was shot in high vacuum, elongated islands were formed, as shown in Fig. 2(a). The islands had a height of about 1 nm, which corresponded to the calculated size of one molecule. The long edges of the islands had three directions, suggesting the epitaxial relation-
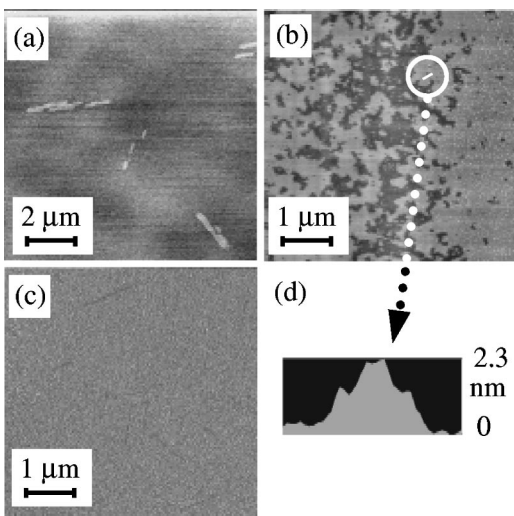

FIG. 2. AFM images of $C_{60}(CH_3)_5H$ films prepared under various conditions: (a) single shot of 5 ms pulse with pump operation, (b) 20 shots of 5 ms pulse at 100 ms intervals with pump operation, and (c) single shot of 200 ms pulse under saturated solvent (toluene) vapor. (d) shows the cross section along the line enclosed by a white circle in (b).
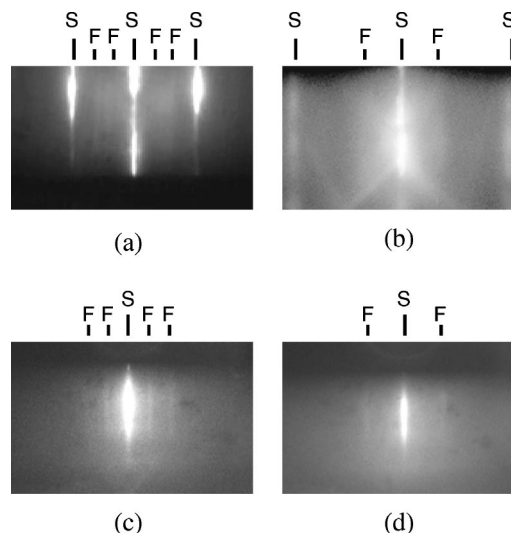
ship between $C_{60}(CH_3)_5H$ and MoS_2 substrate. When sequential pulses of (5 ms on + 100 ms off) $\times 20$ were shot under turbomolecular pump operation, an almost monolayer coverage was achieved, as shown in Fig. 2(b). During the sequential shots, the maximum pressure reached 0.3 Pa as measured by the Pirani gauge calibrated for N_2. Figure 2(d) shows the cross section along the line enclosed by a white circle in Fig. 2(b). As seen in the cross section, the height of most of the film was about 1 nm and a second layer of small triangular shape was also formed. Figure 2(c) shows the morphology of the film formed by a single shot of 200 ms pulse in saturated toluene atmosphere (3×10^3 Pa at room temperature).[3] A dense multiple-layered film was observed and several cracks aligned along sixfold axes are also observed. The size of the area of the surface covered by $C_{60}(CH_3)_5H$ was dependent on the spraying conditions. It was about 15 mm diameter and rounded for multiple shots with 5 ms duration under vacuum, whereas it was reduced to about 8 mm diameter when 200 ms shots were supplied in saturated toluene vapor. Other spraying conditions resulted in an intermediate size of the covered area.

Figure 3 shows RHEED images of $C_{60}(CH_3)_5H$ films formed on MoS_2 (0001) and H–Si(111). The acceleration voltage of incident electrons was 20 kV. Streak patterns from the films were observed on both substrates. Two incident beam azimuths showing symmetrical streak patterns with the first and the second narrowest spacing were chosen in Fig. 3 for each substrate. The positions of the streaks from the substrates and from the films were marked by "S" and "F" outside the images, respectively. Diffraction from the substrates was observed because of the large penetration length of high energy electrons or the partial coverage of the films. Since the spacing of the neighboring streaks changed by a ratio of $\sqrt{3}$ when the incident azimuth was rotated by 30°, single crystalline growth of a hexagonal lattice was concluded on both substrates. From the azimuthal direction

shown in Figs. 3(a) and 3(b), the hexagonal lattice was found to be aligned with the primary axes of the substrate in the case of $C_{60}(CH_3)_5H/MoS_2$. The lattice constant of the film grown on MoS_2 was estimated to be 0.9 ± 0.2 nm from the spacing of the streaks. RHEED patterns of the $C_{60}(CH_3)_5H$ film formed on H–Si(111) [Figs. 3(c) and 3(d)] indicated a hexagonal unit cell corresponding approximately to ($\sqrt{7}$ $\times \sqrt{7}$) R19.1° of the substrate lattice. The lattice constant on H–Si(111) was determined more precisely as 0.97 ± 0.05 nm. This value is close to the lattice constant of C_{60} epitaxial films (1.00 ± 0.02 nm) grown on van der Waals surfaces,[4,5] from which the molecular orientation in the film can be derived. The plane determined by the five methyl groups of a $C_{60}(CH_3)_5H$ molecule should be parallel to the surface since the intermolecular distance would be larger if the methyl groups oriented themselves to face the adjacent molecules. The best streak patterns from $C_{60}(CH_3)_5H$ were obtained by opening the pulse valve once for 200 ms under saturated vapor pressure of toluene, and the lattice constant of the film was not dependent on the film's thickness.

From the AFM images of submonolayer films, the mechanism of the epitaxial growth is speculated as follows. Since the domain shapes of partly covered regions are far different between films grown by a single shot [Fig. 2(a)] and those by multiple shots [Fig. 2(b)], $C_{60}(CH_3)_5H$ molecules must be highly mobile on the surface before crystallization. It is thus suggested that an ultrathin film of the solution of $C_{60}(CH_3)_5H$ is formed, which wets a certain macroscopic area of the substrate. Then, the molecules probably aligned along the substrate lattice when the solution was gradually evaporated by pumping. This mechanism is similar to the "crystallization" of mesoscopic particles partially soaked in a wetting liquid on solid surfaces.[6]

UPS spectra of the films were taken to demonstrate the usefulness of the present technique in characterizing the electronic structure of the molecules. A multilayer film was prepared on MoS_2 (0001) by spraying $C_{60}(CH_3)_5H$ solution twice with 200 ms open time under saturated toluene vapor in order to ensure the complete coverage of the sample surface. The sample was heated at 60 °C for 24 h under ultrahigh vacuum to remove possible inclusion of toluene in the film. For comparison, a multilayer film of C_{60} was prepared in the same way as described above by spraying a saturated solution in toluene, and it was also characterized by RHEED and UPS. Figure 4(a) shows the UPS spectrum of $C_{60}(CH_3)_5H$ grown on MoS_2. He-II UV light ($h\nu = 40.8$ eV) was irradiated onto the sample surface at 25° from the surface normal and electrons that were emitted along the surface normal were detected. The spectrum is compared with those of the C_{60} film and *ab initio* calculation. The RHEED patterns of the "spray-grown" C_{60} film were identical with that of the film grown by molecular beam epitaxy.[4] UPS peak shapes of the C_{60} film [Fig. 4(c)] agreed well with those reported for vacuum deposited films[7] after a shift of the Fermi level. It should be noted that the UPS of $C_{60}(CH_3)_5H$ is different from that of C_{60}, especially in terms of the significant broadening of the peaks.

Figure 4(b) shows the calculated density of states for a $C_{60}(CH_3)_5H$ molecule. The structure of the molecule was op-
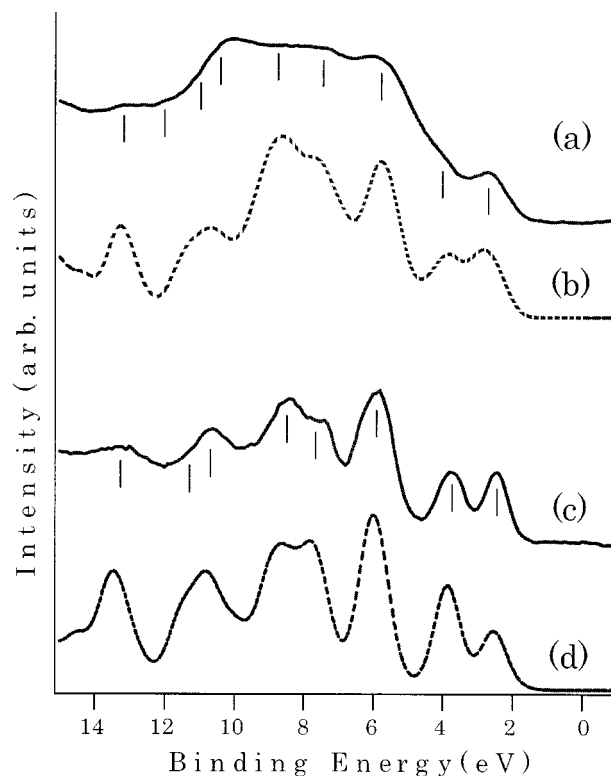

FIG. 4. Valence structure of $C_{60}(CH_3)_5H$ and C_{60}. (a) UPS ($h\nu = 40.8$ eV) of a multilayer film of $C_{60}(CH_3)_5H$, (b) density of states of a $C_{60}(CH_3)_5H$ molecule obtained by *ab initio* calculation, (c) UPS ($h\nu = 40.8$ eV) of a multilayer film of C_{60}, and (d) density of states of a C_{60} molecule obtained by *ab initio* calculation. Bars in (a) and (c) indicate peak positions, which were derived by taking the second derivative of the spectra.

timized by Hartree–Fock calculation using 3-21G basis functions.[8,9] The electronic structure was then calculated by the density functional method B3LYP using 6-31G(d) basis functions.[8,9] The resulting energy levels were obtained relative to the vacuum level of the molecule. Gaussian peaks with full width at half maximum of 0.7 eV centered at calculated energy eigenvalues were summed up to obtain the density of states (DOS). It is widely accepted the molecular orbital levels can be shifted compared to the Fermi level due to the final state charging effect,[10] interface dipole formation,[11] or unintentional doping. The simulated DOS was therefore shifted by 3.2 eV to the lower binding energy (E_B) side to obtain the best fit to the experiment [Fig. 4(a)], thereby resulting in Fig. 4(b). DOS of CH_3 groups distribute mainly in the regions of E_B around 4.8–6.6 and 7.4–9.3 eV.

For comparison, a similar calculation for C_{60} is shown in Fig. 4(d) after a shift by 3.5 eV to fit with Fig. 4(c). It agrees well with more precise calculations previously reported.[12,13] It is noted that the three peaks at $E_B = 2$–6 eV in Fig. 4(b) are broader and less discrete than those in Fig. 4(d). It comes from the broken degeneracy of the molecular levels caused by the lowered symmetry in $C_{60}(CH_3)_5H$. This feature is qualitatively reflected in the UPS peaks of $C_{60}(CH_3)_5H$ being broader than those of C_{60}, although coupling of the vibration of CH_3 groups with the photoemission process may also enhance the broadening. As for the CH_3 groups, the regions of large DOS of CH_3 groups in $C_{60}(CH_3)_5H$ actually show

stronger photoemission than those in the case of C_{60}. These observations, along with the fact that almost all peak positions in Fig. 4(a) are reproduced in Fig. 4(b), indicate the effectiveness of the present technique to study the electronic structure of newly synthesized molecules.

IV. CONCLUSION

We have demonstrated a technique to obtain epitaxial films of a molecular material that cannot be evaporated thermally due to chemical weakness. It involves spraying the solution of the material with a pulse valve under pure environment directly connected to ultrahigh vacuum chambers equipped with surface measurement capabilities. AFM revealed that monolayer films can be formed by choosing the spraying conditions and RHEED indicated that epitaxial films can be obtained by using single crystalline substrates without dangling bonds on the surfaces. The lattice constant and the electronic structure of a recently synthesized C_{60} derivative were determined by RHEED and UPS measurements, respectively.

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