Molecular Layer-by-Layer Growth of C_{60} Thin Films by Continuous-Wave Infrared Laser Deposition

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Abstract

The observation of reflection high energy electron diffraction (RHEED) oscillations has been proved to be a key to open the nano-world of materials, since it definitely verifies that the film growth proceeds in layer-by-layer mode with each layer thickness controllable by simply counting the number of oscillations. This enabled the fabrication of nano-engineered hetero-junctions and devices as commonly practiced for conventional semiconductors and metals. Here we report on the first observation of clear RHEED intensity oscillation in thin film fabrication of a π-conjugated molecular solid. The observation has been achieved by coupling a novel deposition method using a continuous-wave infrared laser for evaporation and a high sensitive RHEED detector, in addition to the combinatorial optimization of film deposition parameters that facilitated our preceding first success in the layer-by-layer growth of oxide thin films. Some details of system design and experimental conditions are presented to discuss the key factors for atomically controlled film growth of molecular solids.

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Due to their mechanical flexibility, light weight, and possible large area coverage, carboneous materials such as diamond and π-conjugated compounds[1–4] have attracted much attention as possible new semiconductors to bridge the gap between soft matter and solid state electronics. In advanced semiconductor electronics, atomically defined hetero-interfaces have been made as artificial superstructures to induce new electronic functionalities by modification of local electronic structure with charge transfer and/or quantum size effects.[5] From the both viewpoints of fundamental research and application to future devices, nano-scale control of carboneous electronic material thin film growth is a critical technology that needs to be established.

Among the fabrication methods that are useful for nanoscale films, we have a choice of either gas-phase methods such as molecular beam epitaxy (MBE), or liquid phase methods such as the Langmuir–Blodgett (LB) technique. Gas-phase methods using high vacuum conditions have advantages of lower contamination levels and compatibility with in-situ monitoring methods, such as reflection high energy electron diffraction (RHEED), photoemission electron microscopy (PEEM), and low energy electron microscopy (LEEM). In particular, the monitoring of specular RHEED can be used to determine the morphology of the film surface from the diffraction pattern.[6] The applicability of the RHEED technique has been well recognized for realtime atomic-level control of thin film growth of conventional semiconductors; RHEED intensity oscillations are an important indicator of layer-by-layer growth. MBE and sputtering were used effectively for atomically controlled epitaxy of metals to verify the giant magnetic resistance in the layered structures.[7] The sharp intensity oscillations for oxide films were realized by the laser MBE film growth on an atomically flat substrate.[8] This technology provided a breakthrough in oxide film growth process and

triggered remarkable progress in oxide electronics.[9–11)]

In contrast to extensive research on film growth of π-conjugated molecules, RHEED observation has been limited to post-deposition analysis of deposited films.[12)] The growth of pentacene and C_{60} films using a conventional MBE chamber (~1×10^{-9} Torr) and a RHEED system (20 keV) neither accompanied any sharp patterns nor RHEED intensity oscillations. However, atomic force microscope (AFM) analysis of thickness gradient [0 – 2 monolayer (ML)] pentacene films, which was fabricated on an atomically flat substrate with a shadow mask action, indicated layer growth up to one ML and subsequent island growth.13) Furthermore, the growth of C_{60} film on 1ML pentacene film gave films with improved surface morphology which in turn used to fabricate field effect transistor (FET) with a highest electron mobility among molecular solid FETs.[4)] In view of these previous results, we have investigated factors necessary for successful layer-by-layer deposition that can be verified with in situ RHEED intensity oscillation on C_{60} film growth.

The three key factors identified from the present study are the following:

(1) Evaporation of source compounds with continuouswave (CW) infrared (IR) laser, instead of conventional thermal evaporation in an MBE chamber.[14)]

(2) The use of atomically flat and lattice-matched substrates.

(3) The use of a highly sensitive micro channel plate (MCP)-RHEED system to reduce electron beamintensity.[15)]

Figure 1 illustrates schematically the CW laser molecular beam epitaxy (CWL-MBE) system that we constructed especially for deposition of π-conjugated compounds by taking into account the above listed factors. Instead of Knudsen-cells, a CW semiconductor laser (980 nm, 6.1– 9.2W/cm^2) was used to focus the laser beam on a mixture of C_{60} and Si

powders contained in a crucible. The base pressure was 1×10^{-9} Torr and the substrate temperature was varied between 50 and 300 °C. Substrates used were mica (001), MoS_2(001), HOPG (001), NaCl(001), KBr(001), KCl(001), LiF(001), CaF_2(001), and CaF_2(111). Their rms roughnesses determined by AFM ranged from 0.07 nm for MoS_2 and 0.19 nm for mica to 0.78 nm for HOPG. The roughest substrate was LiF with the roughness of 2.45 nm.

We found that C_{60} film deposition using a conventional MBE chamber was unstable and the growth rate was hard to control. In contrast, the newly designed CWL-MBE system in Fig. 1 offered excellent deposition controllability. The steady film deposition is synchronized with the laser on/off to enable precise and easy control of the deposition rate by the laser power.

A MCP-RHEED system, which was originally designed to observe insulating surfaces, was installed in the chamber to give the same electron energy (20 keV) but with a much lower electron current as compared to conventional RHEED.[15] The primary electron current can be reduced by four orders of magnitude down to 10 pA, while still allowing the acquisition of RHEED diffraction images of the same intensity as in conventional RHEED. In this manner, the radiation damage and the charge up problem on the growing film surface was eliminated. The C_{60} films thus obtained were characterized by X-ray diffraction (XRD), AFM, and RHEED.

Figure 2(a) shows a θ–2θ XRD pattern of a C_{60} thin film deposited on a mica substrate at 100 °C. Apart from the substrate peaks, the only other peaks observed arise from the (0002) planes of C_{60}, indicating that a phase-pure C_{60} film with the c-axis normal to the surface was obtained. The c-axis lattice constant of the hexagonal C_{60} film was 1.620 nm while the mica *c*-axis length is 2.004 nm.[16] This XRD result indicates that one monolayer of C_{60} has a c-axis length of 0.81 nm. Figure 2(b) shows the six-fold in-plane symmetry of a C_{60} thin film on a

mica substrate.

The rms roughness was determined by AFM to range from 0.97 to 0.55 nm and 1.09 nm for the films deposited at 100 °C on MoS_2, mica, and HOPG, respectively. The LiF substrate gave the the roughest surface of 9.74 nm. On mica substrate, the optimal growth temperature for obtaining a flat surface (rms roughness of 0.55 nm) occurred at about 100 °C.

Figure 3 shows typical RHEED specular beam intensities observed during C_{60} film growth on mica and MoS_2. Films with single RHEED phases were obtained on both mica and MoS_2 substrates, but the RHEED intensity oscillation was observed only for the film grown on a mica substrate at 100 °C. The oscillation period was calculated to be 0.8 nm, which matched well with the value of 0.81 nm, *c*-axis length of oriented C_{60} film evaluated by XRD. The incident direction of electron beam was parallel to the $[10\bar{1}0]$ azimuth of the C_{60} film for specular intensity measurements. When MoS_2 and HOPG (not shown) substrates used, the oscillation was not observed presumably due to larger lattice mismatches.

Analysis of RHEED patterns taken while the substrate was rotating showed that the C_{60} film grew epitaxially on mica and had a hexagonal crystal structure. To our knowledge, this is the first observation of RHEED intensity oscillations during π-conjugated materials film deposition. The clear RHEED oscillation corresponding to molecular layer-by-layer growth of C_{60} is gradually dumped due partially to a slight lattice mismatch (3.1%: this is calculated by using double the substrate lattice parameter) as in the case of oxide early stage of oxide film epitaxy by laser MBE.

Although further refinement is needed, the combination of the CWL-MBE deposition technique and the MCP-RHEED monitoring system has demonstrated the possibility of molecular layer epitaxy of molecular solid films, thus stepping in a way for nanoscale film

growth and surface morphology control. We hope that the combination of this film fabrication method and in-situ monitoring system open the way for new quantum molecular solids and soft matters.

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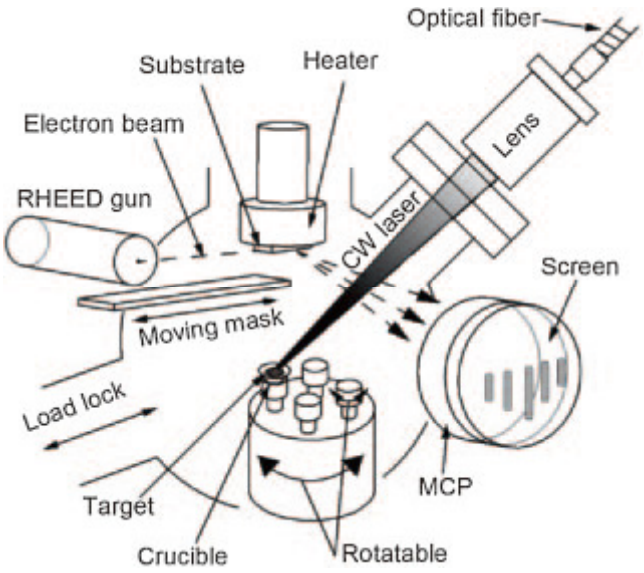
Figure captions

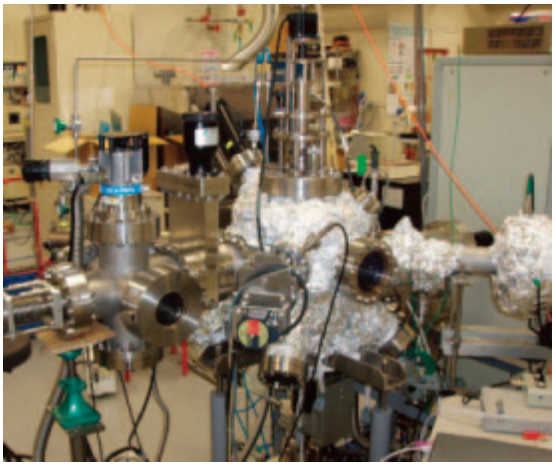
Fig. 1. (a) Schematic illustration of the CWL-MBE system and the layout of the reflection high energy electron diffraction (RHEED) intensity monitoring system with a micro channel plate (MCP) intensifier. (b) The photograph of the chamber.

Fig. 2. XRD of a layer-by-layer deposited C_{60} film. (a) A θ–2θ scan shows only the (000l) peaks of C_{60} in addition to the substrate peaks, corresponding to a phase-pure c-axis-oriented C_{60} thin film. (b) A ϕ scan of the $\left[1\,1\bar{2}0\right]$ C_{60} reflection. The six-fold symmetry indicates that the (0001)-oriented C_{60} film grew epitaxially on the mica substrate.

Fig. 3. Intensity measurements of the RHEED pattern during C_{60} thin film growth on a cleaved natural mica at 50, 100, and 150 °C and MoS_2 at 100 °C. The incident direction of electron beam was parallel to the $\left[10\bar{1}0\right]$ azimuth of the C_{60} film for specular intensity measurements.

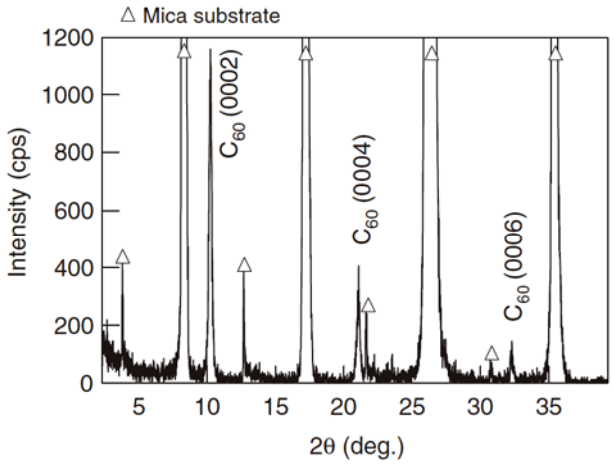

Optical fiber
Substrate
Heater
Electron beam
Lens
RHEED gun
CW laser
Screen
Moving mask
Load lock
Target
MCP
Crucible
Rotatable

(a)

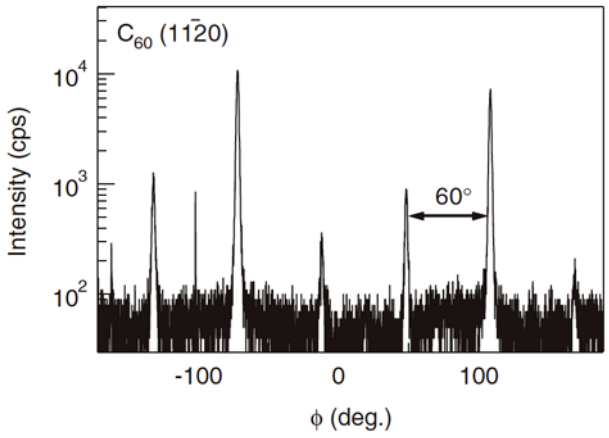


(b)

Fig. 1


△ Mica substrate
1200
1000
800
600
400
200
0
Intensity (cps)
C60 (0002)
C60 (0004)
C60 (0006)
5
10
15
20
25
30
35
2θ (deg.)

(a)


C60 (11$\bar{2}$0)
10^4
10^3
10^2
Intensity (cps)
60°
-100
0
100
ϕ (deg.)

(b)

Fig. 2

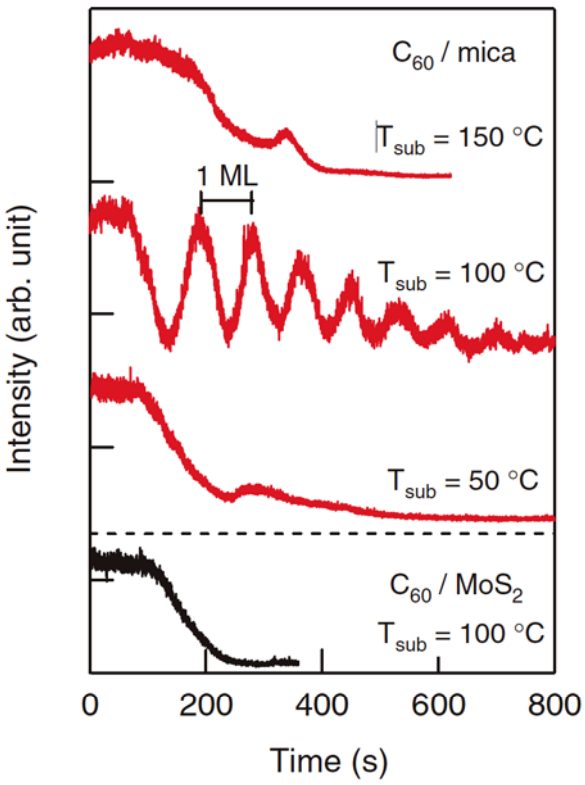

C60 / mica
Tsub = 150 °C
1 ML
Tsub = 100 °C
Tsub = 50 °C
C60 / MoS2
Tsub = 100 °C
Intensity (arb. unit)
0
200
400
600
800
Time (s)

Fig. 3