Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Growth and characterization of epitaxial C_{60} and C_{70} films

Masatoshi Sakurai and Atsushi Koma

Department of Chemistry, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan.

The epitaxial growth features of the C_{60} and C_{70} films on MoS_2 (0001), GaSe (0001), H-terminated Si (111) and CaF_2 (111) have been studied by reflection high energy electron diffraction (RHEED) and by atomic force microscope (AFM). It has been found from RHEED observation that the C_{60} and C_{70} molecules form hexagonal close-packed lattices with bulk lattice constants of 1.00 ± 0.02 and 1.08 ± 0.02 nm, respectively. AFM has revealed that the C_{60} and C_{70} films with monolayer thickness on a MoS_2 substrate consist of domains with diameters as large as ~1μm, which indicates nearly layer-by-layer growth of the fullerene films on that substrate.

1. INTRODUCTION

The epitaxial growth of the fullerenes has attracted much attention since the establishment of synthesizing and purifying methods of a large amount of fullerenes [1]. The need for the fullerene films of good quality is increasing still more for the detailed investigations of their remarkable physical properties and their applications. So far several studies have been made on the epitaxial growth of the fullerenes on various kinds of substrates. Schmicker et al. [2] and Krakow et al. [3] reported the commensurate film growth of C_{60} on mica substrates with the intermolecular distances larger than the bulk value by 3.4%. Li et al. [4] reported the C_{60} film growth on a GaAs (110) substrate where commensurate C_{60} monolayer is formed with certain amount of distortions because of the difference in the symmetry of the C_{60} crystal and that of the GaAs (110) surface. The difference in the lattice constant in the initial film from that of the bulk crystal results in the poor crystallinity in thicker films. Thus it is desirable to get films with bulk lattice constant even in the very early stage of growth. Such growth has been found in C_{60} film growth on a cleaved face of MoS_2 [5,6], which has van der Waals nature. In this case good epitaxial growth become possible even with large lattice mismatch between the grown film and the substrate because of rather weak interaction between them [7]. Here we will report on epitaxial growth of C_{60} and C_{70} on a few kinds of substrate surfaces with van der Waals nature. One is the (0001) surfaces of such layered materials as MoS_2 and GaSe. CaF_2 (111) surface, on which the C_{60} epitaxial growth was reported by Fölsch et al. [8], has been also used since active bonds on its surface are naturally terminated by F atoms, although CaF_2 itself has three-dimensional crystal structure [9]. Epitaxial growth of C_{60} and C_{70} has been tried on quasi van der Waals type Si (111) surfaces, of which dangling bond was terminated with hydrogen. The termination with hydrogen results in growth feature much different from that of direct growth reported by other groups [10-12].

The crystal structures of the grown films were characterized by reflection high energy electron diffraction (RHEED). The surface morphology of the grown film was observed by atomic force microscope (AFM) and the growth mechanisms of the films are discussed on the basis of RHEED and AFM results.

2. EXPERIMENTAL

Details in the experimental apparatus are described elsewhere [6]. The powder specimens of C_{60} and C_{70} with purity of 99.9% or better were prepared according to the well-known method

The present work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

established by Krätschmer et al. [1]. The MoS_2 (0001) and CaF_2 (111) surfaces were prepared by cleavage in the air just before loading into the growth chamber. The GaSe (0001) surfaces were prepared by the epitaxial growth of single-crystalline GaSe films on GaAs (111) substrates [13]. The hydrogen-terminated Si (111) surfaces were obtained by immersion into the boiling water after HF etching [14]. The epitaxial growth of C_{60} and C_{70} films was performed in an ultra-high vacuum chamber with a base pressure of 1 x 10^{-7} Pa. The surface structures of the substrates and the grown films were monitored by RHEED with an incident electron energy of 20 keV. The surface morphology of the grown films was observed by AFM (Seiko SPI3700) under atmospheric pressure.

3. RESULTS AND DISCUSSION

3.1. Characterization with Reflection High Energy Electron Diffraction (RHEED)

Figures 1(a,b), and (c,d) show the RHEED patterns for submonolayer C_{60} and C_{70} films grown on MoS_2, respectively. The incident electron beams were parallel to the [11$\bar{2}$0] and [10$\bar{1}$0] axes in the case of Figs. 1(a,c) and (b,d), respectively. The strong streaks are the diffraction patterns from the substrate. The weak streaks with narrower intervals seen between the substrate streaks are the diffraction patterns originating from the grown C_{60} and C_{70} films. The intervals of the streaks observed for the [10$\bar{1}$0] incidence (Figs. 1(b)) are $\sqrt{3}$ times wider than those observed for the [11$\bar{2}$0] incidence (1(a)) and those patterns appear every 60° rotation around the surface normal. The measured intermolecular distance in the C_{60} film is 1.00 ± 0.02 nm, which is very close to the reported value for the bulk C_{60} crystal (1.002 nm) [1]. This indicates that C_{60} molecules form hexagonal close-packed lattice having bulk lattice constant with its principal crystal axis parallel to the [11$\bar{2}$0] axis of the MoS_2 substrate. Even after the 100 nm-thick film growth, the RHEED patterns maintain the streaks of the C_{60} film indicating good epitaxial growth of the thick C_{60} film. The surface unit mesh of the C_{60} film on MoS_2 is shown in Fig. 2(a).

The C_{70} film, on the other hand, forms different molecular arrangement on the MoS_2 substrate. The narrower interval streaks of the C_{70} film appear in the pattern for the [10$\bar{1}$0] incidence (Fig. 1(c)). The interval of the streaks for the [11$\bar{2}$0] incidence (Fig. 1(d)) is $\sqrt{3}$ times wider than that in Fig. 1(c). Those patterns indicate that

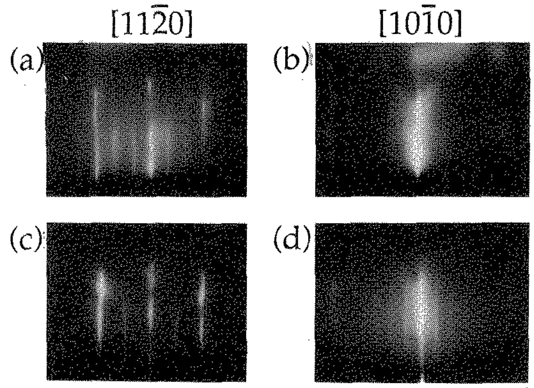
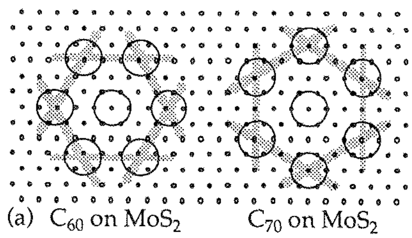


Figure 1. (a),(b) RHEED patterns of submonolayer C_{60} film on MoS_2; (c),(d) submonolayer C_{70} film on MoS_2. The incident beam is parallel to [11$\bar{2}$0] of MoS_2 in (a),(c) and to [10$\bar{1}$0] in (b),(d).



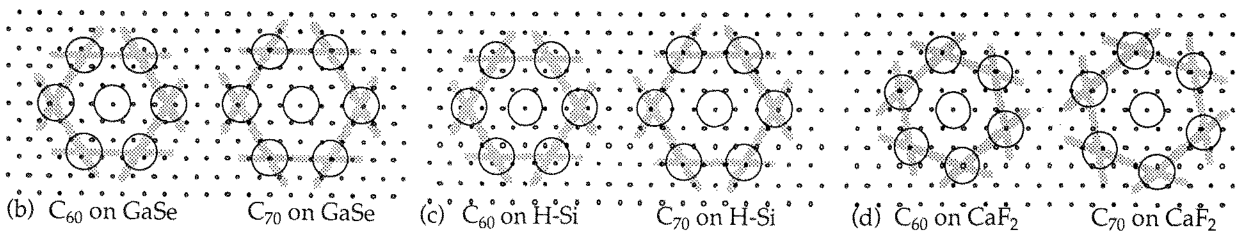


Figure 2. (a) The arrangement of C_{60} and C_{70} molecules on the MoS_2 (0001) ; (b) on GaSe (0001); (c) on H-terminated Si (111) ; (d) on CaF_2 (111). Large circles represent the C_{60} or C_{70} molecules, and small circles are the surface atoms on the substrates.

C_{70} molecules are arranged along the [10$\bar{1}$0] axis of the MoS_2 substrate with the intermolecular distance of 1.08 ± 0.02 nm, which falls near the value of bulk C_{70} crystal (1.056 nm) [15]. Thus the C_{70} film grown on MoS_2 substrate has also the bulk lattice constant.

Figures 2(b), (c) and (d) show the molecular arrangements for the C_{60} and C_{70} films grown on GaSe (0001), H-terminated Si (111), and CaF_2 (111) substrates, respectively. The intermolecular distances calculated from the observed RHEED intervals show good agreement with the bulk value in all cases. It is concluded form those results that C_{60} and C_{70} films with the bulk lattice constants can be grown on the substrates with van der Waals nature regardless of the lattice constants of the substrates.

In the case of C_{60} and C_{70} on GaSe and Si, and C_{60} on MoS_2, the molecules are arranged along the principal axis of the substrate surfaces. C_{70} molecules on MoS_2, on the other hand, are arranged along the axis rotated by 30° from the principal axis around the surface normal. In the case of C_{60} and C_{70} on CaF_2, the axis of the molecular arrangement is rotated by ±19.1° from the principal axis.

The obtained results may be discussed in relation to lattice matching. Figure 3 shows the comparison of lattice constant of fullerene films with those of the commensurate lattices on each substrate. In the cases of C_{70} on MoS_2, C_{60} and C_{70} on CaF_2, the axis of the molecular arrangements in the film is rotated by certain angles from the principal axis of the substrates to form commensurate lattices with the substrates. In the cases of C_{60} on MoS_2, C_{60} and C_{70} on GaSe, C_{60} and C_{70} on Si the arrangements in these fullerene films are parallel to the principal axis of the substrate. The lattice mismatch in C_{60} on GaSe, and C_{60} and C_{70} on Si are not small, and this suggests a possibility of the molecular arrangement along the step edge of the substrate surface, rather than to satisfy the lattice matching condition in those cases.

In conclusion, the molecular arrangements in the C_{60} and C_{70} epitaxial films are considered to be governed by the following two factors. One is

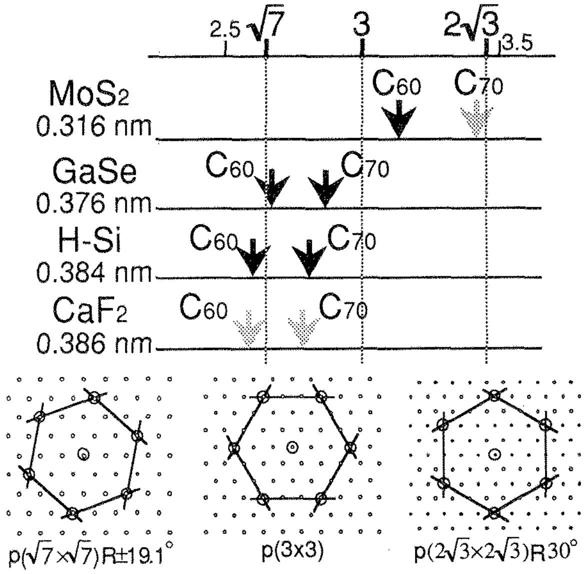


Figure 3. The ratios of the intermolecular distances in the fullerene films to the lattice constants of the substrates. Solid arrow show that the molecules arranged along the principal axis of the substrates, and diffuse arrow show the molecular arrangement along other axis of the substrates. Here $\sqrt{7}$ and $2\sqrt{3}$ correspond to the commensurate lattices rotated by ±19.1° and 30° from the principal axis of the substrate, respectively.

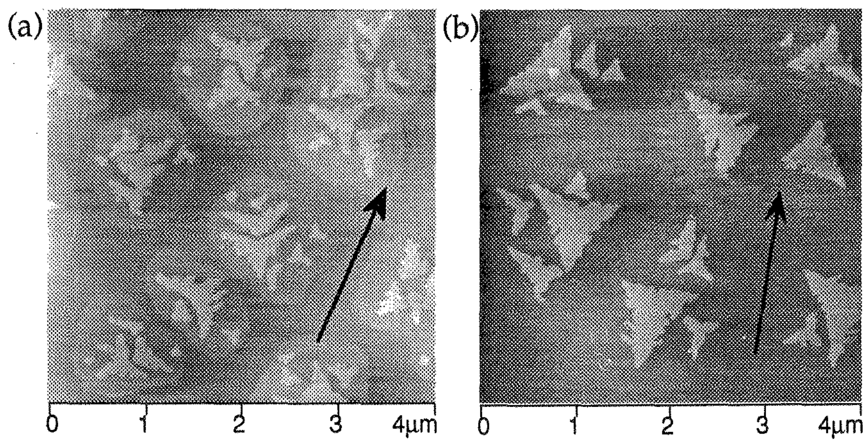


Figure 4. (a) AFM images of a submonolayer C_{60} on MoS_2; (b) C_{70} on MoS_2. The observed area is 4μm by 4μm and the height is 0.8nm in both images. The arrows show the directions of the [11$\bar{2}$0] axis of the MoS_2 substrate.

the alignment of the axis of a grown film with the principal axis of the substrate, and the other is the commensurability between the grown film and the substrate. The actual arrangement seems to be determined by the trade-off of those two factors.

3.2. Characterization with Atomic Force Microscope (AFM)

The direct observation of surface morphology of the grown films is important as well as the diffraction observation in order to get the key for the growth mechanism. Thus AFM images were observed for the C_{60} and C_{70} epitaxial films grown on the MoS_2 surfaces at room temperature, which are shown in Fig. 4. The thickness monitored by a quartz oscillator was 0.5 monolayer in both films. As seen in the figures, domains with diameters of about 1μm are formed in this films. But it should be noted that their height is monolayer thickness (0.8nm) throughout the domains, suggesting the layer-by-layer growth of fullerenes on that substrate. The C_{60} and C_{70} domains on MoS_2 have triangle structures. There exist two triangle orientations which are mirror images to each other, and no other triangle directions is seen. This triangle arrangement reflects well the hexagonal close-packed molecular arrangements as seen in RHEED. However, the triangle orientations relative to the substrate axis are different in the case of C_{60} and C_{70}. The arrows in Fig. 3 show the directions of the principal axis of the MoS_2 substrate. Although the sides of triangular domains of C_{60} are parallel to the principal axis of MoS_2, those of C_{70} are rotated by 30° from the principal axis. The difference in the triangle orientation reflects that in the molecular arrangement of C_{60} and C_{70} films.

Reported domain size in C_{60} film on a mica with the nominal thickness of 2.4 monolayer is 110nm in diameter but 14nm in height [16] which indicates Volmer-Weber type growth mechanism. Similar island formations is observed in the film grown on a CaF_2 substrate. In contrast to those cases, the domain size on a MoS_2 substrate is as large as 1μm in diameter and as thin as monolayer (0.8nm) in thickness. The growth feature on a MoS_2 substrate is much far from Volmer-Weber type and very close to layer-by-layer growth, even though domain formation is seen.

4. SUMMARY

The C_{60} and C_{70} films have been grown epitaxially on such substrates with van der Waals nature as MoS_2, GaSe, H-terminated Si and CaF_2. It has been proved that the films grown on those substrates have the same lattice constant as those of the bulk fullerene crystals. The orientations of the crystal axes of the grown films are along the principal axes of the substrates in most cases. In some cases, however, they are along other axes to satisfy the lattice matching. The best film has been grown on a MoS_2 substrate, on which layer-by-layer type growth occurs forming domains as large as 1μm in diameter.

REFERENCES

1. W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, Nature 347 (1990) 354.
2. D.Schmicker, S.Schmidt, J.G.Skofronick, J.P.Toennies and R.Vollmer, Phys. Rev. B 44 (1991) 10995.
3. W.Krakow, N.M.Rivera, R.A.Roy, R.S.Ruoff and J.J.Cuomo, J. Mater. Res. Vol.7 No.4 (1992) 784.
4. Y. Z. Li, J. C. Patrin, M. Chander, J. H. Weaver, L. P. F. Chibante and R. E. Smalley, Science 252 (1991) 547.
5. M. Sakurai, H. Tada, K. Saiki and A. Koma, Jpn. J. Appl. Phys. 30 (1991) L1892.
6. M. Sakurai, H. Tada, K. Saiki and A. Koma, Chem. Phys. Lett. 208 (1993) 425.
7. A. Koma, Thin Solid Films 216 (1992) 72.
8. S.Fölsch, T.Maruno, A.Yamashita, and T.Hayashi, Appl. Phys. Lett. 62 (1993) 2643.
9. A.Koma, K.Saiki and Y.Sato, Appl. Surf. Sci. 41 (1989) 451.
10. X. -D. Wang, T. Hashizume, H. Shinohara, Y. Saito, Y. Nishina and T. Sakurai, Jpn. J. Appl. Phys. 31 (1992) L880.
11. Y. Z. Li, M. Chander, J. C. Patrin, J. H. Weaver, L. P. F. Chibante and R. E. Smalley, Phys. Rev. B 45 (1992) 13837.
12. Hang. Xu, D. M. Chen and W. N. Creager, Phys. Rev. Lett. 70 (1993) 1850.
13. K.Ueno, H.Abe, K.Saiki and A.Koma, Jpn. J. Appl. Phys. 30 (1991) L1352.
14. Kuang-Yu Liu , K. Ueno, Y. Fujikawa, K. Saiki and A. Koma, Jpn. J. Appl. Phys. 32 (1993) L434.
15. M.A.Verheijen, H.Meekes, G.Meijer, P.Bennema, J.L.de Boer, S. van Smaalen, G. van Tendeloo, S.Amelinckx, S.Muto and J. van Landuyt, Chem. Phys. 166 (1992) 287.
16. H.-G.Busmann, R.Hiss, H.Gaber and I.V.Hertel, Surf. Sci. 289 (1993) 381.