Interface Structure of Epitaxial Polyethylene Crystal Grown on HOPG and MoS_2 Substrates

Yoshiko Takenaka,*,† Hideki Miyaji,† Akitaka Hoshino,† Adam Tracz,‡ Jeremiasz K. Jeszka,‡ and Iwona Kucinska‡

Department of Physics, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan, and Center of Molecular and Macromolecular Studies, PAS, 90-363 Lodz, Poland

Received July 21, 2004
Revised Manuscript Received October 28, 2004

Introduction. Organic crystals including polymers can grow epitaxally on both organic and inorganic substrates.[1−9] At the interface the lattice matching between an epitaxial crystal and a substrate is important. To satisfy the lattice matching, structures different from the bulk structure have been reported to form at the interface.[1,2] This is the case even for the simplest polymer, polyethylene (PE). Although PE crystals usually have the orthorhombic form in the bulk,[12] the monoclinic form of PE is known to form on NaCl,[2] PE fiber,[3] and paper.[4] On the other hand, Tuinstra and Baer reported that PE crystals from the solution grow epitaxially on highly oriented pyrolitic graphite (HOPG).[5] In this case, however, the structure of PE crystals was found to be orthorhombic by using transmission electron diffraction (TED).

Recently, Tracz et al. observed the interface morphology of polyethylene crystallized from the melt on HOPG and molybdenite (MoS_2) by atomic force microscopy (AFM).[6,7] The morphology is similar to the fractured surface of extended chain crystals of polyethylene crystallized under high pressure.[10] The lamellae are much thicker than in the bulk and are arranged in large domains. The chain direction in the neighboring domains differs by 60°. It shows the 3-fold symmetry of the underlying basal plane of the substrate and suggests epitaxial growth.

In the present paper, we investigate the structure of the epitaxial PE crystals using TED and reflection high-energy electron diffraction (RHEED). We prove that PE crystallization on HOPG is indeed epitaxial and that the monoclinic, not the orthorhombic, phase is formed at the interface. On the basis of the results for HOPG, the epitaxial growth of PE on MoS_2 is also discussed.

Experimental Section. The polyethylene (PE) used was Sholex 6009 (weight-average molecular weight (M_w) = 114 000, number-average molecular weight (M_n) = 14 000, Showa Denko Co. Ltd). The substrates were highly oriented pyrolitic graphite (HOPG, Union Carbide Co.) and molybdenite (MoS_2) kindly provided by Professor Shimobayashi of Kyoto University.

Polyethylene thin films were investigated by TED (JEOL 1200EXII) operated at 120 kV and by RHEED (ULVAC BC2952) at 27 kV. The RHEED patterns were observed with use of a microchannel plate 7 cm across in front of the luminescence screen to decrease the radiation damage of specimens. The surface morphology was observed by atomic force microscopy (AFM, Digital Instruments, Nanoscope III[a]).

We prepared three different specimens for TED and RHEED observation. One of them was for TED and gave us the 3D information on PE thin film but needed to be peeled off from the substrate. The other two specimens were for RHEED and gave us only the 2D information but could be observed without peeling off from the substrate. One of them was with no effect of bulk, and the other was with its effect.

PE specimens for TED were prepared in a form of 20−100 nm thick films. They were obtained by spin-casting of *p*-xylene solutions (0.10−1.0 wt %, 130 °C) on the cleaved surface of HOPG preheated in the pure solvent (130 °C). The thin film was melted at 170 °C for 10 min and cooled at a rate 10 °C/min. The thin film was peeled off from the substrate with poly(acrylic acid) (PAA) and was reinforced with a carbon film evaporated in a vacuum. After dissolution of the PAA in water, the carbon-coated PE film was picked up onto an electron microscope grid.

For RHEED, we could use PE specimens without detaching them from HOPG. Two kinds of samples were prepared. (A) A very thin PE film (thinner than 20 nm) was prepared on a cleaved HOPG, preheated in the pure solvent (100 °C), by immersing it into PE solution in *p*-xylene (0.01 wt %, 100 °C) for 20 min. Then the solution was diluted to about $^1/_4$ of the initial concentration by adding the pure solvent (100 °C). The HOPG with PE on it was picked up from the diluted solution.[2] (B) The bulk PE film ca. 0.5 mm thick was crystallized on a cleaved HOPG using the same procedure as for the TED sample described above. A very thin PE layer that remains on HOPG after detachment of the bulk PE film[7] was observed by RHEED. The specimen for AFM was (A).

Results and Discussion. In this section, we show that PE crystallization on HOPG is indeed epitaxial and that the monoclinic, not the orthorhombic, phase is formed at the interface. We also discussed the mechanism of the transition from monoclinic to orthorhombic form.

Figure 1a shows the TED pattern of PE film (about 100 nm thick) grown from the melt on HOPG. We can confirm the orthorhombic PE crystallized epitaxially on HOPG. This pattern determines the epitaxial relation as follows:

$$(0001)\langle 2\ {-1}\ {-1}\ 0\rangle_{\mathrm{HOPG}}//(110)\langle 001\rangle_{\text{orthorhombic PE}} \quad (1)$$

Namely, the chain direction, ⟨001⟩, and the plane {110} of the orthorhombic PE are parallel to the ⟨2 −1 −1 0⟩ direction and the (0001) plane of HOPG, respectively. This agrees with the epitaxial relation reported for PE thin films crystallized on HOPG from solutions using the same technique (TED).[5]

Figures 2 and 3 show an AFM image and an RHEED pattern of a specimen A, respectively. The morphology in Figure 2 is exactly the same as the one observed in refs 6 and 7. AFM observation of a specimen (A) reveals that the orientation of the edge-on lamella in the

* To whom correspondence should be addressed: Tel +81-75-753-3671; Fax +81-75-753-3779; e-mail takenaka.yoshiko@scphys.kyoto-u.ac.jp.
† Kyoto University.
‡ Center of Molecular and Macromolecular Studies.

10.1021/ma0485080 CCC: $27.50
Published on Web 11/20/2004

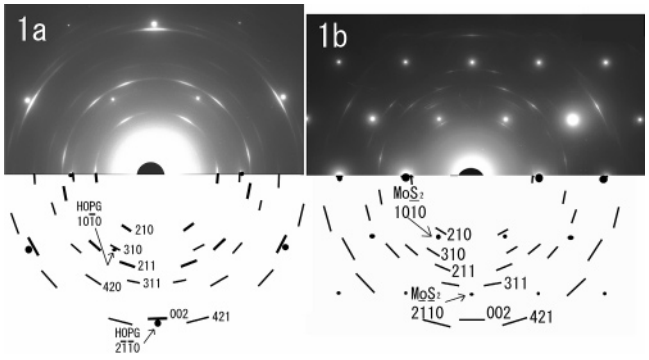

Figure 1. TED patterns of PE thin films about 100 nm thick grown epitaxially on HOPG (a) and MoS_2 (b) (upper half) and their schematic drawings (lower half). These patterns show (a) $(0001)[2\ -1\ -1\ 0]_{HOPG}//(110)[001]_{PE\ orthorhombic}$ and (b) $(0001)[2\ -1\ -1\ 0]_{molybdenite}//(110)[001]_{PE\ orthorhombic}$.

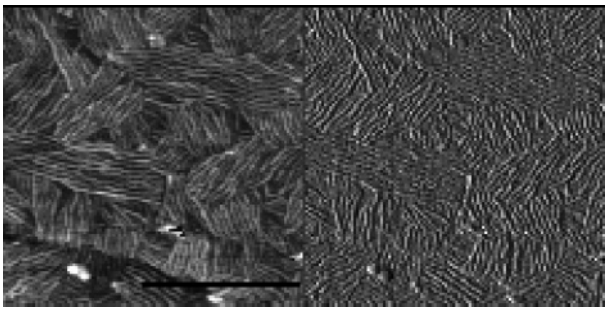

Figure 2. AFM image (tapping mode) of a PE thin film about 2 nm thick grown epitaxially on HOPG: left, height image; right, amplitude image. The scale bar is 1 μm.

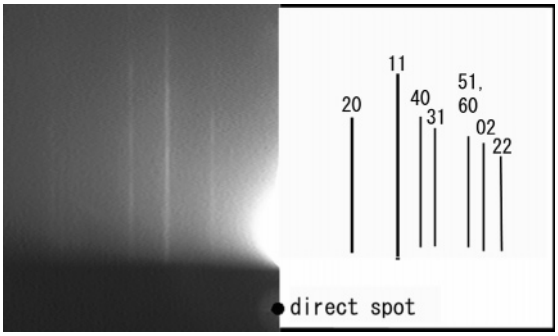

Figure 3. RHEED pattern (left) of the same specimen as in Figure 2 and its schematic drawing (right) with indices of 2-dimensional lattice: $a = 0.809$ nm and $c = 0.253$ nm.

neighboring domains differs by 60°. It reflects the 3-fold symmetry of the underlying HOPG basal plane (Figure 2); it indicates the epitaxial crystallization.

In its RHEED observation, there are many PE crystals in domains of different orientation in the surface area as large as 1 mm^2 irradiated by incident electrons; thus, the RHEED pattern corresponds to that of a rotating crystal with the rotation axis parallel to the c axis of HOPG (Figure 3). In contrast to Figure 1 we can index the streaks using the crystallographic data not for the orthorhombic but for the monoclinic PE:[14] $a = 0.809$ nm, $b = 0.479$ nm, $c = 0.253$ nm (the fiber axis), and gamma = 107.9.

The RHEED pattern shows the following orientational relationship between the PE and substrate crystals:

$$(0001)_{HOPG}//(010)_{monoclinic\ PE} \quad (2)$$

By this RHEED pattern, we could not determine the directional relation between the HOPG surface and the PE chains at the interface because we could never see the patterns of HOPG and PE together. In comparison with (1), however, we assume that chain axis of PE, $\langle 001 \rangle$, is parallel to the $\langle 2\ -1\ -1\ 0 \rangle$ HOPG:

$$(0001)\langle 2\ -1\ -1\ 0 \rangle_{HOPG}//(010)\langle 001 \rangle_{monoclinic\ PE} \quad (2^*)$$

The epitaxial relation 2* gives rise to the PE zigzag plane almost perpendicular to the HOPG surface. Such orientation has been claimed for a paraffin monolayer on HOPG.[8,13]

The PE remaining on HOPG after detachment of the bulk PE, specimen B, also shows the streaks of the monoclinic in RHEED. Therefore, we can conclude that the polyethylene crystallizes epitaxially on HOPG in the monoclinic form.

An important quantity in epitaxy is the lattice mismatch R between an epitaxial crystal and a substrate crystal.[11]

$$R\ [\%] = \frac{d_E - d_S}{d_S} \times 100 \quad (3)$$

where d_E and d_S are spacings of 2-dimensional lattices at the interface of the epitaxial crystal and the substrate crystal, respectively. Using the lattice parameters reported,[12,14] we can calculate the R value for the relations 1 and 2*. Along the chain axis of PE it is +3.0% for both (1) and (2*). Along the direction perpendicular to the chain axis, the R value is +4.3% for the orthorhombic PE (relation 1) and −5.0% for the monoclinic PE (relation 2*).

If the lattice parameters of an epitaxial crystal have to fit to those of substrate, it is easier for the epitaxial crystal to expand than to compress, since the gradient of intermolecular potential is steeper for a negative displacement from the equilibrium position than for a positive displacement. Accordingly, this could account for the formation of monoclinic form ($R = -5.0\%$) rather than orthorhombic form ($R = +4.3\%$) at the interface.

Using TED, we could not observe the monoclinic PE crystallized at the interface. In the case of PE/NaCl, however, the monoclinic PE was observed.[5] In this case, the substrate, solid NaCl, was dissolved on water surface instead of peeling off the PE from the substrate. Therefore, it can be supposed that when PE specimens were peeled off from HOPG, the monoclinic PE transformed to the orthorhombic form by the shear stress.

We also found by TED experiment that the PE film (about 100 nm thick) grown on MoS_2 from the melt (Figure 1b) shows the epitaxial relation

$$(0001)\langle 2\ -1\ -1\ 0 \rangle_{molybdenite}//(110)\langle 001 \rangle_{orthorhombic\ PE} \quad (4)$$

In this case the R value is as large as +8.5%. On the basis of the result of HOPG, however, there is the possibility that a different PE phase exists at the surface of MoS_2. Since the surface of our MoS_2 samples is not so flat as that of HOPG, RHEED experiments were not successful until now.

On the basis of the presented results, we can propose the following model of the crystallization of PE on atomically flat HOPG interface. The crystallization of PE occurs similarly as in the case of PE/NaCl.[2] A very thin transient layer of PE at the interface has the

monoclinic form; further apart from the surface, though the exact thickness cannot be determined, the monoclinic form transforms to the orthorhombic. The monoclinic form is stabilized at the interface due to the energy gain related to the matching of the crystalline lattices.

In conclusion, we proved not only that the epitaxial crystallization of PE from the melt on HOPG results in formation of lamellae much thicker than in the bulk[6] but also that the PE crystal structure at the interface is monoclinic.

Acknowledgment. This work is supported by the Grant-in-Aid for the 21st Century COE "Center for Diversity and Universality in Physics" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. A.T., J.K.J., and I.K. thank gratefully for the financial support by KBN Project T08E 063 22 (2001−2004).

References and Notes

(1) Hashimoto, S. *J. Cryst. Growth* **1995**, *146*, 649.
(2) Wellinghoff, S.; Rybnikar, F.; Baer, E. *J. Macromol. Sci., Phys.* **1974**, *B10*, 1.
(3) Flores, A.; Poeppel, A.; Riekel, C.; Schulte, K. *J. Macromol. Sci., Phys.* **2001**, *B40*, 749.
(4) Furuheim, K. M.; Axelson, D. E.; Antonsen, H. W.; Helle, T. *J. Appl. Polym. Sci.* **2004**, *91*, 218.
(5) Tuinstra, F.; Baer, E. *J. Polym. Sci., Lett. Ed.* **1970**, *8*, 861.
(6) Tracz, A.; Jeszka, J. K.; Kucinska, I.; Chapel, J.-P.; Boiteux, G.; Kryszewski, M. *J. Appl. Polym. Sci.* **2002**, *86*, 1329.
(7) Tracz, A.; Kucinska, I.; Jeszka, J. K. *Macromolecules* **2003**, *36*, 10130.
(8) Rabe, J. P.; Buchholz, S. *Science* **1991**, *253*, 424.
(9) Hoshino, A.; Takenaka, Y.; Miyaji, H. *Acta Crystallogr*. **2003**, *B59*, 393.
(10) Wunderlich, B.; Arakawa, T. *J. Polym. Sci., Part A* **1964**, *2*, 3697.
(11) Hoshino, A.; Isoda, S.; Kurata, H.; Kobayashi, T.; Yamashita, Y. *Jpn. J. Appl. Phys.* **1991**, *34*, 3858.
(12) Bunn, C. W. *Trans. Faraday Soc.* **1939**, *35*, 482.
(13) Baukema, P. R.; Hopfinger, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 399.
(14) Seto, T.; Hara, T.; Tanaka, K. *Jpn. J. Appl. Phys.* **1968**, *7*, 31. We have changed the unique axis from *b* to *c*.

MA0485080