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Notes

Anisotropic-to-Isotropic Change in Lateral Force at the Surface of Single-Crystal Lamellae of High-Density Polyethylene during Low-Temperature Annealing

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Introduction

Single-crystal lamellae of polyethylene (PE) thicken by annealing at temperatures below the melting point. The annealing effect on thickening of the single-crystal lamellae has been investigated mainly by small-angle X-ray scattering measurements and transmission electron microscopic observations.[1−11] These experimental results indicated that the annealing effect was different among at least three temperature ranges. By annealing in a low-temperature range, defect concentration changes and stress relief occurs in the single-crystal lamellae without lamellar thickening.[2,3] By annealing in an intermediate-temperature range, lamellar thickness increases with an increase in annealing temperature (T_a).[4−6] Morphology of the single-crystal lamellae drastically changes accompanying formation of holes. PE stems align perpendicular to the lamellar surface to form the orthorhombic crystal, and the chains fold back along the crystallographic (110) plane at the surface.[7] Therefore, it is considered that the stems possess high and coordinated mobility so that they slide along the crystallographic *c* axis.[8,9] In a high-temperature range below the melting point, the single-crystal lamellae partially melt and recrystallize to form thicker ones by annealing.[10] Recently, local change in morphology of the single-crystal lamellae caused by annealing has been investigated by atomic force microscopy (AFM). For example, Rastogi et al. reported that holes were not formed in stacked regions of the single-crystal lamellae by the intermediate-temperature annealing.[12] Kawaguchi et al. found that the morphology of the single-crystal lamellae was little changed on Pt/Pd-evaporated silicon substrates by the high-temperature annealing.[13] These results implied that lamellar thickening behaviors would be influenced by not only the T_a but also lamellar surface and interface environment during annealing. Because the folding part of chains is not in the crystal state, molecular aggregation structure at the lamellar surface may change even by low-temperature annealing below the crystallization temperature (T_c). However, details of the annealing effect on the single-crystal lamellae have not been revealed yet. The purpose of this study is to clarify the low-temperature annealing effect below T_c on isolated single-crystal lamellae of PE on the nanometer scale. In the low-temperature annealing process, the morphology and physical properties at the surface were directly evaluated for the lamellae by in-situ AFM observations and lateral force microscopic (LFM) measurements.

Experimental Section

The sample used in this study was a high-density polyethylene (HDPE, Marlex 9, $M_w = 520$k) with a broad molecular weight distribution. Single-crystal lamellae were prepared from a 0.01 wt % *p*-xylene solution of the HDPE by an isothermal crystallization method. First, the solution was kept at 411 K for 1 h to have the HDPE dissolved completely in *p*-xylene. Next, the thus-prepared solution was rapidly cooled to a T_c of 358 K and then kept at the T_c for 24 h for crystallization. Afterward, the solution was slowly cooled to 293 K. A small amount of the solution containing HDPE single-crystal lamellae was dropped onto the crystallographic (111) plane of original silicon substrates with a native oxide layer and onto Pt/Pd-evaporated ones. Afterward, the lamellae on the substrates were allowed to air dry at 293 K.

AFM observations and LFM measurements were simultaneously performed for HDPE single-crystal lamellae using a SPA300HV (Seiko Instrument Industry, Co. Ltd., Japan) in the contact operation mode. Each of the cantilevers used in this study was a rectangular-shaped one with a quadrangular pyramidal Si_3N_4 microtip (Olympus, Co. Ltd., Japan). The bending spring constants of the cantilevers were 0.09 and 0.006 N m^{-1}. The long axis of the cantilevers was perpendicular to the scanning direction. The torsion angle of the cantilevers reflected the magnitude of lateral force between the microtip and the sample surface. The magnitude of lateral force was determined based on the measurement under bidirectional scanning. AFM observations and LFM measurements were carried out for as-prepared lamellar crystals at 293 K in air under a repulsive force of 0.088 nN at a scanning rate of 1.4 μm s^{-1}. In-situ experiments were performed for lamellar crystals at various T_a from 293 to 363 K in vacuo just after annealing them for 30 min at each T_a in vacuo.

Results and Discussion

Figure 1a and 1b show AFM and LFM images observed for an as-grown single-crystal lamella of HDPE on an original silicon substrate at 293 K, respectively. Figure 1c shows a schematic representation of the adjacent-reentry sharp chain folding at the lamellar surface and the scanning direction of a cantilever perpendicular to the crystallographic (110) plane in a sector of a single crystal. The brighter part in the AFM image corresponds to the higher part in height and that in the LFM image to the larger part in lateral force. A lozenge-shaped lamella with a flat surface is observed in Figure 1a. The thickness of the single-crystal lamella

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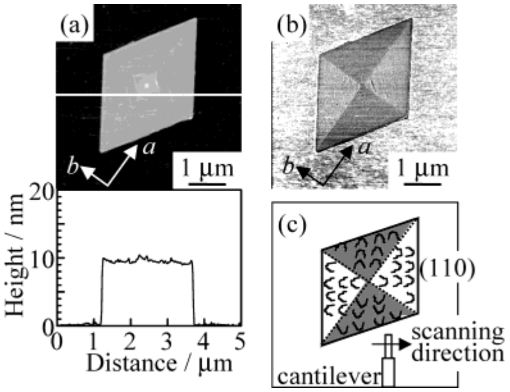

Figure 1. AFM image with its height profile (a) and LFM image (b) of a single-crystal lamella of HDPE crystallized at T_c = 358 K and the relationship between the scanning direction of a cantilever and the chain folding direction at the lamellar surface (c). AFM/LFM observations were performed at 293K in air.

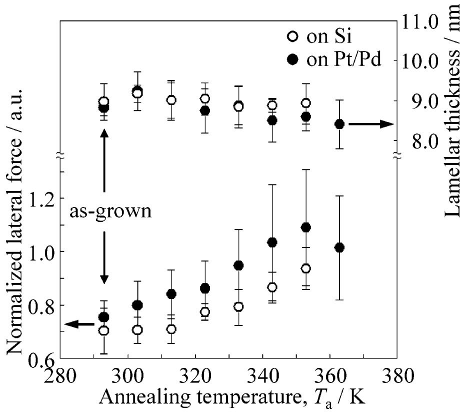

Figure 2. Lamellar thickness and lateral force evaluated for as-grown and annealed single-crystal lamellae of HDPE on original and Pt/Pd-evaporated silicon substrates by in-situ AFM observations and LFM measurements.

was ca. 9 nm, which was determined on the basis of the maximum in a height histogram of the lamellar crystal computed from its AFM image. This lamellar thickness was smaller than the already reported lamellar thickness evaluated for stacked lamellae by SAXS and TEM.[11] In Figure 1b the contrast in lateral force between the adjacent sectors of the single crystal is clearly observed. Kajiyama et al. investigated the lateral force at the lamellar surface as a function of the scanning angle for a HDPE single crystal prepared by a self-seeding method. The scanning angle was defined as an angle between the scanning direction and the (110) plane. It was revealed that the magnitude of lateral force in a sector of a single crystal increased with an increase in scanning angle from the crystallographic (110) plane. This suggested that the contrast in lateral force between the adjacent sectors would be attributed to the sharp and regular chain folding along the (110) plane.[14−16] Therefore, the HDPE chains at the surface of single-crystal lamella prepared by the isothermal crystallization would also consist of the adjacent-reentry chain folding along the (110) plane with the sharp loop as shown in Figure 1c.

Figure 2 shows lamellar thickness and lateral force evaluated for as-grown and annealed single-crystal lamellae of HDPE on original and Pt/Pd-evaporated silicon substrates by in-situ AFM observations and LFM measurements. The magnitude of lateral force in a sector of a single crystal was measured in the perpendicular direction to the (110) plane and normalized on the basis of that at the substrate surface. As shown in Figure 2, the magnitude of lateral force in the perpendicular direction of the (110) plane increased with an increase in T_a. The lateral force and lamellar thickness changed reversibly in a T_a range from 293 to 363 K for the single-crystal lamellae on original and Pt/Pd-evaporated silicon substrates. The lateral force can be attributed to friction and adhesion forces between the microtip and the lamellar surface. In other words, the magnitude of lateral force reflects molecular aggregation structure and molecular motion at the lamellar surface. In the α_c relaxation temperature range of PE, the 180° flip motion of the stems occurs around the chain axis with the forward and backward chain sliding motion and it is activated with an increase in T_a.[17,18] It was considered that the molecular motion in the folding part of chains at the lamellar surface in a T_a range from 293 to 363 K would be connected with the 180° flip motion of the stems. On the other hand, the thickness of the single-crystal lamellae evaluated by in-situ AFM observations slightly decreased with an increase in T_a. Moreover, the adhesion between the microtip and the lamellar surface evaluated with an atomic force microscope slightly increased in magnitude with an increase in T_a. These experimental results implied that an increase in the magnitude of the lateral force would be due to an increase in the contact area between the microtip and the lamellar surface under a scanning condition at a constant applied load. Elastic deformation of the lamellar surface might be caused by the microtip during scanning.

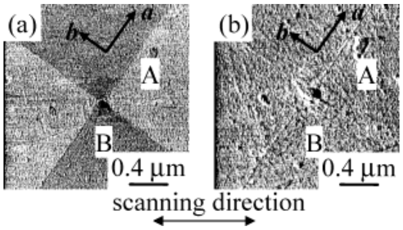

Figure 3. In-situ LFM images for a single-crystal lamella of HDPE measured on an original silicon substrate at an ambient temperature of 293 K (a) and at a T_a of 363 K (b).

Figure 3a and 3b show in-situ LFM images for a single-crystal lamella of HDPE measured on an original silicon substrate at an ambient temperature of 293 K and a T_a of 363 K, respectively. The sector where the (110) plane was perpendicular to the scanning direction was defined as sector A, and another sector was defined as sector B. The contrast in lateral force between the adjacent sectors, sectors A and B, was clearly observed at 293 K. However, such a contrast was hardly observed for the lamella at T_a = 363 K. Also, it should be mentioned that this contrast appeared again when the lamella was cooled slowly from 363 to 293 K. The magnitude of the contrast corresponds to the degree of anisotropy in lateral force at the lamellar surface. Figure 4 shows the $LF_{SectorA}/LF_{SectorB}$ measured for as-grown and annealed single-crystal lamellae of HDPE on original silicon substrates and Pt/Pd-evaporated ones. Here, $LF_{SectorA}/LF_{SectorB}$ indicates the ratio of lateral force in sector A to that in sector B. The magnitude of $LF_{SectorA}/LF_{SectorB}$ was ca. 1.1 in a T_a range below 323 K and decreased to ca. 1.0 with an increase in T_a from 323 to 363 K. On the basis of analysis of the lateral force, it was revealed that the degree of anisot-

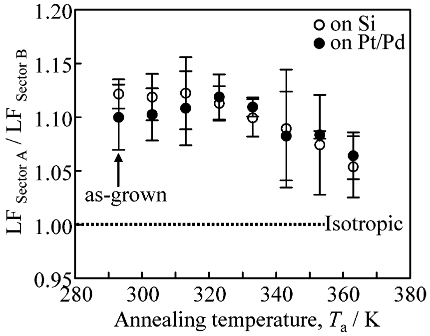

Figure 4. $LF_{SectorA}/LF_{SectorB}$ measured for as-grown and annealed single-crystal lamellae of HDPE on original silicon substrates and Pt/Pd-evaporated ones.

ropy in lateral force at the lamellar surface began to decrease around T_a = ca. 323 K. This implied that the chain folding direction at the surface would become apparently the same between sectors A and B against the scanning direction. In the annealing process, molecular motion in the folding part of chains would be activated and conformational disordering of the chains would occur in the near-surface region of the lamellae. Therefore, it is reasonable to consider that the sharp loop at the lamellar surface would change to the loose loop during low-temperature annealing. As shown in Figures 3 and 4, the low-temperature annealing effect on the HDPE single crystals was directly revealed for the first time by in-situ LFM measurements. As defect concentration was considered to change without lamellar thickening in this T_a range,[2] structural disordering of the chain-folded lamellar surface might be necessary for the chains to form a thermally more stable structure.

Conclusions

The low-temperature annealing effect was directly evaluated for isolated single-crystal lamellae of HDPE on original silicon substrates and Pt/Pd-evaporated ones by in-situ AFM observations and LFM measurements. We found, for the first time, the anisotripic-to-isotropic change in lateral force at the surface of the single-crystal lamellae during the low-temperature annealing. With an increase in T_a from 293 to 363 K, lamellar thickness evaluated by in-situ AFM decreased only by a few angstroms. On the other hand, the magnitude of lateral force in the scanning direction perpendicular to the crystallographic (110) plane remarkably increased with an increase in T_a . At the same time, the contrast in lateral force between the adjacent sectors diminished. These experimental results indicated that molecular motion in the folding part of chains would be activated and conformational disordering of the chains would occur in the near-surface region of the lamellar crystals. Therefore, it is reasonable to consider that the sharp loop at the lamellar surface would change to the loose loop during the low-temperature annealing.

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