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AFM observation of polyethylene single crystals: selective handedness of screw dislocations in a chair type

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Abstract

The three-dimensional morphology of polyethylene single crystals grown from dilute solution has been examined by atomic force microscopy. Single crystals were deposited on a soft ground of aqueous solution of poly(vinyl alcohol) (PVA) to avoid the collapse of thin lamellar crystals with thickness of 10 nm. The observation of single crystals on dried PVA clarifies the morphology of a chair type crystal as well as well-known hollow pyramidal type. It has been confirmed that the screw dislocations in the chair type follow a selection rule of the handedness in a manner to relieve the distortion in the chair type.

Keywords: Polyethylene; Single crystal; Chair type

1. Introduction

Within a polyethylene single crystal, polymer chains tilt at an angle of 15–30° to the folding surfaces of the lamellar crystal [1]. The tilting direction is different for each growth sector, and hence the single crystals take a characteristic three-dimensional form. Well-known morphology is the shape of a tent called hollow pyramidal type (Fig. 1(a)). In fact, single crystals of the form called chair type also exist at a rate of 1-to-1 together with the hollow pyramidal type when grown from dilute solution [2].

As shown in Fig. 1(b), the right-and-left half of a chair type crystal is considered to take a convexo-concave form with the border of sector boundary parallel to the *b* axis. Since the two halves of convexo-concave form join as the chair type, the crystal holds distortion in its inside. The distortion in a chair type crystal can be relaxed by the introduction of screw dislocation with the Burgers vector of selective directions. Consequently, spiral terraces with the selected handedness will develop from the screw dislocations, as shown in Fig. 1(c). Spiral terraces with the selected handedness were actually observed in the chair type single crystals of polyethylene grown from the melt [3] and of poly(vinylidene fluoride) grown from the melt and from the blend with an amorphous polymer [4]. Concerned with the three-dimensional shape of the chair type, however, there is very limited information obtained by optical-microscopy of a chair type single crystal in a solvent [2], and the actual three-dimensional shape has many unknown points especially on the distortion of its shape.

In terms of the introduction of screw dislocations, Schultz and Kinloch [5] presented a model calculation of the twisting correlation of crystallites in a banded spherulite (a spherulite showing periodic extinction bands under polarizing optical microscope) with the row of screw dislocations of the same handedness. Based on their argument, we proposed the possibility of the twisting correlation due to the introduction of the selective screw dislocations in the chair type for the formation of banded spherulites of poly(vinylidene fluoride) [4]. However, there is a criticism about the possibility, based on the argument that the stress in the chair crystal will not be large enough for the creation of a screw dislocation with such a large Burgers vector corresponding to the lamellar thickness [6].

Under those situations, we consider that the direct observation by atomic force microscopy (AFM) will be the most reliable evidence for the three-dimensional shape of a chair crystal and for the selective creation of screw dislocations in the chair type crystals. Since polyethylene

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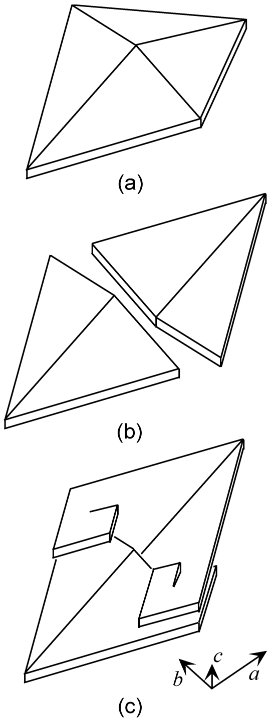

Fig. 1. Schematic representations of polyethylene single crystals: (a) hollow pyramidal type, (b) two halves of chair type, and (c) spiral terraces from screw dislocations, the handedness of which is selected to relieve the distortion in the chair type. In order to highlight the three-dimensional shape, the drawing assumes the {312} folding surfaces with tilting angle of 29°, which is expected at higher crystallization temperatures.

single crystals are thin lamellae of the thickness about a few 10 nm, only the collapsed form is observable in the usual sampling. In the present report, we deposit single crystals on a soft ground (aqueous solution of poly(vinyl alcohol) to avoid the collapse. The same method has been utilized by Ishihara and Imura [7] in the sample preparation for a transmission electron microscopy, and the hollow pyramidal type judged from the shadowing contrast was successfully reported [7].

2. Experimental

Polyethylene was NIST SRM 1483 of $M_w = 32,100$ and $M_w/M_n = 1.11$. Single crystals were obtained by isothermal crystallization at 83.0 °C from 0.01 wt% xylene solution. After isothermal crystallization, the dispersion of single crystals was dropped on a aqueous solution of poly(vinyl alcohol) (PVA). Aqueous solution of PVA is from Diax Co., Ltd, and was 7 wt%. After drying PVA at room temperature, the single crystals distributed on the surface of PVA were observed with an atomic force microscope (SPI3800N, Seiko Instruments, Inc.) in a dynamic force mode in air. Silicon cantilevers (SI-DF20, Seiko Instruments, Inc.) with a resonance frequency of 110–150 kHz were used for the observations.

3. Results and discussion

Fig. 2 shows the topographic (height) image of single crystals; Fig. 2(a) shows a convex hollow pyramidal type, Fig. 2(b) a concave hollow pyramidal type, and Fig. 2(c) a chair type single crystal; the single crystals in Fig. 2(a) and (b) are made up of two sheets of lamellae. The lamellar thickness of those single crystals was about 10 nm. The tilting angle of each growth sector was in the range of 10–17° and corresponds to the angle of the {314} surfaces (~15°), which is the folding surface of the crystals grown at relatively lower temperatures from xylene solution [2]. As shown in Fig. 2(c), the actual three-dimensional shape of a chair type crystal was clearly observed by the present method. It is confirmed that the shape is greatly distorted in the central region from the original two halves of convexo-concave form.

Concerned with the screw dislocations (and the consequent spiral terraces), the following results were obtained. Firstly, the frequency of screw dislocations in the hollow pyramidal type is very low. The location is mostly restricted to the center of the single crystals. In the chair type, the frequency is higher, and the spiral terraces were mainly formed in the neighborhood of the sector boundaries parallel to the *b* axis, where the distortion will concentrate.

Fig. 3 shows an example of the spiral terraces in a chair type crystal. In Fig. 3, bright portion is convex and dark portion is concave, and hence the coexistence of the bright and dark portions in the central region of a single crystal indicates that the crystal is chair type. It is seen that the spiral terrace in the upper part (Fig. 3(b)) turns clockwise from the center and counter-clockwise in the lower part (Fig. 3(c)). The selection of the handedness agrees with the expected manner shown in Fig. 1(c), in which the distortion in the chair crystal is relaxed by the formation of the screw dislocations with the selected handedness. Spiral terraces contrary to this rule have not been observed.

The absence of spiral terraces in Fig. 2(c) and the existence in Fig. 3 are mainly due to the size difference between those crystals; the length of the crystals in the direction of *a*-axis is about 3 and 12 μm in Figs. 2(c) and 3, respectively. With increasing size, screw dislocations were more easily introduced probably because of increasing total distortion with the growth of the size.

It should also be noted that, in the upper part of the spiral terrace in Fig. 3(c), a new spiral terrace is created and turns clockwise. This selection of handedness also follows the above rule if the chair type form is preserved in the spiral terrace. Similar evidences are seen in other crystals and suggest the preservation, though the direct information about the three-dimensional shape of the spiral terraces was not obtainable due to the collapse of the spiral terraces on the mother crystal.

Finally, it needs to be mentioned that the single crystals were grown from diluted solution, and hence the mechanism proposed by Keith and Padden [8] as an alternative

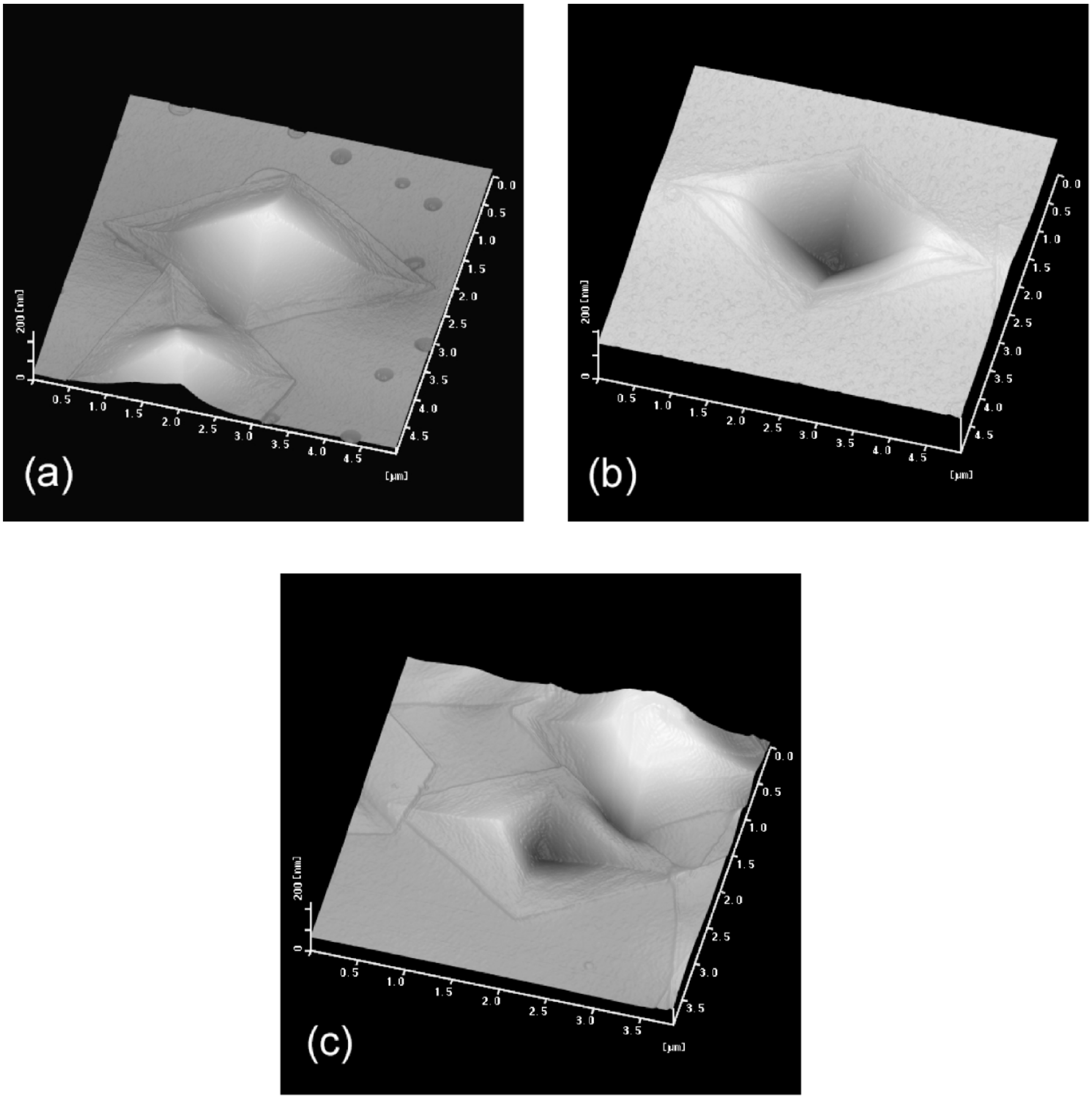

Fig. 2. Topographic images of polyethylene single crystals grown from dilute xylene solution: (a) convex hollow pyramidal type, (b) concave hollow pyramidal type, and (c) chair type. The height difference is exaggerated in the images.

explanation for the selection of the handedness of screw dislocations does not apply to the crystals because the mechanism postulates slow diffusion of the centroid of polymer chains in the melt.

4. Conclusion

By the direct observation by AFM of the three-dimensional shape of polyethylene single crystals grown from dilute solution and deposited on a soft ground, the morphology of the chair type was clarified. Furthermore, it has been confirmed that the screw dislocations and the consequent spiral terraces were preferentially produced in the chair type with the selection of the handedness in accordance with the relief of the distortion in the chair type. This is the direct proof of the selection mechanism of the handedness of the screw dislocations in the chair type single crystals.

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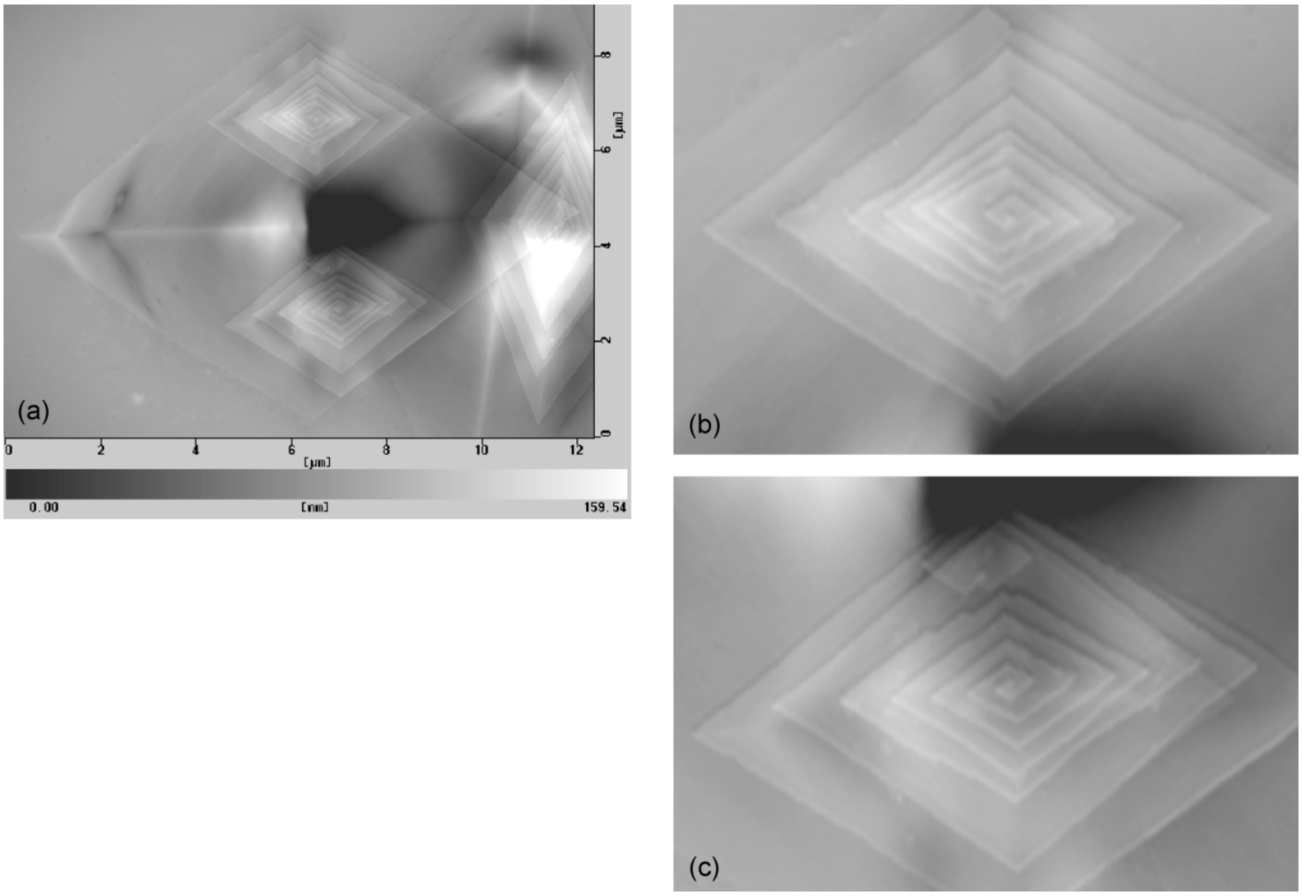

Fig. 3. Top view of the topographic image of a chair type crystal with a pair of spiral terraces. The magnified images of the spiral terraces are shown in (b) and (c).

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