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Annealing behavior of solution grown polyethylene single crystals

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Abstract

The morphology evolution of solution grown polyethylene single crystals has been studied upon annealing below their melting temperature by using atomic force microscopy (AFM). AFM investigations have been performed ex situ, which means AFM investigations at room temperature after the annealing treatment, and in situ at real temperature. Beside the well-known Swiss-cheese and picture frame appearance a novel morphological feature has been observed: the formation of saw-tooth-like patterns at the edges of the crystals, which become more and more pronounced with increasing annealing temperature. Controlled dissolution experiments have resulted in similar saw-tooth-like edge patterns of the single crystals, which indicate that the initial organization of the crystals influences the reorganization. This reorganization behavior upon annealing can be related to the presence of nano-sized fold defects, which have been monitored using the technique of *n*-alkane surface decoration.
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1. Introduction

In contrast to the equilibrium crystalline state, which is the extended chain crystal, a folded-chain crystal is metastable; and it tends to reorganize during an annealing treatment below its melting temperature. The annealing behavior of solution grown single crystals has been studied intensively. The main techniques used in those studies are small angle X-ray diffraction (SAXS), Raman spectroscopy and transmission electron microscopy (TEM) including electron diffraction [1–3]. From these investigations main result is that with raising the annealing temperature near to but below the melting temperature the lamellar thickness increases. A similar thickening behavior is observed with time for annealing at constant but elevated temperatures near the melting temperature.

For SAXS as well as Raman spectroscopy experiments single crystal mats were used, which means that the data obtained represent the average behavior of a large quantity of crystals. In contrast, studies related to the reorganization of individual crystals were performed using TEM. Local features related to the reorganization of annealed solution grown polyethylene (PE) single crystals are, e.g. the formation of a so-called Swiss-cheese morphology, which means that cavities are formed throughout the entire lamellae having a pronounced thicker rim [4], and the formation of a picture frame morphology [5] after the annealing treatment. However, the main drawback of TEM is that monitoring of individual crystals during annealing experiments cannot be performed, mainly for the reason that sample damage is caused by the electron beam.

To overcome the limitations of TEM, in the present study we have applied atomic force microscopy (AFM) as main investigation technique. Most of the AFM studies related to the development of the morphology in polymer systems are performed at room temperature [6–8]. Recently, some appealing investigations have shown that using intermittent-contact mode AFM equipped with a hot-stage, it is possible to follow, e.g. the annealing/melting of polymer crystals in situ at real temperature [9–16]. However, the continuous capturing of data related to the morphological evolution of polymer crystals remains a challenge, since the surface of the measured substrate tends to become softer with elevated temperature, which causes, e.g. penetration of the tip in the sample.

It is generally accepted that the reorganization behavior during annealing experiments is associated with the initial organization of the polymer chains within a single lamella. In another part of our study, we have followed the formation of

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solution grown PE single crystals and have analyzed their lamellar organization depending on the preparation conditions used [17]. In the present part, we investigate the annealing behavior of such crystals, which were prepared from solution by using the self-seeding procedure [18].

2. Experimental

2.1. Preparation of solution-grown polyethylene single crystals

The material used in the present study was a linear polyethylene with a molecular weight of 112 kg/mol and a polydispersity of 1.1 (NIST, USA). Polyethylene single crystals were prepared from dilute xylene solution (0.01 wt%) using the technique of self-seeding [18]. The solution was obtained by dissolving PE into the hot solvent at a temperature slightly below the boiling temperature of xylene. The hot solution was transferred to an oil-bath, which had a temperature below the dissolution temperature of PE, and held for 2 h for pre-crystallization (in principle, it is now crystals in solvent suspension). Then it is heated to the seeding temperature with a heating rate of 10 °C/min and held for 15–20 min to form stabilized and uniform nuclei. Subsequently, the solution was transferred to another pre-heated oil bath having the temperature for isothermal crystallization. The crystals were removed from the solution by simply dipping freshly cleaved mica in the solution followed by subsequent drying the samples in a vacuum oven at 40 °C for 24 h. The substrates used were pre-heated by immersing in a fresh solvent, which had a temperature similar to the crystallization temperature of the single crystals. This procedure was chosen to prevent the formation of non-isothermal crystallization of the remaining crystals in the solution due to the introduction of a cold substrate.

2.2. n-Alkane decoration

Some of the single crystals were decorated with *n*-alkanes following the route as described by Refs. [19,20]. A detailed description of the experimental set-up can be found in [17]. Concisely, a small piece of PE was placed on an Ω-type wire in an evaporator and was uniformly decomposed. The resulting *n*-alkanes were condensed on the surface of the single crystal substrate and have formed rods by means of crystallization. After decoration, and in the preferred case, the rods were aligned and have formed specific patterns, which may reflect the local organization of the fold surface of the crystal.

2.3. Intermittent-contact atomic force microscopy (AFM)

AFM investigations of the morphology evolution of PE single crystals were performed using a Smena P47H (NT-MDT Ltd, Moscow, Russia), which is specially designed for scanning force microscopy measurements in a controlled environment, and which is equipped with a hot-stage. The hot-stage is controlled to a temperature stability of better than 0.1 °C. The symmetric design of the hot-plate fixation greatly reduces vertical expansion or contraction, leading to a low thermal drift during AFM imaging. The AFM was operated in intermittent mode in air using silicon cantilevers with spring constant $k = 11$–15 N/m, which are coated with a gold layer for higher laser beam reflectivity. Typical resonance frequencies are 210–230 kHz. The AFM has been calibrated using a 25 nm height standard grating produced by NT-MDT Ltd, Moscow, Russia. The temperature of the hot-stage integrated in the AFM was calibrated using standard test materials, such as azobenzol ($T_m = 68$ °C), acetanilid ($T_m = 115$ °C), phenacetin ($T_m = 135$ °C) and benzanilid ($T_m = 163$ °C).

Imaging of the single crystal samples was performed ex situ or in situ at real temperature. For ex situ experiments, the samples were annealed on a Linkam hot stage at the desired temperature for different times, and subsequently cooled to room temperature and investigated by AFM. In situ imaging was performed at the desired temperature. For all images the phase shift difference, represented by the different grey levels in the phase-contrast images, was kept constant. Acquisition of images always has started after 2 min of temperature equilibration, and time for complete imaging was in the order of 6 min.

3. Results

Annealing of solution grown PE single crystals near to but below the melting temperature forces the reorganization of the lamellae. Fig. 1 shows a representative AFM image obtained in height-contrast mode, and its corresponding line scan of a crystal annealed in air at 120 °C for 30 min. The initial crystal thickness is 11.7 nm for crystallization from solution at a temperature of 80 °C. After the annealing treatment, the image is recorded at room temperature. Obviously, the Swiss-cheese morphology can be observed. From the AFM line scan the height of the remaining lamella body, the thickened rims and the crystal edges can be measured quantitatively (Fig. 1(b)). For the present experimental conditions, the remaining lamella body still has a thickness of 11.7 nm, and the thickness of the rims and edges could be determined to be ~24 nm, which is approximately twice the initial thickness. These results are in accordance with TEM investigations of Roe et al., who have shown that the rims around the wholes are twice as high as the lamella body [4].

Fig. 2 shows a series of height- and phase-contrast mode images of single crystals. To follow their morphology evolution the annealing experiment has been performed in situ. Beside a single lamella (center) two stacked lamellae (left bottom) can be seen. Especially the phase-contrast images show clear contrast of the edges of the crystals. The as-crystallized single lamella has a central pleat and some corrugation lines indicating the initial hollow pyramidal shape of the crystal before deposition (Fig. 2(a) and (b)). For the crystallization conditions used the initial crystal thickness of the lamella is approximately 12.3 nm.

The appearance of the crystals did not change significantly for annealing temperatures up to 118 °C (Fig. 2(c) and (d)); only the corrugation lines close to the central pleat become

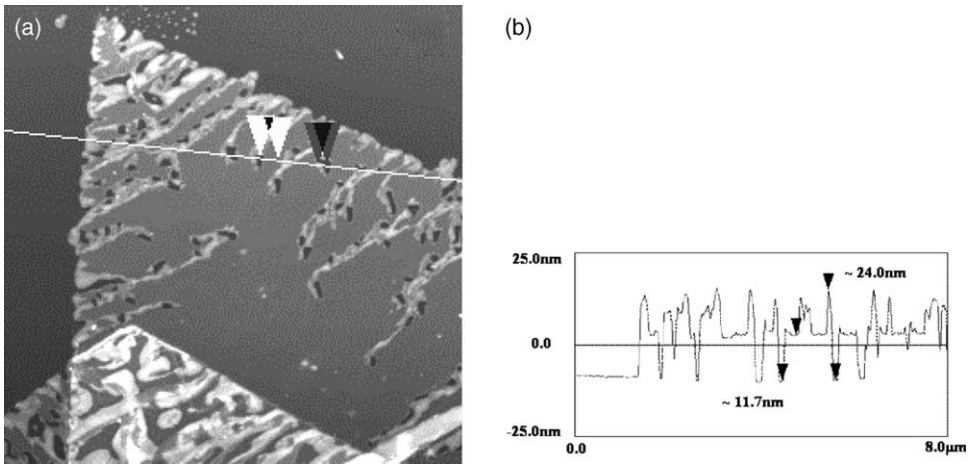

Fig. 1. (a) Height-contrast AFM image and (b) the corresponding line scan of a part of a PE single crystal after annealing at 120 °C for 30 min; scan size is 8 μm × 8 μm, the grey scale corresponds to a height difference of 100 nm.

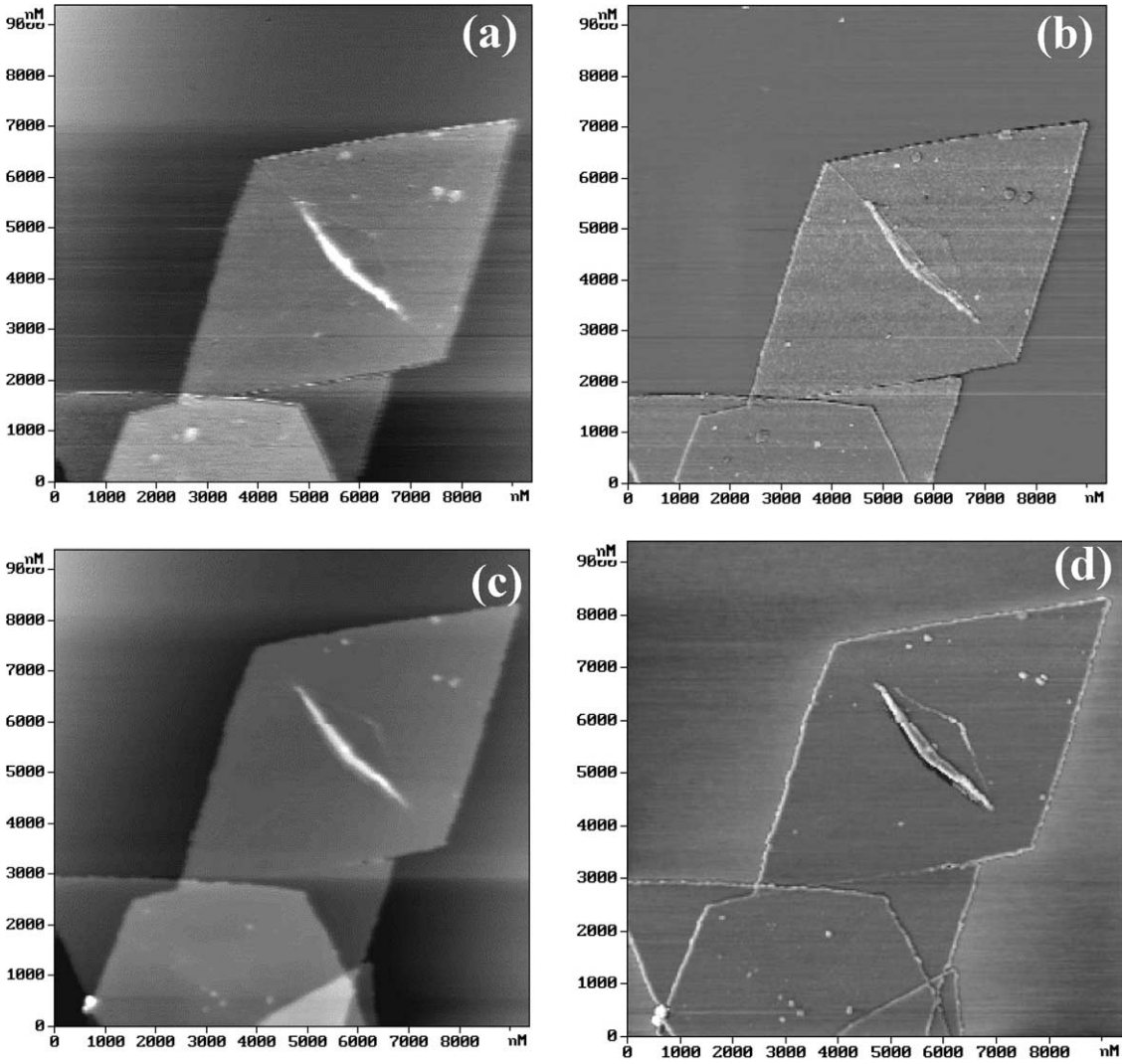

Fig. 2. Series of height- and phase-contrast images obtained during an in situ annealing experiment observed at real temperature. Annealing temperatures are (a and b) 25 °C, (c and d) 118 °C, (e and f) 119 °C, and (g and h) 120 °C, respectively. The grey scale corresponds to a height difference of 50 nm and the phase difference is 15°, respectively. Each image is acquired within ~6 min.

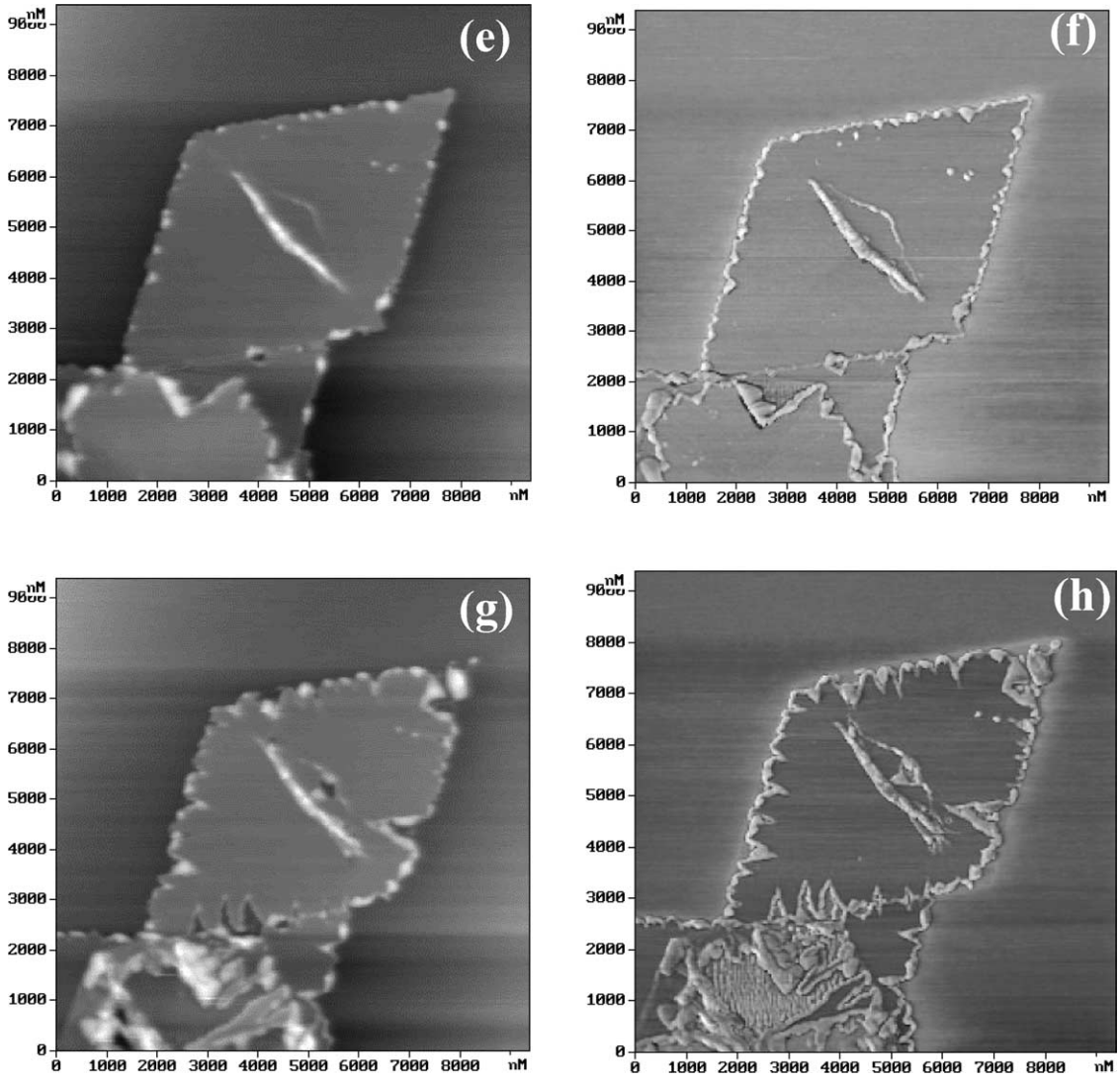

Fig. 2 (*continued*)

more pronounced. Annealing to 119 °C (Fig. 2(e) and (f)) results in a roughening and a distinct contrast enhancement of the lamella edges. The top lamella of the stacked crystals in the left bottom corner of the images shows a serrated, saw-tooth-like reorganization at the edge. For further annealing at 120 °C, all the edges of the three lamellae visualized in the images are serrated and form saw-tooth-like patterns (Fig. 2(g) and (h)). The crystal bodies of the two crystals in contact with the substrate still seem to be unchanged; in contrast the top one of the stacked crystals might be already melted and recrystallized, even at the temperature of 120 °C.

Fig. 3(a) is a high magnification height-contrast image of the edge region of the single lamella introduced in Fig. 2(g), and the corresponding topography line scan (Fig. 3(b)), which shows the increased thickness of the edge compared to the lamella core. The thickness of the edges can be measured to be approximately 30 nm, whereas the remaining and unchanged crystal body has still its initial thickness of about 12.5 nm. Similar observations based on in situ AFM investigations at real temperature have been published recently, indicating a melting/recrystallization process during annealing starting at the edges of the crystals [14].

Besides edge thickening, in our present in situ annealing experiment the formation of serrated, saw-tooth-like patterns at the edges of the crystals has been observed. Fig. 3(c) and (d) (Fig. 3(d) is a phase-contrast image corresponding to Fig. 3(b)) show in detail the regular organization of these serrated areas. Starting from the original {110} grow edge of the single crystal the two other sides of the triangular-shaped area are approximately parallel to the crystallographic *b*-axis and the ⟨310⟩ direction, which has an angle of 72–76° relative to the *b*-axis. The formation of the saw-tooth-like edges has been observed also for crystals initially grown at different crystallization temperatures and is independent of the substrate used (e.g. mica, oxidized Si-wafer, amorphous or crystalline carbon; results not shown) as indicated also by the reorganization behavior of the top of the two stacked crystals in Fig. 2(e) and (f).

For better understanding the origin of this reorganization behavior further experiments have been performed; single

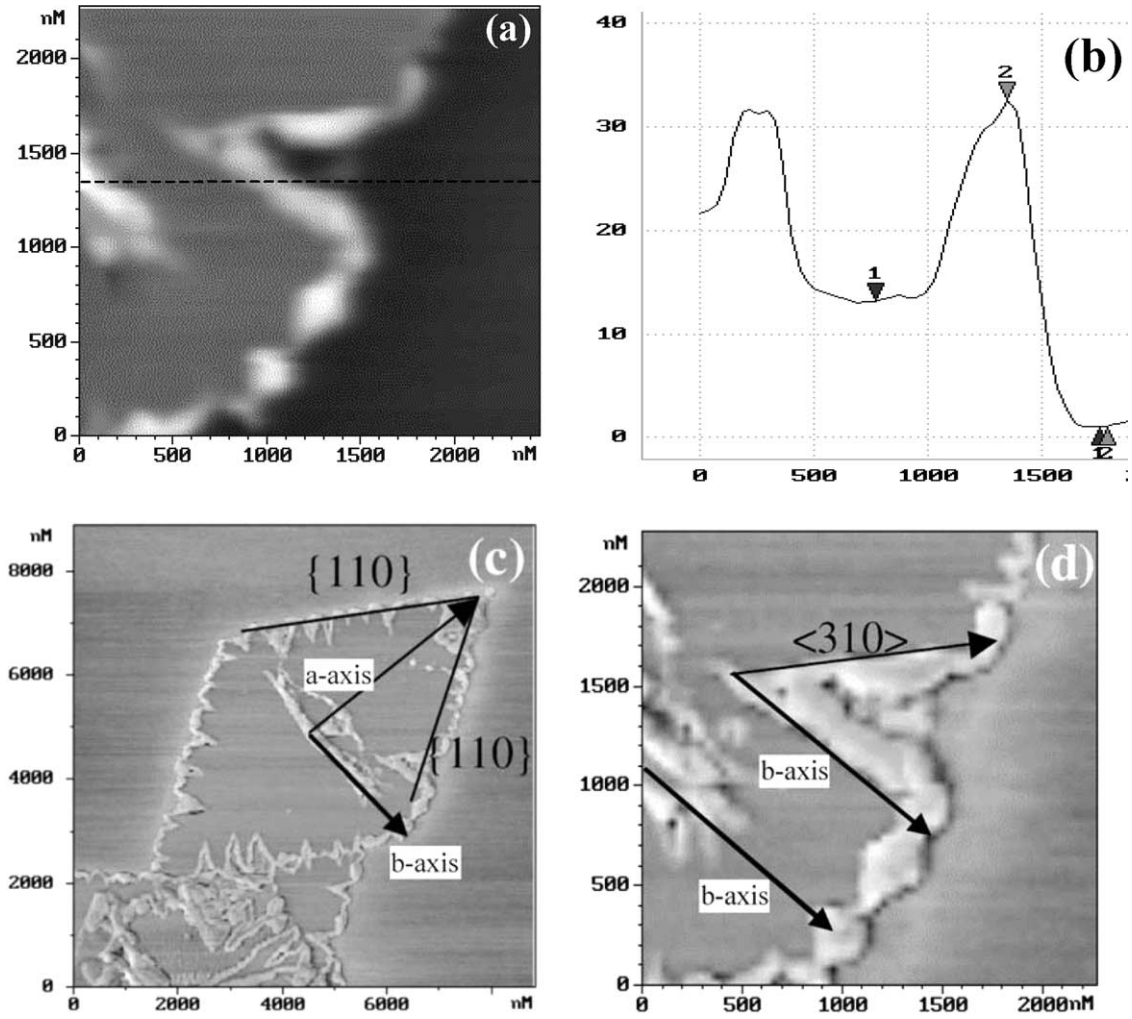

Fig. 3. (a) High magnification height-contrast image and (b) the corresponding topography line scan of the edge region of the lamella during an in situ annealing experiment at 120 °C; (c) overview (same as Fig. 2(h)) and (d) high magnification phase-contrast images showing the characteristic crystallographic directions found after annealing at 120 °C.

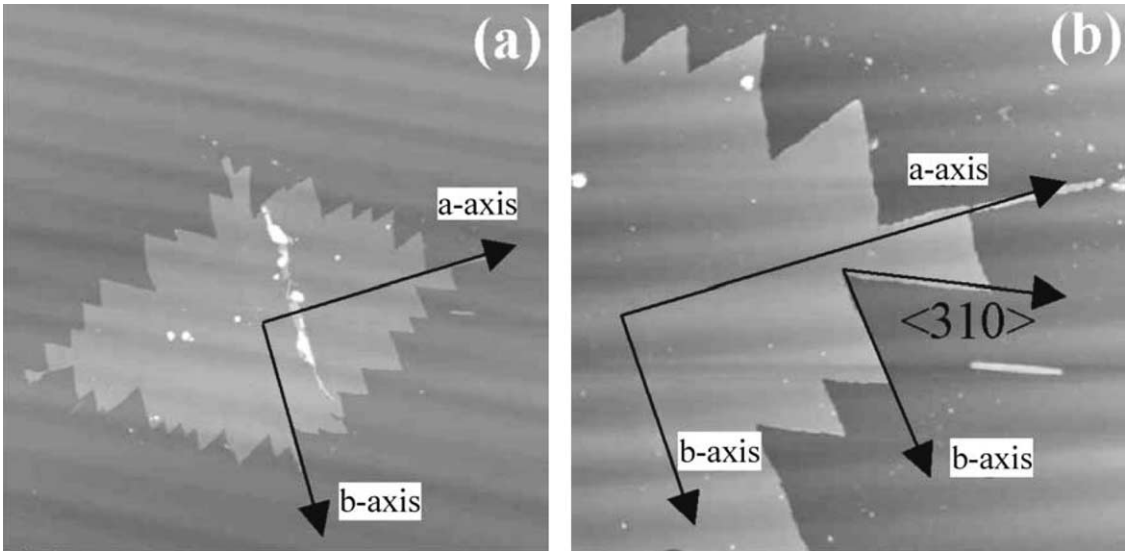

Fig. 4. (a) Low magnification and (b) high magnification height-contrast AFM images of a PE single crystal after annealing in decalin at 90 °C; scan sizes are 20 μm×20 μm and 6 μm×6 μm, respectively, the grey scale corresponds to a height difference of 100 nm.

crystals are transferred from the growing solution to decalin, dispersed, annealed and subsequently deposed on mica. Fig. 4(a) shows a single crystal, which is annealed at a temperature of 90 °C, which is slightly below its dissolution temperature in decalin. Still, the central pleat and the original lozenge shape of the crystal are detectable. At higher magnification evidently the saw-tooth-like edge patterns are present having the same crystallographic orientation as discussed for the annealing experiments in air: one edge is approximately parallel to the ⟨010⟩ axis of the single crystal, and the other edge is parallel to the ⟨310⟩ direction (Fig. 4(b)). In contrast to the experiments performed in air, annealing in solution does not result in a thickening of the edges; only parts of the crystal are dissolved, and the characteristic saw-tooth patterns are formed. This might be another indication that the edge thickening observed for annealing in air is caused by a melting/recrystallization process.

It is expected that the initial organization of the single crystals as grown from solution strongly influences the morphological evolution during the described experiments. Therefore, further experiments are performed to gain information on the local organization of the as-grown lamellae; observation of the fold surface of the crystals after *n*-alkane decoration was performed using high-resolution AFM.

Fig. 5(a) and (b) shows the height- and phase-contrast images of a lozenge-shaped solution-grown single crystal after *n*-alkane decoration. In both images the four (110) growing sectors are evidently visible. The contrast in the phase image is enhanced due to the pronounced phase shift difference between the sectors, which is caused by the different orientations of the *n*-alkane rods with respect to the AFM tip scanning direction. At the first glance, the *n*-alkane rods are aligned perpendicular to the {110} growth front in each sector.

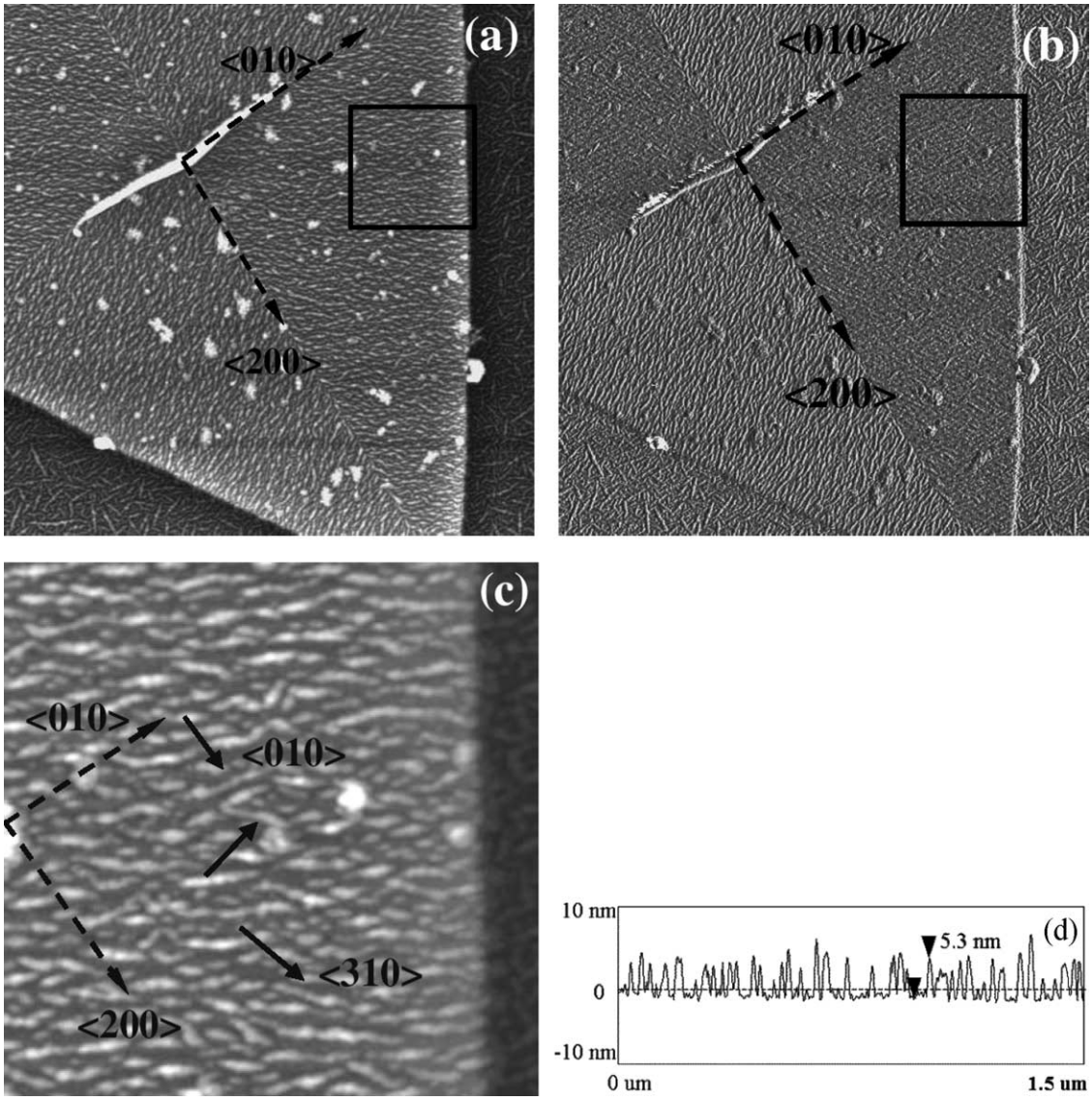

Fig. 5. (a) Height-contrast and (b) phase-contrast AFM images of PE single crystal decorated with *n*-alkane rods; (c) high magnification height-contrast AFM image and (d) the corresponding topography line scan of the area marked by the square in the images (a) and (b). Arrows indicate important crystallographic directions. Scan sizes are 8.0 μm×8.0 μm for (a) and (b), and 1.5 μm×1.5 μm for (c), respectively.

The high magnification image, which is recorded at the position marked by the square in the images 5a and b, shows more details of the local organization and orientation of the *n*-alkane rods (Fig. 5(c)). Because of the low amount of decorating material used, individual rods can be easily distinguished, which have average heights of 5.3 nm and widths of 10 nm, respectively, (Fig. 5(d), topographic line scan of Fig. 5(c)). Most of the rods are aligned perpendicular to the {110} growth plane of the sector, however, apparently some of the rods are arranged in a different fashion. Accurate orientation analysis has demonstrated that these rods are aligned almost parallel to the ⟨010⟩ or to the ⟨310⟩ directions, respectively.

4. Discussion

The presented data are the results of careful AFM measurements performed at various conditions: the influence of oscillation amplitude and applied force used in intermittent-contact mode (from soft to hard tapping), scan rate and direction as well as accurate calibration of the *x*-, *y*- and *z*-axes of the scanner used and the temperature control of the heating stage guarantee that the observed morphological features (e.g. directions of the *n*-alkane rods, direction of the edge borders during/after annealing) are authentic and the quantitative height measurements are reliable.

Because the in situ annealing experiments are performed at real temperature using single crystals deposited on a substrate, the substrate may influence the reorganization behavior observed. However, we have used several different substrates and the separated crystals are randomly distributed on the substrate; and always a similar reorganization of the crystals during in situ annealing experiments has been observed. Moreover, crystals annealed in a solvent show similar morphological features so that an influence of the substrate can be neglected.

The decoration experiments have shown the presence of *n*-alkane rods being aligned almost parallel to the ⟨010⟩ or ⟨310⟩ directions not only at the edges of the crystals; these rods are distributed over the entire crystal surface, which indicates that a possible high defect concentrations at the edges of the crystals is not the reason for the formation of the saw-tooth-like edge pattern. Besides regular back and forth folding of the chains to form the four {110} growth fronts of lozenge-shaped single crystals, fold defects should be always present and have to be taken in account to explain the presented results. On basis of previous dark-field TEM studies it is suggested that within one {110} growth sector micro-sectors are present having different fold directions [21–24]. Mainly internal boundaries in ⟨010⟩ and ⟨200⟩ direction could be visualized. At these boundaries folds might be rotated slightly about their normal. These fold asymmetries immediately might result in the formation of {310} fold planes, as present, e.g. in dendritic grown crystals. Further, the occurrence of fold irregularities forces the formation of domains within a (110) sector, which have the same fold pattern as the initial irregularity, parallel to the ⟨010⟩ or ⟨310⟩ direction.

Because of the additional intra-sector boundaries and the imperfect folding of the micro-sectors their thermal stability during annealing experiments is lower than that of the regular folded micro-sectors, which causes local melting or reorganization of these irregular folded domains, especially when they are located at the edges of the single crystals. This feature might explain the observation of the saw-tooth-like edge patterns after annealing of single crystals in air or in dispersion (Figs. 2–4). However, it cannot explain the large size of the reorganized saw-tooth-like areas.

5. Conclusions

In the present part of our study, the morphological evolution of solution grown polyethylene single crystals during annealing has been analyzed. Beside the common behavior, the formation of Swiss-cheese and picture frame morphology at annealing temperatures below but near to the melting temperature of the crystals, a novel morphological feature has been observed: the reorganization of the crystal edges to form a saw-tooth-like edge pattern. With increasing annealing temperature, the edges of the crystals become more and more serrated, both annealing in air or on a solvent. The saw-tooth edge patterns are initiated by the presence of nano-sized fold defects. These fold defects are detected by applying the technique of *n*-alkane decoration on the initial as-grown single crystals. Both the edges of the saw-tooth patterns as well as some *n*-alkane rods are aligned almost parallel to the ⟨310⟩ and ⟨010⟩ crystallographic directions. Besides the observation of the reorganization behavior, the performed experiments indicate high chain mobility within the crystals below their melting temperature.

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