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Two types of graphoepitaxy of tellurium onto uniaxially-oriented polyethylene

F. KATZENBERG, I. LIEBERWIRTH, J. PETERMANN*
Lehrstuhl für Werkstoffkunde, FB Chemietechnik, Universität Dortmund, Emil-Figge-Str.66, 44221 Dortmund, Germany
**E-mail: petermann@chemietechnik.uni-dortmund.de*

The growth of vapour-deposited tellurium on uniaxially oriented polyethylene substrates of various crystallinity is examined. Two orientations of the tellurium appear, depending apparently on the crystallinity of the respective substrate. That these individual orientations are of various origins is concluded from our investigations. On totally amorphous films, obtained after electron irradiation of the substrate films, only one preferred orientation of the Te remains in accordance with our model, which is presented to explain the mechanisms of the respective orientations of tellurium onto polyethylene. © *1998 Kluwer Academic Publishers*

Introduction

The orientation of tellurium and other metals (Sn, Sb, Bi, Tl, etc.) on uniaxially oriented polymer substrates (PE, PP, sPS, etc.) [1, 2, 3] is supposed to be an "artificial" epitaxy (graphoepitaxy) [4, 5, 6], because lattice matching in accordance with the conventions of L. Royer [7, 8] can be excluded for most of the systems. Artificial epitaxy occurs on surface steps of the substrate by a preferred nucleation of the deposit and has been observed on crystalline substrates having monoatomic surface-steps [9, 10] as well as on amorphous substrates having surface steps up to a few nanometers in height [11, 12]. The question remains, which kind of surface steps on the polymer substrate are responsible for the appearance of the artificial epitaxy. Jandt et al. [13] supposed strain-induced ledges at the amorphous/crystalline interfaces of the lamellar morphology perpendicular to the molecular direction (Fig. 1) and processing induced ridges along straining direction. Consequently, two different (perpendicular) preferred orientations of the Te deposits are expected and observed. It is the purpose of this investigation, to differentiate between several surface topologies, which may cause artificial epitaxies by varying the degree of crystallinity of the substrate.

Experimental

The uniaxially oriented semi-crystalline polyethylene substrates were prepared according to the Petermann-Gohil method [14]. Commercial HDPE (Lupolen 6021D) and LDPE (Lupolen 1840H) granulate, both from BASF AG Ludwigshafen (Germany), was dissolved in xylene (0.5 wt %) at a temperature of 423 K. Some droplets of the solution were spread on a preheated glass slide, where the solvent evaporated. The temperature of the glass slide was heated well above the crystallization temperature of the polymer. From the remaining polymer melt a highly oriented ultra-thin polymer film was drawn using a motor-driven cylinder. Small sections ($3 \times 3\,\mathrm{mm}^2$) were mounted onto conventional copper TEM-grids. Furthermore, some of these uniaxially oriented HDPE films were irradiated by an electron beam using a radiation dose of about 400 $\mathrm{C/m}^2$ at 200 kV. The substrates were subsequently vapour-deposited with 25 nm tellurium at a substrate temperature of 383 K and a nominal deposition rate of 1nm/min in a Balzers BAE080T vapour-deposition facility under high-vacuum conditions (1×10^{-3} Pa). The nominal layer thickness as well as the deposition rate were monitored with a quartz crystal oscillating microbalance. The subsequent TEM examinations were carried out in a Philips CM200 at 200 kV. The crystallinity of the LDPE and HDPE was estimated from a quantitative enthalpy-analysis in a TA instruments DSC.

Results

It is known, that Te crystallizes at elevated temperatures ($>$353 K) in shapes of needle-like crystals, with the c-axis of the hexagonal lattice of the Te in needle direction [15, 16, 17, 18]. Therefore, preferred orientations of the Te crystals already can be recognized in bright field (BF) TEM micrographs. Fig. 2 shows Te crystals on oriented HDPE and LDPE substrates, obtained under exactly the same conditions (substrate temperature, deposit thickness, evaporation rate). The molecular directions of the substrate films are indicated by an arrow. Two preferred orientations can be seen: parallel and perpendicular to the molecular directions of the substrate films. Furthermore, the sizes of the Te crystals differ significantly on the HDPE and LDPE substrates, but even more important, the number of Te crystals parallel to the molecular direction of the substrate film is considerably higher on the HDPE. More precisely, the orientation of the Te crystals can be monitored on the

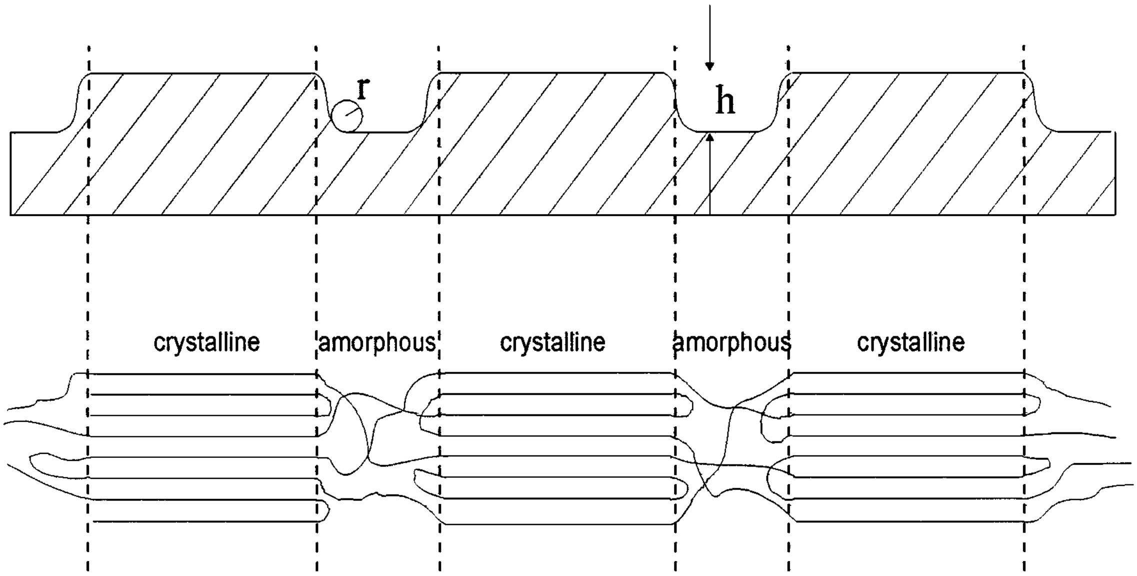

Figure 1 Sketch showing super-molecular surface steps of a melt-spun, ultra-thin uniaxially oriented polyethylene substrate, steps which are caused by protrusion of the crystalline parts from the rest of the surface.

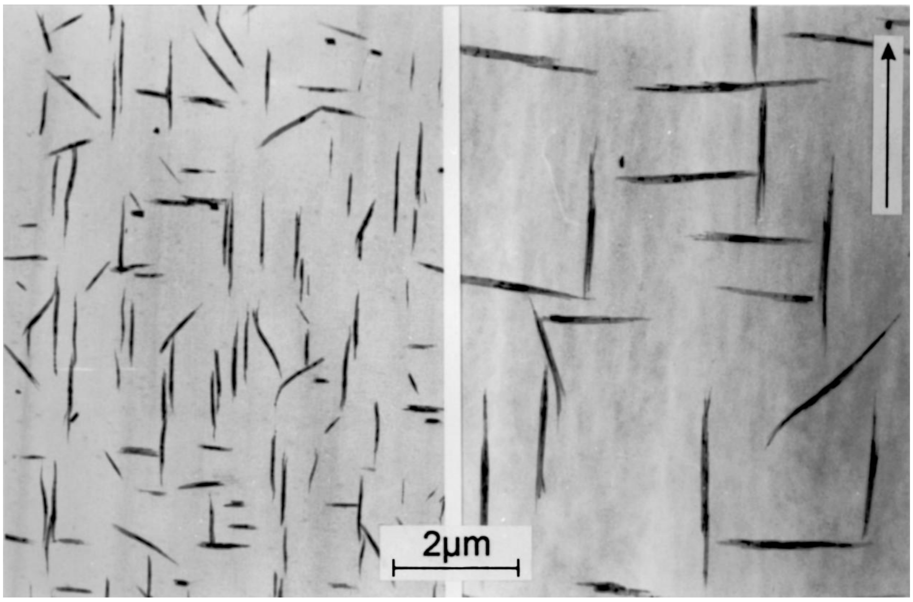

Figure 2 TEM brightfield micrograph of an uniaxially oriented HDPE- (left) and LDPE-substrate (right) evaporated with 25 nm tellurium at a substrate temperature of about 483 K. Two preferred crystallographic orientations of the tellurium needles, parallel and perpendicular to the molecular c-directions of the substrates (indicated by an arrow) are visible.

electron-diffraction diagrams (Fig. 3). Te-(003) diffraction spots can be seen either parallel or perpendicular to the (002) diffraction spots of the PE. Except for the $(003)_{\mathrm{Te}}$ spots, all other electron-diffraction spots belong to the oriented PE-substrate film. Speaking more quantitatively:

- On the HDPE substrate, the [0 0 1]-direction of the tellurium orients mostly parallel (approx. 80%) to the molecular c-direction of the substrate (Fig. 2 (left)). Both preferred orientations are also visible in the corresponding electron-diffraction pattern (Fig. 3 (left)), in which the $(003)_{\perp}$-reflection appears very weakly.
- On the LDPE substrate, the two preferred orientations appear however in a ratio of 50/50 (Fig. 2 (right)). The corresponding electron-diffraction pattern (Fig. 3 (right)) also exhibits both preferred orientations. The $(003)_{\perp}$-reflection of the tellurium appears in the shape of an arc, whereas the $(003)_{\|}$-reflex is visible as a discrete diffraction spot.
- Only the preferred orientation perpendicular to the original c-direction of the polymer substrate appears on the amorphous HDPE (Fig. 4 (left)). No tellurium needles, oriented parallel to the original c-direction, are visible. The electron-diffraction pattern (Fig. 4 (right)) reveals expanded reflections, which indicate a lower degree of tellurium-orientation. Due to the amorphization of the PE during the irradiation, no diffraction spots of the PE are visible.

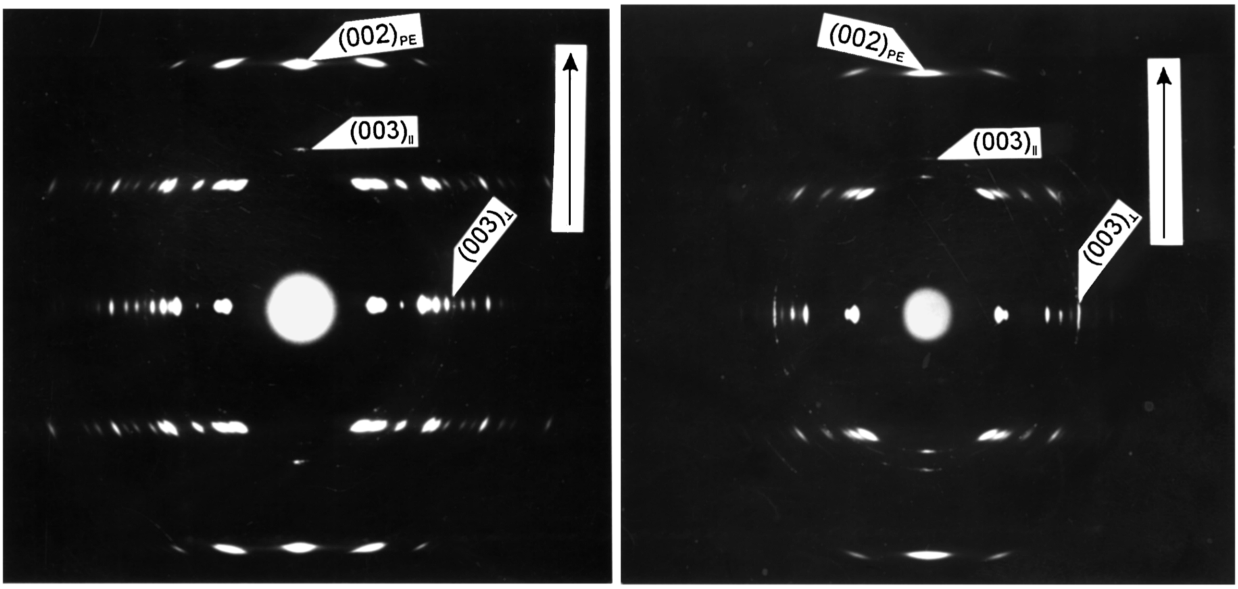

Figure 3 Corresponding electron-diffraction patterns of Fig. 2. Both preferred orientations of the tellurium on uniaxially oriented HDPE (left) and LDPE (right) can be seen. The molecular c-directions of the polymer substrates are indicated by arrows. Nearly all reflections (except the indicated) belong to the PE-oriented substrate film.

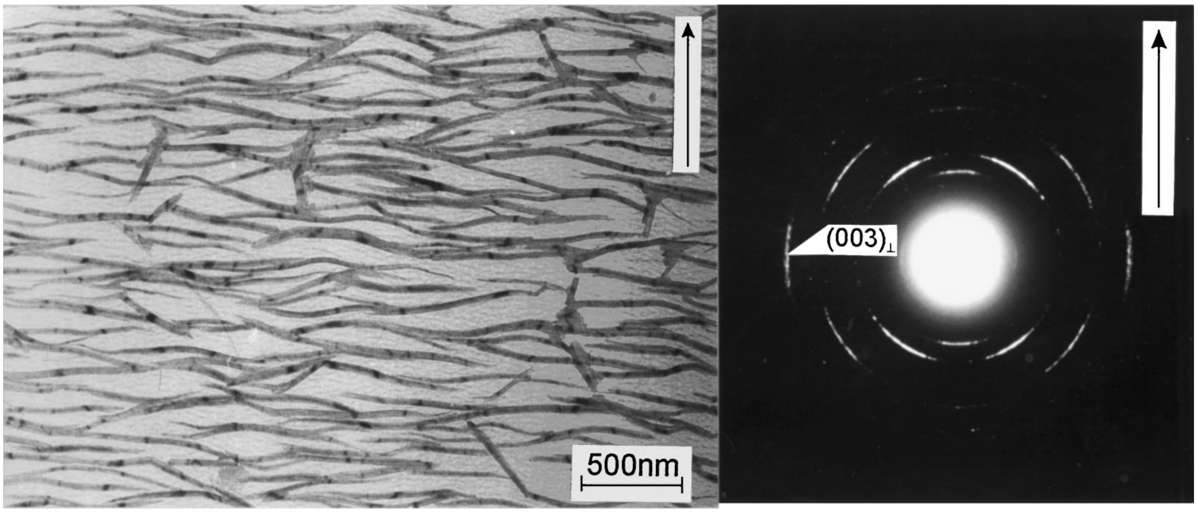

Figure 4 TEM brightfield micrograph (left) and corresponding electron diffraction pattern (right) of an electron beam irradiated and 100% amorphous polyethylene substrate, which is evaporated with 25 nm tellurium at a substrate temperature of 483 K. All of the tellurium needles exhibit an orientation perpendicular to the super-molecular orientation of the polymer substrate. The original molecular c-direction is indicated by an arrow.

Discussion

Because the appearance of the preferred orientation parallel to the molecular c-direction is apparently proportional to the crystallinity of the polyethylene substrate, the assumption of the following hypothesis seems to be reasonable: Both observed orientations of tellurium onto polyethylenes are graphoepitaxial orientations, in which, however, the respective orientations of the needle-crystals are of different origins. It is supposed, that the [0 0 1]-direction of the tellurium crystals parallel to the c-direction of the polyethylene is initiated by an alignment along molecular steps (Fig. 5a) on the surface of the polymer crystals (molecular surface topology). The orientation of the tellurium [0 0 1]-direction perpendicular to the c-direction of the substrate may be caused by alignment along super-molecular surface-steps of the amorphous/crystalline interface (Fig. 5b) of the stacked lamellars morphology (super-molecular topology). In polyethylene, the super-molecular surface topology remains after irradiation and therefore, the graphoepitaxy caused by this structure remains after amorphization, while the molecular steps disappear. Process-induced surface steps seem to play no role in the preferred nucleation events, because they also remain after irradiation but do not induce a preferred orientation in processing (molecular) direction.

During the formation of the preferred orientation along super-molecular topologies, not only preferred orientation but also preferred growth selection of the crystals may be involved (Fig. 5c). Small randomly oriented Te needle-crystals, hindered in growth by the protruding polymer-crystals, may be rotated by growth along their hexagonal c-axis in the direction of the super-molecular surface topology of the polymer substrate.

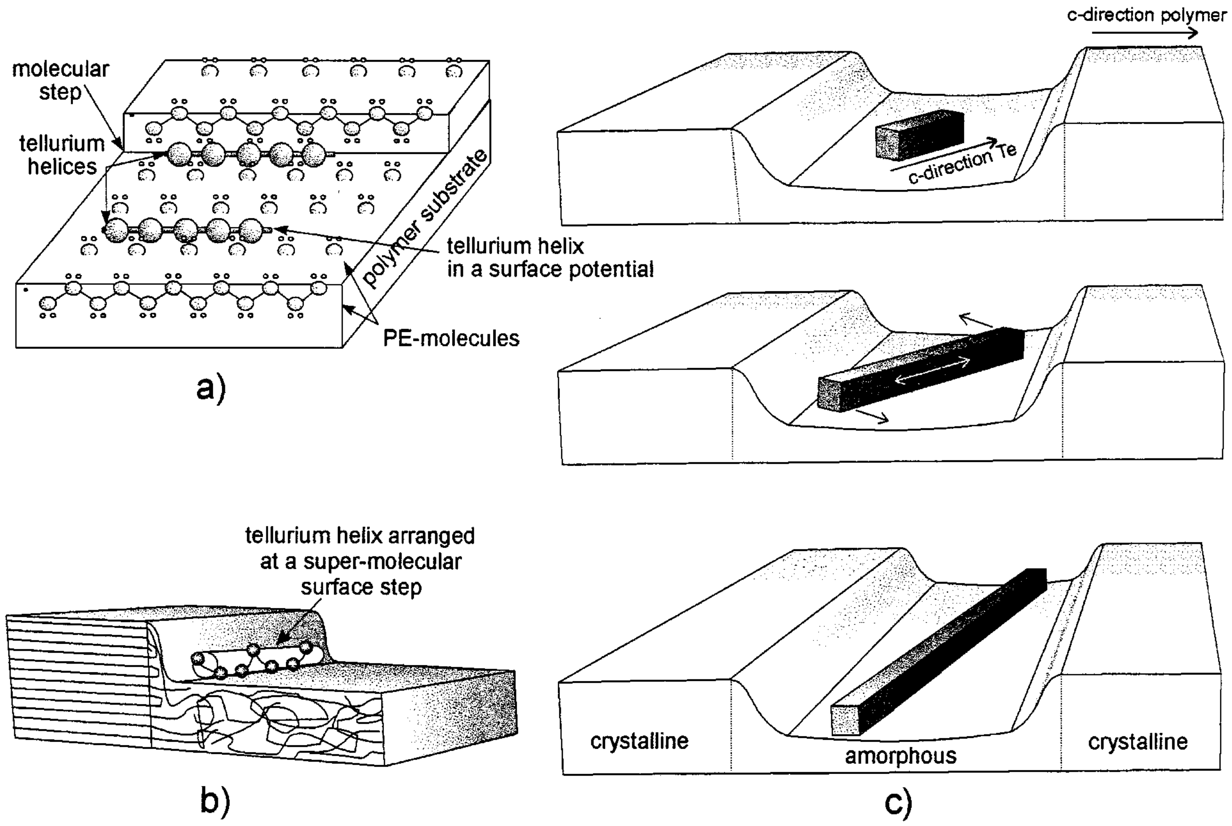

Figure 5 Sketches elucidating the different conceivable mechanisms of tellurium orientation: (a) by alignment along molecular steps on polymer crystals, (b) by alignment along super-molecular steps of the stacked lamellae morphology and (c) by rotation of small statistically oriented tellurium needles due to needle-crystal growth.

The different average sizes and densities of tellurium needles on LDPE- and HDPE-substrates give information about the surface diffusion of tellurium-atoms (chains), a diffusion which is higher on LDPE than HDPE [12].

Acknowledgement

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