Decoration of the Fold Surfaces of Polyethylene Single Crystals with Tellurium and Tin

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ABSTRACT: The folded-chain surfaces ((001) surface) of polyethylene (PE) single crystals were decorated with tin (Sn) and tellurium (Te) by physical vapor deposition. Since it is known that Sn and Te particles grow epitaxially on (*hk*0) lattice planes of PE, the attempt is made to find evidence for crystallogrphic order in the fold surfaces of PE single crystals from a crystallographic register of the metal particles compared to the PE crystal lattice. Sn particles do not give such evidence, but Te particles align with their [001] lattice direction parallel to the [020] and [110] lattice directions of the PE single crystals. This register is found only under specific experimental conditions.

1. Introduction

Investigations of polymer surfaces by the decoration technique has been the subject of many activities.[1-5] Initially, the method was used to study surface topologies of ionic crystals.[6] Metal atoms, mostly gold (Au), were evaporated as an extremely thin layer onto the surface of a crystal, and by preferred nucleation of the metal atoms on surface steps, topologies even of atomic height were decorated with small Au spheres ($\approx$3 nm).

Recently, it was reported that the decoration of cleavage surfaces of KCl with tin (Sn) particles not only decorates the monoatomic steps but also leads to an epitaxial crystallographic lattice relationship between the surface atoms of the KCl crystals and the Sn particles.[7] Further on, in parallel experiments using NaCl instead of KCl, similar effects were observed, but from the misfit calculations, pure epitaxy was ruled out and graphoepitaxy was used to explain the experimental results. In graphoepitaxy, anisotropic surface energies lead to a preferred lattice orientation during nucleation. The phenomenon can be observed even on surfaces of amorphous materials structured by microlithography.[8,9]

Anisometric molecules (polyethylene (PE) and paraffin) were used to decorate the fold surfaces of PE and paraffin single crystals,[5,10] and physical vapor deposition of some metals on uniaxially oriented thermoplastic polymers[11] resulted in, besides decorational effects, crystallographic lattice orientation relationships between the polymer and metal crystals. Additionally, the anisotropic growth of some metals like tellurium into whisker-shaped crystals with the long axis of the whiskers parallel to the polymer chain direction can give further information on surface structures of polymers.

Hence, information about surface topologies and structures can be obtained by the sample technique of evaporating small amounts of metals onto the surfaces under investigation and analyzing the nucleation, growth, and orientation of the metal particles. Experiments were performed using the fold surface of PE single crystals for the investigations. The folded chain structure of the PE single crystals has been studied extensively in the past by various methods,[12] and it is now a general belief that the chain folds in the surface of the PE single crystals have a somehow ordered structure.[5,12] It is the purpose of this paper to demonstrate that the metal decoration technique can give additional information compared to the Au decoration when metals that exhibit, besides the preferred nucleation, preferred orientational and growth effects are used.

2. Experimental Section

Single crystals of HDPE with low ($M_w \approx 8 \times 10^3$) and high molecular weights ($M_w \approx 3 \times 10^5$) (A409 from Hüls AG and Lupolen 6041D from BASF-AG, respectively) were prepared from 0.001 wt % xylene solutions by isothermal crystallization at 85 °C. The Te was obtained from Aldrich Chemical Co. and Sn from Merck. Single crystals to be decorated were taken from the xylene suspensions on carbon-film-supported TEM grids and mounted onto a heating stage (accuracy ±1 °C) of a Balzers (BSV 080) high-vacuum evaporation unit. Sn and Te were evaporated from tungsten boats at 10^{-5} mbar.

The samples were investigated in a transmission electron microscope (Philips 400T) operated at 100 kV.

3. Results

3.1. Sn on PE Single Crystals. In Figure 1 (top), an A409 single crystal decorated with a 13 nm thick layer of Sn is seen. The single crystal was kept at room temperature during the evaporation. The Sn crystals which are covering the surface of the single crystal are somewhat larger than Sn crystals on top of the carbon-support film. Figure 1 (bottom) shows the corresponding electron diffraction pattern. From the intensities of the Debye–Scherrer rings a statistical distribution of the Sn crystals is concluded. Closer inspection reveals that not all expected (*hkl*) rings of the tetragonal β-Sn are visible on the diffraction pattern, resulting from the fact that the (100) crystallographic plane of the β-Sn is the contact plane to the surface of the PE single crystal (polar orientation). The same orientation of the β-Sn particles is seen on the supporting carbon film. Qualitatively, the same results were obtained when single crystals of Lupolen 6041D were used, irrespective of annealing up to a temperature of 115 °C and subsequent decoration at room temperature or at elevated temperatures (up to 115 °C) of the carbon-support films.

3.2. Te on PE Single Crystals. Somewhat different results were obtained when Te was used as the decorating

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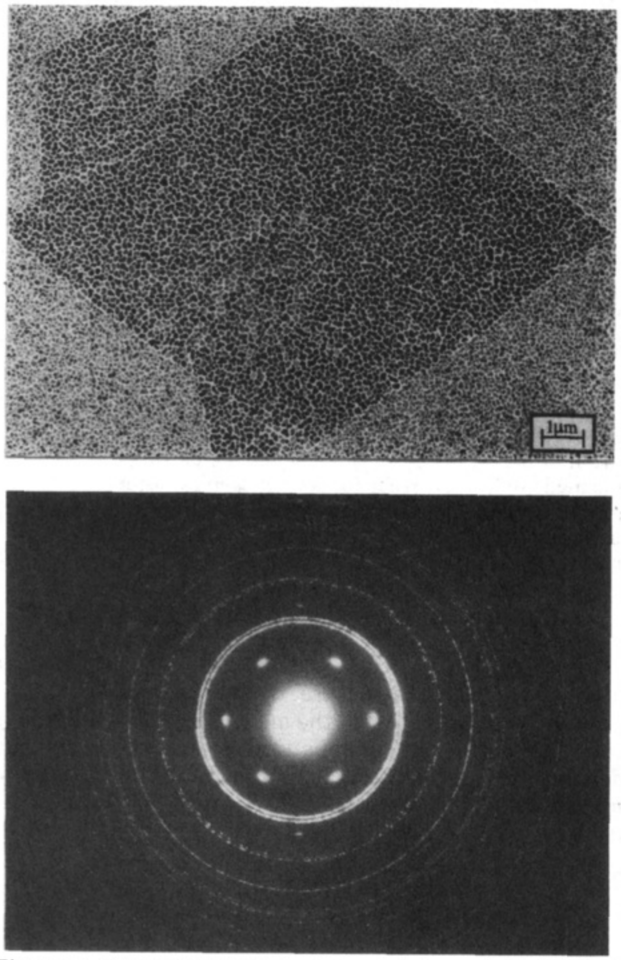

Figure 1. (Top) PE (A409) single crystal, decorated with Sn at room temperature and (bottom) its electron diffraction pattern.

metal. The experimental parameters (annealing temperature and temperature of the supporting carbon film during decoration) were the same as with Sn.

In Figure 2 (top), a nonannealed single crystal is seen, decorated at room temperature, and Figure 2 (bottom) is the corresponding electron diffraction pattern. As in the case of the decoration with Sn, the Te particles have different shapes and sizes on the carbon supporting film compared to those on the surfaces of the PE single crystals. Also, the diffraction pattern from the Te shows random orientation. Contact planes of the Te to the PE single crystal surfaces are all (*hk*0) planes (as on the carbon supporting film). Annealing *A409* single crystals at 105 °C for 1 h and evaporating the Te onto the single crystal keeping the supporting carbon film (and the surface of the single crystal) at the same temperature result in a surface decoration of the PE crystals with whisker-like shaped Te particles having their long axes parallel to the [020] direction of the PE single crystals (Figure 3 (top)). From the electron diffraction patterns (Figure 3 (bottom)) it can be concluded that the [003] direction of the Te is parallel to the [020] direction of the PE; contact planes can be all (*hk*0) planes of the Te. The decoration of the annealed A409 single crystals at room temperature leads to the same results as for nonannealed crystals (Figure 2). When the PE single crystals are annealed close to their crystallization temperature ($\approx$85 °C) and the Te is evaporated at this substrate temperature, a less pronounced but clearly visible orientation of the Te is observed (Figure 4). The orientational effect was found to be independent of the annealing time. The onset of the orientational decoration of the Te on the A409 PE single

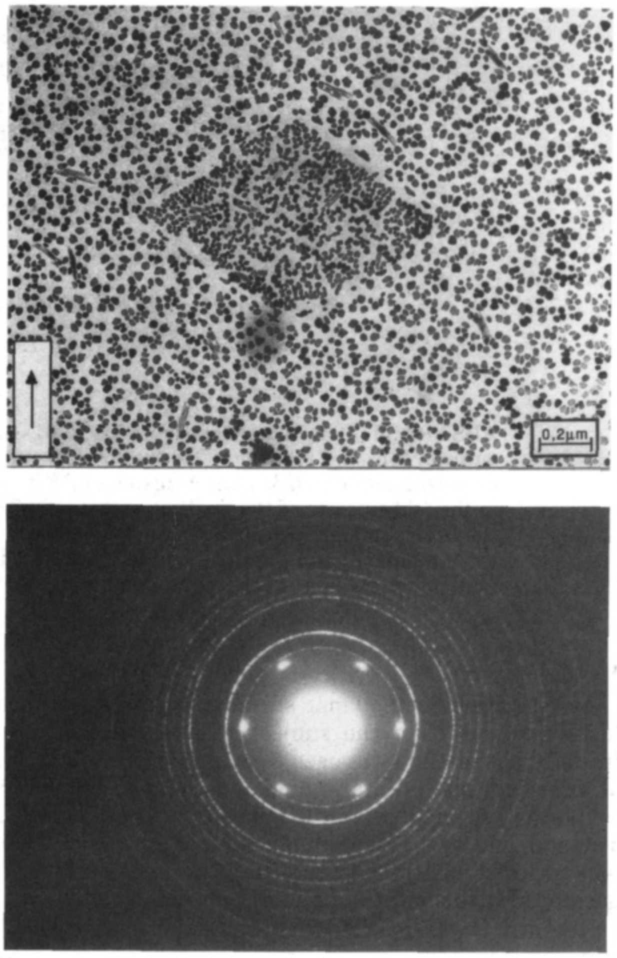

Figure 2. (Top) PE (A409) single crystal decorated with Te at room temperature. The arrow indicates the [020] direction of the single crystal. (Bottom) electron diffraction pattern of a PE (A409) single crystal, decorated with Te at room temperature.

crystals starts at a substrate temperature of about 80 °C, and the perfection of the orientation is increased with increasing substrate temperature.

When PE single crystals from *Lupolen 6041D* are decorated under the experimental parameters used for A409 crystals, the whisker-like growth of the Te particles is maintained but the long axes of the whiskers are oriented along the [110] and [020] directions of the PE single crystals (Figure 5).

Finally, some of the A409 single crystals, which were annealed at 105 °C, were subsequently irradiated with 100 kV of electrons to their end point dose (no more crystalline reflections are visible in the electron diffraction patterns) and decorated at a substrate temperature of 105 °C (Figure 6). Whisker-like Te particles are seen with their long axes randomly distributed in the surface of the crystals. The same experimental observations account for the Lupolen 6041D PE single crystals.

Decoration experiments on normal paraffin ($C_{32}H_{66}$) single crystals at room and elevated temperatures of the substrates (maximum temperature used was 60 °C) failed to exhibit orientational decoration of the Te particles, which is propably due to the too low temperature of the substrate (see above).

4. Discussion

Evidence of some long-range order of the chains in the fold planes of PE single crystals has previously been obtained from decoration experiments in which long-chain molecules were evaporated onto the fold surfaces.[5,10] The

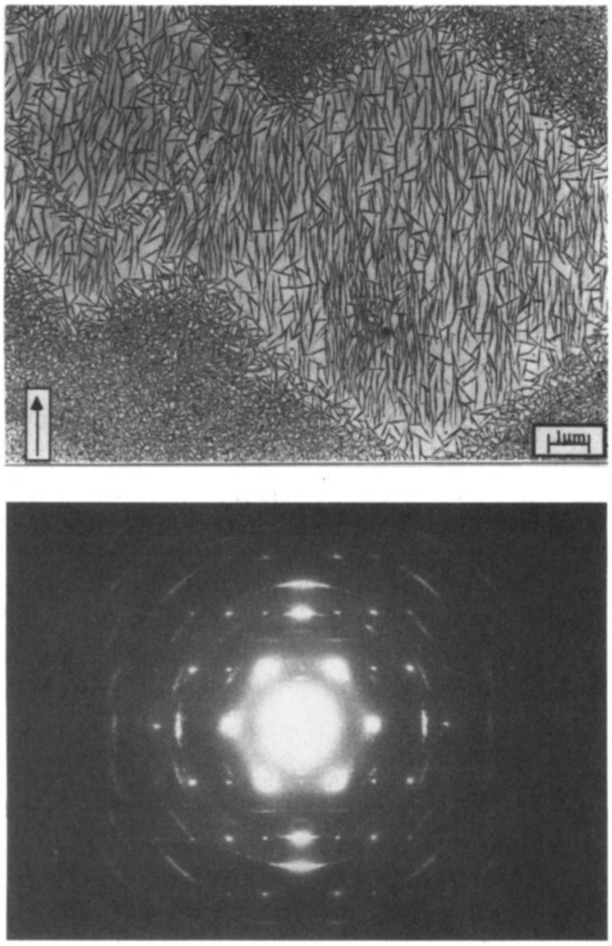

Figure 3. (Top) PE (A409) single crystals decorated with Te at 105 °C and (bottom) their electron diffraction pattern.

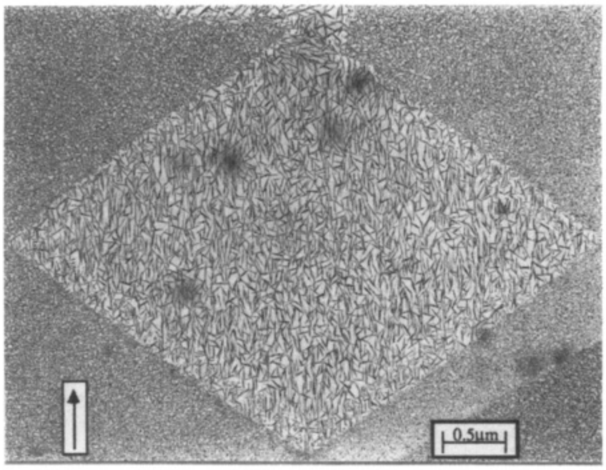

Figure 4. PE (A409) single crystal decorated at 90 °C.

interaction forces between the long-chain molecules and the macromolecules on the fold surface average over the distance of the length of the long-chain molecule and, hence, do not give any information about nearest-neighbor order. Using smaller molecules or single atoms in the decoration technique may give additional information about the nearest-neighbor order. In our experiments with the Te particles, information about the existence of adjacent or nonadjacent reentry of the macromolecules in the fold surface may be obtained. The metals Sn and Te were chosen because they exhibit lattice orientational relationships when evaporated onto (*hk*0) crystal surfaces of uniaxially oriented PE.[11]

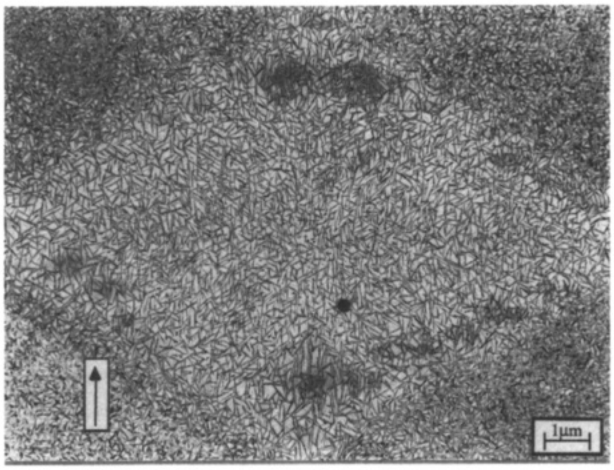

Figure 5. PE (Lupolen 6041D) single crystal, decorated at 115 °C.

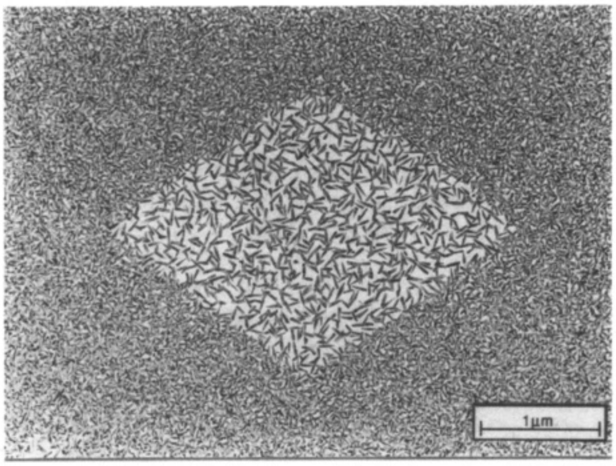

Figure 6. PE (A409) single crystal, electron irradiated to its final end point dose and subsequently decorated with Te at 105 °C.

The decoration of the fold surfaces of PE single crystals with Sn does not give any indication of order in the fold surface. The different sizes of Sn particles on the carbon and PE result from different critical nucleation sizes and/or different surface diffusion rates of the Sn atoms on both surfaces. The polar orientation of the Sn particles is a common feature of Sn on many surfaces including the carbon supporting film. Surface steps, for example, the boundaries between the carbon and the PE single crystals, are not very well decorated with the Sn particles.

The remarkable results are the decoration of the single crystals with the Te whisker-like particles at substrate temperatures above 80 °C. The whisker-like shape of the Te particles at elevated temperatures is independent of the substrate and a property of the crystal growth mechanism.[13] But their parallel alignment is certainly induced by the PE single crystal's surfaces. Since there is different alignment on the single crystals of A409 and Lupolen 6041D, a difference in surface structure of the low and high molecular weight PE single crystals must be concluded. Due to the shorter length of the chains in the low molecular weight PE, the orientation of the Te whiskers may be influenced primarily by chain ends located at the surface, while in the higher molecular weight PE the fold directions are the main contribution to the whisker orientation. The experiments of the evaporation at 80 °C without prior annealing indicate that the increase of the orientational effect of the Te particles at elevated temperatures results from an improved decoration at higher temperatures[11] rather than a reorganization of the fold surfaces. The sectorization[14] of the PE single crystals, which has been made visible by the decoration with long-chain molecules, has not been observed in our experiments. The sectorization is a result of a crystallographic direction of the chain folds, but adjacent reentry of the PE molecules is not a necessary assumption for it. With paraffin or short-chain polyethylene as decorating material, the resolution limit is in the order of the length of the molecules and adjacent reentry cannot be concluded from it (approximately 5–10 nm), while with the Te a much higher resolution can be expected and the orientational effect is likely induced by crystallographic order in the surface of PE single crystals (tight folds with adjacent reentry or chain ends). Te evaporates as molecules of Te_n,[15] where n ranges between 1 and 7, and the dimer Te_2 is the predominant species. The shape of this molecule is unisotropic, and its long axis is 0.27 nm. It is not clear, yet, why the Te decorates crystallographically with its c axis parallel to the [020] direction of the low molecular weight PE single crystals (A409) and parallel to the [110] direction of the higher molecular weight PE single crystals (Lupolen 6041D). Neither Te (hexagonal: $a = 0.446$ nm, $c = 0.593$ nm) nor Sn (tetragonal: $a = 0.583$ nm, $c = 0.318$ nm) exhibits any kind of lattice matching with the PE single crystals. The fact that the surface of the A409 PE single crystals contains a considerable number of chain ends while in the surface of Lupolen 6041D PE single crystals the number of chain folds must be much higher (due to the much higher molecular weight of the Lupolen 6041D) indicates that chain ends in the surface of the single crystals favor the growth of the Te particles in [020] direction of the PE single crystals while the chain folds favor the [110] direction. The latter is reasonable, as the [110] directions are assumed as fold directions in PE single crystals. The linear shape of the Te_n molecules in the vapor phase (in contrast to the Sn atoms) may be one reason that PE single crystals are orientationally decorated with Te and not with Sn. As the long size of the Te_n molecules does not exceed intermolecular distances of polymer crystals, a crystallographic-like order in the PE single crystal surfaces is very likely.

In electron-irradiated single crystals, this kind of order is destroyed, and consequently no crystallographic alignment of the Te particles is expected. This is consistent with our observation that electron irradiation suppresses the oriented decoration.

5. Conclusions

Surface decoration of PE single crystals of low and higher molecular weight with Te at elevated temperatures exhibits a crystallographic correlation between the PE and Te crystallographic lattices. As it must be assumed that the interaction forces between the PE and Te are of short-range nature, the crystallographic order of the Te in the fold surface of the PE is a result of an order in intermolecular arrangement of the PE macromolecules in the fold surface. It is therefore assumed that the chain folds in PE single crystals are of a tight regular reentry nature. On electron-irradiated PE single crystals, the decorational effect is not observed anymore.

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Registry No. PE (homopolymer), 9002-88-4; Sn, 7440-31-5; Te, 13494-80-9.