Polymer Bulletin 39, 761–765 (1997)

Polymer Bulletin

Oriented overgrowth of vapour deposited tin on highly oriented PTFE substrates

F. Katzenberg, J. Petermann*

Fachbereich Chemietechnik, Lehrstuhl für Werkstoffkunde, Universität Dortmund,
Emil-Figge-Strasse 66, D-44221 Dortmund, Germany

Received: 19 September 1997/Revised version: 30 October 1997/Accepted: 31 October 1997

Abstract

The vapour deposition of tin on highly uniaxially oriented PTFE causes an oriented overgrowth of tin islands. The origin of this orientation is not clear. Classic epitaxy as well as graphoepitaxy seems to be an explanation for the occurring orientation. The appearance of this orientation was observed in a temperature range from -80°C to 90°C. An orientation by crystallization from the melt could not be achieved so far. In this short communication, a metal/polymer system is introduced which offers new possibilities to investigate the origin of oriented overgrowth.

(Keywords: metal/polymer interface, friction transfer, ultra-thin films)

Introduction

Oriented overgrowth of numerous metals on semicrystalline polymer substrates is well known since about one decade. The reason for this orientation is still under debate. For some metal/polymer systems [1], a possible explanation seems to be classic epitaxy, which bases on lattice matching and misfits less than 15% [2,3]. On the other hand, artificial epitaxy (graphoepitaxy) seems to be a possible explanation for metal/polymer systems (e.g. Sn, Te, In, on to PE, PP ,PB-1 ,sPS), because no lattice matching exists [4,5,6,7]. For this kind of epitaxy, the surface topology seems to be responsible for the preferred orientation. It is still not clear yet, if a nucleus orients at the surface topology due to the semicrystalline character of the substrate (super-molecular steps) or at the topology of the crystal (molecular steps). With PTFE a new substrate that causes oriented overgrowth is found. Oriented PTFE is known to orient many organic layers [8] and for some of the materials, lattice matching can be excluded for the ordering [9]. But it is the first time to our knowledge, that the orientation of a metal on PTFE is reported. Its properties, especially the high-temperature stability, promise new possibilities to examine the mechanisms of oriented overgrowth of metals on polymeric substrates.

Experimental

Highly uniaxially oriented PTFE films are obtained according to the friction transfer method of Tabor et al. [10,11]. With this method, a PTFE bar is slipped over a clean glass

---

* Corresponding author

slide at room temperature and leaves a thin layer of PTFE on the glass. The resulting layer is floated off on water and picked up on copper TEM grids. The pressure and sliding speed of the bar are varied in that manner till homogeneous thin layers arise. The tin was evaporated under a pressure of $5*10^{-4}$ Pa at room temperature and in a temperature range from -100°C to 150°C, in order to determine the substrate temperature dependence for the appearance of the epitaxy.

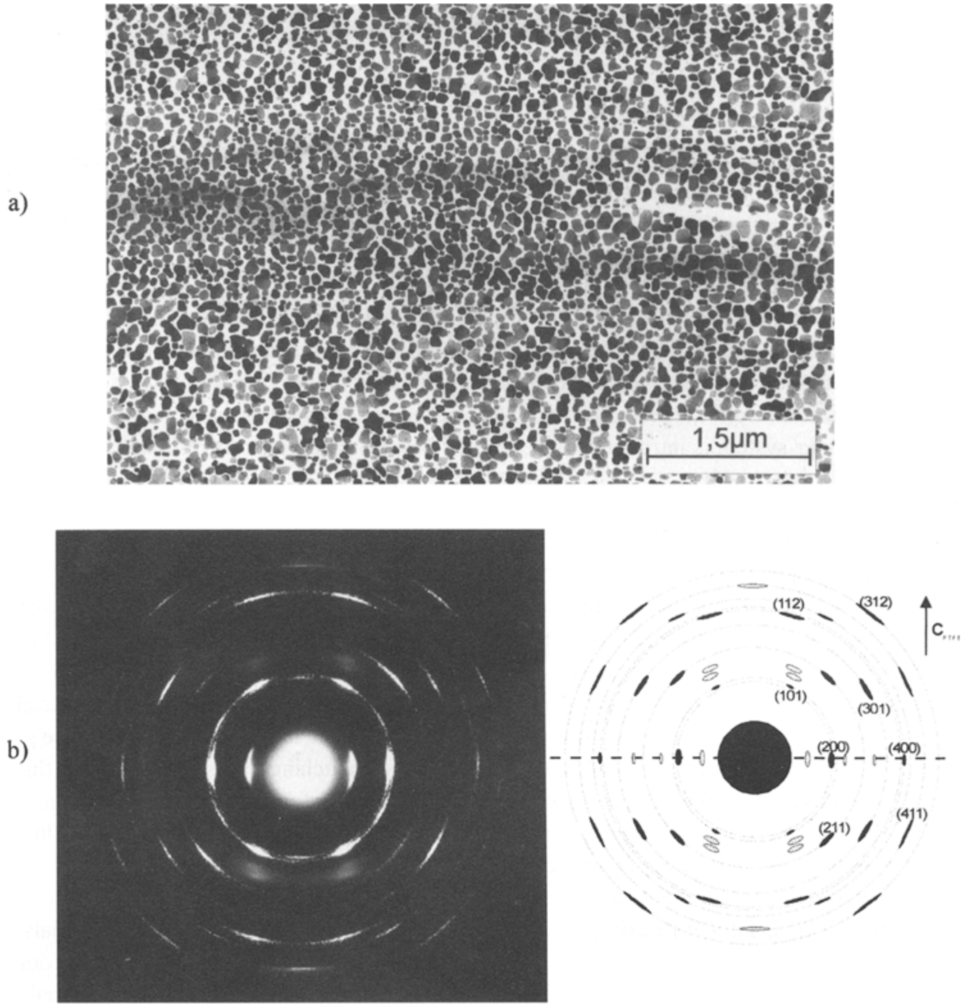

Fig. 1. a) TEM bright field micrograph of the uniaxially oriented PTFE layer deposited with 20nm tin at 20°C substrate temperature.

b) Corresponding electron diffraction pattern of the sample shown in Fig. 1a. (left) and a sketch indicating the Sn-diffraction pattern (right). The open circles are indicating the PTFE and the filled circles the tin, respectively. The arrow indicates the chain direction of the PTFE.

Furthermore, a tin deposited PTFE sample was heated up to 250°C (above the T_m of Sn) under high vacuum conditions and the tin was subsequently crystallized from its molten state on the PTFE substrate.

Results

The electron diffraction patterns in Fig. 1a,b exhibit the fiber texture of the PTFE and a preferred crystallographic orientation of the tin. The [100]-direction of the tin crystals orients perpendicular to the [001]-direction of the PTFE crystals.

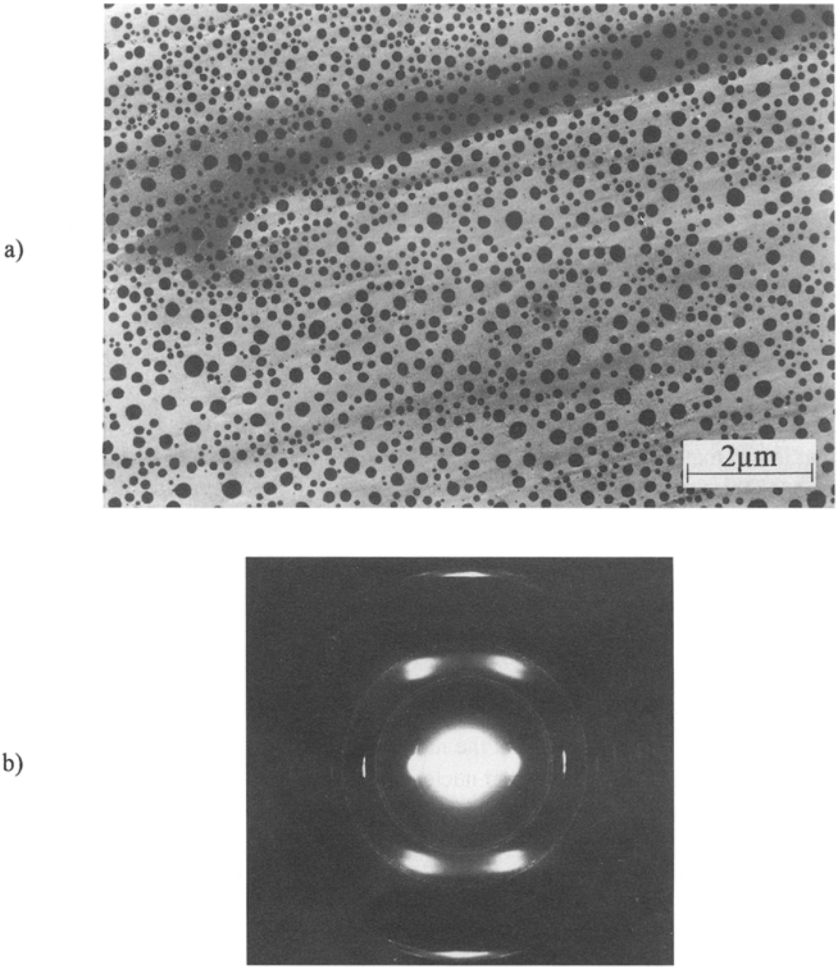

Fig.2: a) TEM bright field micrograph of the tin deposited PTFE-layer, heated up to 250°C (above T_m of Sn) and crystallized from the melt by quenching the sample to room temperature.
b) Corresponding electron diffraction pattern of the same sample shown in Fig.2a. No preferred orientations of the tin crystals occur.

Additionally, a second but less pronounced orientation of the Sn crystals with $[100]_{Sn} \| [001]_{PTFE}$ is visible. Contact planes of the tin crystals are (010) which are parallel to (hk0)-planes (fiber texture) of the PTFE crystals.

The oriented crystallisation of the Sn occurs in a temperature interval between -80°C and 90°C. When heating the Sn deposited samples above the melting point of Sn (232°C) and crystallizing it from the melt by quenching it to room temperature instead from the vapour, no preferred orientations of the tin crystals were observed (Fig.2a,b). Also, the morphologies of the melt and vapour crystallized Sn islands differ considerably. The relative mismatches between the Sn and PTFE crystals are given in Table 1.

Lattice constants PTFE [Å]	Lattice constants Sn [Å]	Contact plane substrate‖adsorbate	Orientations	Mismatch δ[%]
hexagonal	tetragonal	$(hk0)_{PTFE} \| (010)_{Sn}$	$a_{PTFE} \| a_{Sn}$	3
			$c_{PTFE} \| 6c_{Sn}$	2,7
a=5,66, c=19,5	a=5,831		$c_{PTFE} \| 3a_{Sn}$	-10
	c=3,182		$a_{PTFE} \| 2c_{Sn}$	-11

Table 1: Crystallographic data and relative mismatches of deposit and substrate.

Discussion

The fact, that the crystallographic orientation of Sn crystals obtained by vapour deposition on several uniaxially oriented polymers (PE, sPP, iPP, PB-1, sPS) is the same regarding the contact planes $(010)_{Sn} \| (hk0)_{Polymer}$ and the lattice directions $[100]_{Sn} \| [001]_{Polymer}$, let suppose, that lattice matching is not the dominant factor for the occurrence of the oriented crystallization of the Sn crystals despite large differences for the atomic positions in the planes and along the directions of the polymer crystals. This suggestion is further supported by the experimental observation, that independent of the substrate temperatures in the range of -80°C to 90°C the epitaxial orientation is not changing despite the fact, that the PTFE undergoes a phase transition [12]. An alternative explanation was given by Jandt et al [4], who supposed the oriented crystallization along super-molecular and process induced-surface steps (graphoepitaxy), as it is also known for some atomar crystals (Sn on NaCl and KCl [13]) and amorphous substrates having artificial microscopic structured surfaces [14]. It remains the question upon the molecular nature of the surface structure in polymer crystals responsible for the oriented nucleation of the metal islands. Striation along the sliding direction of the PTFE substrate has been observed by replication of the PTFE surfaces. But we cannot claim that these striatings are the location of the epitaxial nuclei. For the most efficient oriented nucleation event, the radii of curvature at the corner of a step and the size of the critical nucleus are supported to be in the same order of magnitude. This may explain, why oriented crystallization occurs in a temperature interval and only by crystallization from the vapour: at too low substrate temperatures, the critical nucleus is too small and at high temperatures too large concerning the radii of curvature of the surface step, respectively (Fig.3). When crystallizing the tin from the melt, the supercooling is too low for the appropriate small nucleus size. Experiments, which reveal the molecular nature of steps in polymer crystal surfaces are under way.

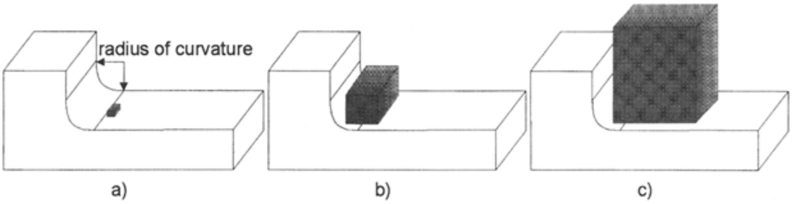

Fig.3: Surface steps and critical nuclei with different orders of magnitude. Corresponding to high supercoolings the nucleus is too small concerning the radius of curvature at the corner of the step (a). The nucleus and the step radius are in the same order of magnitude; oriented overgrowth is possible (b). Corresponding to low supercoolings the nucleus is too large (c).

Acknowledgement

The financial support of the Volkswagen Foundation is gratefully acknowledged.

References

1. Torii H, Tsuji M, Kawaguchi A (1996) J Mater Res 11: 970
2. Royer L (1928) Bull Soc Fr Miner Cristallogr 51: 7
3. Royer L (1954) Bull Soc Fr Miner Cristallogr 77: 1004
4. Jandt K D, Buhk M, Petermann J (1996) J Mater Sci 31: 1779
5. Petermann J, Broza G (1987) J Mater Sci 22: 1108
6. Schultz J M, Peneva S K (1986) APS-meeting, Las Vegas, Bulletin: 511
7. Schultz J M, Peneva S K (1987) J Polym Phys B, Polym. Phys. 25: 185
8. Wittmann J C, Smith P (1991) Nature 392: 414
9. Fenwick D, Smith P, Wittmann J C (1996) J Mater Sci 31: 128
10. Rachel Makinson K R, Tabor D (1964) Proc Roy Soc London A281: 49
11. Pooley C M, Tabor D (1972) Proc R Soc London A329: 251
12. Sperati C A (1989) Physical Constants of Fluoropolymers, In: Brandrup J, Immergut E H, pp. V/35
13. Kasukabe Y, Osaka T (1986) Thin Solid Films 146: 175
14. Osaka T, Kasukabe Y (1985) J Crystal Growth 73: 10