Epitaxial deposition of metals on uniaxial oriented semi-crystalline polymers

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The evaporation of certain metals (tin, indium, bismuth, tellurium) onto uniaxially oriented semi-crystalline polymer films leads to strongly textured lattice orientations of the metals. The contact planes differ in character from the common epitaxy because the polymer surface planes are $(h\,k\,0)$ planes having only the $[0\,0\,1]$ direction in common, and a single polymer crystallite has a surface area of $\sim 100 \times 20\,\text{nm}^2$ only, while the metal film has a "single crystalline" texture over the entire surface.

1. Introduction

It is well known that the surface structures of solid materials can be decorated with metals [1–5], and gold decoration of polymer crystal surfaces has been used to obtain information on the surface topography of polymer crystals [2]. Decoration patterns can arise from reduced nucleation energy barriers at steps and edges of crystals, or areas with decreased interfacial energies [6]. Different surface diffusion coefficients can also lead to distinct arrangements of the metals on the polymer surfaces but, in general, the decoration of polymer surfaces with metals is not connected with a preferred orientation of the lattices of the metal crystals. Electron diffraction patterns of decorated surfaces reveal a random orientation of the metal crystallites (Figs 1a and b).

On the other hand, it is well established that the nucleation and growth of metal particles on certain crystallographic surfaces of molecular, metal, ionic and covalent crystals can lead to epitaxial interfaces [6]. Little work has been done on the epitaxy of metals on macromolecular crystals. Recently, a lattice correlationship between uniaxially oriented polypropylene and tin particles, which were evaporated on to polypropylene, has been reported [7]. It is the purpose of this paper to extend the number of metals or semi-metals which exhibit lattice orientation correlationships on uniaxially oriented polymer substrates. Additionally, the influence of the chemical nature of the polymeric substrates and their lattice structure upon the occurrence of epitaxial crystallization of the metal particles is investigated by using many different uniaxially oriented polymer substrates. Some indications of the reason for the epitaxies obtained by high resolution transmission electron microscopy (HRTEM), are discussed.

2. Experimental procedure

The oriented polymer substrates were prepared according to the method of Petermann and Gohil [8]. The ultra thin ($< 50\,\text{nm}$) uniaxially oriented polymer films were washed in distilled water, cut into $3 \times 3\,\text{mm}^2$ pieces and mounted on electron microscope grids. The metals were evaporated on to the thin films
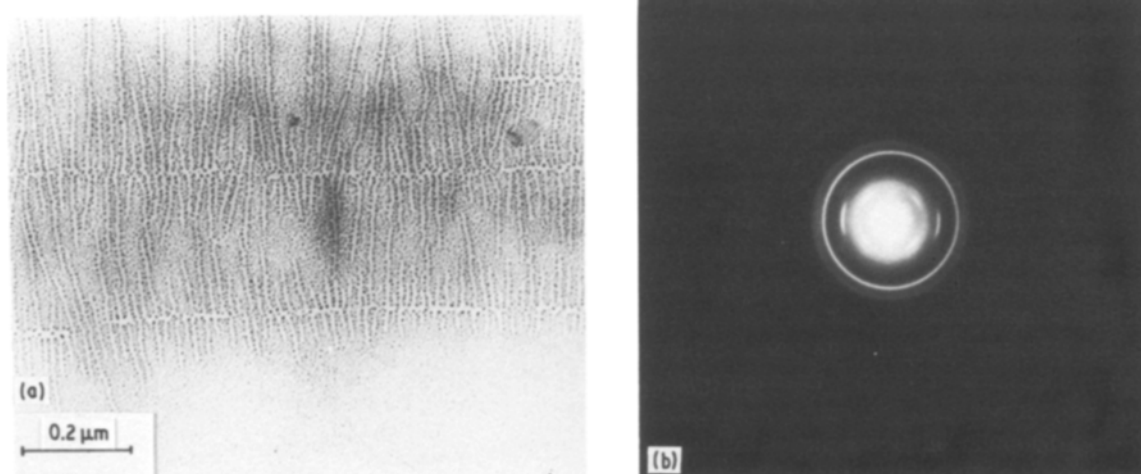

Figure 1 (a) Transmission electron micrograph of gold-decorated shish-kebab crystals in isotactic polystyrene. The horizontal pattern corresponds to the shish crystals, the vertical pattern to the kebab crystals. (b) Electron diffraction pattern of the gold-decorated isotactic polystyrene (iPS) crystals. The molecular direction of the iPS is horizontal. The diffraction rings result from the gold.

TABLE I Substrate films and layers of the materials used in the investigations

Substrate: oriented polymer films		Metal Layers									
		Sn (tetr)	Te (hex)	Bi (hex)	In (tetr)	Zn (hex)	Au (fcc)	Ni (fcc)	Co (hex)	Ge (orthorhom)	Sb (rhom)
Polyethylene	Epitaxy* Orientation Relationship†	s [c] ‖ [1 0 0]	s [c] ‖ [0 0 1]	s [c] ‖ [1 0 2]	none	none	none	none	none	none	none
Polypropylene	Epitaxy Orientation Relationship	vs [c] ‖ [1 0 0]	s [c] ‖ [0 0 1]	vs [c] ‖ [1 0 2]	(w) [c] ‖ [1 0 1]	none	none	none	none	none	none
Polybutene-1	Epitaxy Orientation Relationship	vs [c] ‖ [1 0 0]	vs [c] ‖ [0 0 1]	vs [c] ‖ [1 0 2]	s [c] ‖ [1 0 1]	(w)	none	none	none	none	none
Polystyrene Isotactic	Epitaxy Orientation Relationship	w [c] ‖ [1 0 0]	none	[–]	(w) [c] ‖ [1 0 1]	[–]	none	[–]	[–]	[–]	[–]
Polyvinylidene Fluoride	Epitaxy Orientation Relationship	none	none	[–]	[–]	[–]	[–]	[–]	[–]	[–]	[–]

*Epitaxy: vs = very strong, s = strong, w = weak. [–] Not investigated.
†[c] = chain direction.

in a Balzers BAE 080 at a pressure of 10^{-6} torr. The thickness of the metal layers on the polymeric substrates was approximately 30 nm. The samples were examined by transmission electron microscopy (TEM) and electron diffraction using a Philips EM 400 T and a JEOL 2000 DX microscope, operated at 100 and 200 kV, respectively.

3. Results and discussion

In contrast to conventional experiments for the investigations of epitaxy, the substrate material is not a single crystal but an arrangement of very small lamellar or fibrillar crystals having only one crystallographic axis in common, the direction of the molecules (fibre texture). In Fig. 2 the morphology of a lamellar substrate is shown schematically. Figs 3a and b are electron micrographs of lamellar polyethylene (PE) and fibrillar polybutene-1 (PB-1) films, with their electron diffraction patterns inserted. The metals evaporated on those substrates were tin, tellurium, bismuth, indium, zinc, gold, nickel, cobalt, germanium and antimony. No preferred crystal orientations of the metal layers were observed on polyvinylidenefluoride, the strongest orientations were obtained with tin, tellurium and bismuth on PB-1 films. Table I summarizes the experimental observations. In order to illustrate the epitaxial orientation effect, Figs 4a to d show electron diffraction patterns of tin on a carbon film substrate and tin, tellurium and bismuth on PB-1 substrate films. On the carbon substrate, the tin crys-
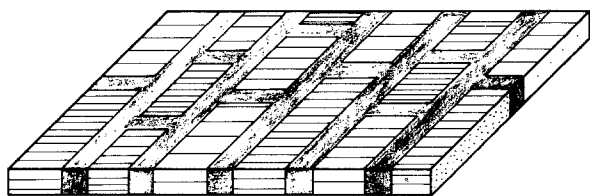
tals have random orientations as seen from the homogeneous intensities of the Debye–Scherrer rings. On PB-1 substrates, tin crystallites have a preferred orientation with the [1 0 0]-axis of the tetragonal tin parallel to the chain direction of the polymer, as indicated by the intensity maximum on the (2 0 0) Debye–Scherrer ring parallel to the (0 0 3)-reflexion of the pseudohexagonal PB-1 unit cell. Similar intensity maxima are seen from the hexagonal tellurium on PB-1 with hexagonal axes (c-axis) of tellurium parallel to the chain direction, but with the hexagonal axis perpendicular to the polymer chain axes in the case of bismuth. From the observation that different lattice planes of the polymer crystals (see Fig. 2), different unit cells of the polymer crystals (PE, orthorhombic; PP, monoclinic; PB-1; pseudohexagonal), and different conformations of the polymer chains (PE, planar zig-zag; PP and PB-1, $2 \times 3_1$-helix) lead to preferred orientations of the same metal, it must be concluded that neither a matching of lattice planes nor the conformation of the polymer chains (matching along chain direction) are the reason for epitaxial crystallization. On the other hand, the crystalline nature of the polymeric substrate is a necessary requirement for the occurrence of preferred orientation of the metal layers. Disturbing the long-range order of the polymer crystals by electron irradiation prior to the evaporation of the metals, suppresses the preferred orientation of the layered materials. The empirical observation that the epitaxy is enhanced by the CH_3 and C_2H_5 side groups (PP, PB, respectively) in the chain configuration (see Table I) may be of importance.

Additional information was obtained from electron micrographs of tellurium and tin on PB-1 substrates. In Fig. 5a the tellurium layer on PB-1 can be seen. The tellurium consists of rather dense packed small spheres with diameters of approximately 25 nm. From the extinction contours it can be concluded that the lattices of neighbouring spheres have exactly the same lattice orientation. The lattice coherency is extended
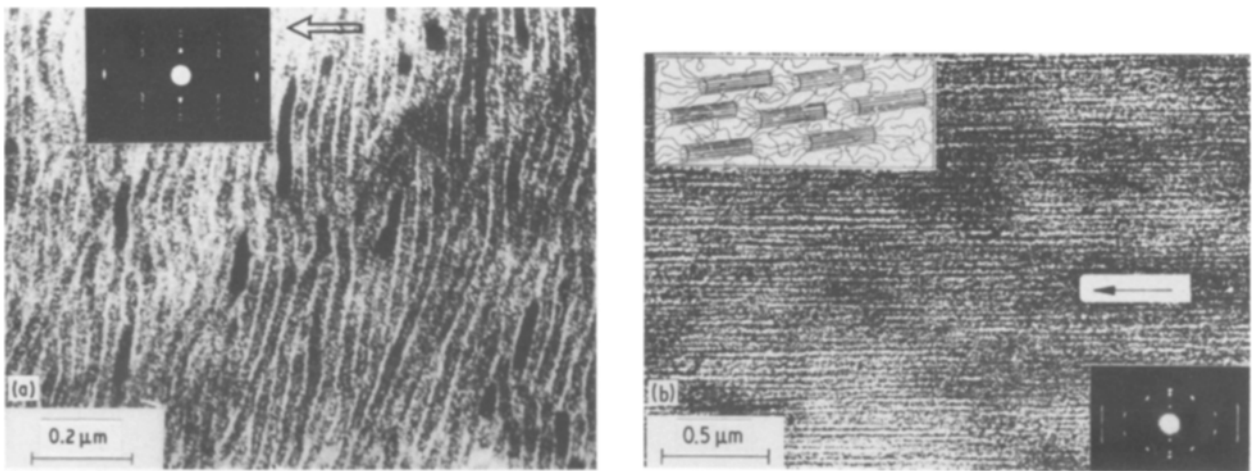

Figure 2 Schematic sketch of the morphologies and molecular orientation of the lamellar polymer substrates.

Figure 3 (a) Transmission electron micrograph of a PE lamellar substrate. The white lines are amorphous regions, the dark ribbons the lamellar crystals. The black areas within the dark ribbons are "Bragg-reflecting" crystals. The arrow indicates the molecular direction. (b) Transmission electron micrograph of fibrillar polybutene-1 films.

over areas of about $1000 \times 1000 \, nm^2$. Fig. 5b shows a diffraction pattern of such a "single-crystal-like" domain. Fig. 6 shows a high resolution electron micrograph of tin particles on a PB-1 substrate. The parallel fringes within the particles represent the $(2\,0\,0)$ lattice planes of the tetragonal tin. Haloes can be seen around the particles, which differ in their TEM contrast from the tin and from the substrate. The appearance of the domains and the haloes leads to speculation that the information of the polymer chains is transferred to the metals via a very thin layer, the nature of which cannot be identified by TEM techniques. Those layers may
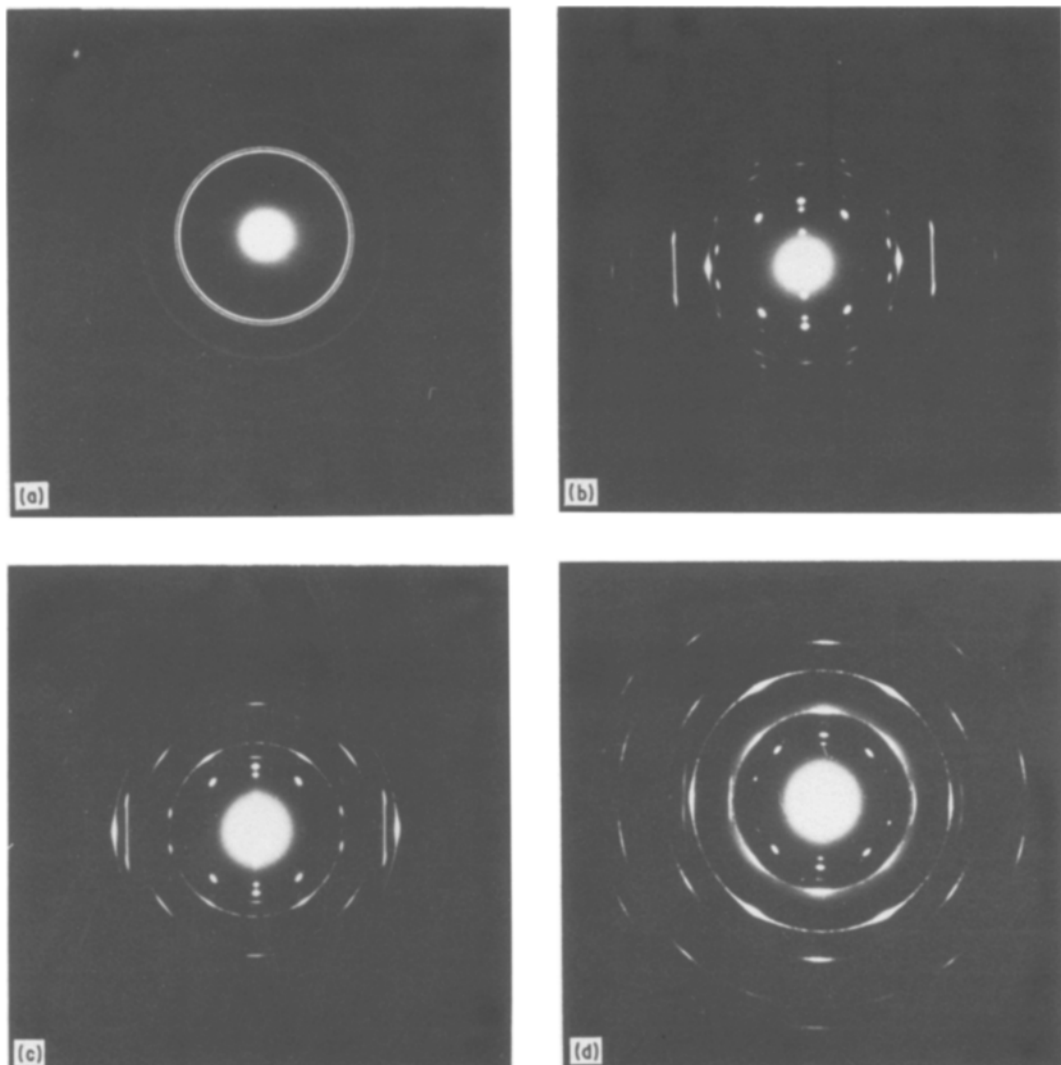

Figure 4 (a) Electron diffraction patterns of tin deposited on a carbon film substrate. (b) to (d) Electron diffraction patterns of tin, tellurium and titanium on a PB-1 substrate. The molecular directions of the substrate films are horizontal.
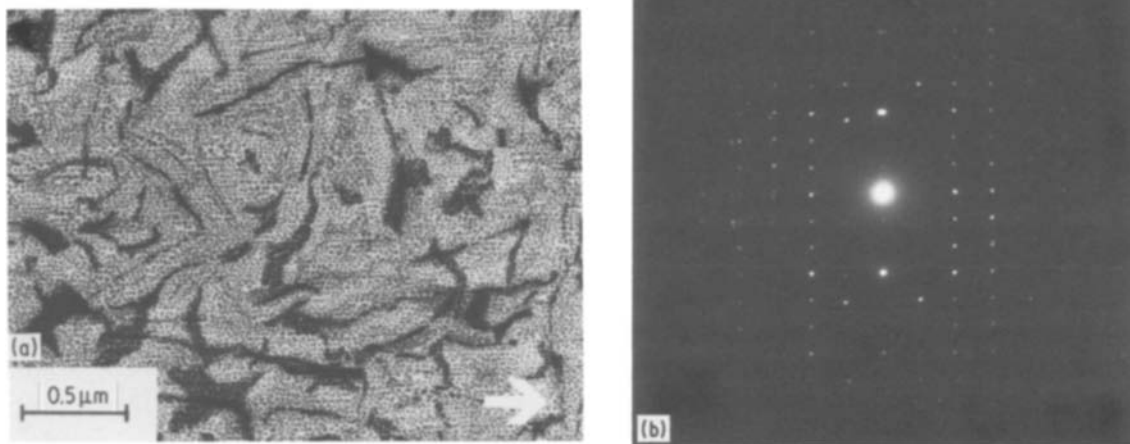
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Figure 5 (a) Bright-field transmission micrograph of electron tellurium on PB-1. The dark "clouds" are regions within the crystal, orientations of the tellurium spherical particles do not deviate more than 0.1° (Bragg extinction contours). The arrow indicates the molecular direction of the PB-1 film. (b) Selected-area electron diffraction pattern from a dark domain of (a).

consist of metal/methyl complexes formed by the interaction of the highly energetic metal atoms from the thermal evaporation source hitting the surface molecules. Electron spectroscopy for chemical analysis (ESCA) investigations may yield further details [9].

For the other epitaxial systems, the epitaxy of metals on the polymers can be enhanced by heating the substrate. Evaporating the metals at substrate temperatures of 80° C leads to a narrowing of the intensity maxima in the electron diffraction patterns of the metals. This observation holds for all metals and substrates used in this work. On the other hand, cooling the substrates to −80° C can even suppress the epitaxy.

Fig. 7 shows tellurium on PB-1, evaporated at a substrate temperature of +80° C. Compared to Fig. 5a, a change in geometric shape of the tellurium particles can be seen easily. The tellurium particles are rod-shaped with their long axis (which corresponds to the c-axis of the hexagonal unit cell) preferentially

parallel to the chain axes of the polymer substrate. This kind of morphological transition was only observed with tellurium and may be due to the $1 \times 3_1$ helical structure of tellurium and its polymerization [10].

4. Conclusion

Interactions of uniaxially oriented polymer substrates and metal layers can be of an epitaxial nature. The polymeric substrates must be semi-crystalline with $(h k 0)$ surfaces, and the lattice orientations of the metal layers are determined by the chain direction of the polymer; atomic or molecular matching of lattice planes or directions are not required. Polymer chain configurations having methyl or dimethyl side groups enhance the texture of the metals. These special metal/polymer surface interactions are empirically observed with metals which can form metal organic compounds. It is supposed that molecular surface layers of those compounds transfer the epitaxial orientations from the polymer to the metal.
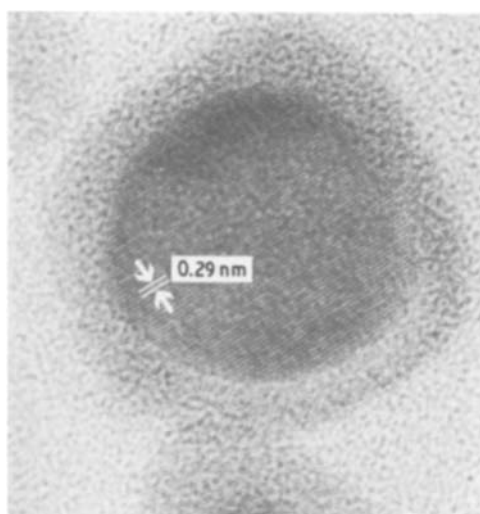
Figure 6 High resolution electron micrograph of a spherical tin particle on a PB-1 film. The parallel fringes correspond to (2 0 0) lattice planes of the tin.
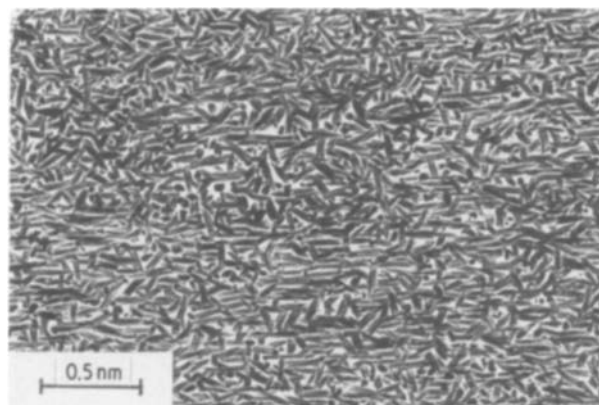

Figure 7 Transmission electron micrograph of tellurium on a PB-1 film, evaporated at a substrate temperature of +80° C. The molecular direction of the PB-1 is horizontal.

Microscope Centre of the TUHH with the experimental parts of the investigations, and JEOL Ltd, Tokyo with the HRTEM.

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