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Epitaxial growth of *para*-hexaphenyl on GaAs(001)-2 × 4

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Abstract

para-Hexaphenyl grows on GaAs (001) in well-defined, three-dimensional islands of a needle-like shape. The needles are oriented in ⟨100⟩ with respect to GaAs. The orientation of the hexaphenyl molecules within the needles has been studied using electron diffraction techniques. Two different orientations of the epitaxially grown hexaphenyl molecules on GaAs are identified. One with the (10 0 1) plane and the other one with the (11 0 $\bar{2}$) plane of hexaphenyl parallel to GaAs (001). In both cases, the *b*-axis of hexaphenyl is parallel to ⟨100⟩. The epitaxial growth of the needle-like hexaphenyl is explained in terms of micro and rotation twinning. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The molecule *para*-hexaphenyl ($C_{36}H_{26}$) is an electroactive organic molecule with high potential for future applications. The blue colour of the photoluminescence in combination with reasonable charge carrier and mobility values make this material suitable for opto-electronic devices, e.g. light-emitting devices with high efficiency and tuneable colour are realised [1–3]. Thin films of hexaphenyl are the electroactive layers in these opto-electronic devices. Since the optical as well as the electric properties of hexaphenyl are highly anisotropic, the orientation of the molecules within the thin film plays an essential role in the performance of these applications [4]. Therefore, the growth of hexaphenyl crystallites has been studied in detail: on isotropic substrates three different preferred orientations could be found [5,6]. The hexaphenyl molecules are either parallel aligned or tilted by an angle of 73° with respect to the substrate. Highly ordered hexaphenyl layers are prepared by growth on rubbed surfaces or by rubbing the hexaphenyl layer itself [7–9]. One further method to orient the hexaphenyl molecules is the epitaxial growth on potassium chloride substrates [10,11]. The epitaxial growth of hexaphenyl on a suitable semiconductor, e.g. GaAs(001)-2 × 4 is demonstrated by atomic force microscopy [12]. At elevated substrate temperatures Vollmer–Weber or 3D-growth is observed. Hexaphenyl forms elongated islands oriented in [100] and [010] direction of GaAs. The size of the needle-like crystallites as

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well as the nucleation on the GaAs substrate depends exponentially on the substrate temperature (T_s) during the deposition.

This paper is focused on the internal arrangement of the hexaphenyl molecules within the crystallites which are epitaxially grown on GaAs(001)-2 × 4 substrates. In addition, the orientation of the hexaphenyl molecules with respect to GaAs (001) is determined.

2. Experimental section

Hexaphenyl ($C_6H_5-(C_6H_4)_4-C_6H_5$) of high purity was purchased from Tokyo Chemical Industries Ltd. The thin films were prepared by molecular beam epitaxy (MBE) on epiready GaAs surfaces which are cut 2° relative to the (001) surface. The substrates were thermally deoxidised in ultrahigh vacuum at 650°C. Since the desorption rate of As exceeds the desorption of Ga at the deoxidation temperature, the surface preparation was performed in As atmosphere of 1×10^{-4} Pa. During the MBE growth of hexaphenyl the base pressure corresponded to 1×10^{-6} Pa. Using a source temperature of 230°C and a deposition time of 10 min, a mean film thickness of 42 nm was found up to a substrate temperature of 150°C. On changing the substrate temperature from 90 to 170°C, the island density follows exactly an ideal Arrhenius curve. In the same manner, the mean thickness of the hexaphenyl islands increases from 120 to 400 nm [13].

To prepare the crystallites for electron microscopy, a carbon layer was deposited onto the hexaphenyl surface. This carbon layer mainly supports the hexaphenyl layer and transports charges generated by the electron beam. Poly(acrylic acid) $[-CH_2CH(CO_2H)-]_n$, (25 wt% solution in water) was used to remove the hexaphenyl layer from the substrate. Furthermore, it helps to float the layer onto a water surface, before it is placed onto a copper grid. The investigation of the hexaphenyl crystallites was performed using transmission electron imaging and diffraction. A Philips CM12 electron microscope working at a tension of 120 kV was used. The diffraction patterns were obtained at a spot size of 100 nm using a condenser aperture of 50 μm and a selected-area aperture of 50 μm. All images were recorded on Agfa Scientia EM films.

Indexation of the experimental diffraction pattern was carried out using the Cerius2 program of Molecular Simulations. The computations are based on the crystal structure of hexaphenyl as it is well known from single crystal investigations: Hexaphenyl crystallises in the monoclinic space group $P21/c$ with $a=2.6241$ nm, $b=0.5568$ nm, $c=0.8091$ nm and $\beta=98.17°$ [14].

Since the crystallite size is large compared with the diffracting beam, the diffraction pattern was taken from one crystallite only. Defocusing the image in diffraction mode does not significantly change the orientation of the image with respect to the sample but helps to orient the diffraction pattern with respect to the corresponding crystallite. Hence, the relative orientation of the crystal and the diffraction pattern can be unequivocally verified.

The graphical representation of the relative orientation of the hexaphenyl molecules with respect to the substrate surface was carried out with the software PowderCell [15].

3. Results

Fig. 1a shows a defocused image in diffraction mode of a hexaphenyl island on GaAs (001). The two directions of the needle-like islands are clearly visible. The bright spot in the centre represents the area selected to form the diffraction pattern given in Fig. 1b. It shows that the diffraction pattern was taken from one crystallite island only. This diffraction pattern represents a regular arrangement of clear diffraction spots. Consequently, the hexaphenyl island consists of one well-defined crystallite. Fig. 1c shows the simulation of a diffraction pattern with the zone $[20\bar{3}]$ parallel to the beam direction. The simulated positions of the reflections and their calculated intensities are in excellent agreement with the reflections of the diffraction pattern (Fig. 1b). The weak reflection with a d spacing double that of the 020 must be indexed as 010, which is normally absent but appears in electron diffraction of thick specimens as a result

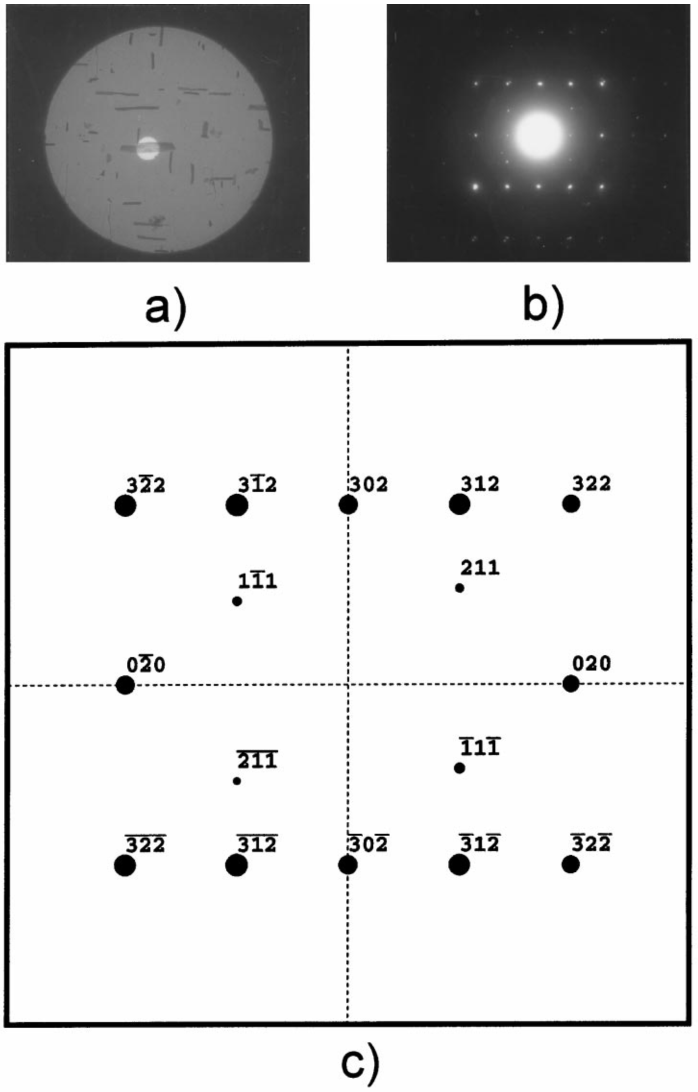

Fig. 1. (a) Defocused image in diffraction mode of hexaphenyl islands on GaAs (001) at $T_s = 130°C$. (b) Electron diffraction pattern of the hexaphenyl crystallite selected in the defocused image. (c) Simulated electron diffraction pattern (with indexing) for the $[20\bar{3}]$ zone axis, in correct relative orientation.

of multiple diffraction. Very weak higher-order reflections of the strong reflections (604, 624, 644) are also visible. The contact plane according to the zone $[20\bar{3}]$ is found to be $(11\ 0\ \bar{2})$. The long axis of the diffracting island is parallel to the [010] direction, hence, the *b*-axis of the hexaphenyl unit cell.

The defocused image (Fig. 1a) shows two orientations of the hexaphenyl islands at right angle to each other. The diffraction patterns relative for both islands are similar. The two populations have identical contact planes and the right angle orientation reflects the cubic symmetry of the substrates.

Fig. 2a shows another type of diffraction pattern which was also found for some hexaphenyl islands on GaAs (001). The strong diffraction spots can be indexed assuming a zone [304] parallel to the beam direction (Fig. 2b). The positions and rela-

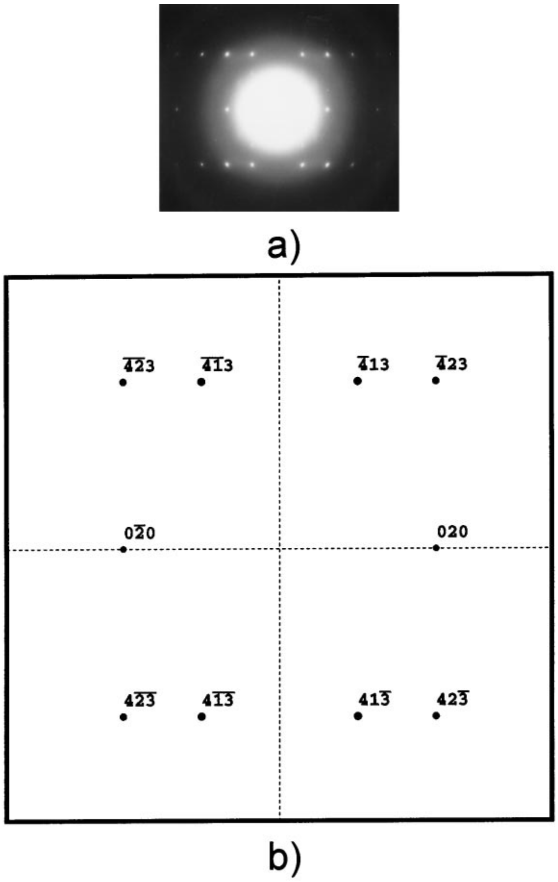

Fig. 2. (a) Electron diffraction pattern of a hexaphenyl island on GaAs (001) at $T_s = 140$°C. (b) Simulated electron diffraction pattern for the [304] zone axis.

tive intensities of the strong reflections (020, $41\bar{3}$, $42\bar{3}$) in Fig. 2b match very accurately with the experimental pattern. Since the diffraction pattern was taken from one crystallite island, it is evident that [010] is in direction of the long axis of the hexaphenyl islands. The *b*-axis of the unit cell is like that in the previous case — depicted in Fig. 1 — again parallel to the long axis of the hexaphenyl island. The contact plane indicated by the [304] zone axis is (10 0 1).

4. Discussion

The analysis of the single crystal diffraction pattern indicates that the *b*-axis of the hexaphenyl unit cell, which is parallel to the needle's long axis, is always parallel to the substrate. Since the growth direction of the hexaphenyl needles with respect to the substrate is GaAs [100] and [010], it is evident that the *b*-axis of the unit cell is parallel to GaAs [100] and [010]. The spacing of the atoms at the surface of the GaAs along [100] ($a_{\mathrm{GaAs}} = 0.565$ nm) matches nearly the *b*-axis of hexaphenyl ($b_{\mathrm{HP}} = 0.5563$ nm). The lattice mismatch is about 1.44%. It is well within the accepted range for epitaxy of organic molecules ($<10\%$).

The diffraction pattern indicates that the growth of the hexaphenyl islands on the substrate is well defined. Fig. 3 shows the orientation of the molecules with respect to the GaAs (001) substrate. The vertical orientation of the hexaphenyl molecules, shown in Fig. 3a, corresponds to the (10 0 1) contact plane. In Fig. 3b the molecular orientation corresponding to the $(11\ 0\ \bar{2})$ contact plane is shown. The molecular chains form an angle of about 40° to the surface of the substrate.

To sum up therefore the experimental evidence, we are dealing with two orientations of the hexaphenyl lattice relative to the substrate. They are characterised by contact planes of the type (10 0 1) and $(11\ 0\ \bar{2})$ and correspond to tilts of the hexaphenyl molecules of 0 and 50° relative to the substrate normal. Both orientations should be accounted for in terms of hexaphenyl structure and crystal growth mechanisms and hexaphenyl/substrate interactions.

4.1. (10 0 1) contact plane

The *vertical* orientation of the molecules observed in the present investigation raises a fundamental problem if 'simple' epitaxy is to be assumed. Indeed, the (10 0 1) contact plane *intersects* the hexaphenyl molecules, and therefore cannot be a natural contact plane: the (100) one would be more logical. Since this plane is only 17° away from the (10 0 1) one, a plausible mechanism may be put forward, which relies on *micro twinning* with a $(30\bar{2})$ twin plane, which is parallel to the long axis of the molecules (Fig. 4a). The twinned crystallites would thus be composed of small sectors parallel to *b* with the tilt of the *c*-axis at +17° and −17° to the surface. Macroscopically the contact plane would be (10 0 1) but composed locally of (100) planes.

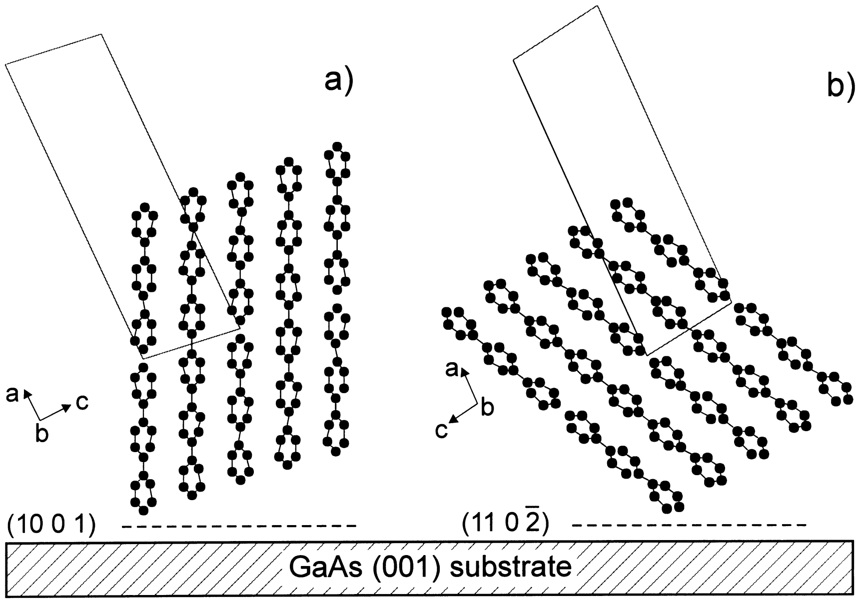

Fig. 3. Orientation of the hexaphenyl molecules with respect to the substrate surface for (a) the (10 0 1) plane and (b) the (11 0 $\bar{2}$) plane parallel to the surface.

4.2. (11 0 $\bar{2}$) contact plane

The orientation at 50° to the substrate normal of the hexaphenyl molecules appears as 'unnatural' as the vertical orientation discussed above: indeed, the substrate plane intersects the molecules, which means again that no 'straightforward' contact plane emerges. Several possible mechanisms have been considered to account for this population of crystals. The most likely one involves a rotation twin between the previous orientation and the present one. Specifically, the suggested homoepitaxy can be described as a rotation twin with the (010) as the contact plane and the rotation twin parallel to the *a*-axis. The amount of rotation is such as to re-create a strong overlapping of phenyl rings across the contact plane (Fig. 4b). As a result of this homeopathy, a novel orientation of the hexaphenyl molecules is generated, which suggests an 'apparent' (11 0 $\bar{2}$) contact plane.

Rotation twins of the type just described are well known in the field of polymer and elongated molecules' crystal structure and growth habit. They are observed in particular in the α phase of isotactic polypropylene, and give rise to a characteristic lamellar branching [16]. They are also included in the crystal structure (at the unit-cell level) of the γ phase of the same polymer. The hexaphenyl structure shares several features with these other systems (long chain character, nearly lozenge symmetry of the phenyl rings location in the rotation twin contact face, which mimics the disposition of methyl groups in the (010) twin planes of isotactic polypropylene, cf. Fig. 4b).

AFM images characterising the island morphology show parallel stripes along the islands [12]. These stripes may be explained by the micro twinning. Since the (30$\bar{2}$) twinning plane is perpendicular to the GaAs surface and in the direction of the needle-like crystallites, the stripes occur due to the micro twinning planes.

Thus the GaAs (001) surface acts as the substrate for growth of a micro-twinned crystal in the first orientation (Figs. 3a and 4a). The orientation of the molecule in this first orientation promote the growth in the second orientation by rotational twin growth as depicted in Fig. 4b.

Interestingly, the crystal structure of quaterphenyl, quinquephenyl and septiphenyl are very similar to hexaphenyl. The molecules are also packed

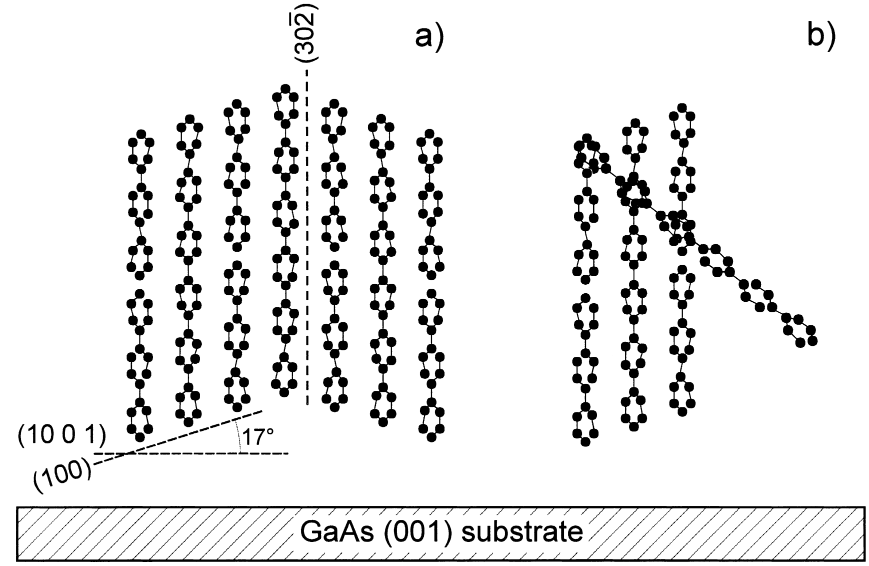

Fig. 4. Interpretation of the observed epitaxial growth of hexaphenyl molecules. (a) Micro twinning of the crystals with a $(30\bar{2})$ composition plane. (b) Rotation twinning with (010) as twinning plane and rotation twin axis (in the plane of the paper) parallel to the *a*-axis.

in layered structure, so *b*- and *c*-axes are nearly identical. It would be of interest to perform similar experiments with other members of this series in order to study the resulting molecular orientation and in particular the nature of the hexaphenyl contact plane with the substrate.

5. Conclusion

The samples prepared under different growth conditions show only two orientations of the *para*-hexaphenyl molecules with respect to the GaAs (001) substrate surface, for which either the (10 0 1) or the $(11\ 0\ \bar{2})$ planes are parallel to the GaAs (001). Since for both orientations the *b*-axis of the hexaphenyl unit cell is parallel to the needle direction, we conclude that the two orientations must be closely related to each other. This relationship cannot be explained by a simple model or by geometrical considerations: the relative orientations must be interpreted by a micro twinning and a homoepitaxial growth or rotation twinning.

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