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Molecular beam epitaxy of *p*-hexaphenyl on GaAs(111)

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Hexaphenyl grows on GaAs(111) in elongated three-dimensional islands several micrometres long. The characteristic island shape (a drop-like or pyramidal head with a thinner tail) is demonstrated by atomic force microscopy. Using x-ray diffraction and transmission electron diffraction, the three-dimensional islands are found to be perfectly crystalline. On the basis of the bulk structure of hexaphenyl, three contact planes of hexaphenyl with GaAs(111) are identified: $(\bar{3}12)$, $(11\bar{2})$ and $(\underline{10}01)$. These results suggest that the epitaxial hexaphenyl islands consist of differently orientated domains. It is shown that the techniques used are appropriate for the characterization of stable organic epitaxial islands. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: hexaphenyl; GaAs(111); molecular beam epitaxy; x-ray diffraction; transmission high-energy electron diffraction; atomic force microscopy

INTRODUCTION

Hexaphenyl ($C_{36}H_{26}$) is a promising luminescent organic material for potential applications in optoelectronic devices such as light-emitting diodes or thin-film transistors.[1,2] Because these applications are usually based on high-purity heterostructures, the detailed study of island formation and defect structure of hexaphenyl becomes necessary. The preparation of hexaphenyl films on amorphous substrates is relatively easy, and one can even obtain highly crystalline films with preferred orientations of the molecules.[3] The deposition of hexaphenyl on single crystals such as GaAs(001) results, however, in well-defined three-dimensional (3D) epitaxial islands.[4] Although the epitaxy of hexaphenyl is an intended effect, the 3D shape of the islands is problematic for any application as active material in organic light-emitting diodes. Therefore, we would like to extract how far the 3D islanding of hexaphenyl on GaAs is determined by the physicochemical interactions of single molecules with the substrate material. A possible solution is the present investigation of hexaphenyl growth on a different GaAs surface, namely GaAs(111).

At low coverage (∼40 nm) hexaphenyl forms 3D islands of drop-like shape. Atomic force microscopy (AFM)[5] reveals stripes on top of the islands indicating their epitaxial character. At higher coverages the island morphology changes: A tail is developed on each island, as shown in Fig. 1 for a 500 nm thick film. The 150 μm × 150 μm AFM image proves that the hexaphenyl islands are homogeneously distributed on GaAs(111). The AFM images on the 10 μm scale show well-defined head facets with stripe features parallel to the tail. On the tail, however, the stripes are rotated by 90°, therefore we assume that the crystalline structure of the head differs from that of the tail. In order to prove our assumption we have performed x-ray and electron diffraction. The main advantage of electrons with respect to x-rays is their high cross-section due to the strong interaction even with organic matter. Furthermore, the beam diameter of ∼1 μm in the case of transmission electron diffraction (TED) enables us to study just one island or even parts of it. On the other hand, the sample preparation for transmission electron microscopy may cause artefacts. Moreover, the electron beam can significantly alter the organic material, therefore a detailed structural analysis of the hexaphenyl islands has to be based on a combination of different techniques, e.g. AFM, x-ray diffraction (XRD) and electron diffraction.

EXPERIMENTAL TECHNIQUES

Hexaphenyl (C_6H_5-$(C_6H_4)_4$-C_6H_5) of high purity was purchased from Tokyo Chemical Industries Ltd. The hexaphenyl islands were prepared by molecular beam epitaxy (MBE) on epiready GaAs surfaces cut 2° relative to (111). The substrates were thermally deoxidized at a substrate temperature of 650 °C under ultrahigh vacuum conditions. Because the desorption rate of As exceeds that of Ga at the deoxidization temperature, the surface preparation was performed in an As atmosphere of 1×10^{-4} Pa. During the MBE growth of hexaphenyl, the base pressure

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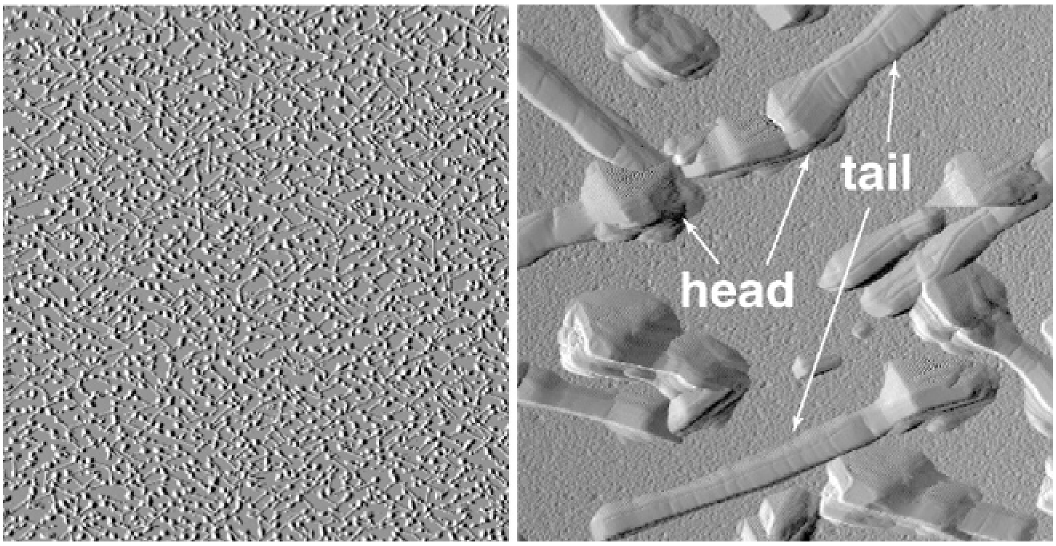

Figure 1. Atomic force microscopy images of hexaphenyl islands grown on GaAs(111) of size: (left) 150 × 150 μm^2, (right) 10 × 10 μm^2.

did not exceed 1×10^{-6} Pa. Using a source temperature of 230 °C and a deposition time of 120 min, an average film thickness of ~500 nm was found. During deposition the substrate temperature was kept constant at 150 °C.

The morphology of the hexaphenyl islands is studied *ex situ* by AFM (Topometrix Explorer) in both contact and transmitting mode. Damage or displacement of the deposited hexaphenyl islands due to the AFM tip was not observed. Several repetitions of the measurements reveal that the islands are stable under atmospheric conditions.

The hexaphenyl islands were studied as deposited on GaAs(111) by XRD. The $\Theta/2\Theta$ scans in Bragg–Brentano geometry with a Siemens D501 powder diffractometer are performed using Ni-filtered Cu Kα radiation.

The preparation of the hexaphenyl islands for transmission electron microscopy and diffraction included the deposition of carbon onto the hexaphenyl/GaAs(111). This carbon layer incorporates the hexaphenyl islands and avoids sample charging by the electron beam. Poly(acrylic acid) ($[-CH_2CH(CO_2H)-]_n$, 25 wt.% solution in water) was used to remove the hexaphenyl islands 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 islands was performed by a Philips CM12 electron microscope using an accelerating voltage of 120 kV. The different diffraction patterns were obtained at a spot diameter of ~100 nm using a condenser aperture of 50 μm and a selected-area aperture of 50 μm. The detected images were recorded on Agfa Scientia EM films. Because the hexaphenyl island sizes are large compared to the beam size, the diffraction pattern can be taken easily just from a part of a single 3D island. Defocusing the image in diffraction mode does not change significantly the orientation of the image with respect to the sample, but helps to orient the diffraction pattern with respect to the corresponding island. Hence, the relative orientation of the crystalline island and the diffraction pattern can be verified unequivocally. Indexation of the experimental diffraction pattern was carried out using the Cerius^2 program of Molecular Simulations based on the crystal structure of hexaphenyl.[6] Hexaphenyl crystallizes in a monoclinic lattice (space group 2_1/c) with $a = 26.24$ Å, $b = 5.565$ Å, $c = 8.091$ Å and $\beta = 98.17°$. The graphical representations of the relative orientation of the hexaphenyl molecules with respect to the substrate surface are carried out with the software package PowderCell.[7]

STRUCTURAL CHARACTERIZATION OF HEXAPHENYL ISLANDS ON GaAs(111)

The XRD pattern is depicted in the top right part of Fig. 2. Two clearly distinct peaks are observed. The peak at $2\Theta = 27.31°$ is related to the GaAs(111) reflection. The relatively small intensity of this reflection is explained by the fact that the (111) plane of the GaAs substrate is not fully parallel to the surface of the substrate, due to the 2° miscut. The second peak of the diffraction pattern is found at $2\Theta = 28.17°$, which fits exactly the position of the $(\bar{3}12)$ reflection of hexaphenyl (calculated at $2\Theta = 28.18°$) according to the crystal structure of hexaphenyl.[6] The occurrence of the $(\bar{3}12)$ reflection in the $\Theta/2\Theta$ diffraction pattern indicates that the $(\bar{3}12)$ planes of hexaphenyl crystallites are parallel to the surface of the

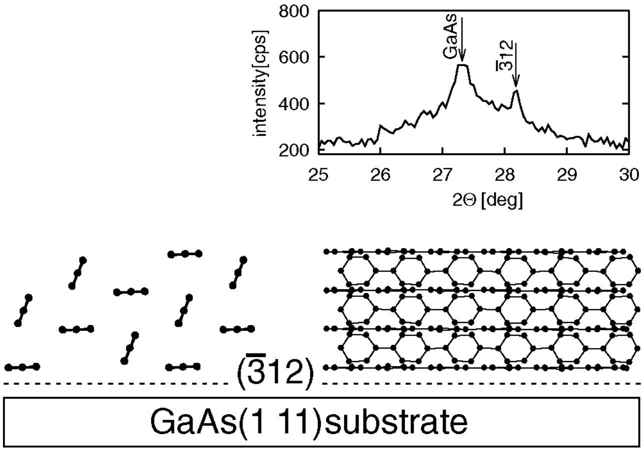

Figure 2. Orientation of the molecules relative to the GaAs(111) substrate in top view (left) and side view (right) as obtained by x-ray diffraction; the $\Theta/2\Theta$ scan of the hexaphenyl GaAs(111) sample is given in the top right part of the figure.

GaAs(111) substrate, as shown in Fig. 2. The $(\bar{3}12)$ plane is sketched with a dotted line and the orientation of the hexaphenyl molecules relative to the substrate is drawn in top view as well as in side view. The orientation of the hexaphenyl molecules is explained by two ingredients: the long axes of the molecules are aligned parallel to the substrate, suggestive especially for the early stages of growth; and every second molecule has its molecular plane (plane built by the six phenyl rings of hexaphenyl) exactly parallel to the GaAs surface. Note how one phenyl ring fits nicely the As–As or Ga–Ga distance of 0.4 nm.

It is possible to perform the TED study on an individual hexaphenyl island. However, owing to the thickness of the head, the different diffraction pattern are only taken from the tail of the islands and at the outer circumference of the head, respectively. Figure 3(a) shows one of the two different diffraction patterns observed. The insert of Fig. 3(a) represents the related defocused image. The bright spot onto the tail of one hexaphenyl island exhibits the area selected for the diffraction pattern in Fig. 3(a). The diffraction pattern consists of well-defined spots. Our simulation of this diffraction pattern is shown in Fig 3(b) and demonstrates an excellent agreement with the experimental data. The deviation is within a few per cent. The agreement between observed and calculated intensities is even seen in Fig. 3: in the zero layer line the $(\bar{6}00)$, $(\underline{12}00)$ and $(\underline{13}00)$ reflections are dominating; and $(\bar{1}11)$ and $(\bar{2}11)$ are diffraction spots of high intensity. Because the interplanar distances as well as the spot intensities of the experiment correspond exactly to the simulations, we believe that the underlying crystal structure of hexaphenyl is uncovered as the observed crystal structure. The simulation of the diffraction pattern is performed with the [203] zone parallel to the incident electron beam, therefore the contact plane of the hexaphenyl island to the GaAs substrate is $(11\bar{2})$. The tail of the hexaphenyl island is in the [021] direction of the crystallite.

Another characteristic diffraction pattern is given in Fig. 4(a). A highly symmetric pattern of the diffraction spots is observed. Just as in the diffraction pattern of Fig. 3, the observed interplanar distances and intensities agree with the simulated ones given in Fig. 4(b). Only the symmetry-forbidden reflections (010) and $(0\bar{1}0)$ are present. These reflections arise due to multiple scattering of the electrons (dynamic scattering), as already observed for anthracene, which is symmetry equivalent to hexaphenyl.[8] The diffraction pattern was simulated with the zone axis $[01\bar{1}]$, resulting in a contact plane of $(\underline{10}01)$.

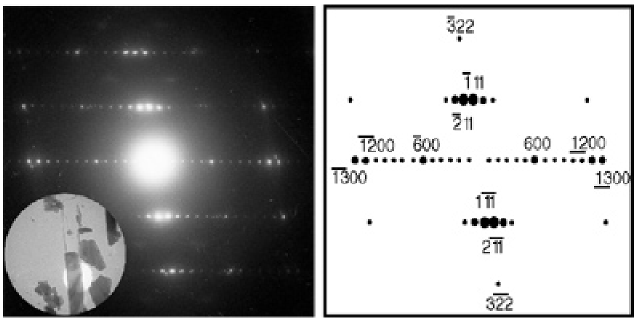

Figure 3. (a) Transmission electron diffraction pattern from the tail of a hexaphenyl island. The insert gives the defocused image. (b) Simulated electron diffraction pattern for the $[01\bar{1}]$ zone axis.

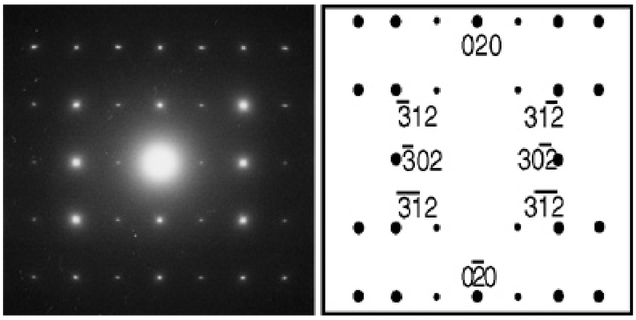

Figure 4. (a) Transmission electron diffraction pattern from another tail of a hexaphenyl island. (b) Simulated electron diffraction pattern (with indexing) for the [203] zone axis.

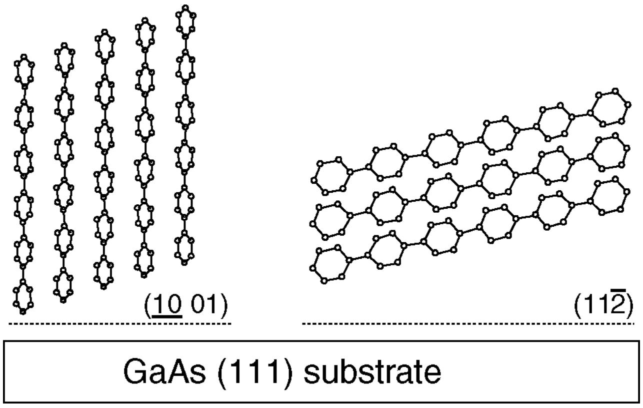

Figure 5. Two different orientations of molecules relative to the surface of the GaAs(111) substrate as obtained from the transmission electron diffraction data. The dotted line represents the contact plane of the hexaphenyl crystallite with respect to the substrate.

Surprisingly, the tails of the hexaphenyl islands exhibit two different orientations, as represented in Fig. 5 relative to the GaAs(111) substrate. The first orientation is described by the $(11\bar{2})$ contact plane indicated by a dotted line. The molecules are inclined towards the substrate and the long axis of the molecules is tilted by 14° with respect to the substrate surface. The contact plane of the other orientation is $(\underline{10}01)$. Here, the molecules are perpendicularly oriented to the substrate surface. In both cases the contact planes through the hexaphenyl crystal intersect the hexaphenyl molecules. A simple description of the growth of these highly anisotropic organic molecules that form such extended islands (crystallites) with the uncovered crystalline structure cannot be given here.

DISCUSSION AND CONCLUSION

As found on GaAs(001), hexaphenyl grows on GaAs(111) in the 3D fashion (Volmer–Weber mode). Because the islands are homogeneously distributed on the substrate and do not show any preferential orientation on a scale of 17 nm (cf. Fig. 1) or larger, we can surely exclude the possible influence of the miscut of 2°.

The island densities and heights are comparable, whereby the island shape reflects the substrate symmetry. For hexaphenyl/GaAs(111) the 3D islands consist of a massive head and a thinner tail. The tails exhibit a constant height and width, which is attributed to the compressive strain of the islands.[9] Transmission electron diffraction performed on the tails reveals two different orientations that are identified as the $(11\bar{2})$ and the $(\underline{10}01)$ contact planes. Owing to the thickness of the massive heads of the hexaphenyl islands, TED patterns were impossible to obtain. X-ray diffraction in a $\Theta/2\Theta$ scan shows a $(\bar{3}12)$ contact plane of the hexaphenyl crystallites, presumably only present in the head. The absence of XRD peaks of the orientations observed by TED is related to their low intensity in the case of the $(11\bar{2})$ reflection or the extinction of the $(\underline{10}01)$ reflection. On the other hand, if one assume that the massive heads of the hexaphenyl islands are responsible for the $(\bar{3}12)$ orientation, this orientation cannot be found by TED because the heads are too thick for this type of diffraction experiment. Thus, the preferred orientation of organic islands cannot be identified by an individual technique. One has to combine the appropriate diffraction and real-space techniques for a complete characterization of epitaxial organic films.

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