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Structure and morphology of sexiphenyl thin films grown on aluminium (1 1 1)

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Abstract

The epitaxial growth of sexiphenyl ($C_{36}H_{26}$) on an atomically clean aluminium (1 1 1) surface is studied on the basis of thin films grown at different substrate temperatures. Thin films with an average thickness of 350 Å are investigated by X-ray diffraction techniques and atomic force microscopy. Grown at room temperature the films show epitaxial order. It is found that the aromatic planes of sexiphenyl are oriented parallel to Al(1 1 1) and the long axes of the sexiphenyl molecules are aligned along a $\langle 1\ {-1}\ 0\rangle$ azimuthal direction at the Al(1 1 1) surface. The films grow in islands with average lateral dimensions up to of 200 nm and to 50 nm in height, the areas between the islands are observed as rather flat. The films grown at 150 °C show a completely different morphology: occasional large islands and irregularly distributed segmented needles with a relatively constant width of about 0.5 μm, lengths up to 100 μm and heights of about 600 nm. Although the film appears as crystalline, no epitaxy could be verified.

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1. Introduction

The wide gap organic "semiconductor" sexiphenyl ($C_{36}H_{26}$) has attracted interest for applications in opto-electronic devices such as organic light emitting devices and organic field effect transistors [1,2]. The operation of devices is strongly determined by the electron injection from the metal electrodes to the organic material. In most cases aluminium electrodes are used. Therefore, the properties of the aluminium/sexiphenyl interface are important for device performance [3,4]. Especially the orientation of the molecules relative to the current flow has an influence on the charge transport through and along the interface [5,6]. Quite recently, the growth of sexiphenyl on Al(1 1 1) surfaces was investigated by photoelectron spectroscopy and low energy electron

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diffraction (LEED) [7,8]. The first monolayer as well as thicker films were investigated as a function of the substrate temperature (25 and 150 °C). It was found that the formation of the first monolayer is independent of the substrate temperature, since the LEED pattern one observed to be identical for monolayers grown at different substrate temperatures. However, strong differences were observed in both LEED and valence band photoemission in the subsequent growth of the sexiphenyl film. The thin films, which are grown at room temperature show an unchanged LEED pattern at a thickness up to 80 Å. In contrast, 80 Å thick films grown at a substrate temperature of 150 °C show LEED patterns, which are drastically different from the monolayer. A number of different ordered domains and polymorphism were concluded [7].

This paper presents results about the above mentioned two types of sexiphenyl thin films investigated by X-ray diffraction and atomic force microscopy. The epitaxial order as well as the morphology of the films are investigated. Both properties can have strong influence on the performance of devices.

2. Experimental technique

Thin films of sexiphenyl on Al(1 1 1) were prepared under UHV conditions at a base pressure of 1×10^{-10} mbar. In a first step the Al(1 1 1) surface was cleaned by Ar^{+}-sputtering and subsequently annealed at 700 K. The purity of the surface was checked by means of UV photoemission, since the line shape of the valence band of aluminium is extremely sensitive to contamination. LEED reveals a 1×1 pattern of the Al(1 1 1) surface. Sexiphenyl was purchased from Tokyo Chemical Industries and throughly degassed in situ. The deposition was controlled by a quartz microbalance assuming a density of 1 g/cm^3. Deposition rates of 0.2 nm/min were used. Two different types of sexiphenyl thin films were prepared. In one case the temperature of the substrate was kept at room temperature, while in the second case a temperature of 150 °C was used. The nominal thickness of the films was 350 Å. After the preparation procedure, X-ray diffraction (XRD) experiments and atomic force microscopy (AFM) were performed ex situ.

XRD was performed by symmetrical $\theta/2\theta$ scans and by pole figure technique in reflection geometry using CrK_α radiation. The pole figures were taken in step intervals of $\Delta\Psi = 1°$ and in continuous intervals of $\Delta\varphi = 3°$, the collecting time for a single pair of Ψ, φ was 15 s. In order to obtain information on the orientation of the aluminium single crystalline substrate, a single pole figure of the 200 reflection of Al was recorded. The X-ray data was analyzed on the basis of the cubic structure of aluminium with a lattice constant of 4.050 Å [9] and by means of the monoclinic structure of sexiphenyl with lattice constants of $a = 8.091$ Å, $b = 5.568$ Å, $c = 26.24$ Å and $ß = 98.17°$ [10]. Note, only one single phase of sexiphenyl is available as a fully solved crystallographic structure. The diffraction patterns were calculated by the software POWDERCELL, the spherical projections of the crystals are obtained from STEREOGRAM [11,12].

AFM investigations were performed with a Digital Instruments Multimode Nanoscope IIIa microscope in tapping mode using advanced AFM tips for high resolution imaging. Low tip velocity was used in order to image large differences in height of the individual islands.

3. Experimental results

3.1. Growth at room temperature

$\theta/2\theta$ scans reveal one single quite intensive peak arising from sexiphenyl at an interplanar distance of 3.166 Å; no trace of any additional peak of sexiphenyl could be found. Pole figures of the three most intense reflections of sexiphenyl were taken. The pole densities of 21–3, 20–3 and 11–1 were measured. Fig. 1 shows the three pole figures, enhanced pole densities are given by light grey and dark grey areas for elevated and high intensity values, respectively. Spherical projections of the sexiphenyl crystallites are calculated and assigned to the enhanced pole densities. Within Fig. 1 their calculated positions are given by three-bar symbols. Totally 12 different alignments of the sexi-

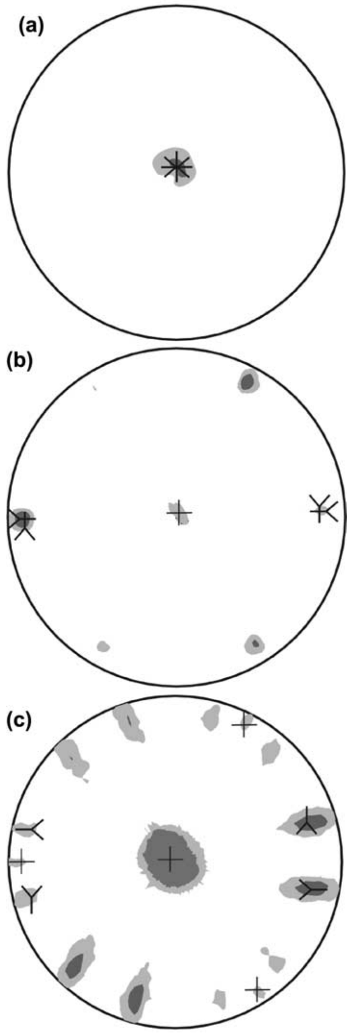

Fig. 1. Three pole figures of sexiphenyl thin films grown on an Al(1 1 1) surface: 21–3 (a), 20–3 (b), and 11–1 (c). Enhanced pole densities are represented by light grey and dark grey areas for elevated and high densities, respectively. Four relationships between epitaxially grown sexiphenyl crystallites and the Al(1 1 1) substrate are found, they are indicated by different three-bar symbols (⅄,≻,Y,≺). The positions of the symbols within the pole figures are obtained from a spherical projection of a sexiphenyl crystal. Crosses mark intensities arising from scattering on the Al single crystal.

phenyl crystallites are required to explain the enhanced pole densities. Taking the three-fold symmetry of the Al(1 1 1) substrate into account, the 12 different alignments can be reduced to four independent alignments of the sexiphenyl crystallites relative to the Al(1 1 1) substrate. The corresponding four epitaxial relationships are listed in Table 1. Please note that the pole figures clearly indicate a three-fold symmetry of the sexiphenyl thin film, which reflects the symmetry of the Al(1 1 1) substrate.

From the crystal structure of sexiphenyl the arrangement of the molecules within the unit cell is known. The combination of this knowledge with the four epitaxial relationships reveals the orientation of the molecules on the Al(1 1 1) surface. For all four types of epitaxial alignments two common elements are found: (i) the aromatic plane of sexiphenyl is parallel to the Al(1 1 1) surface and (ii) the long molecular axes of the molecules are aligned parallel to the $\langle 1\ -1\ 0\rangle$ azimuthal directions on the Al(1 1 1) surface (i.e. parallel to the close packed atomic rows of the substrate surface). Fig. 2(a) gives the alignment of a sexiphenyl molecule on an Al(1 1 1) surface in a right scale. The aluminium atoms of the Al(1 1 1) surface are drawn by dark grey circles which are connected by dashed lines and a single sexiphenyl molecule is drawn along one azimuthal direction.

What is the reason for observing exactly four different epitaxial alignments? The reason is connected with the growth of sexiphenyl crystallites starting from sexiphenyl molecules ordered in he manner described above. There are exactly four possibilities how a crystal can be arranged around an aligned molecule. A schematic picture of these four growth possibilities is given in Fig. 2(b). On one hand, next neighbor molecules (denoted as in-plane molecules) arrange themselves in the same plane (the (21–3) plane). However, there is a shift of the molecules relative to each other, the angle between the long molecular axis and the terminal ends of in-plane neighboring molecules can be 80° or 100° (this is 90° ± 10°). On the other hand the stacking of the molecules upon each other is also connected with an angular shift. The terminal ends of the “stacked” molecules built up the (0 0 1) plane; the angle between the (0 0 1) and (21–3) planes can take the angles 76° or 104° (this is 90° ± 14°). Combining these possibilities of mutual molecular arrangement, four possibilities of crystal growth are possible. These are exactly the four observed types of epitaxial growth (Table 1).

Table 1
Epitaxial relationships between the epitaxially grown crystallites of sexiphenyl (PSP) and the Al(1 1 1) substrate

Notation	Relation between planes	Relation between directions
⅄	$(21-3)_{\mathrm{PSP}}\|(1\,1\,1)_{\mathrm{Al}}$	$[031]_{\mathrm{PSP}}\|[-321]_{\mathrm{Al}}$
≻	$(-2-13)_{\mathrm{PSP}}\|(1\,1\,1)_{\mathrm{Al}}$	$[031]_{\mathrm{PSP}}\|[-1-23]_{\mathrm{Al}}$
Y	$(21-3)_{\mathrm{PSP}}\|(1\,1\,1)_{\mathrm{Al}}$	$[031]_{\mathrm{PSP}}\|[-13-2]_{\mathrm{Al}}$
≺	$(-2-13)_{\mathrm{PSP}}\|(1\,1\,1)_{\mathrm{Al}}$	$[031]_{\mathrm{PSP}}\|[-312]_{\mathrm{Al}}$

The four epitaxial relationships are denoted by following three-bar symbols: ⅄,≻,Y,≺.

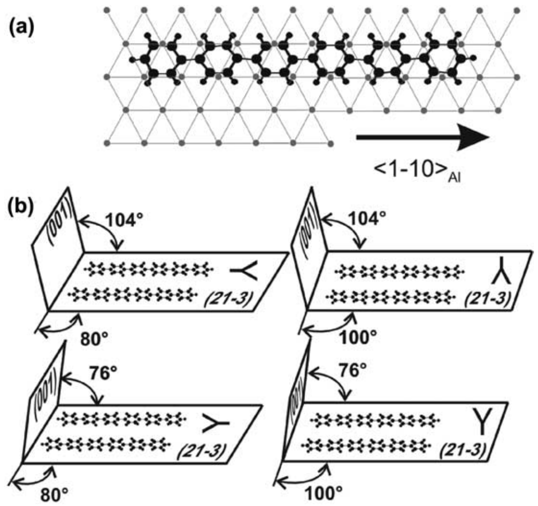

Fig. 2. Orientation of a sexiphenyl molecule on an Al(1 1 1) surface (a). The aromatic planes are parallel to Al(1 1 1) and the long molecular axis of the molecule is aligned along ⟨1 −1 0⟩ directions. Around a single oriented sexiphenyl molecule, four growth directions of sexiphenyl crystallites are possible (b). For a detailed explanation see text.

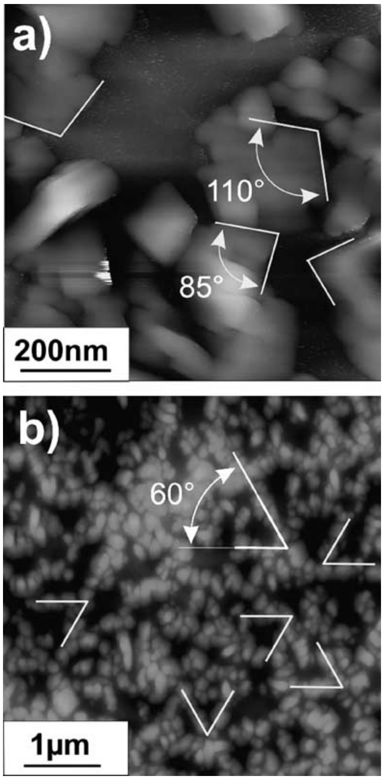

Fig. 3. Morphology of the 35 nm of PSP on Al(1 1 1) grown at room temperature imaged by atomic force microscopy. Two micrographs are depicted at different magnifications, the *z*-scale is 150 nm and 200 nm for (a) and (b), respectively. One typical feature is the quite regular shape of the islands (a); the arrangement of islands in rows and the typical angle between the rows are indicated (b).

The typical morphology of a 350 Å thick film is depicted in Fig. 3. Islands with typical lateral dimensions of about 200 nm are visible. The height of the islands is of about 50 nm, an rms-roughness of 23 nm is observed. The islands show a regular shape with clear edges, typical observed lateral angles are 85° and 110° (Fig. 3(a)). The areas between the islands are flat without any detectable differences in height. This flat inter-island area does not correspond to the bare Al surface, as concluded from photoemission measurements of growth from sub-monolayer to multilayer coverage [8]. The island shapes do not reflect the threefold symmetry of the substrate, the angles reflect rather the margins of close packed rows of sexiphenyl molecules at the (21–3) plane. Interestingly, the islands show a tendency to agglomerate in lines which seem to reflect the substrate symmetry, the lines enclose angles of 60° (Fig. 3(b)). It is remarkable that the morphology appears only weakly regular, whereas the crystallites show a high degree of crystalline order.

3.2. Growth at 150 °C

Symmetrical $\theta/2\theta$ scans of a 350 Å film grown at 150 °C are depicted in Fig. 4(a). Diffraction peaks of sexiphenyl appear at interplanar distances of about 25 Å and at 3.17 Å, which can be indexed with 0 0 1 and 21–3 of the sexiphenyl bulk structure. It seems that at least two different types of orientations are present in the films grown at 150 °C. Please note, that additional peaks appear in the $\theta/2\theta$ scans. They arise from scattering of higher harmonics of CrK_α on the Al(1 1 1) plane. Extended pole figure investigations do not reveal any additional information about the order in the sexiphenyl thin film. Probably the structural order is (in comparison with the room temperature sample) much less developed, so that it cannot be detected by X-ray diffraction pole figure technique. The morphology shows large structures which are visible even with an optical microscope. A typical AFM micrograph is given in Fig. 4(b). Segmented, long needle-like islands, are observed. The needles have a typical width of about 500 nm and a length of up to 100 μm and a height of up to 600 nm. No preferential orientation of the needles is observed. The needles are originated from central islands. These islands show typical heights of over 600 nm.

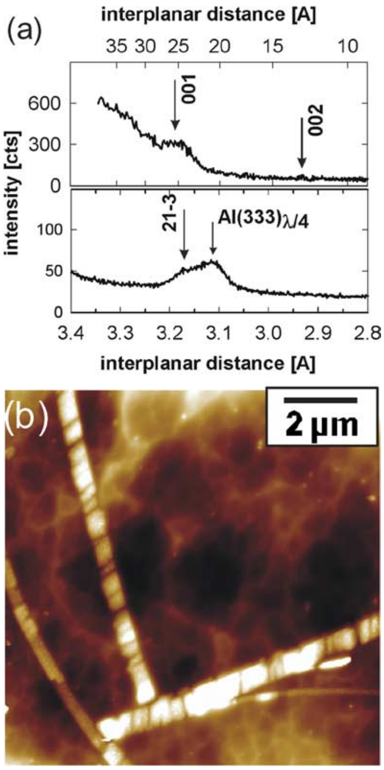

Fig. 4. $\theta/2\theta$ scans of 35 nm thick film on Al(1 1 1) grown at 150 °C reveal weak diffraction peaks at interplanar distances of 25 and 3.17 Å originated from PSP (a). Atomic force microscopy reveals extended islands and segmented needles (b). The *z*-scale is 200 nm.

4. Discussion

Sexiphenyl films grown on Al(1 1 1) at room temperature show epitaxial order, while thin films grown at high temperatures (150 °C) do not show high order by XRD. Films prepared at 150 °C reveal multiple molecular orientations and polymorphism from LEED investigations. These multiple orientations with the long molecular axes perpendicular and parallel to the surface can be verified by the observation of $0\,0\,\ell$ reflections and the 21–3 reflection, respectively (Fig. 4(a)). However, the crystallographic order within the films is too weak for detection by XRD pole figure technique which is experimentally limited by the low scattering probability of the organic material and by the requirement of large domain sizes unlike LEED which indicates upright standing molecules with epitaxial order [7]. On the other hand, films prepared at room temperature show epitaxial order with an unique alignment of the molecules: the aromatic plane of the molecule is parallel to Al(1 1 1) and the long molecular axes are aligned along azimuthal directions on the Al(1 1 1) surface. It is obvious that the alignment of the sexiphenyl molecules has to be similar in the first monolayer. The LEED pattern of the first monolayers reveals a surface unit cell of 8×25 Å^2 [7]. This fits quite well to the area requirements of a sexiphenyl molecule which is arranged “flat on” the Al(1 1 1) surface, the estimated van der Waals area is 6.7×27.2 Å^2.

The Al(1 1 1) surface, unlike Au(1 1 1), does not show any reconstructions. This may explain the observed differences in the molecular alignments of sexiphenyl on these two surfaces. While in the case of Al(1 1 1) surface the long axes of the molecules are aligned along ⟨1 −1 0⟩, on a Au(1 1 1) surface the long molecular axes are aligned along ⟨1–20⟩ [13]. Also the small differences in the lattice constants of Al ($a_{\mathrm{Al}} = 4.050$ Å at room temperature) and Au ($a_{\mathrm{Au}} = 4.079$ Å) can have influence to the molecular alignment [9].

The Al(1 1 1) substrate has a three-fold symmetry. Also the epitaxially grown sexiphenyl crystallites show a three-fold symmetry, like it is evident from the pole figure measurements (Fig. 1(b) and (c)). Although all four epitaxial alignments have the same common element (the aromatic planes are parallel to Al(1 1 1) and the long molecular axis is parallel to ⟨1 −1 0⟩), the fraction of epitaxially aligned crystallites is not distributed equally for these four epitaxial alignments. Two types of epitaxial alignments are less favored (Y,≺) than the other two (λ,≻). Less favored epitaxial alignments correspond to lower pole densities in Fig. 1(b) and (c) which reveal three-fold instead of six-fold symmetry. This fact reveals that not only the uppermost layer of the Al(1 1 1) surface is responsible for the epitaxial growth of sexiphenyl, but also the layer of Al-atoms beneath the top layer has influence on the epitaxial growth of sexiphenyl.

No information is obtained about the influence of step edges of the substrate surface on the epitaxial growth. It is known that the directions of step edges on highly polished metal surfaces are along close packed rows of atoms and that the agglomeration of molecules happens at step edges [14,15]. However, the observation of a densely closed monolayer of sexiphenyl on Al(1 1 1) at a thickness of 6 Å suggests, that the step edges are not the source of epitaxial order in this system [8]. Nevertheless, the arrangement of the islands along straight lines (compare Fig. 3(b)) could be the effect of step decoration.

The morphology of the two types of films is extremely different. In case of films grown at room temperature simple islands with a height of 50 nm are observed, whereas samples prepared at 150 °C show elevated island heights of one order of magnitude. It seems that the higher migration mobility of the molecules at elevated temperatures favor more pronounced 3D growth. However, it is interesting to note, that the films prepared at room temperature show a high degree of crystallographic order while those prepared at elevated temperatures do not. This suggests that the commonly used practice of growth at elevated temperatures to promote structural order may be erroneous.

5. Conclusion

The outstanding result of this work is the evidence of epitaxial order in thin films of sexiphenyl (grown at room temperature with an average thickness of 350 Å) on an Al(1 1 1) substrate. Four different types of epitaxial relationships between the sexiphenyl crystallites and the Al(1 1 1) substrate are observed. Taking the three-fold symmetry of the Al(1 1 1) substrate into account, totally 12 alignments are present. The alignments can be referred to one common structural element: the (on average) planar molecule sexiphenyl is arranged parallelly to Al(1 1 1) surface and the long molecular axes are aligned along the azimuthal ⟨1 −1 0⟩ direction of the Al(1 1 1) surface. This experimental result suggests that this orientation of the molecules is also present within the first monolayers of the film. The morphology of the thin film reveals island type morphology with a height of about 50 nm. Thin films prepared at 150 °C show no epitaxial order by XRD. Also an island type morphology could be observed with a height of the islands of about 600 nm.

Thin films prepared at room temperature show better features for application in the field of organic electronics than films prepared at 150 °C, since high structural order is observed and the morphology appears rather homogenous, which is suitable for a planar technology.

Acknowledgements

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