

Temperature-induced epitaxial growth modes of para-sexiphenyl on Au(111)

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We focus on the epitaxial growth of para-sexiphenyl on a Au(111) single-crystal surface. The films are prepared by molecular beam epitaxy at different temperatures (300 K, 330 K, and 430 K), and their thicknesses are 30 nm. X-ray diffraction investigations of these films show that the growth is strongly dependent on the substrate temperature. Lying molecules are always observed and lead to sexiphenyl crystals with their $\pm(21-3)$ plane parallel to the surface which corresponds to *flat-on* molecules with respect to the substrate. The in-plane alignment of the crystallites is determined by pole figure measurements, at which it is shown that it varies with the growth temperature. While standing molecules, which are only observed at 430 K, are aligned arbitrarily, lying molecules lead to preferred in-plane alignments. It is shown that the type of epitaxy changes from a molecule alignment (along distinct gold directions) on samples grown at 430 K and 330 K to an alignment of crystallites on the 300-K film, which is obviously driven by a lattice match. In the latter case the molecule long axes are tilted by 3° to the $\langle 11-2 \rangle$ direction of the gold surface. This experimentally observed in-plane alignment could be verified by a lattice mismatch calculation. The excellent agreement between experiment and calculated results reveals that in the latter case the bulk structure of the film is retained down to the interface and that its alignment is affected by the lattice match of the interface surface lattices.

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I. INTRODUCTION

As a blue-light-emitting semiconducting material with high quantum yield, para-sexiphenyl (p-6P) is a very promising material in the field of organic semiconductors.^{1,2} P-6P needlelike structures are of large interest for applications such as nano light-emitting devices (nano-LED's), waveguides, and lasers.³⁻⁸ Since optical and electronic properties are strongly dependent on the orientation of the crystallites, it is essential for applications to control the crystal growth. This makes an understanding of the fundamental growth mechanisms indispensable.

For sexiphenyl molecules the highest energy gain is achieved by arranging them within herringbone layers with their long molecule axes parallel to each other.^{9,10} The mainly observed crystal structure is the β phase (Baker phase) of para-sexiphenyl which is a monoclinic crystal consisting of herringbone layers of approximately the thickness of one molecule length.¹¹

Previous studies of p-6P thin films grown on different substrates (aluminum, glass, KCl, NaCl, KBr, GaAs, mica, gold, etc.), under varying growth conditions (growth method, substrate temperature, growth time), yield different types of growth.¹²⁻²⁹ From the morphological point of view there are mainly two different kinds of growth: namely, needlelike growth and terracelike growth. It is to say that there are different kinds of needles concerning their shapes and their sizes as well as their alignments.¹⁹⁻²⁹ Structural analyses yield a number of different preferred *contact planes* (planes parallel to the surface).¹⁸ Some of them lead to molecular alignments with molecules lying on the surface either *flat-on* or *edge-on*; others yield molecules that are standing on the surface (*end-on*). Some studies correlate the morphology and the crystal structures so that it is seen that standing molecules mainly form terraces whereas lying molecules tend to form needles.^{19,24}

Also varieties concerning the crystal in-plane alignment are observed. In some cases an arbitrary in-plane distribution of sexiphenyl is observed; in others, there are preferred in-plane alignments. The in-plane alignments are determined by different matters: sometimes the molecule long axes, sometimes the herringbone layers, and sometimes the lines of the adjacent molecules are found parallel to a certain surface direction.^{18-21,24,27-29} On the other hand, there are systems where the lattice match seems to determine the in-plane alignment of the thin film.²⁹⁻³³

Concerning the epitaxial growth there exist methods to calculate the most probable in-plane alignment and to describe the alignment by an epitaxial matrix.³⁰⁻³³ This matrix is a transformation matrix between two surface unit cells with a defined rotational angle between each other. The lattice mismatch is calculated for two different surface unit cells by variation of the in-plane angle. Furthermore, the lattice constants can be varied to find a better lattice match at the cost of strain in the organic layer. A more advanced calculation takes the energy gain into account, but so far these calculations are only done for flat lying molecules.³¹⁻³³ Epitaxy is defined in Ref. 43 as any structure-dependent intergrowth (overgrowth) of two chemically and/or structurally different crystalline or subcrystalline phases. Explaining epitaxy in terms of lattice match one has to distinguish between different types of coincidence: point-on-point, point-on-line (two types), and line-on-line. However, this way of description does not always lead to a satisfying result, because there are incommensurable lattices that show a well-defined epitaxial order.²⁴ This can be understood because the lattice-matching condition is drastically relaxed in the case of organic epitaxy where large differences between the involved structures exist and van der Waals interactions play a major role.^{41,42}

Previous studies of p-6P on Au(111) show a molecular alignment within the first monolayer at which the molecule long axes are almost parallel to the $\langle 11-2 \rangle$ direction (intera-