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Morphology and crystallographic properties of rubrene thin films grown on muscovite(0 0 1)

T. Djuric [a,*], A. Thierry [b], W. Grogger [c], Sh.M. Abd Al-Baqi [d], H. Sitter [d], R. Resel [a]

[a] Institute of Solid States Physics, Graz University of Technology, Austria
[b] Institut Charles Sadron, Centre National de la Recherche Scientifique, Strasbourg, France
[c] Institute for Electron Microscopy, Graz University of Technology, Austria
[d] Institute of Semiconductor and Solid States Physics, University Linz, Austria

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ABSTRACT

Thin films of the organic semiconductor rubrene were deposited on muscovite (0 0 1) substrates by hot wall epitaxy. The morphology of rubrene thin films in combination with their crystallographic properties was characterized by transmission electron microscopy. The initial growth proceeds in a partially wetting regime where amorphous droplets are formed. Through diffusive interactions the droplets merge together in partially crystalline open networks. At a more advanced growth stage, spherulites are formed and a variety of crystalline morphologies appears. Platelet- and needle-like morphologies can be assigned to the orthorhombic phase of rubrene with the [3 0 1] and [1 1 0] zone axes, respectively.

1. Introduction

Rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene) is a conjugated molecule consisting of a tetracene backbone and four phenyl sidegroups. The overlap of the π-orbitals of phenyl rings belonging to adjacent molecules provides an extended system of delocalized electrons. Hence, rubrene shows one of the highest charge carrier mobilities measured in organic single crystal transistors (20 cm^2/Vs [1]) and has recently become a focus of interest. To achieve similar electronic properties in thin films as well, crystalline films with a high molecular order are required. In contrast to other conjugated organic small molecules like sexithiophene and pentacene [2,3], rubrene mostly yields highly disordered films. Numerous attempts to grow well-structured rubrene thin films on different substrates resulted in amorphous films with small spherulitic-shaped crystalline areas [4–8]. The reason for this unfavourable growth behaviour can be found in the molecular conformation of rubrene. The phenyl rings are twisted in respect to the tetracene backbone and cause a nonplanarity of the molecule, which impedes a crystalline growth from the first monolayer [9].

Rubrene crystallizes in three different polymorphic phases. The first characterization of its crystal structure was already reported in 1936 by Taylor [10], who observed a monoclinic structure with lattice constants $a = 1.550$ nm, $b = 1.010$ nm, $c = 0.880$ nm and $\beta = 90.55^\circ$. In 1962, Akopyan et al. [11] described the triclinic polymorph with lattice constants $a = 0.915$ nm, $b = 1.160$ nm, $c = 0.716$ nm and angles $\alpha = 103.53^\circ$, $\beta = 112.97^\circ$ and $\gamma = 90.98^\circ$. An orthorhombic unit cell was first reported by Henn et al. (1971) [12] and all following structure solutions of rubrene (e.g. [13,14]) revealed the same unit cell with the lattice constants $a = 0.7184$ nm, $b = 1.4433$ nm, $c = 2.6897$ nm. A full structure solution is available for the orthorhombic polymorph only.

This work presents a study of the different growth stages of rubrene thin films on muscovite(0 0 1) surfaces together with their crystallographic characterisation.

2. Experimental methods

Rubrene was purchased from Sigma Aldrich (elemental purity >98%) and additionally purified by gradient sublimation. Freshly cleaved muscovite (0 0 1) was used as substrate. Rubrene thin films

* Corresponding author. Tel.: +43 316 873 8477; fax: +43 316 873 8466.
E-mail address: tatjana.djuric@tugraz.at (T. Djuric).

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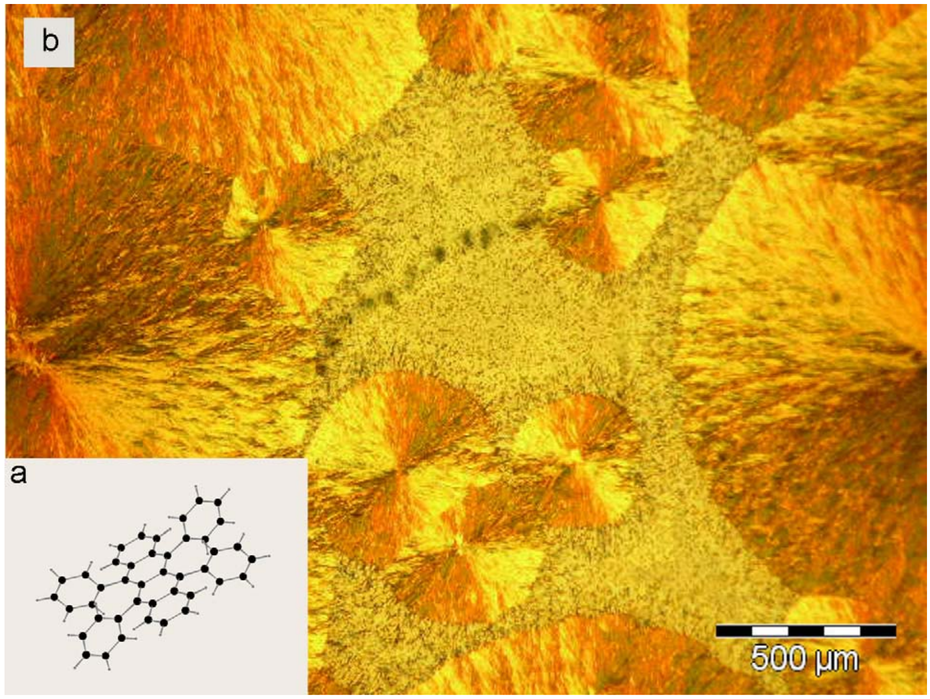

Fig. 1. Polarized optical microscopy image of a rubrene thin film grown for 3 h at a substrate temperature of 393 K. The inset shows the chemical structure of a rubrene molecule.

were deposited by hot wall epitaxy in a vacuum chamber with a base pressure below 10^{-4} Pa under systematically varied growth conditions. The deposition rate corresponds to temperatures $T_{source} = T_{wall} = 508$ K. The substrate temperature was varied between 344 and 393 K and the growth time from 5 min to 3 h.

The samples were examined by polarized optical microscopy (POM) and transmission electron microscopy (TEM). POM was performed with an OLYMPUS BX51 microscope in crossed polar mode. For transmission electron microscopy investigations, a PHILIPS CM 12 microscope operated at 120 keV was used. The diffraction patterns were recorded in the selected area electron diffraction (SAED) mode, where the size of the diffracting region is limited to diameters between a tenth and few µm. Some of the reported images were taken in the defocused diffraction (DD) mode to preserve the relative image and diffraction orientation. A double exposure mode is used, in such a way that the diffracting region appears as an enlightened circle within the real space image. As the DD mode misses the size information, additionally bright field (BF) images were recorded to allow a scaling of the morphologies. The SAED patterns were evaluated with the software Cerius2 by ACCELRYS and CaRIne crystallography 3.0. For TEM observations, the rubrene films are removed from muscovite by floating on water or on diluted hydrofluoric acid (HF) (5%) water solution and baked with carbon. As some thin films strongly adhered to the substrate, the films could not always be fully removed.

3. Results and discussion

Fig. 1 shows a representative optical micrograph of a rubrene thin film grown for 3 h on muscovite held at 393 K. At this microscopic scale, two different morphologies are readily identifiable. Spherulites in the millimetre range are embedded in a porous film wetting the substrate surface. Films grown for shorter growth times only display the porous morphology films with a lack of spherulites. Identical growth behaviour was already reported on SiO_2 by Luo et al. (2007) [6].

3.1. Initial growth stage

The samples studied in this work cover a broad range of growth conditions. The evolution of the thin film morphology is evidenced by observing samples grown at the same substrate temperature ($T_{sub} = 363$ K) but at different growth times (Fig. 2). In the early stage of deposition ($t_{growth} = 5$ min) (not shown in Fig. 2), rubrene grows in a partially wetting regime forming spherical cap-shaped droplets with an average diameter of about 20 nm. Other isolated morphologies like thin needles or small platelets are rarely found. With increasing growth time ($t_{growth} = 15$ min), droplets grow bigger and attain an average diameter of approximately 200 nm (Fig. 2a). By means of used experimental methods (TEM and X-ray diffraction (XRD)), no statement about the existence of a wetting layer is possible. Since the evolution of a wetting layer for conjugated molecules deposited on muscovite is frequently reported [15–17], its existence has to be regarded as realistic.

The subsequent stage in the evolution of rubrene thin films is driven by diffusive interactions that cause deformations of the droplets. Coalescence of neighbouring droplets starts forming open networks (Fig. 2b). At this advanced growth stage, other morphologies like needles and platelets are emerging more frequently.

The same successive growth stages are found by observing samples grown at a given time ($t_{growth} = 15$ min) but with different substrate temperatures. At lower substrate temperatures ($T_{sub} < 363$ K), thin films show many different morphologies like platelets and needles. In contrast, at high substrate temperatures ($T_{sub} > 363$ K) the development of morphologies other than droplets is suppressed.