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Initial stage of crystalline rubrene thin film growth on mica (0 0 1)

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ABSTRACT

We have studied the morphology and the spatially resolved photoluminescence of rubrene thin films at the early stage of crystallization. The initial growth proceeds via the formation of a wetting layer and the nucleation of islands with an amorphous structure. Crystallization starts when the amorphous islands coalesce and needle like crystalline fibers are formed in the gap between islands. The crystalline fibers then grow on top and in between the original amorphous islands leading to an "open network" of islands. The latter acts as the basis for the growth of semi-crystalline spherulites.

1. Introduction

Increasing scientific and technological interest is devoted to organic materials for their promising applications in optoelectronic devices such as organic field effect transistors (OFETs) [1,2], light-emitting diodes (OLEDs) [3,4], and photovoltaic cells [5]. Because of the favorable overlapping of the π-orbitals of the adjacent molecules, rubrene ($C_{42}H_{28}$, 5,6,11,12-tetraphenyltetracene) constitutes one of the most promising candidates for the realization of high performance OFETs. Indeed, OFETs based on rubrene single crystals exhibit a very high carrier mobility [6,7]. On the other hand, it is still a great challenge to fabricate OFETs based on rubrene thin films with satisfying electronic properties by organic molecular beam deposition (OMBD) [8,9]. Käfer et al. have shown that the different molecular conformation in gas (nonplanar) and bulk phase (planar) results in a disordered seed layer on the substrate which impedes the growth of ordered thin films [10]. Accordingly, the growth of crystallites with a bulk structure can occur only at particular nucleation sites [10]. Progress has been achieved in improving the crystallinity of rubrene thin films by deposition on organic single crystal substrates [11] or inorganic substrates pre-covered by organic layers [12], deposition on passivation layer of self-assembled octadecyltrimethylsilane on silica [13], prolonged annealing of amorphous thin films in vacuum [14,15] and by using hot-wall epitaxy (HWE) [16,17]. However, a detailed understanding of the growth mechanism is still missing. It is thus very important to study the growth, especially at its initial stage. It is well known that the crystallinity of rubrene not only influences its electronic performance but also its optical properties [14,15,18–23]. Characteristic photoluminescence (PL) spectra have been reported for amorphous [14] and crystalline phases of rubrene [18,19], respectively. Particularly, it has been demonstrated that the PL spectrum can be used as a sensitive probe for the transformation of thin rubrene films from the amorphous to the polycrystalline phase [15].

In the present study, we have investigated the morphology and PL emission of rubrene thin films deposited on muscovite mica (0 0 1) substrates by HWE using a combination of atomic force microscopy (AFM), fluorescence microscopy (FM) and laser scanning confocal microscopy (LSCM). Special attention was devoted to the initial stage of crystallization in rubrene thin films. The spatially resolved PL emission measured by LSCM allows us to determine the location and the onset of crystallization.

2. Experimental

Rubrene thin films were deposited on the (0 0 1) surface of muscovite mica using hot-wall epitaxy (HWE) [24]. The mica substrates were cleaved in air and then transferred into a vacuum chamber with a base pressure of 10^{-6} mbar. Before rubrene deposition, the substrate was thoroughly degassed by heating for 30 min at 150 °C in vacuum. During deposition, the substrate was kept at 150 °C, while the source and wall temperature was 160 °C. AFM measurements were performed with a Veeco Dimensions S3100 microscope with super sharp silicon tips (Nanosensors SSS-NCHR-50) operated in tapping mode. Fluorescence microscopy was performed with an inverted microscope (Nikon Eclipse Ti) using a Hg lamp for illumi-

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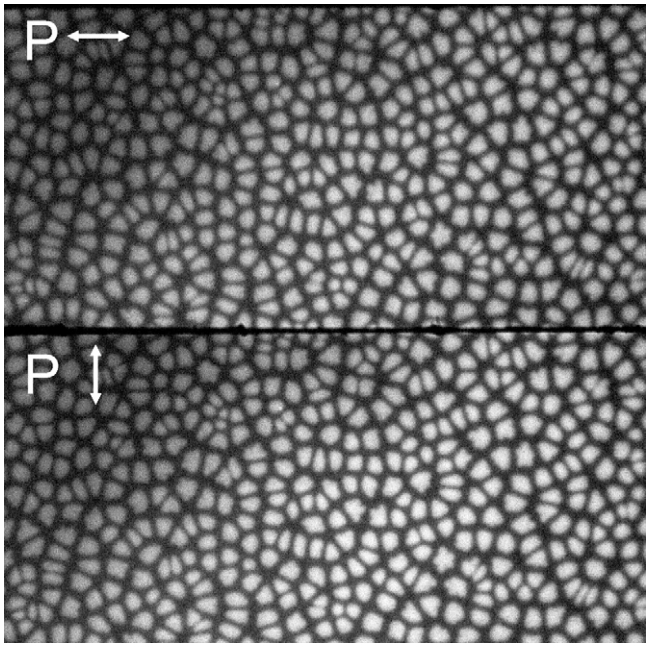

Fig. 1. Fluorescence images recorded from ultrathin rubrene films on mica. The two panels show the same 130 μm wide area but with the polarization of the fluorescence signal oriented along two orthogonal directions as indicated by the arrows in the images.

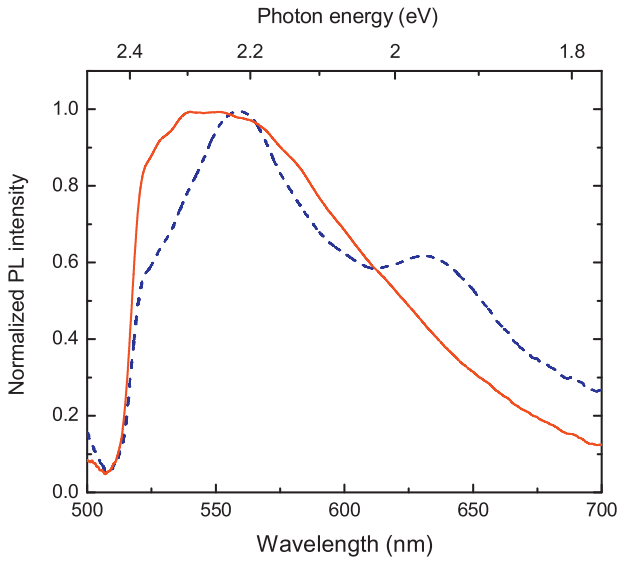

Fig. 2. Spatially integrated PL spectra recorded from the images presented in Fig. 1 (solid line) and Fig. 3a (dashed line), respectively.

nation. The excitation wavelength can be selected within a wide range from UV to red by using different filter cubes. Fluorescence images were acquired with an electron multiplying CCD camera (Luca EMCCD from Andor Technology). In order to investigate the polarization state of the fluorescence signal, a beam splitter (Cairn Research Optosplit II), which allows dual polarisation imaging, was attached in front of the camera. For acquiring the PL spectrum from the field of view of the microscope, a high-resolution spectrometer (HR4000 from Ocean Optics) can be attached to the eyepiece of the microscope. Furthermore, a Nikon Eclipse C1si confocal microscope system equipped with a spectrometer using 32 channel photomultiplier tube detectors was used to record spatially resolved PL spectra.

3. Results and discussion

Fig. 1 shows the fluorescence image of rubrene grown on the (0 0 1) surface of muscovite mica. A medium band blue excitation filter (Nikon B-2A, excitation wavelength 390–450 nm) was used for the experiment. The image shows that the surface is covered by islands with an average size of about 3 μm and an average height of about 300 nm. The islands are distributed homogeneously on large terraces over most of the substrate area. From the eyepiece, one can see clearly that the emission of these islands is green under irradiation with blue light. Although the shape of the islands is not really uniform, no preferential orientation of the island is observed. Besides, the top and bottom panels in Fig. 1, which are taken from the same area but with polarization along two orthogonal directions as marked by the arrows, show equal intensities. This observation demonstrates that the rubrene molecules in the islands are randomly oriented, suggesting an amorphous structure of the islands. Indeed, the corresponding PL spectrum plotted in Fig. 2 is very close to that of amorphous rubrene thin films reported by Park et al. [14,15], characterized by a broad peak around 560 nm. Based on the unpolarized nature of the emission and its spectral line shape, we can conclude that the structure of the islands shown in Fig. 1 is amorphous. This conclusion fully agrees with the results of transmission electron microscopy (TEM) and transmission electron diffraction (TED) measurements obtained from samples prepared under similar conditions [25]. Thin films with similar morphology and structure have also been observed before the onset of crystallization [12,13,26–29]. The not completely round appearance of the islands is characteristic of the very late stage of amorphous growth [29].

In addition to the typical image presented in Fig. 1, occasionally, areas with different morphology and emission properties can be found on the same sample. Fig. 3a shows such an area containing an open network of islands which emits yellow light. Indeed, the corresponding PL spectrum measured from the same area reveals additional emission features peaked at 570 nm and 645 nm (Fig. 2). In fact, on single crystal rubrene samples, PL emission at the same wavelengths has been reported. According to Mitrofanov et al., the 570 nm and 645 nm features are contributed by the emission from crystalline rubrene and its oxidation state, respectively [18,19]. The central area of the network structure shows a particularly strong emission at these wavelengths with some degree of polarization. To have a closer look at the network structure, the area surrounded by white frame in Fig. 3a was imaged using an objective with larger magnification (60×) and the result is presented in Fig. 3b. In this figure one can clearly see that the yellow islands are those covered and connected by strongly emitting fibers. Besides, it is the emission from these fibers which shows a dependence on the polarization. The morphology of the islands and the fibers on top of them can be seen more clearly in Fig. 3c, which displays an AFM image recorded from the area marked by the white frame in Fig. 3b. Comparing Fig. 3b with Fig. 3c, it is evident that the islands which emit yellow light are those covered by fibers. The thick fibers located in the central area of the network exhibit sharp and straight edges indicating a crystalline structure. The line profile taken from the AFM image in Fig. 3c along the line AB is plotted in the same figure. From this, the cross-sectional profile of the fibers can be resolved, yielding a height of about 50 nm and a width of around 250 nm. Most importantly, from the morphology revealed by AFM and the spectral emission detected by fluorescence microscopy, we conclude that the fibers are crystalline rather than amorphous. Consequently, the open network of yellow islands observed here can be assigned to the initial stage of growth of microcrystalline rubrene films. Similar structures have been reported recently by different authors [13,25]. Particularly, Djuric et al. have investigated samples prepared under