

Rubrene on mica: from the early growth stage to late crystallization

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Abstract. The fabrication of Rubrene thin films is of interest because of the high mobility observed for Rubrene single crystals. Here, we report on an atomic force microscopy (AFM) investigation of the growth of Rubrene thin films by Hot Wall Epitaxy on mica(001). During the initial formation of amorphous islands, a non-constant growth rate is observed due to temperature dependent changes in the sticking coefficient. Furthermore, the contact angle of these islands – also measured by AFM – depends on temperature. With continuous deposition, island coalescence starts resulting in ramified surface aggregates. The final growth stage is characterized by the formation of crystalline spherulites which also analyzed by AFM.

1. Introduction

Rubrene is known for its large carrier mobility in single crystal form. Values of up to 20 cm²/Vs have been reported [1,2]. Although this would make it an interesting candidate for various devices, thin films grown from Rubrene have shown hole mobilities lower by 7 orders of magnitude [3]. Unfortunately, very often these thin films are amorphous. Recent studies have shown that in crystalline or polycrystalline films grown with a large overpressure of Rubrene or by utilizing heterostructures, mobilities of up to 0.2 cm²/Vs can be reached [4-6]. Recent work using the weakly interacting substrate SiO₂ and an OTS layer to tune the surface energy of the substrate demonstrated mobilities between 0.1 cm²/Vs and 2.5 cm²/Vs [7].

Here, thin films of Rubrene are grown on mica(001) by means of hot wall epitaxy (HWE). The initially formed amorphous islands as well as the morphologies in crystalline spherulites, observed in thick films, are characterized by atomic force microscopy (AFM). The behavior of the growth rate, the contact angle of the Rubrene islands, and their fractal dimension are analyzed in dependence on growth temperature and film thickness.

2. Experimental Methods

Mica(001). The (001) surface used is a cleavage plane of 2M₁ muscovite. It allows easy ex situ cleavage offering large (>100 μm) atomically flat terraces. Fur-

thermore it has shown the capability to align organic molecules by the a strong surface dipole [8]. Standard quality mica was cleaved before insertion into the HV chamber, thus a fresh cleaved surface with only a few cleavage steps is used.

Hot Wall Epitaxy (HWE). HWE is a high vacuum variant of physical vapor deposition with a base pressure of 10^{-6} mbar [9]. In contrast to many other growth techniques it utilizes the near field of the molecular beam by moving the sample close or even into the hot wall tube that holds the film material. The walls of the tube can be heated separately and are held on a higher temperature than the sample and the source. This prevents deposition on the tube wall and helps to create a uniform flux of molecules. The main advantages of HWE are that the films are grown close to the thermodynamic equilibrium. The main drawback is that the position of the sample close to the evaporator makes an in situ characterization of the film growth impossible.

Rubrene. This organic semiconductor consists of a tetracene core with four additional phenyl groups connected by single bonds. In contrast to the desired crystalline phase the amorphous one is not stable against oxidation [10]. The two states can be distinguished easily, since the amorphous phase lacks the typical red color found for crystalline films.

Atomic Force Microscopy (AFM). We used an Digital Instruments MultiMode IIIa AFM in intermittent mode to avoid damage to the organic thin film. Conventional Si probes with opening angles of 20° and tip radii of less than 10 nm have been employed. The typical resonance frequency of the used cantilevers is 300 kHz and the force constant is about 40 N/m.

3. Results and Discussion

Figure 1 shows two series of AFM images obtained from amorphous Rubrene (or more likely oxidized Rubrene [10,11]) thin films grown with a substrate 363 K (a-d) and 393 K (e-h). The deposition times for both image sequences ranged between 2 min and 24 h. First, small circular islands of rather uniform size are formed which then grow (a,b,e,f) and start to coalesce (c,g,h).

In fig. 2 the distribution of island height and island base area for the case of 363 K is presented. The island height changes from 50 nm after 2 min to 120 nm after 60 min. While the width of the height distribution remains constant (20 nm) with ongoing deposition, the width of the island area distribution, however, broadens dramatically as soon as coalescence starts. The same holds for the films grown at higher temperature (lower row of fig. 1). However, in this case the island density is much lower which can be related to the increased mobility of the molecules on the surface at higher temperatures.

Figure 3(a) shows the nominal film thickness (f) vs. deposition time. These thickness values are obtained by calculating the total volume of Rubrene divided by the image area of at least three independent images. For the sample grown at higher temperature, f ranges significantly below the film thickness obtained under identical conditions at lower temperature. We can explain this by a change in sticking coefficient for Rubrene on mica(001). From the power law fits indicated we obtain exponents of nearly unity (linear dependence as expected) for the higher temperature growth and 1/2 for the low temperature growth. We can understand

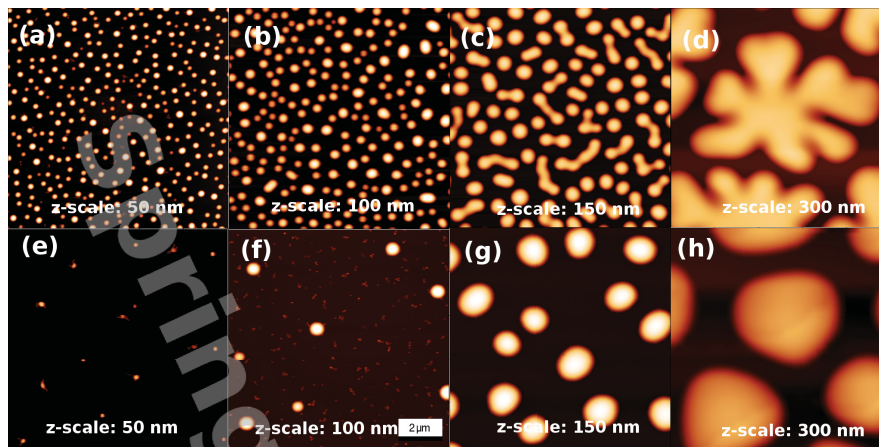


Figure 1: AFM images of Rubrene thin films grown by HWE on mica(001). Top row samples grown at 363 K, bottom row sample temperature 393 K. Deposition times are (a,e) 2 min, (b,f) 15 min, (c,g) 60 min, and (d,h) 24 h.

this behavior if we assume different sticking coefficients, namely a high one for Rubrene on mica(001) and a low one for Rubrene on Rubrene.

The observed change in lateral shape of the islands can be evaluated by the fractal dimension D . Figure 3(b) shows the change in D vs. deposition time, where D is calculated by applying a linear fit to the power spectrum [12] of the corresponding $10 \mu\text{m} \times 10 \mu\text{m}$ AFM images. Again, the growth of the amorphous Rubrene islands can be divided in three stages. First, the compact islands are formed and the highest fractal dimension is obtained. Then coalescence starts, and the fractal dimension is reduced as more one-dimensional aggregates are formed. The last stage shown in fig. 1(d) leads to a further reduction of the dimensionality as the islands become more ramified.

From the islands three dimensional shape we can make qualitative estimations on the surface free energy. As the Rubrene islands in the initial stage have the shape of a droplet it is assumed that they are amorphous which is confirmed by several techniques [3,13]. Thus, AFM allows measuring the contact angle Θ , like for liquids, by analyzing cross sections through the island center [3]. Figure 4 shows two cross sections through islands grown at different temperatures. Both sections are taken from samples with deposition times shorter than the deposition time re-

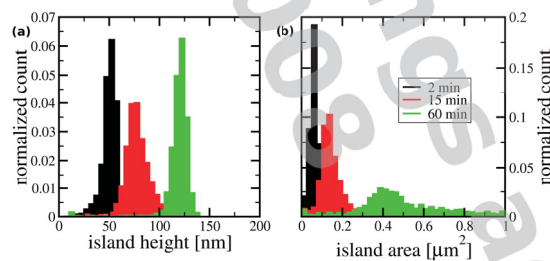


Figure 2: Island height (left) and island size histograms for Rubrene films grown at 363 K.

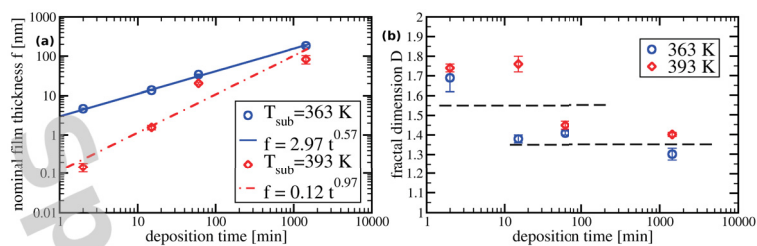


Figure 3: (a) Nominal film thickness f from AFM images vs. deposition time. (b) Fractal dimension of the Rubrene islands vs. deposition time. Dashed lines separate the regimes.

quired for coalescence to allow the largest possible drop volume but before changes in island shape might influence the contact angle. Besides the obvious size difference, the contact angle for the film grown at elevated temperature is larger than the one grown at lower temperature. This is contrary to what would be expected at first glance, since surface energy in general decreases with increasing temperature. The observed behavior can be explained when considering different temperature dependencies of surface energies for Rubrene and mica(001). It seems that the surface energy of Rubrene decreases slower with increasing temperature as the one of mica. As a result the surface becomes more *rubrenophobic* with increasing temperature.

The later growth stage is characterized by the formation of large spherulites [14]. Figure 5 shows AFM images obtained from different parts of a spherulite typically found after 1 hour of Rubrene deposition with a source temperature of 508 K and a sample temperature of 363 K. Three areas can be distinguished optically: a dark red center region, a lighter iris region, and a transparent matrix. Already from the red color impression we conclude that the spherulites are crystalline. The matrix, however, has turned transparent when the sample was removed from the high vacuum system because the amorphous Rubrene film is not stable against oxidation. The center (fig. 5(a)) is formed by a rough (rms-roughness: 33 nm), highly crystalline and faceted area that exhibits a slight radial orientation. The surrounding iris area (fig. 5(b,c)) rms-roughness 10 nm) shows branched, strongly radial orientated structures, typical for spherulitic growth. The edge of the spherulite is separated from the amorphous matrix by a deep trench (fig. 5(c)). Furthermore, there is a significant change in height between the spherulite and the matrix region. Both observations are indications of a large mass transport towards the spherulite since it is fed from the amorphous matrix. Fig. 5(d) finally represents the amorphous matrix (rms-roughness 0.7 nm) which is covered by many small holes of a few nanometer depth. These holes could be either due to the mentioned

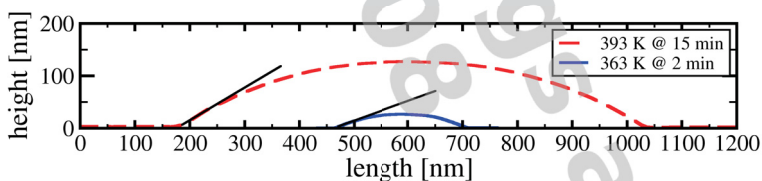


Figure 4: AFM cross section through Rubrene islands. The contact angle is 27° for 393 K and 22° for 363 K.

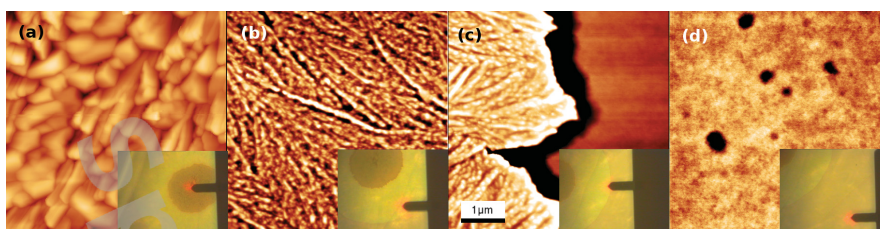


Figure 5: Details of a Rubrene spherulite. (a) Center, (b) Iris, (c) spherulite rim, and (d) surrounding amorphous matrix. Z-scale: (a) 300 nm, (b) 50 nm, (c) 30 nm and (d) 5 nm. The insets show the cantilever position relative to the spherulite center.

massive mass transport but are more likely a result of the oxidation process, since they exit all over the surface.

4. Conclusions

Quantitative morphological AFM analysis of HWE growth of Rubrene on mica(001) allowed to draw the following conclusions with respect to sticking coefficient and surface energies: Material and temperature depended sticking coefficients lead to non-linear growth rates for amorphous Rubrene on mica. The sensitivity of Rubrene growth with respect to the growth temperature is also reflected in the observed increase of the contact angle for Rubrene on mica(001) with increasing deposition temperature.

Acknowledgments. Funding by Austrian Science Fund Projects S9707, S9706.

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