

Rubrene Thin Film Characteristics on Mica

Sh.M.Abd Al-Baqi^a, G.Henandez-Sosa^a, H.Sitter^a,
B. Th. Singh^b, Ph. Stadler^b, N. S. Sariciftci^b,

a)Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria

b)Institute of Physical Chemistry and Linz Institute For Organic Solar Cells (LIOS), Johannes Kepler University, Linz, Austria

E-mail: shaimaa.abd-al-baqi@jku.at

Abstract. Rubrene thin films were deposited by Hot Wall Epitaxy on mica substrates. To optimise the growth conditions, the growth rate and the substrate temperature were changed systematically. The surface morphology of the grown rubrene layers was investigated by polarized optical microscopy (POM), electron microscopy (SEM) and atomic force microscopy (AFM). After an initial nucleation and coalescence stage a continuous amorphous layer is formed. In a later stage of growth, spherulites embedded in the amorphous matrix are found, which furthermore cover the whole surface. It could be proven that the spherulite consist of polycrystalline material, which could be used for the fabrication of organic field effect transistors.

1. Introduction

Many attempts were made to fabricate organic field effect transistors from rubrene thin films [1-4]. The largest mobility obtained so far in rubrene OFETs is $2.5 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is still much less than in monocrystalline bulk material [5]. The main difference between bulk and thin film material is the crystalline property. Consequently, the main effort goes in the direction of improving the crystallographic order in the rubrene layers. Since there is no lattice matched substrate available, the only chance to approach the goal of highly ordered structures is to use an optimised growth regime. Due to the weak Van der Waals type bonds of the molecules, a deposition process as close as possible to thermodynamic equilibrium seems to be appropriate. The local dynamic equilibrium at the growing surface allows a manifold impingement and re-evaporation of the molecules. Supported by an enhanced surface mobility the rubrene molecules can find the optimum position on the substrate to form a highly ordered structure, which can lead to a layer of enhanced crystallinity. The method of choice to provide such growth conditions is the Hot Wall Epitaxy (HWE).

2. Experimental Procedure

The rubrene source material was purchased from Aldrich (purity >98%) and purified by threefold sublimation under dynamic vacuum conditions. The rubrene layers were evaporated in a standard HWE reactor on freshly cleaved $2M_1$ muscovite mica. Two different growth rates were used by employing different

source temperatures (T_s) for the evaporation of rubrene ($T_s=180^\circ\text{C}$ and 235°C). The surface mobility of the rubrene molecules was influenced by the substrate temperatures ($T_{\text{sub}}=80^\circ\text{C}$, 90°C or 120°C).

The surface structure of the rubrene layers was investigated routinely by polarized optical microscopy. Atomic Force Microscopy (AFM), (VEECO Di3100) in tapping mode was employed. In the case of high surface roughness SEM was used to investigate the surface morphology. The crystalline property of the rubrene layers was probed by polarization depend Raman spectroscopy and x-ray diffraction experiments reported in detail elsewhere [6, 7].

3. Results and Discussion

Since mica substrates can be freshly cleaved before evaporation and therefore provide a very clean surface, we selected this substrates to investigate the growth process of rubrene layers. The cleaving process was done ambient air, which means that some dust particles can still contaminate the substrate surface. In the early stage of growth single rubrene islands are formed which coalesce and form an amorphous layer [8]. The later stage of growth is dominated by the formation of spherulites. Fig (1) summarizes the optical micrographs to demonstrate the surface structure after different growth times. Very similar rubrene surface structures were observed previously on SiO_2 substrates [9]. The development of spontaneously nucleated spherulites is clearly seen, which are embedded in an amorphous matrix. By increasing the deposition time, the spherulites grow in diameter and consist of an inner disc surrounded by an outer ring. Finally the spherulites coalesce and cover with the outer ring structures the whole substrate. Depending on their growth mechanisms spherulites can be divided into two categories nucleated either from single nucleation site or bunch of needles and both categories have been found in these thin films from TEM measurement [10]. The radii of the central disc and the outer rings are plotted as a function of growth time in Fig (2), showing a linear increase with the onset of a saturation due to coalescence of the spherulites.

The nucleation of the spherulites can be caused by static impurities or dynamic heterogeneities [10]. If the pin holes in the amorphous matrix would act as nucleation centers, as assumed in ref [9], the density of spherulites should be the same as the density of the pinholes, which is by far not the case. On the other hand, if the spherulites are originated by defects in the amorphous larger, the spherulites would grow on top of the amorphous matrix which is also not the case. As shown by the AFM picture in Fig (3), the spherulites are embedded in the amorphous matrix. The cross section across the border of the spherulite (see Fig (3)) shows the same height for the spherulites as for the amorphous matrix and a clear trench at the borderline. So we assume that starting from an impurity the amorphous matrix undergoes a phase change by forming poly crystalline structures. In that way the material of the amorphous matrix is consumed until the whole substrate is covered with spherulites.

Optical microscopy using polarized light gives a first hint on the crystallinity of the obtained structures. A typical result of optical micrographs obtained without polarization, parallel and perpendicular orientation of the polarizer and analyzer are shown in the Fig (4). If the relative position of the polarizer and analyser is

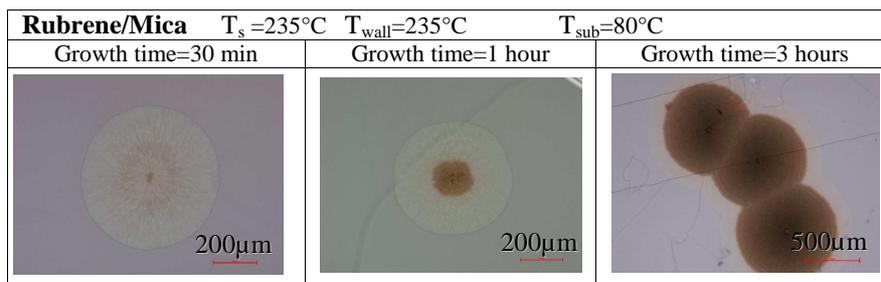


Fig.1. Optical Micrographs of the surface structure with increasing growth time.

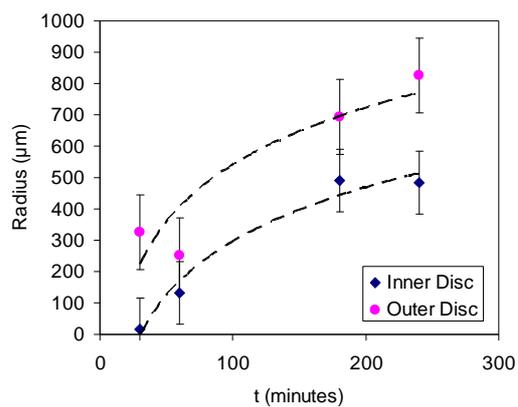


Fig.2. Diameter of the inner disc and outer rings as a function of growth time, $T_s = 235^\circ\text{C}$, $T_{\text{wall}} = 235^\circ\text{C}$, $T_{\text{sub}} = 90^\circ\text{C}$.

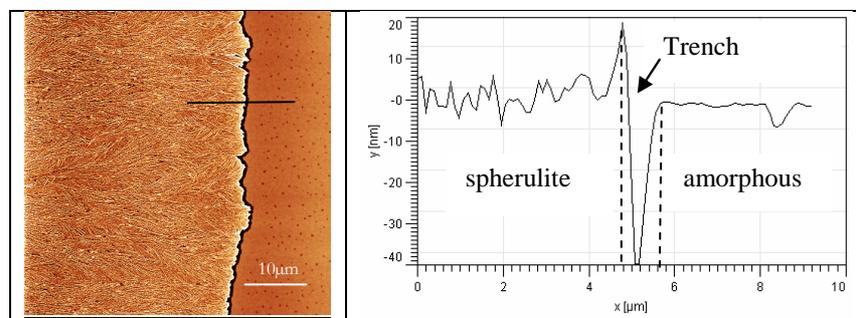


Fig.3. AFM image of rubrene on mica together with a cross section across the border.

changed ; the different regions of the spherulites change their colour, while the surrounding amorphous matrix stays unchanged. This can be interpreted, that the spherulites consist of small crystallites oriented in a radial direction. A detailed investigation of the crystallographic order inside the spherulite was performed by polarization dependent micro Raman spectroscopy and x-ray diffraction [6, 7]. Due to the higher surface roughness inside the spherulite the morphological details were studied by SEM. Fig (5a) shows the typical structure of the inner disc of a spherulite. Zooming into the central part two different features can be observed. Out of a layer consisting of similar elongated mosaic blocks, (Fig 5b) whisker like faceted structures grow in the third dimension (Fig 5c). During the growth of the spherulites in lateral direction by recrystallization of the amorphous material, the flux of impinging rubrene molecules continuous. The additional molecules hitting the amorphous matrix contribute to the continuous growth of this part of the layer. The other molecules impinging on the polycrystalline spherulites find crystalline mosaic blocks as seeds for the formation of whiskers, pointing out of the surface in the central part of the sphurlites. Fig (4c) clearly shows the faceted structure of such whiskers.

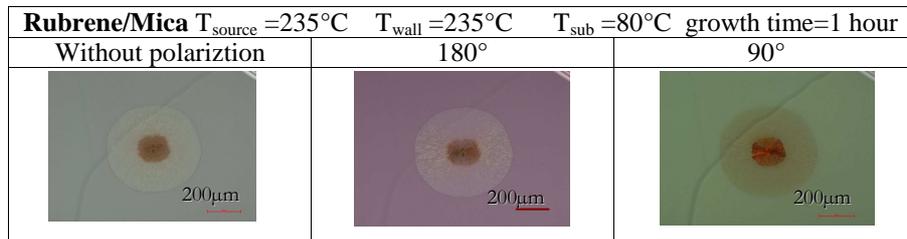


Fig.4. Rubrene thin film on mica substrate under polarized optical microscope.

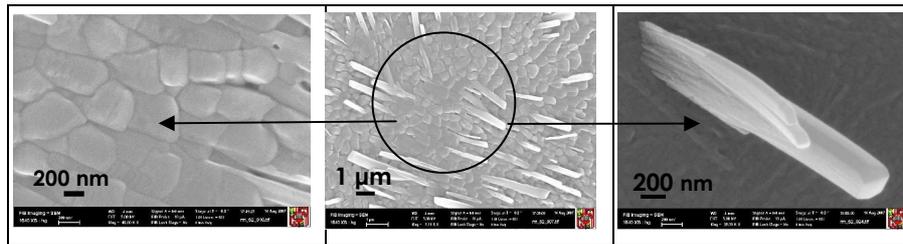


Fig.5. SEM pictures for rubrene on mica substrate $T_s=230^{\circ}\text{C}$, $T_{\text{wall}}=240^{\circ}\text{C}$, $T_{\text{sub}}=120^{\circ}\text{C}$, $T_{\text{pre-heat}}=90^{\circ}\text{C}$.

Acknowledgements. The work was supported by the Austrian Science Foundation (FWF) within the National Research Network (NFN) “Interface controlled and Functionalized Organic Films”.

4. Conclusions

Rubrene thin films were evaporated by HWE on mica. After the formation of an amorphous matrix, spherulite structures start to grow, which finally cover the whole surface. Due to their polycrystalline property the spherulites are resistant against oxidization while the amorphous matrix becomes transparent upon exposure to air, which is a clear sign for oxidation. The rubrene spherulites provide therefore a promising material for the fabrication of OFETs.

5. References

1. Se-W. Park, et.al., Appl. Phys. Lett. **90**, 153512 (2007).
2. Se-W. Park, et.al., Appl. Phys. Lett. **91**, 033506 (2007).
3. M. Nothaft et.al., Phys. stat. sol. (b) Volume **245**, Pages 788 - 792, (2008).
4. C. H. Hsu, et.al., Appl. Phys. Lett. **91**, 193505 (2007).
5. V. Podzorov, et.al., Phys. Rev. Lett. **93**, 086602, (2004).
6. T. Djuric, et.al., E-MRS proceedings 2008,(in print).
7. B. A. Paez, et.al., E-MRS proceedings 2008,(in print).
8. Gregor Hlawacek, et.al.; E-MRS proceedings 2008, (in print).
9. Y. Luo, et.al., phys. Stat. Sol. (a) **204**, No. 6, 1851 –1855 (2007).
10. László Gránásy, et.al., Physical Review **E 72**, 011605 (2005).