

Research Article

Study of Factors Effecting Growth Rate and Grain Density of Rubrene Deposited on Different Substrates Using Hot Wall Epitaxy

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Abstract

Rubrene is a promising hydrocarbon for organic thin film transistors due to its remarkable carrier transport capabilities in the active semiconducting layer. Room temperature hole mobilities for single crystals have been high and are the reason for increased attention towards this material. In our work here we report on the thin films of rubrene deposited on two dielectric materials, SiO_2 and mica which resulted in nominal film thicknesses starting from sub monolayer. A study of island growth dependence on substrate temperatures has also been conducted. In order to understand the molecular growth dynamics of rubrene thin films on these two substrates, we made use of Atomic Force Microscopy for the characterization of these films and studied the pattern of island growth dependence on different substrate temperatures and substrates.

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Keywords:

Hole mobility, Nominal film thickness.

1. Introduction

The field of optoelectronic devices using organic materials is gaining an increase in attention of researchers due to applications like organic field effect transistors (OFETs) [1, 2], photovoltaic cells [3] and light-emitting diodes (OLEDs) [4, 5]. One reason for this interest is the high performance of single crystal based OFETs using organic materials like rubrene (5,6,11,12-tetraphenyltetracene - $\text{C}_{42}\text{H}_{28}$) which have shown an interestingly high carrier mobility [6, 7]. The challenge, however, remains to achieve sufficiently high carrier mobilities using rubrene thin films as are seen for the single crystal-based devices [7–14].

Continuous attempts are being made to grow rubrene thin films of a crystalline nature, but results have showed spherulites which are small polycrystalline areas in the mostly amorphous films [15–17]. In order to fully understand the reason behind such a morphology, a detailed study of the different stages of thin film growth for rubrene is necessary. Research has been conducted into the initial stages of island formation [8–10, 16–

28] and the consequent stage of coalescence and thin film development followed by the nucleation of crystalline areas namely spherulites [29]. Island formation of an amorphous nature on an amorphous wetting layer might be the most interesting stage of growth to be studied for the best understanding of morphology of rubrene thin films as it is followed by crystalline nucleation in between islands [30]. Here we put forward a similar study using substrates of mica and SiO_2 to see rubrene growth dependence on varying substrate temperatures.

2. Materials and Methods

Rubrene, an organic substance, was purchased from Aldrich and purified even further using thermal sublimation. The material was 98% pure. Rubrene was moved into the Hot Wall Epitaxy apparatus and placed in a quartz tube. Muscovite Mica substrates measuring $15 \times 15 \text{ mm}^2$ that were acquired from Segliwa GMBH were manually split fresh in the air before being placed in the HWE vacuum chamber. Subsequent to attaining a vacuum of 10⁻⁶ mbar, a 15-minute preheating process was conducted at the substrate deposition temperature. All materials that have been adsorbed onto the substrate surface are totally removed by this in situ heat treatment. Subsequently, at a vacuum

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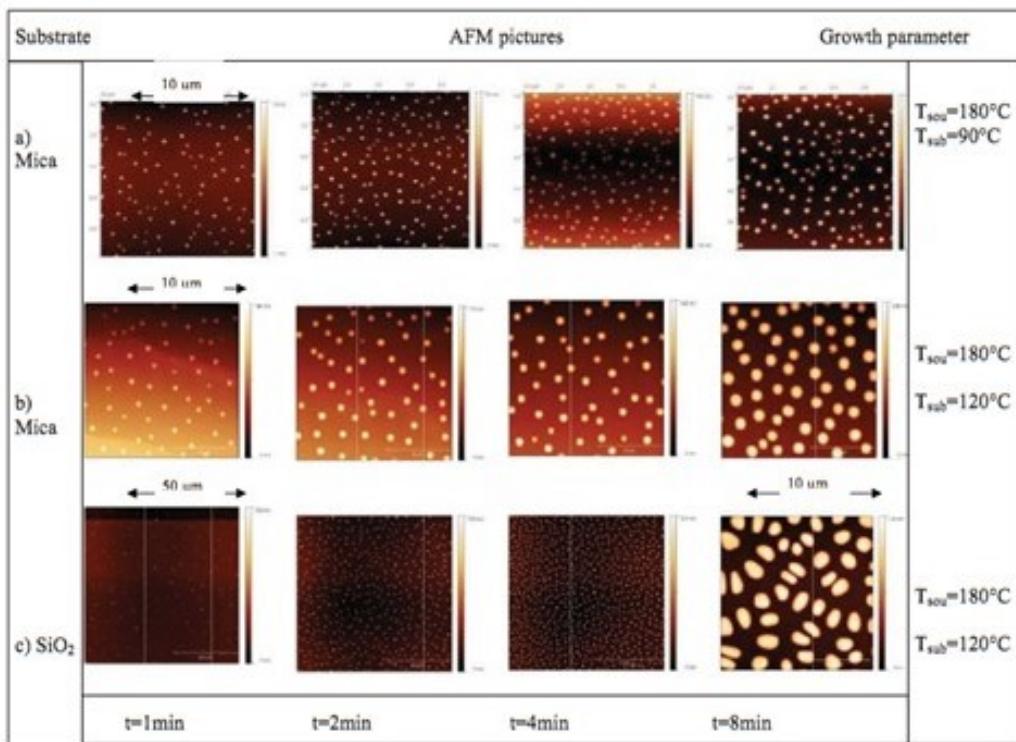


Figure 1. AFM images of rubrene grown on (a) mica surface at $T_{sou} = 180^{\circ}\text{C}$ and $T_{sub} = 90^{\circ}\text{C}$, (b) mica surface at $T_{sou} = 180^{\circ}\text{C}$ and $T_{sub} = 120^{\circ}\text{C}$, and (c) SiO_2 surface at $T_{sou} = 180^{\circ}\text{C}$ and $T_{sub} = 120^{\circ}\text{C}$, for growth times 1, 2, 4 and 8 minutes. The magnifications of images are (a) $10 \times 10 \mu\text{m}^2$, (b) $10 \times 10 \mu\text{m}^2$ and (c) $50 \times 50 \mu\text{m}^2$.

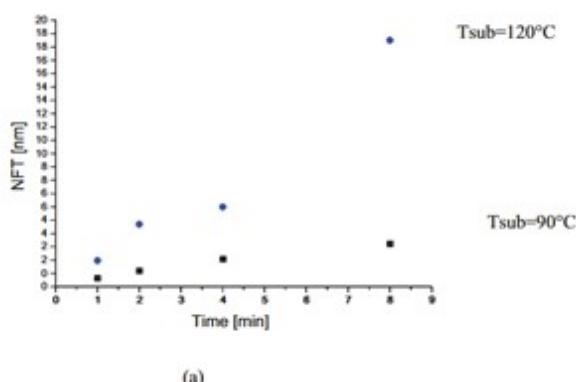
of 10-6 mbar, rubrene was placed on mica (001) and recently cleaned SiO_2 wafer (SiO_2 coated Si wafer) substrates. The substrate temperatures that were utilised were 90°C and 120°C for mica and 120°C for SiO_2 . In all situations, the wall temperature was maintained at 180°C in addition to the source temperature. The samples' growth times were 1, 2, 4, and 8 minutes. Using a SiC tip on regions measuring $10 \times 10 \mu\text{m}^2$ and $50 \times 50 \mu\text{m}^2$, morphology studies were conducted by acquiring atomic force microscopy (AFM) pictures of the deposited organic thin films using the tapping mode of a Digital Instruments Dimension 3100 microscope. These AFM images of rubrene placed on muscovite mica and SiO_2 substrates are displayed in Fig. 1. The following analysis was done on this set of AFM scans. To calculate the island density, one might count the number of grains per $10 \times 10 \mu\text{m}^2$. The average height of these islands was determined by analyzing a significant number of cross sections, and this information was then utilized to calculate the distribution of island heights.

3. Results and Discussion

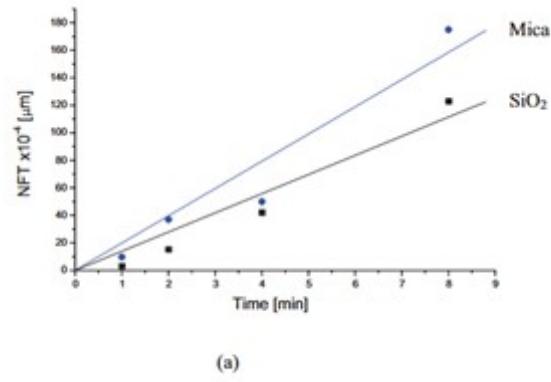
We obtained 98% pure rubrene from Aldrich which was further purified using thermal sublimation. Rubrene was deposited on freshly cleaved mica (001) and on freshly cleaned SiO_2 wafer substrates using hot wall epitaxy keeping substrate temperatures at 90°C and 120°C for mica and 120°C for SiO_2 at a vacuum of 10-6 mbar whereas the source temperature was maintained at 180°C for both cases. Digital Instruments Di-

mension 3100 in tapping mode was used to obtain AFM scans for morphology assessment as shown in Fig.1.

The nominal film thickness (NFT) was plotted versus growth time to find growth rate in each series of samples. Figures 2 and 3 show these plots of samples whose AFM scans are shown in Fig. 1. The results in Fig. 2 show a clear dependence of the amount of material deposited on the substrate temperature. Keeping the source temperature constant at 180°C the same number of molecules evaporated. The increased substrate temperatures in the first two series for mica increase the growth rate which can be attributed to greater diffusion lengths of rubrene molecules. Consequently, the nominal layer thickness was less at lower substrate temperatures. However, the grain count increase with time is prominent only at lower substrate temperature. The grain density is almost independent of growth time for the high substrate temperature while it increases in the beginning of growth at lower substrate temperatures and reaches a saturation. A similar comparison was made for samples grown at the same source and substrate temperatures but on different substrates of SiO_2 and mica. By performing the same evaluation procedure as described above, the results shown in Fig. 1 were obtained. The smaller growth rate for SiO_2 can be interpreted in terms of a smaller sticking coefficient of rubrene molecules on SiO_2 as compared to mica substrates. This assumption can also explain the increasing grain density on SiO_2 . If the rubrene molecules cannot reach the next island within the time before they evaporate again only a small number of islands will be formed in the beginning. With increasing growth



(a)



(a)

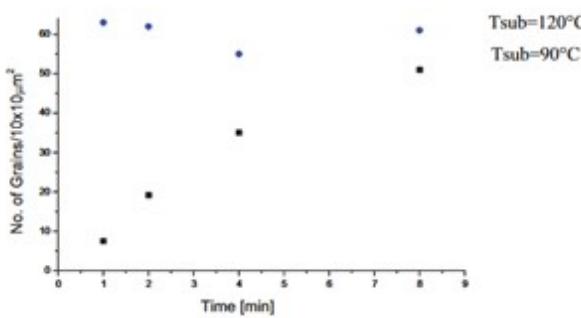


Figure 2. Comparison of (a) nominal film thickness (NFT) (b) grain count per $10 \times 10 \mu\text{m}^2$ for samples prepared on mica at substrate temperature of 90°C and 120°C.

time more and more islands will provide stable positions for the rubrene molecules reducing the re-evaporation and resulting in an increased growth rate.

4. Conclusion

We have studied the early phases of growth of rubrene layers that are deposited on various substrates at varying substrate temperatures using Hot Wall Epitaxy. The findings indicate that whereas grain density is dependent on both substrate material and substrate temperature, thin film thickness at constant source temperature directly correlates with substrate temperature.

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