

Pattern Formation in Organic Thin Films

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Abstract

The performance of organic devices is highly sensitive to the different pattern formed in organic thin films on different substrates. The diverse morphologies and structural properties of organic thin films make the subject fascinating but simultaneously very complex. The morphology of thin films depends upon the delicate balance of the interactions between the molecules and the substrate. Linear planar organic molecules and non planar molecules, all of these consist of π - π stacking however the linearity enhances the overlapping between the adjacent molecules, thus the carrier mobility. The non planarity of the molecules hinders the formation of crystalline films resulting poor mobility. The linear molecules (Pentacene) show highly crystalline layer by layer morphology, whereas the non-planar molecules like Rubrene show very complex and diverse morphology, such as spherulites in thicker films and spinodal decomposition in thinner films.

1. Introduction

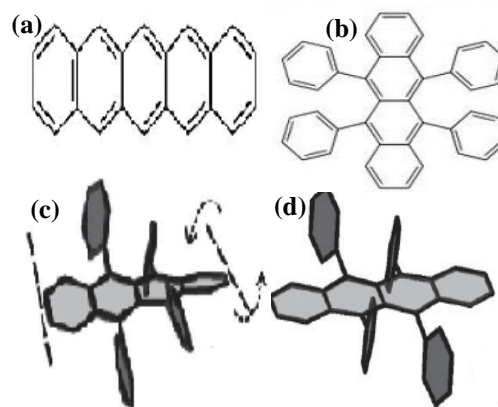
Thin film transistors (TFTs) based on organic material as active layer have recently received considerable interest. Organic based TFTs offer advantages compared to traditional amorphous silicon transistors, like mechanical flexibility and weight reduction [1, 2]. Also the organic TFT is a powerful tool to investigate the charge carrier transport properties of organic materials, including the density of states distribution, charge carrier mobility.

Pentacene and Rubrene are interesting semiconducting organic materials for TFTs. Pentacene has attracted considerable interest due to its high mobility in thin film form [3], which makes it an excellent candidate for device application as thin film transistors. Rubrene on the other hand being highly soluble is a good candidate for devices based on solution processing. The highly crystalline structure of the thin films allows Pentacene TFTs to serve as a model system [4] for charge carrier transport studies.

2. Structure of Pentacene and Rubrene

Pentacene and Rubrene are different in molecular structure, anisotropy and symmetry. Pentacene is a member of acenes family, consisting five fused benzene rings. It is a linear planar p-type molecule (Fig. 1a).

Figure 1: (a) Schematic structure of Pentacene (b) Rubrene (c) molecule structure of Rubrene in gas phase (d) in crystalline phase.



Rubrene

($C_{42}H_{28}$, 6,6,11,12-tetraphenyl-naphthacene), a non-planar organic molecule with p-type semiconducting properties consists of a tetracene backbone and four phenyl side groups. This highly anisotropic non-planar character provides additional degrees of freedom which triggers change in internal conformational orientation during thin film growth. Rubrene molecules possess a different molecular confirmation with twisted backbone in gas phase (Fig. 1c) with D_2 symmetry leading to an axial symmetry; however in crystalline phase Rubrene adopts a confirmation with planar backbone (Fig.1d) which has C_{2h} symmetry without any chirality [5].

3. Experimental Details

Triple sublimed Pentacene and Rubrene were procured from Sigma-Aldrich Co. USA and used without further purification. Thin films of Pentacene and Rubrene have been deposited on SiO_2 and H-passivated Si substrates. All thin films were grown under high vacuum ($\sim 10^{-6}$ torr) using oil free thermal evaporation system at substrate temperature $30^\circ C$ and at deposition rate 0.1 \AA/s . The thickness of the film and deposition rates are monitored and controlled by Quartz crystal microbalance. The thin film morphology was analyzed using Park Systems XE 70 atomic force microscope (AFM) in non-contact mode.

4. Morphological Characterization

We have studied systematically the effect of growth conditions on the surface morphology of thin films of Pentacene and Rubrene. Thin films of Pentacene consist of discoid, pyramidal islands [6].

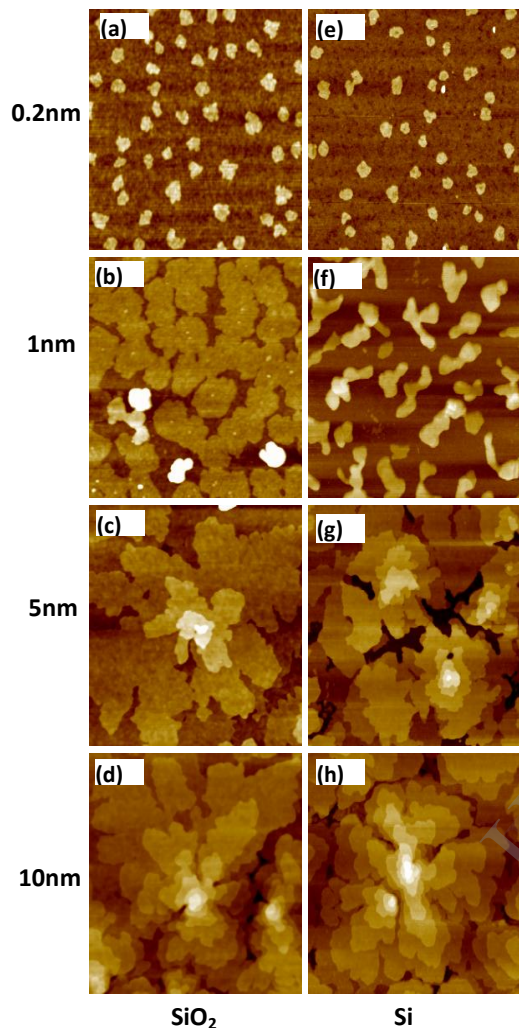
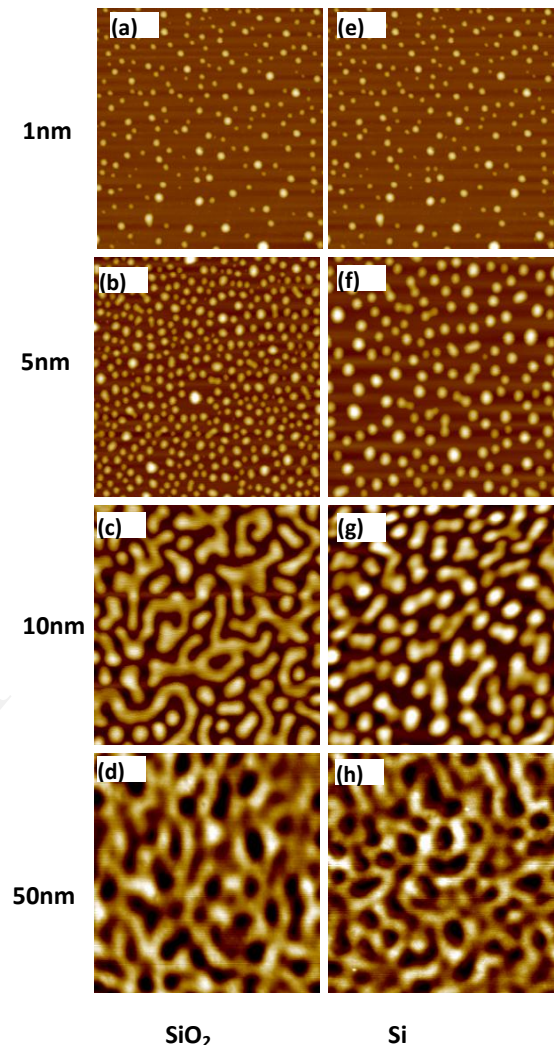


Figure 2: AFM topographic images (2 μm x 2 μm) of Pentacene thin films deposited at room temperature and deposition rate 0.1 $\text{\AA}/\text{s}$.

Fig.2 summarizes the effect of substrate interaction on the morphology of Pentacene thin films. At very low thickness (Fig.2) the film shows small islands uniformly distributed on the surface. With increasing film thickness the island grow across the surface meeting other existing nuclei (Fig.2c). The shape of the islands at lower coverage is not strictly as of fractal type but rather compact. With increasing film thickness the second layer nucleation is observed before the coalescence of first layer. Thus the film consists of ordered layer by layer growth with upward pyramidal growth i.e. horizontal DLA type with vertical mound growth. Till 10 nm substrate is not fully covered.

Figure 3: AFM topographic images (10 μm x 10 μm) of Rubrene thin films deposited at room temperature and deposition rate 0.1 $\text{\AA}/\text{s}$.

Figure: 3 compares the differences of



morphologies acquired by the Rubrene thin films in the immediate vicinity of substrate to study the effect of substrate interaction. The growth starts with the formation of three dimensional islands distributed uniformly on entire surface. On subsequent deposition these islands grow in height and size. At a film thickness of around 10 nm the coalescence of islands takes place which give rise to connecting network similar to spinodal decomposition between two phases.

There is also a modification in the film morphology with the hydrophobicity of the substrate. At high film thickness when the substrate interaction get screened the film consists of similar structures as obtained for the films at SiO₂ substrate. On comparing with the growth on H-passivated Si we observe that the diffusion is strongly enhanced on Si [7] observed as the less coverage. As the diffusivity is increased correlation between two neighbouring islands can occur even

at longer inter edge distances and a lower thickness is sufficient to trigger the transition from dendritic to compact shaped islands. Similarly in case of Rubrene less density of islands as well as connecting network requires high film thicknesses.

5. Conclusion

We have studied the effect of growth conditions on surface morphology of thin films of Pentacene and Rubrene. The AFM images show that the morphology of vacuum evaporated thin films is strongly dependent on the substrate surface and the film thickness. Thus the results indicate that the thin film phase is a substrate induced phase. The different morphologies lead to difference in their device performance. In view of this it would be interesting to look into the possibility of getting different types of morphology for a specific device application.

6. Acknowledgement

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7. References

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