Chapter 4
Morphology of Rubrene thin films: Role of nonplanarity

4.1. Introduction

Rubrene (C\textsubscript{42}H\textsubscript{28}, 6,6,11,12, tetraphenynaphthacene) has been identified as a versatile molecule showing highest mobility of 40 cm\textsuperscript{2}/Vs in single crystal based transistor at room temperature [1] and efficient application as a dye or dopant in white OLEDs [2,3]. Apart from this, a high solubility of Rubrene makes it a good candidate for devices based on solution processing. Rubrene (shown in Fig. 4.1a), which is a non-planar organic molecule with p-type semiconducting properties consists of a tetracene backbone and four phenyl side groups. This highly anisotropic nonplanar character provides additional degrees of freedom which triggers change in internal conformational orientation during thin film growth. Rubrene molecules have been shown to possess a different molecular conformation with twisted backbone in gas phase (Fig. 1.1b) with \(D_2\) symmetry leading to an axial symmetry, however in crystalline phase Rubrene adopts a conformation with planar backbone (Fig. 1.1c) which has \(C_{2h}\) symmetry without any chirality [4]. The calculated energy difference of both molecular conformations is around 200 meV. In the crystalline phase this energy which is required for planarization of the backbone is compensated by the lattice energy. But this diverse molecular conformation makes it difficult to grow thin films at room temperature. To circumvent this, high substrate temperature is required to grow ordered Rubrene thin films. The twisted geometry of the molecules is preserved for thin films and only above a critical film thickness a change of the molecular conformation takes place [4], thus making it difficult to get a high performance thin film transistor (TFT) as the accumulation region is centred only in the first few monolayers above dielectric. So far the best mobility in TFT is found to be five or six orders of magnitude lower than single crystal [5, 6]. This has become an obstacle limiting practical applications of Rubrene in organic electronics. In order to fabricate polycrystalline thin films of Rubrene, one approach is annealing a hypereutectic mixture of Rubrene and 9,10-diphenylanthracene [7]. Besides this solution processing and several special techniques associated with vapour phase deposition, such as “hot wall” deposition where a large number of collisions are likely
to assist a conformational change, [8] in situ vacuum annealing, [9] and slowly ramping substrate temperature during film deposition, [5] have been developed to grow polycrystalline films of Rubrene. In addition to these approaches, growths of polycrystalline thin films of Rubrene have been attempted on the top of a single crystal of tetracene [10] or a polycrystalline layer of pentacene [11, 12]. Recently it has been found that heteroepitaxy is of great potential in controlling molecular ordering of organic semiconductors [13,14] and fabricating highly ordered and aligned structures on different substrates for organic electronics [15,16]. However, using a semiconductor molecule like Pentacene thin film as the template to induce the crystallization of Rubrene in TFTs [11, 12] brought a new problem while solving the old one, because it is not Rubrene but Pentacene that formed the first few molecular layers at the interface between organic semiconductors and dielectric, which is the region of accumulation and responsible for current modulation in organic field effect transistors (OFETs). Using an insulating molecule 6,13-pentacenequinone (PQ) as an template has found a success in order to produce the crystallinity in Rubrene thin films on subsequent deposition [17].

**Figure 4.1:** (a) Schematic structure of Rubrene molecule. (b) Molecular geometry of Rubrene molecule in gas phase and (c) in crystalline phase. [Image is taken from Ref.4]

Molecular self assembly at surfaces is determined by surface chemistry, molecular confirmational flexibility and nonplanarity of molecules. An intense amount of research has been focused on unraveling the principles governing the growth of soft molecular materials on hard inorganic substrates. A detailed understanding of the adsorption and self assembly of Rubrene on dielectric surfaces is important for controlling the growth of Rubrene thin films which are required for
exploring the potential of this molecule for ordered nanoscale structures as well as for optimizing its use in organic electronic devices. This chapter deals with above mentioned problems focusing on the growth mechanism and pattern formation in Rubrene thin films under different growth conditions.

4.2. Experimental details

Triple sublimed Rubrene (99.999%) was procured from Sigma-Aldrich Co. USA and used without further purification. Thin films of Rubrene have been deposited on various substrates Si, SiO$_2$, quartz and ITO. All thin films are grown under high vacuum (~10$^{-6}$ torr) in an oil free evaporation system at different substrate temperatures and deposition rates. The thickness of thin films 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. The pattern evolutions in thin films have been visualized by Olympus Fluoview FV1000 confocal microscope. The excitation wavelengths used are 405 nm (blue emission), 488 nm (green emission) and 543 nm (red emission).

Crystalline nature of the thin films has been characterized by XRD in the reflecting mode at grazing angle using PANalytical Xpert Pro System in grazing incidence mode with incident angle of 2°. A filtered CuKα radiation (λ=1.54Å) has been used. The data was collected from (2θ=) 5° to 60°. The X-Ray tube voltage and current were 45 kV and 45 mA, respectively. The optical properties of thin films have been investigated in spectral range of 200-1000 nm using Shimadzu UV-2401PC spectrophotometer. All optical and XRD measurements are carried out at room temperature under ambient conditions.

4.3. Optical properties of Rubrene thin films

4.3.1. Absorption spectroscopy

In order to study the effect of possible conformational changes of the molecule in solid phase we have compared the absorption spectra of Rubrene in solution and thin film phase, shown in Figure 4.2. The solution phase spectra shows the characteristics of twisted isomeric phase of Rubrene favorable in free form. The characteristic UV-vis spectrum of Rubrene consists of four characteristic peaks at 530
nm (2.34 eV), 490 nm (2.5 eV), 460 nm (2.7eV) and 430 nm (2.9 eV). In particular, the 530 nm peak must be from the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) gap [18]. The double-hump structure at 2.3 eV and 2.54 eV belong to Davydov splitting [19]. Davydov splitting arises due to the interaction of 4 molecules in the unit cell which is double the primitive cell. The Rubrene absorption spectra show clear vibronic bands with a separation of about 0.18 eV, which can be attributed to a C-C stretching vibration [20]. There is apparently no shift in absorption maxima in thin film. There are two more peaks in low wavelength side in thin film at 407 nm (3.04 eV) and 385 nm (3.22 eV) attributed to vibrational progressions. The continuous increase in the peak width in vibronic progression is assigned to the involvement of more than one vibrational mode [21].

![Image of Rubrene absorption spectra in thin film and solution phase](image)

**Figure 4.2:** Absorption spectra of Rubrene in thin film and solution phase in the wavelength range 350-600 nm. Rubrene is dissolved in trichloroethylene (TCE) at 10 µM concentration. Rubrene thin film (600 nm) is deposited on quartz at substrate temperature of 80°C and at deposition rate of 10 Å/sec.

Figure 4.3 shows the absorption spectra of Rubrene thin films for different thicknesses and at two deposition rates of (a) 1 Å/s and (b) 10 Å/s. At low deposition rate with increasing film thickness, the intensity of higher wavelength peak at 530 nm decreases while the absorption bands on shorter wavelength side becomes significant. At high deposition rate the intensity of higher wavelength peak at 530 nm decreases while there is no significant change corresponding to the shorter wavelength bands.
The increase in absorption intensity infers the increase of crystallinity of Rubrene in thin film phase [22]. The absorption intensity increases with film thickness as the coverage with crystalline disk shaped spherulites that will be discussed in next section increases with film thickness for both deposition rates. Similar effect has been observed with annealing time by S. W. Park et al. [23]. The absorption maxima are sharper for the films grown with high deposition rate inferring better crystalline growth at high deposition rate. These results are consistent with the findings of Y. Yoon et al. [24].

4.3.2. Photoluminescence (PL) spectroscopy

Figure 4.4 displays PL spectra of Rubrene thin films grown at different deposition rates for thickness 300 nm (a) and 600 nm (b). The emission spectra of Rubrene consists of mainly two peaks at 560 nm (2.21 eV) and 598 nm (2.07 eV) in solution phase [25]. In comparison to solution phase emission spectra from Figure 4.4 we observe that the Rubrene thin films (300 nm) grown at low deposition rate do not show the peak at 598 nm. However with increasing the deposition rate a shoulder at
598 nm is appeared. For the high thickness samples (600 nm) there is signature of peak at 598 nm even at low deposition rate which becomes significant at high deposition rate. Similar change is observed in thin films grown on ITO substrates shown in Figure 4.5. The structure less and broad emission spectra are attributed to triclinic and orthorhombic phases of Rubrene [26]. Thus the films undergo a phase change from triclinic to orthorhombic phase with increasing the deposition rate or the film thickness. The origin of peak at 640 nm is not known. The strong PL emission in organics originates from the amorphous phase, and the PL intensity reduces with the increase in crystalline ordering [27]. The PL intensity is low for the films with low thickness 300 nm at all deposition rates signifying the ordering in thin films. However as the thickness is increased the films grown with high deposition rate shows an intense PL emission indicating the amorphous character of thin film. On SiO$_2$ substrates the low deposition rate thin films show better crystallinity however on ITO substrates thin films grown under high deposition rate shows better crystallinity.

![Figure 4.4: PL emission spectra of Rubrene thin films grown on Si substrate at substrate temperature 80°C and variable deposition rate with thickness (a) 300nm and (b) 600nm. Excitation wavelength is 488 nm.](image_url)
4.4. Structural characterization

4.4.1. X-ray diffraction

The crystalline nature of Rubrene thin films deposited under different growth conditions is determined by the XRD, as shown in Figure 4.6. Rubrene crystallizes in three different polymorphic phases [26]: monoclinic ($a = 8.7397 \text{ Å}, b = 10.125 \text{ Å}, c = 15.635 \text{ Å}, \alpha = \gamma = 90^\circ, \beta = 90.55^\circ$); triclinic structure ($a = 7.0196 \text{ Å}, b = 8.5432 \text{ Å}, c = 11.948 \text{ Å}, \alpha = 93.04^\circ, \beta = 105.58^\circ, \gamma = 96.28^\circ$) and orthorhombic structure ($a = 26.775 \text{ Å}, b = 7.1680 \text{ Å} \text{ and } c = 14.258\text{Å}, \alpha = \beta = \gamma = 90^\circ$). The XRD data reveal that the thin films of Rubrene in both conditions grown with low and high deposition rates possess polycrystalline spherulites consisting polymorphic crystal entities. The films are crystalline (grown at high deposition temperature) consisting of mixed orthorhombic and triclinic phase. On SiO$_2$ substrate the films deposited with low deposition rate shows a predominantly orthorhombic phase. At deposition rate of 10 Å/s the films show triclinic phase to be prevalent. The films grown under very high deposition rate of 20 Å/s shows very poor crystallinity. Thus an appropriate balance between
deposition rate and substrate temperature is required for the growth of highly ordered crystalline films.

The films grown on ITO substrates (Fig. 4.6b) show opposite crystalline order compared to the films that are grown on SiO\textsubscript{2} substrate. At low deposition rate the triclinic phase is prevalent while at 10 Å/s the orthorhombic phase is prominent. But thin films on ITO substrate with very high deposition rate of 20 Å/s show poor crystallinity as in case of SiO\textsubscript{2} substrate.

![XRD pattern of Rubrene thin films grown on (A) SiO\textsubscript{2} and (B) ITO substrate at substrate temperature 80°C and variable deposition rate with thickness 600 nm.](image)

**Figure 4.6:** XRD pattern of Rubrene thin films grown on (A) SiO\textsubscript{2} and (B) ITO substrate at substrate temperature 80°C and variable deposition rate with thickness 600 nm.

### 4.4.2. Morphological characterization

The growth of Rubrene thin films takes place in two steps depending on thickness.

1. In the initial growth stage amorphous islands are formed till a critical thickness and
(2) when a critical thickness is achieved the grains merged and coalescence happens and an amorphous porous film is formed that works as a template for spherulitic growth.

Figure 4.7 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. This represents Volmer Weber growth mode [28] which dominates when surface energy of substrate is less than the sum of surface energy of deposited material and the interfacial energy between the organic material and substrate. On subsequent deposition these islands grow in height and size. At a film thickness of around 10 nm (Fig. 4.7) the coalescence of islands takes place which give rise to connecting network similar to spinodal decomposition between two phases [29]. Similar growth also occurred on Si except that less density of islands as well as connecting network requires high film thicknesses. This type of the morphology in Rubrene thin films can be attributed to the difference in sticking coefficient being high for Rubrene on substrate and low for Rubrene on Rubrene [30]. This morphology resembles with the inverse spinodal decomposition (phase separation of incompatible materials) in unstable thin films when the second derivative of the excess intermolecular free energy with respect to the film thickness is negative [31].

![AFM images (scan area 10μm X 10μm) of Rubrene thin films of variable thickness grown under identical conditions at room temperature under a low deposition rate of 0.1 Å/s. Top row samples were grown on SiO₂ surface while bottom row samples were grown at hydrophobic H- passivated Si surface.](image-url)
This perspective whether the competition between gas phase and crystalline phase provide a perturbation to stimulate the unstablity in thin film, requires a detailed understanding and is subject of future study.

On subsequent deposition the islands coalesce and form an amorphous layer which acts as template for spherulite growth. The later stage of growth after 20 nm on SiO$_2$ is dominated by the formation of spherulites. Spherulites are aggregates of microcrystals, which arrange in radially growing fiber-like structures. Figure 4.8 summarizes the complex growth stages of spherulite formation. The spontaneous development of spherulites can be seen in Figure 4.8a. On increasing the deposition time the growth starts with threadlike fibres (dark red colour lines in Fig. 4.8a) which subsequently form crystalline “sheaves” which further spreads out until a rough spherical shape is achieved (Fig. 4.8b). The spherullites grow in size resulting inner disc like pattern surrounded by an outer ring (Fig. 4.8c). Finally the spherullites coalesce and cover the whole substrate (Fig. 3.8d).

![Figure 4.8: Optical microscopy images of evolution of spherulitic growth at different stages of Rubrene thin film on SiO$_2$ substrate at substrate temperature of 80°C.](image)

Figure 4.9 shows AFM images obtained from different parts of a spherulite in Rubrene film with thickness of 100 nm. The spherulite starts to grow with an embryo formation (Fig. 4.9 a) at a random nucleation site, on subsequent deposition it takes the form of a spherulite. The spherulite growth can be divided into three parts: (i) surrounding amorphous matrix; composed of two dimensional connected networks, (ii) the outward boundary of spherulite, which is highly crystalline consisting of small crystallites arranged in radially oriented manner; and (iii) central part, composed of
small crystallites (~300 nm) arranged in random orientation with radially outward fashion. We observe that even before the completion of one spherulite rim, another layer of spherulite growth starts in similar fashion. These layers are separated by a step of ~20 nm (cursor position in green line) which is equal to the step of outer rim with amorphous matrix (cursor position in red line).

Figure 4.9: Details of Rubrene spherulite. (a) embryo; Beginning of an spherulite formation, (b) Spherulite sheaf, (c) Iris, and (d) surrounding amorphous matrix. And (e) Center Scan area: (a) 30µm X 30µm, (b) 40µm X 40µm and (c-e) 5µm X 5µm . The spherulitic growth consists of layered structures showing a step of 20 nm at each growth stage as seen in the height profiles along the lines in (b).

Figure 4.10 shows the wide range of spherulitic crystallization patterns observed during the growth of a thin film of Rubrene viewed by confocal microscope.
Figure 4.10: Various spherulite morphologies observed in thin films of Rubrene using confocal microscope.

Figure 4.10a shows the birth of a type 2 spherulite (embryo) consisting of fibres randomly oriented from a nucleation site. These threadlike fibres subsequently form the grains at the growth front. This branching leads to a crystalline sheaflike pattern (Fig. 4.10b) which plays out during growth (Fig. 4.10d). At prolonged exposure these sheaves develop “two eyes” (uncrystallized region) on each side of primary nucleation (Fig. 4.10d). Finally it settles down into a spherical growth pattern (Fig. 4.10c and d). Figure 4.10e shows the morphology of thick Rubrene film with many nucleation sites. The two spherulite regions have been separated by the sharp boundaries (arrows) indicating that their growth rates are similar. Figure 4.10f shows
the crystallites embedded in amorphous matrix (orange colour). This kind of morphologies has been described by L. Granasy et al. [32] considering disorder by static or dynamic heterogeneities and crystalline branching induced by a misoriented grain boundaries. The diversity of spherulitic growth morphologies arises from a competition between the ordering effect of discrete local crystallographic symmetries and randomization of the local crystallographic orientation that accompanies crystal grain nucleation at the growth front (GFN).

The two growth stages (i) island growth that leads to amorphous matrix and (ii) spherullite growth that leads to polycrystalline thin film arise because of conformational changes in Rubrene molecule in thin films. At low thickness, in the immediate vicinity of substrate the Rubrene molecules exhibit a different molecular geometry same as in gas phase with twisted tetracene backbone however in crystalline phase, the molecules arrange in herringbone pattern with planar tetracene backbone optimizing $\pi-\pi$ interaction. The conformational change in molecular geometry explains the difficulty in growing high quality of Rubrene thin films for device applications.

(a) Effect of substrate surface

As already discussed in chapter 2 and 3 substrate interaction plays an important role in deciding the morphology. We have chosen ITO and glass substrates to observe the resultant patterns. Figure 4.11a shows the optical image of Rubrene thin film consisting of three spherullites grown on $\text{SiO}_2$ or glass surface. The films show spherulite patterns (discussed in previous section) consisting of crystalline array which increases the coverage with film thickness. Figure 4.11(b) shows the edge of such spherulite. The edges of a spherulite show the small crystallite indicating GFN. The middle region of the spherulite consists of branched fibres which are surrounded by nanowire structure at the edges (Fig. 4.11e). These nanowires consist of $\sim 50$ nm thick disc shaped crystals arranged in side by side manner (Fig. 4.11f). The two spherulites are separated by a boundary created by the different oriented crystals. Figure 4.12 shows the morphology of Rubrene thin film grown on ITO substrate. Surprisingly the film does not show the usual spherulitic pattern although both the substrates are hydrophilic in nature. Rather it shows bunches of platelets with thickness 30 nm and width 100 nm and hence provide a good template for an ordered
growth. The difference in morphology could lie in the roughness of the substrate template which needs to be explored further.

Figure 4.11: Detailed structure of Spherultic thin film growth. The film is grown at 80°C and with deposition rate 10 Å/s.
Figure 4.12: (a) Confocal image, (b) and (c) AFM image of 100 nm thick Rubrene film grown on ITO substrate grown at substrate temperature 80°C and with deposition rate of 10 Å/s.

4.5. Morphology and Device

The role of morphology on transport properties of thin films and devices will be discussed in details in chapter 6 and here, we demonstrate a device which could be achieved due to certain thin film morphology of Rubrene.

Figure 4.13 shows the room temperature I-V characteristics of Au/Rubrene/Au and ITO/Rubrene/Au sandwiched structures. Exploring Au/Rubrene/Au device in which Rubrene thin film was grown on Au (60 nm) coated glass (Fig. 4.13b). We observe that in the first bias scan, current increases slowly with bias, but at a threshold voltage ($V_T$), current increases sharply by several order of magnitude and the device
undergoes a conductance transition from an insulating state to a conducting state. In second bias scan, the device retains the insulating state. Similar switching effect is also observed when current injected from bottom Au electrode. When the applied bias is increased by 3V (forward or reverse) the current increases by three orders of magnitude. This switching effect is reversible and shows same transition in subsequent scans. This switching is stable even after a no. of bias scans. However the Rubrene devices deposited on ITO electrodes does not show switching behavior (Fig. 4.13a). The detailed characterization for this device is given in chapter 6.

Figure 4.13: Current-voltage (I-V) characteristics of Rubrene single layer devices sandwiched between (a) ITO/Au and (b) Au/Au contacts. Rubrene thin films are grown on ITO/Au substrate at 80°C substrate temperature and at 1Å/sec deposition rate. Insets show morphology of Rubrene thin films on ITO (inset a) and Glass/Au (inset b) substrates. The scan size of AFM topographic images are 5µm X 5µm.
In the insulating state current follows SCLC ($J \propto V^\alpha$) and in the conducting state, current shows an Ohmic behavior ($J \propto V$). Figure 4.14a shows log-log plot of

**Figure 4.14:** (a) $\ln I - \ln V$ characteristics of Rubrene single layer devices sandwiched between Au/Au in ON and OFF state. (B) Resistance vs voltage ($R-V$) plot of the ON and OFF states. Resistances are extracted as $R=I/V$. Rubrene thin films are grown on ITO/Au substrate at substrate temperature of 80°C and at deposition rate of 1 Å/sec.

In the insulating state current follows SCLC ($J \propto V^\alpha$) and in the conducting state, current shows an Ohmic behavior ($J \propto V$). Figure 4.14a shows log-log plot of
I-V characteristics. Straight line fits to insulating (OFF-state) and conducting (ON-state) states shows the slope $m \sim 2$ and $m \sim 1$ respectively confirming the SCLC behavior in insulating and Ohmic conduction in conducting states. Nonconducting state shows high impedance of the order of 100 $G\Omega$, while conducting state shows low impedance of order of 100 $M\Omega$. The irreversible switching effect in Rubrene thin films have been previously reported by Li et al. [33] and assigned to the charge carrier trapping at the OTS/Rubrene interface. It is to be noted that no SAM layer has been used between substrate and Rubrene layer.

Here we propose that the switching effect in Rubrene thin films is assigned to its unique morphology. Similar mechanism has been proposed for the charge trapping at the discontinuous patches of pentacene [34]. However the memory effect is unerasable in Pentacene based switching devices. Rubrene thin films evolve in the form of spherulites on glass/Au substrates which are uniformly distributed on the surface. The charge carriers got trapped at the two spherulite boundaries whereas the films on ITO substrate consists of crystallites (as shown in Fig. 4.12 and 4.13) with platelet structure and do not lead to switching effects. Hence, switching effect can only be observed in thin film with spherulitic morphology. The memory effect here is reversible due to trapping and detrapping of carrier at shallow states as the devices are grown at low deposition rates [35]. Another possible mechanism could be due to the formation of metallic filament providing low resistance pathways between electrodes exhibiting Ohmic conduction [36]. Here we have found that the resistance of ON state decreases with applied voltage (Fig. 4.14b). This presents a non-Ohmic conduction behavior, suggesting that the filament formation is not a possible mechanism for switching. Moreover filament formation is equally probable in Au/Rubrene/Au and ITO/Rubrene/Au structures.

4.6. Conclusions

In this chapter we have studied the effect of growth conditions on morphology of thin films by optical, AFM and confocal microscopic images. Although the conformational change in Rubrene owing to its nonplanar structure in thin film evolution does not affect the absorption and morphological properties however the growth conditions effectively modify the structure at the interface. The films on SiO$_2$ substrates show spherulitic structure while on ITO substrate platelet like crystals are
achieved. High substrate temperature and high deposition rate are required to induce high crystallization in Rubrene thin films. With high deposition rate, the films consist of stable polymorphs orthorhombic and triclinic phases. This induced crystallization largely affects the transport properties of thin film. The two terminal devices consisting spherulitic patterns with low deposition rate shows reversible switching effect.
4.7. References