



Role of kinetic energy of impinging molecules in the α -sexithiophene growth

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ABSTRACT

We report on the α -sexithiophene sub-monolayer growth with supersonic molecular beam deposition by investigating how the kinetic energy of the impinging molecules influences the growth on substrates with different surface wettabilities and temperatures. The results show that the energy of the impinging molecules affects the morphology of the molecular film increasing the coverage and the island size, and reducing the fractality of the sub-monolayer islands. The possibility of directing growth of more ordered islands could improve the performances of electronic devices, which are greatly affected by the structure of the first monolayers.

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1. Introduction

Organic semiconductors have a number of properties that make them ideal for applications in fields ranging from photonics [1] up to devices and sensor realisation [2]. With the study of fundamental properties, it is important to understand the principles that characterise these compounds [3] and to overcome some of the limitations still present. Notably, in order to achieve good electrical properties, an overlap between the delocalized π -conjugated systems is required. This can be achieved through a right molecular assembly in a crystalline structure [4]. Such ordered films are indeed quite hard to obtain, because the intrinsic asymmetry of the molecules, compared with atoms in inorganic thin films, gives rise easily to different polymorphs and molecular orientations. The presence of these grain boundaries [4], regions where the π -orbitals of the molecules have a low overlap, becomes the bottleneck of the charge carrier mobility along the thin film [5]. To limit these problems a higher control during the growth process is required.

Previous works showed that the energetic state of the molecules plays an important role in the collision processes and in the energy transfer between molecules and substrate [6]. We developed a deposition technique based on supersonic beams (SuMBD) that allows us to improve the control on the state of the impinging molecules, widening the range of tunable parameters (i.e. kinetic

energy, momentum, internal energy, etc.) [7] increasing the control on the assembling processes in the island formation and coalescence [8]. By changing the carrier gases (Ar, He, H₂...) and the degree of seeding, it is possible to tune the E_K of the impinging molecules from thermal energy (typical of an effusive source) up to several tens of eV, depending on the mass of the seeded molecules. This supersonic expansion gives rise to a higher directionality and a narrower energy distribution of the molecular beam, with a cooling of the roto-vibrational energy levels [3,9]. This technique produces a better morphology and structure of the organic thin film and thus enables better performances from the organic device [10,11].

This work involves the sub-monolayer growth of α -sexithiophene (α -6T), a common molecule used for the realisation of prototypical field effect transistor based on organics [12] that can be appealing for several applications (OLEDs, OFETs, and sensors) [13]. We conducted a detailed investigation on the influences of the main growth parameters (kinetic energy of the impinging molecules, substrate wettability and temperature) on the morphology of the molecular islands.

2. Experimental

The growth of α -6T films was made in a home-built SuMBD apparatus [7] that includes a time-of-flight (ToF) spectrometer used to check the energetic parameters of the seeded molecules, the beam purity and the intensity of the supersonic molecular beam flux. The source settings were adjusted to keep constant the deposition conditions (nominally the flux) along the whole series of experiments [8]. High and low kinetic energy (E_K) beams were utilised, seeding the α -sexithiophene in helium and in argon, respectively. The comparison

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between the low and high E_K has been examined on both hydrophobic and hydrophilic (same substrate, treated by UV(O₃) for 12 min) silicon oxide (100 nm thick, Jocam) substrates. The wettability of the as-grown and the UV(O₃) treated SiO_x/Si was characterised by the sessile drop method, resulting in a $63^\circ \pm 3^\circ$ and $10^\circ \pm 2^\circ$ contact angle, respectively [14]. The sub-monolayer organic films were grown at room temperature (RT=25 °C) and at 90 °C to check how the substrate temperature affects their morphology [15].

3. Results and discussion

Fig. 1 shows the α -T6 islands grown during 5 min (first row) and 40 min (second row) of exposure to the supersonic beam. The first two columns concern hydrophilic substrates, while the third and fourth columns refer to hydrophobic substrates. The first and third columns show films grown at 2.2 eV, while the second and fourth columns show films grown at 13.1 eV, respectively. Molecular island height is the same for all the samples, and from the AFM analysis, results to be 2.4 ± 0.1 nm. This value agrees with the current literature for standing α -T6 molecules [16]. AFM micrographs allow us to extract information about the coverage and its evolution during the growth process. The coverage and fractality values were calculated with WSxM software [17] averaging on 5 AFM images. It is important to note that the coverage value is directly connected to the sticking coefficient of the molecules because the molecular flux was kept constant during all the depositions.

Fig. 1 shows the effect of E_K on island growth. It is clear that E_K affects both island size and island density: the former parameter is proportional to the beam E_K while the latter decreases. This means that an increase in E_K gives rise to an increase surface mobility of the molecules [18], and to a reduced number of nucleation sites. These effects are more evident on hydrophobic substrates (see Fig. 1).

A more accurate analysis of the AFM pictures shows that for both substrates, the sticking coefficient is higher for the films grown at higher E_K , particularly for films deposited onto hydrophilic substrates as reported in Fig. 2a. The greater sticking coefficient (measured at higher E_K) can be explained as an increase of the probability that the highly energetic molecules break through the surface potential barrier, thus achieving a stronger interaction with the surface [19].

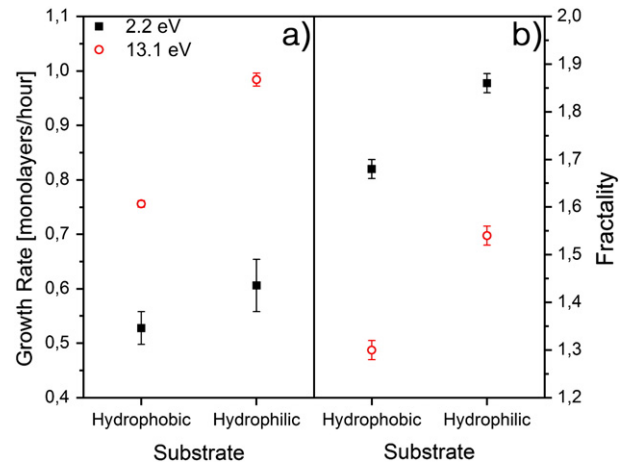


Fig. 2. a) Growth rate (monolayers per hour) and b) fractality of the islands after 40 min, at room temperature. Each point has been obtained averaging the values from 5 AFM images ($10 \mu\text{m} \times 10 \mu\text{m}$).

The high E_K is dissipated via a series of processes that increase the molecule surface diffusion and its interaction with the surface. The surface energy also affects the molecule–surface interaction [20]. In fact, the higher pinning centre density of the hydrophilic surface gives to the moving molecules many aggregation positions, improving their probability to nucleate and also increasing the coverage.

From the analysis of AFM data, the island fractality can also be extracted. The islands grown at higher E_K result to be less fractal and have a more rounded perimeter on both types of substrate as it is reported in Fig. 2b. The effect is due to the partial conversion of the impinging kinetic energy in surface mobility. This, in turn, increases the probability of the molecules to reach the sites with less nucleation energy and rearrange in a more ordered structure [19].

The fractality value on hydrophilic substrates is always larger with respect to the films grown on hydrophobic substrates. This is due to the higher surface pinning centre density present on hydrophilic substrates which restricts the surface mobility, increasing the fractality of the growing molecular islands (Fig. 2b). Due to lower

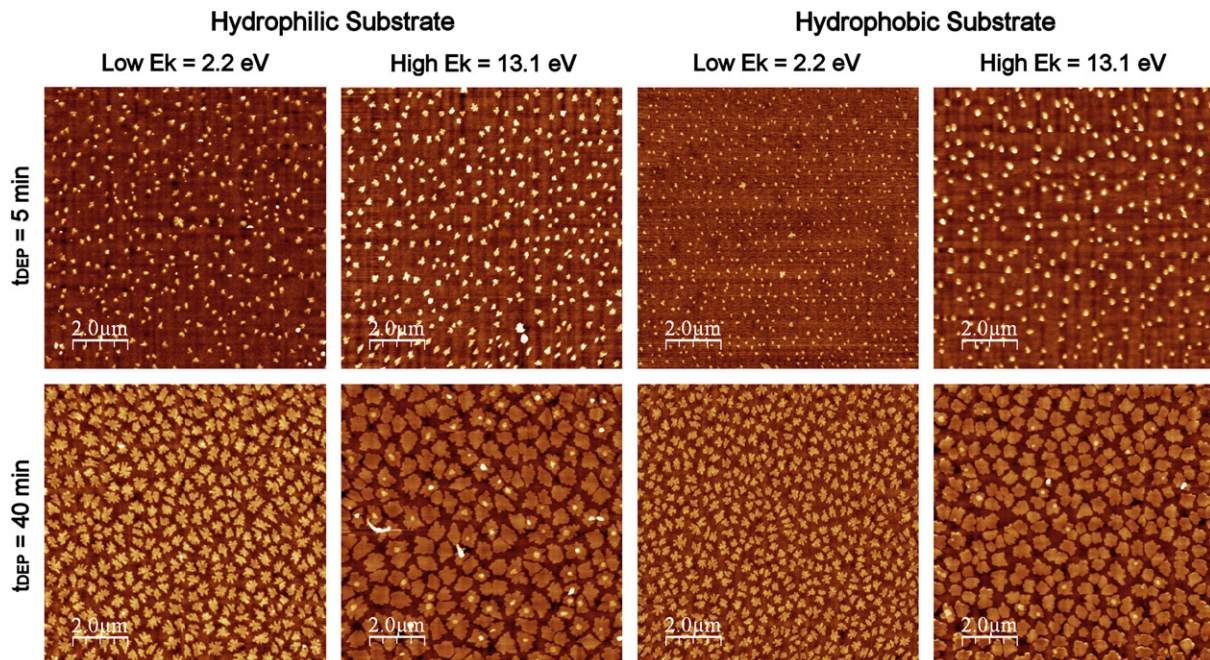


Fig. 1. AFM images of submonolayer α -6T islands time-evolution at room temperature. The first row shows the situation after 5 min, while the second one shows the islands after 40 min.

mobility, the sexithiophene molecules cannot reach the inner part of the “star-island”, and stop on a “branch”, increasing the fractality of the molecular island.

At RT, one of the major effects of the E_K of the impinging molecules is to increase the surface mobility with a better rearrangement of the molecules in the thin film, as a consequence we have an improvement of the thin film crystallinity.

Another method used to improve both the crystallinity and electrical properties of α -6T films, is to increase the substrate temperature during the deposition. Even in this case, an increase of the molecular surface mobility allows the molecules to configure a better rearrangement, giving rise to an increase of the film crystallinity. Fig. 3 shows the effect on morphology of combining E_K and substrate temperature (deposition made at 90 °C) keeping constant all the other deposition parameters. Fig. 3 shows the α -6T islands after 5 min (first row) and 40 min (second row). If compared with the RT depositions, larger islands and a reduced number of nucleation sites are formed, due to the increased surface molecular mobility. The two conditions reported in Fig. 3 (after 5 min and 40 min of deposition) show the importance of the different steps in the thin film growth. In particular, after 5 min the pictures show the situation after the initial nucleation process. On the hydrophobic surface the island size and density follow the behaviour observed for all cases at RT. On the hydrophilic surface we observe instead an opposite situation. In particular at low E_K the island size is larger and the density lower compared to the high E_K . We ascribed this different behaviour to different nucleation mechanisms [8,16]. After 40 min the AFM pictures of Fig. 3 (second row) show the island growth and in some cases their initial coalescence.

Comparing Figs. 2a and 4a, we can observe that there is no large difference in the coverage. In more detail, while the effect of the kinetic energy on the growth rate is still present on hydrophobic substrates, on hydrophilic substrates it seems to be weakly affected by the E_K of the impinging molecules. We can argue that this effect is probably due to a non negligible re-evaporation process rate, due to the increased temperature. These re-evaporation processes overcome the effect of the kinetic energy making the sticking coefficient practically independent from E_K .

Also in this case the island fractality, as in the case of RT growth, is strongly depending on the E_K of impinging molecules. Working at

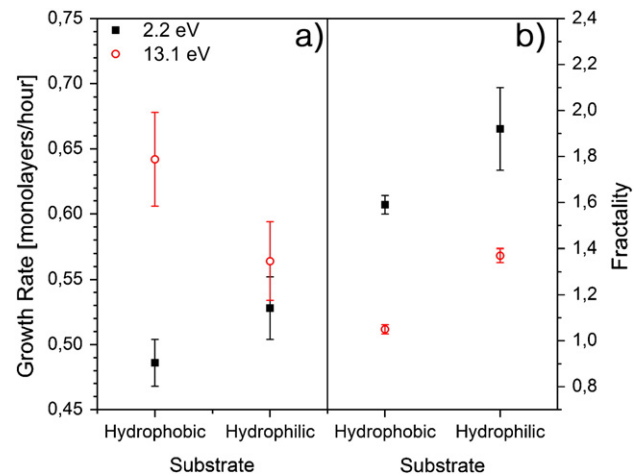


Fig. 4. a) Growth rate (monolayers per hour) and b) fractality of the islands after 40 min, at 90 °C. Each point has been obtained averaging the values from 5 AFM images ($10 \mu\text{m} \times 10 \mu\text{m}$).

13.1 eV, we obtained less fractal islands on both hydrophobic and hydrophilic substrates, as it is reported in Fig. 4b. Finally we see, as for the RT deposition, that the effect of the stronger interaction of the molecules with the hydrophilic surface gives rise to higher fractality values, both at low and high kinetic energy.

4. Conclusions

In summary, we have investigated the sub-monolayer growth of sexithiophene on silicon oxide, focusing on three main growth parameters: the kinetic energy of the impinging molecules, substrate temperature and substrate wettability. We found clear effects of the kinetic energy on island formation (size, density and fractality). The possibility to increase the kinetic energy, allows for the growth of greater islands with reduced fractality even at room temperature. This is due to a partial conversion of the energy of the seeded molecules in additional surface mobility, which permits the molecules to find better nucleation sites. The hydrophilic surface presents higher coverages and fractalities because its higher pinning centre density

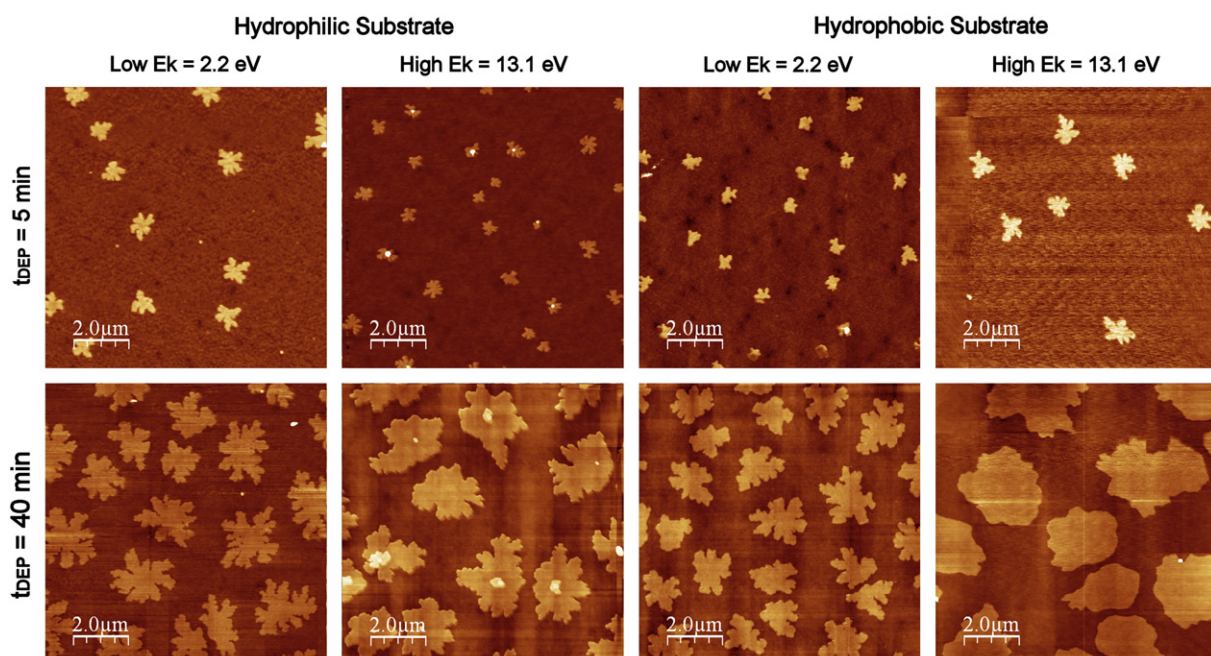


Fig. 3. AFM images of submonolayer α -6T islands time-evolution at 90 °C. The first row shows the situation after 5 min, while the second one shows the islands after 40 min.

offers a stronger interaction with the α -6T molecules. The same effects are present at 90 °C, where the synergy between E_k and temperature gives rise to bigger islands.

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