

**Molecular-Scale Events in Hyperthermal Deposition of
Organic Semiconductors Implicated from Experiment and
Molecular Simulation**

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Supporting Information (10 [pages](#))

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Results and Discussion

The kinetics of pentacene thin film growth

Incident molecular flux

In the experiments described here, we have examined the kinetics of thin film growth using supersonic molecular beam techniques, and a combination of *ex situ* atomic force microscopy and ellipsometry [S-1]. More recently we have also employed *in situ* real time synchrotron x-ray scattering to examine this same system [S-2]. Here we have maintained a fixed incident molecular flux while both the incident kinetic energy and the angle of incidence are varied. This is accomplished by changing appropriately the temperature of the evaporator that holds the pentacene. To calibrate/verify the incident molecular flux we measured the line-of-sight intensity of the pentacene molecular beam prior to each experiment using a quadrupole mass spectrometer, QMS (Extrel). The incident kinetic energy was measured in a separate experiment using time-of-flight techniques. The QMS is a density detector, thus, the molecular flux is a product of the density and the velocity. For deposition at variable angles of incidence, the beam deposits over an area of $A_{\text{beam}}/\cos\theta_i$, where A_{beam} is the area illuminated at normal incidence. To maintain a fixed incident flux, therefore, the quantity, $\text{QMS intensity} \times (E_i)^{1/2} \times \cos\theta_i$, should be constant. In Fig. S-1 we plot this quantity as a function of beam kinetic energy, and for a series of angles of incidence for the experiments reported in the main text, Figs. 1(a) and (b). We also plot the value of the mean, and the mean \pm the standard deviation. As may

be seen the values for this quantity are nearly constant, with a mean of 2.070×10^5 , and a standard deviation of 0.101×10^5 , i.e., about 5%.

Surface coverage and morphology

For the same sets of conditions detailed in Fig. 1(b), we have also acquired AFM images. One set of images is displayed in Fig. S-2, and these are for growth at $E_i = 6.7$ eV, $\theta_i = 0^\circ$. As may be seen for this set of conditions, the first monolayer grows to a coverage of about 0.75 ML (150 s) before growth of the second monolayer is observed. After the deposition of an additional ~ 1.6 ML (300 s, total coverage > 2 ML), the underlying substrate is nearly covered. After 600 s total exposure an additional 3.1 ML have been deposited (total coverage > 5 ML), and the surface is essentially covered.

Thermalization and Diffusion in Simulations

We analyzed the thermalization and diffusion properties of our system using a bulk surface (i.e. no step edge present). The surface consisted of 3 layers of 5x5 unit cells (5400 atoms in total). Again the bottom layer was frozen in bulk coordinates and the top two layers were free to move. For each incident energy ($E_i = \text{thermal}, 1\text{eV}, 2\text{eV}, 5\text{eV}, 10\text{eV}$) 10 molecules were fired at the bulk pentacene surface. All incident molecules were randomly orientated but the incident angle was always 0 degrees. The results are summarized in Table S-1 and Figs. S-3 & S-4 . When considering these results it must be remembered that there are only a maximum of 10 trajectories at each incident energy and that the statistical error will be relatively high.

Table S-1 shows the destination of the incident molecules. The results are consistent with our “bulk” collision point in the main article. Figure S-3 shows the average displacement of molecules still on the surface after 50ps (at least 2.5-5 times as long as the collision trajectories used in the main article). For molecules that adsorb on the surface the average displacement is largest for the 10eV collisions (45 Å) but not greatly larger than the thermal collisions (25 Å) remembering that pentacene is 15Å in length). When insertions are also considered this value decreases significantly because the inserted molecules remain static in an interstitial site and the average displacement is more or less constant over all energies. Importantly, looking at Figure S-4, the increased displacement of the higher energy molecules is due to the movement in the 1st 10 ps. From visualizations of these trajectories it is apparent that this is when the molecule is not “bound” to the surface but is on a secondary bounce. It would be hard to describe this as surface diffusion but more a part of the collision event itself. After 10 ps there is very little difference in the trend of displacement versus time across all energies. The temperature of the system was also stable by 10 ps with none of the system temperatures rising above 310K.

References

- [S-1] Killampalli, A. S., T. W. Schroeder and J. R. Engstrom, *Nucleation of pentacene on silicon dioxide at hyperthermal energies*, Appl. Phys. Lett. **87**, 033110/1-033110/3 (2005).

- [S-2] Hong, S., A. Amassian, A. R. Woll, S. Bhargava, J. D. Ferguson, G. G. Malliaras, J. D. Brock and J. R. Engstrom, *Real time monitoring of pentacene growth on SiO₂ from a supersonic source*, Appl. Phys. Lett. **92**, 253304/1-253304/3 (2008).

Figure Captions

Figure S-1 Incident flux of pentacene (arb. units) as measured by line-of-sight quadrupole mass spectrometry as a function of beam kinetic energy.

Figure S-2 A series of AFM images ($20 \times 20 \mu\text{m}^2$) of pentacene thin films grown at $E_i = 6.7$ eV, $\theta_i = 0^\circ$ on SiO_2 . The exposure time to the molecular beam is shown for each image.

Figure S-3 Average displacement (Angstroms) from collision point after 50ps for molecules that remain on surface at 5 different incident energies and $\theta_i = 0^\circ$.

Figure S-4 Displacement (Angstroms) as a function of time for all molecules that adsorb onto the pentacene surface (i.e. Not including insertions or ejections).

Table S-1 Destination of incident molecule after 50ps for 5 different energies.

Figure S-1

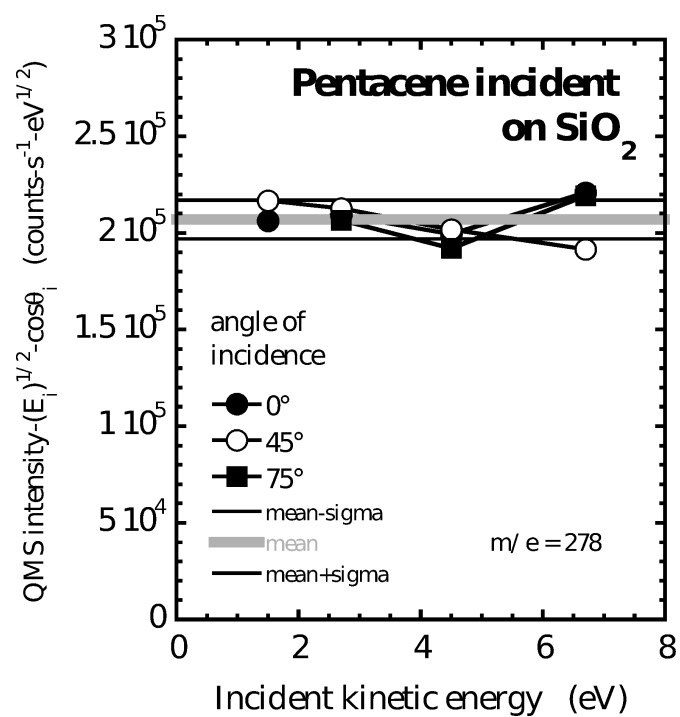


Figure S-2

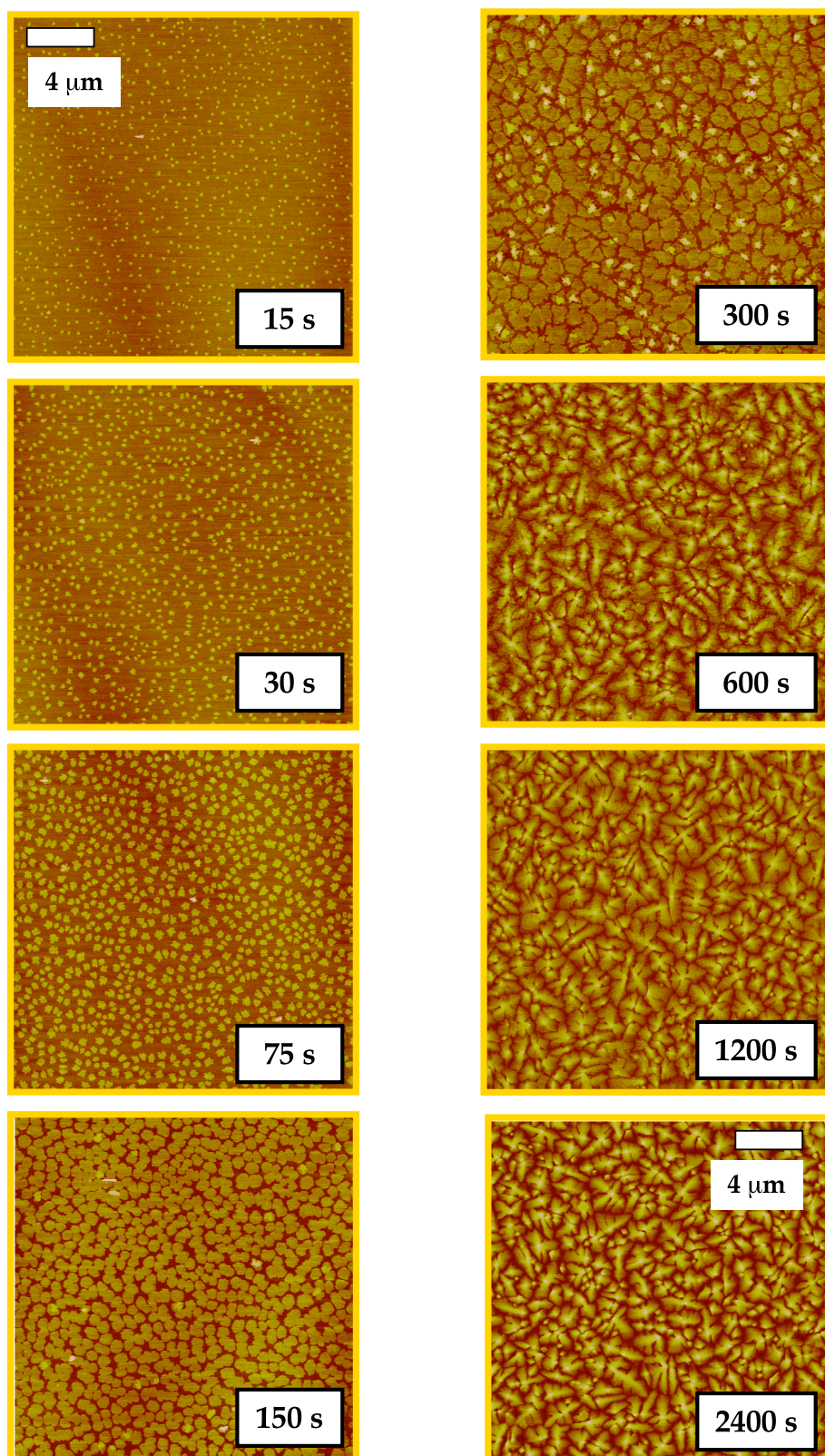


Figure S-3

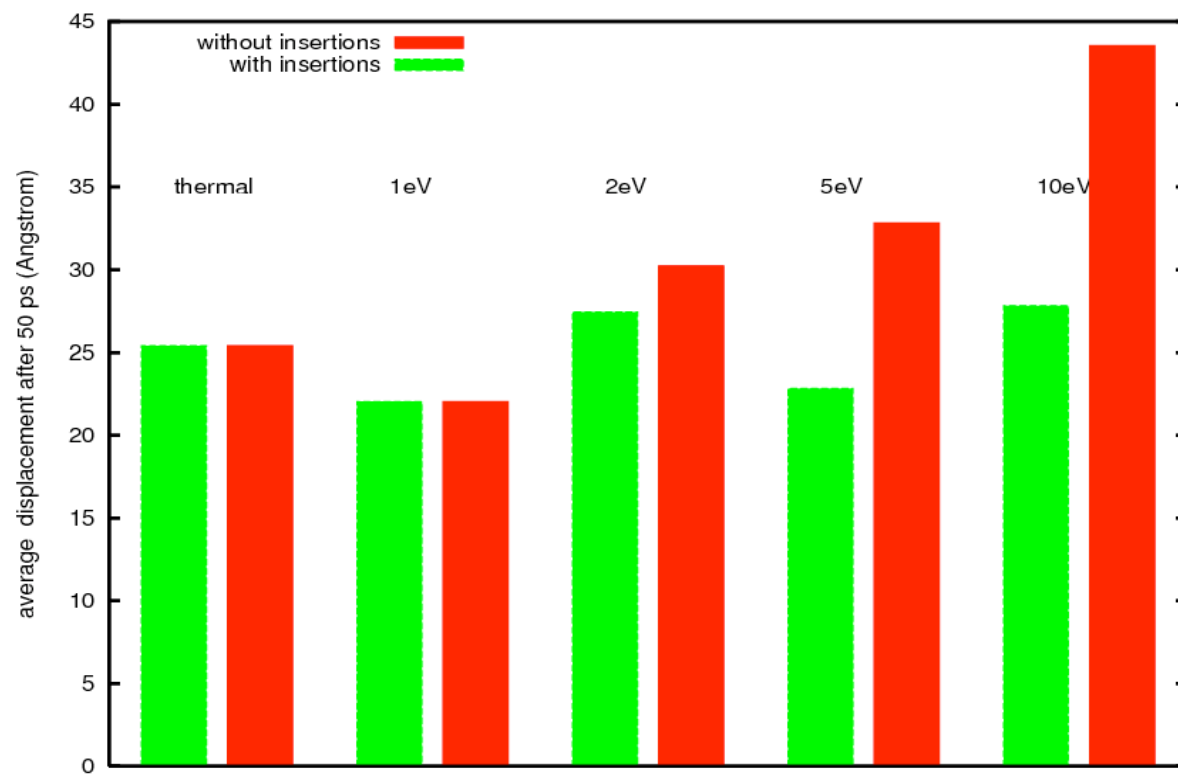


Figure S-4

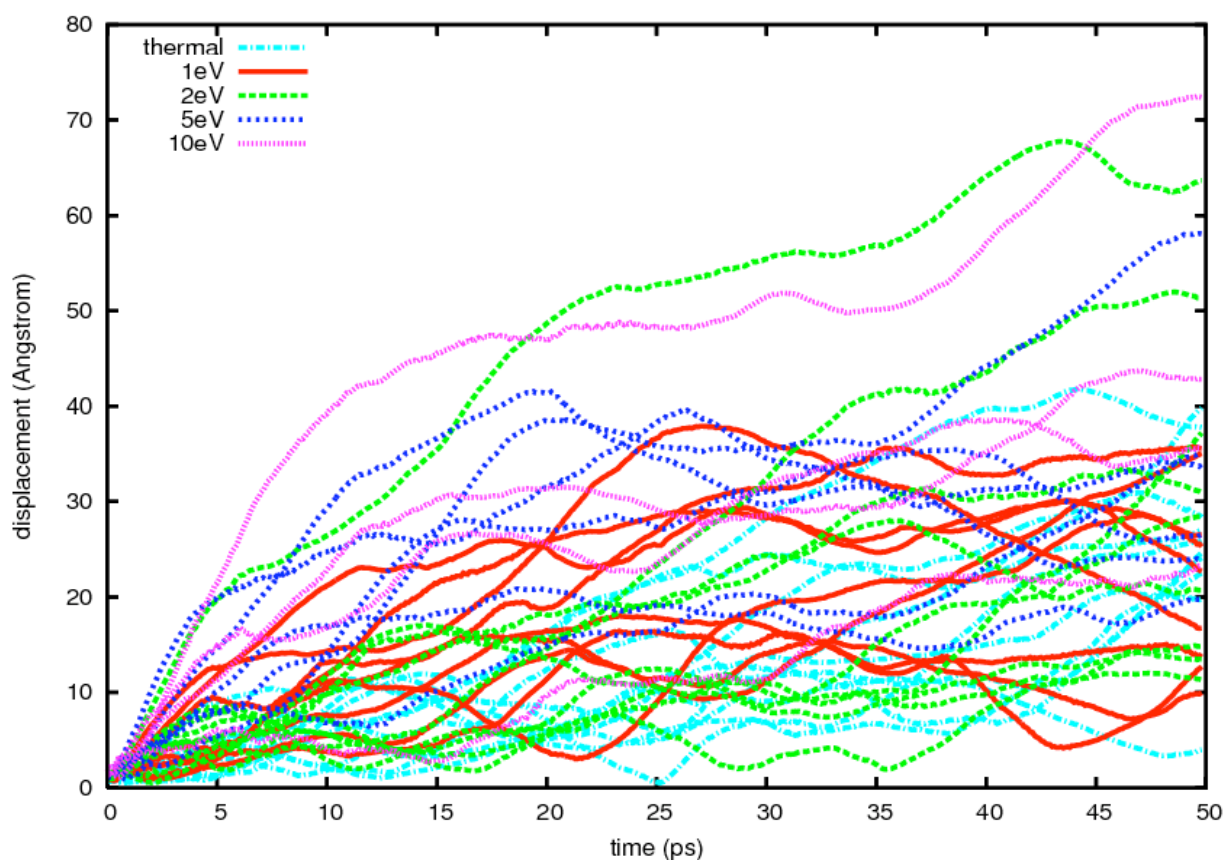


Table S-1

Energy (eV)	Ejected	Inserted	Adsorbed
thermal	0	0	10
1	1	0	9
2	0	1	9
5	1	3	6
10	3	3	4