Light control over polymorphism in evaporated molecular thin films

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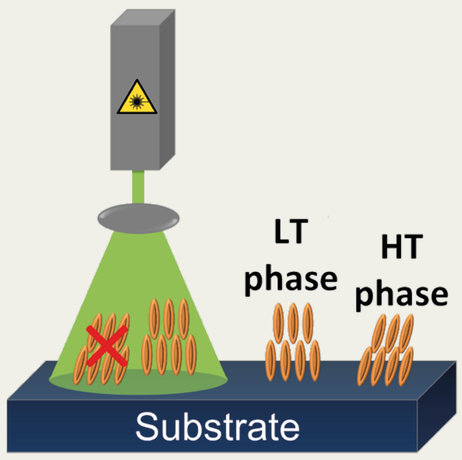
Growth Control through Light



Controlling the growth and crystallinity of organic molecules helps to increase the efficiency of organic thin film devices such as OLEDs or OFETs and has been addressed as one of the current challenges in organic semiconductor research. Besides substrate temperature and molecular deposition rate there is an ongoing quest for additional ways to influence the molecular growth process [2]. With our study [1] we introduce light as a new control parameter for the crystal structure in thin films of α-sexithiophene (6T) and pentacene.

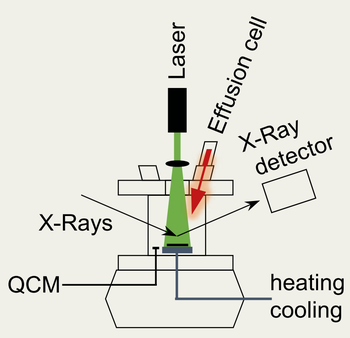
Methods

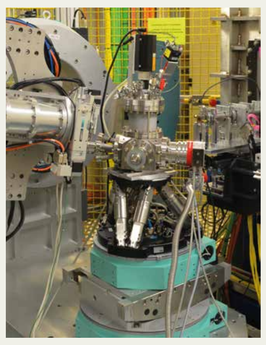
Growth
- Organic Molecular Beam Deposition (OMBD), base pressure of 10^{-8} mbar
- 6T on cleaved potassium chloride (KCl) substrate
- Pentacene on silicon wafer with native oxide layer

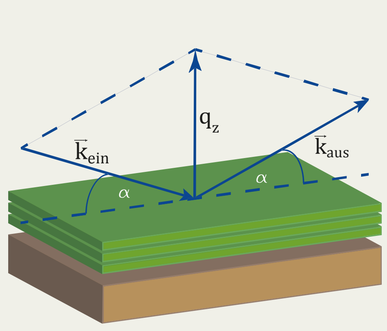
Growth Monitoring
- Real time *in situ* x-ray experiments for 6T at MS beamline, Swiss Light Source
- Reflectivity & θ/2θ scans for pentacene at I07, Diamond, UK

Growth Control
- 532nm Laser Light Source (1W/cm²)

Simulation
- Optical properties simulated with **`exciting`** code in the framework of density-functional and many- body perturbation theory (MBPT) [3]

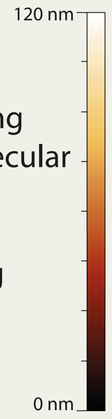


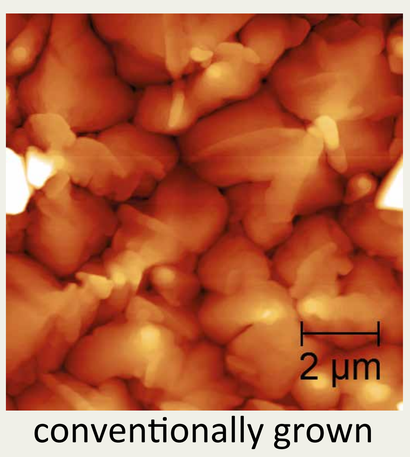




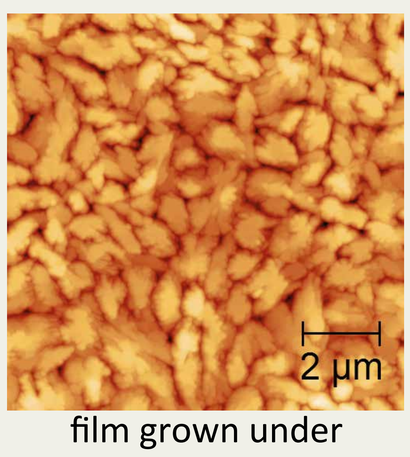
Pentacene: Light Influences Morphology & Crystallinity

- AFM shows strong decrease in molecular island size of pentacene films irradiated during growth

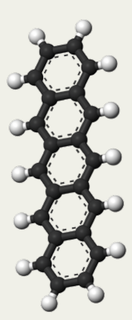


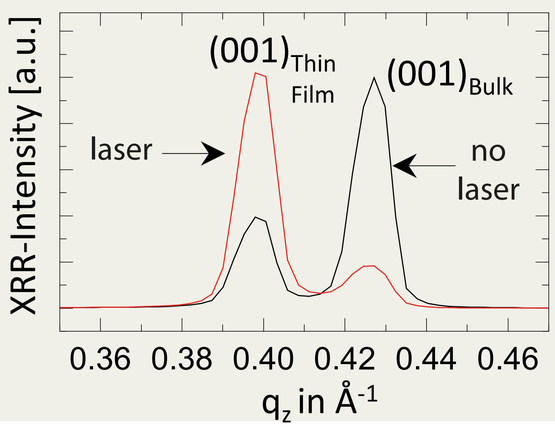


conventionally grown film



film grown under illumination

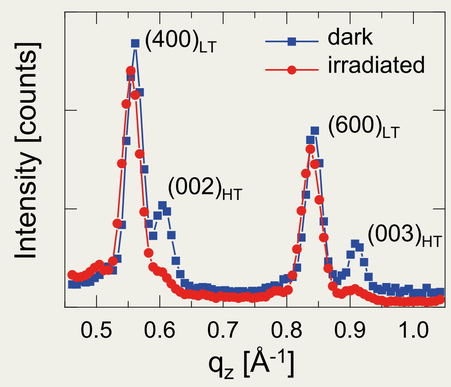


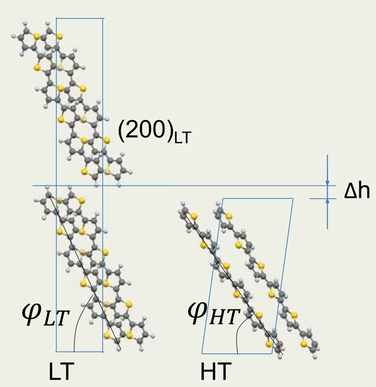


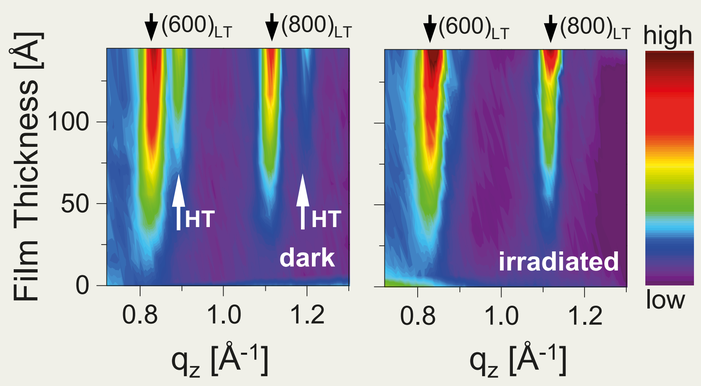
- Phase purity enhancement through light favouring the pentacene thin-film phase

6T: Phase-Purification in Thin Films through Light

- HT & LT polymorph of 6T coexist on KCl
- Irradiation with light reduces occurrence of the 6T HT phase

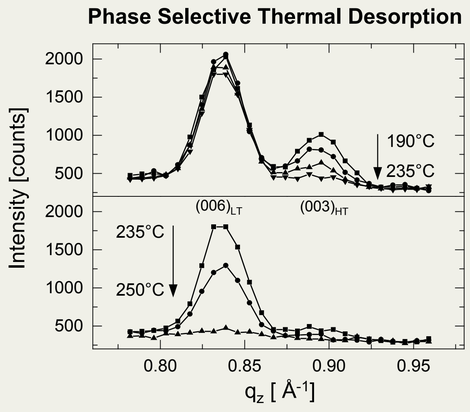


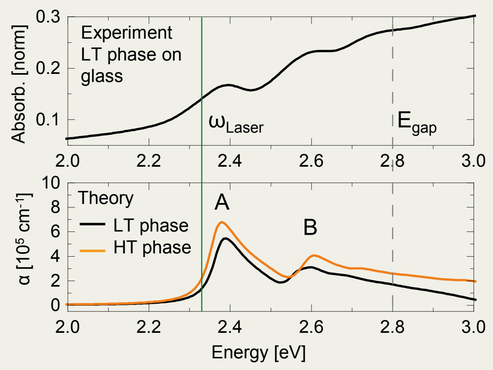




- Real-time *in situ* x-ray diffraction experiments highlight the suppression of the 6T HT crystal phase through light during the whole growth process

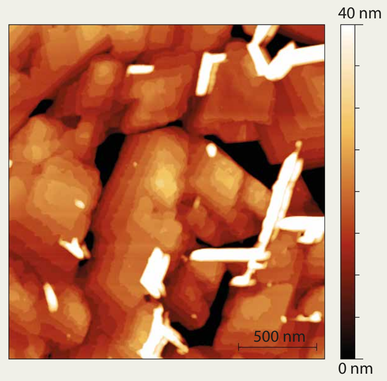
- Differing desorption temperatures for LT and HT phases of 6T on KCL:
  HT phase desorbs between 190 and 235 °C,
  LT phase desorbs between 235 and 250 °C





- Separate simulation of the absorption spectra of the 6T HT and LT polymorphs, since there is no experimental access to the isolated HT phase absorption spectrum

- Differing molecular tilt angle of the two phases leads to 20 % higher optical absorption of the HT phase



Mechanisms & Conclusion

- Light is a promising control parameter in molecular thin film growth, as shown for the organic semiconductors pentacene and α-sexithiophene (6T)

Mechanisms
- Phase selective optical absorption for 6T (but not for pentacene)
- Different thermal stability of the occuring polymorphs of 6T and pentacene

Perspective
- Demonstration that light acts as a control parameter during growth for a wider range of organic molecules
- Patterning through local, optical growth control

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Acknowledgments

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