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Structural and dynamical transitions in molecular ultra thin films for charge transport.

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The objectives of this experiment were to study the early stages of growth of organic semiconductor thin films in high vacuum (HV). The molecule chosen for this study was Sexithienyl (T6), a well known conjugated material employed for the preparation of high performance organic thin film transistors (OTFTs). This research was motivated by the importance of the structure of the first few layers of the organic material for performance of the actual devices. It has actually been suggested that only the first two monolayers of these films are actually involved in the electrical conduction in OTFTs.

We have thus designed an experimental set up for the real time in-situ study of the growth of T6 thin films. This system is based on a vacuum chamber fitted with a Be window on which we have adapted an home-made Knudsen cell optimised for organic materials. Such a cell actually allows us to control the growth rate better than 0.05nm/min. The substrate was fitted onto a sample heater located close to a quartz micro balance in order to control the impinging molecular flux.

Experimental Results

The reflectivity curves recorded for very thin films prepared at 120 °C (ca 10nm) showed that these samples contained two phases of T6, on one hand a phase where the T6 molecules stand exactly normal to the substrate (observation of (h 0 0) reflections exactly corresponding to the molecular length of T6) and on the other hand a phase where the molecules are slightly tilted with respect to the normal (fig. 1). The angle of tilt c.a. 25° is compatible with the one observed in the bulk structure of T6. The beam damage tests we realized on a 10nm thick film showed that the standing molecules phase (the thin film phase) is much more prone to degradation than the tilted one. Since the beam damage is essentially caused by secondary electrons that are emitted by the substrate and thus have a major impact on the very first layers we interpret the different stabilities as an indication that the standing molecule phase grows first at the contact of the substrate and is followed by the tilted phase.

Time resolved measurements were then realized during the growth at different substrate temperatures (Ts) with a growth rate 0.55Ang/min. Typical reflectivity curves are shown in fig. 2 for Ts=80°C. The results we obtained may be summarised as follows: for Ts=34°C, only Kiessig fringes were observed during the growth

of the film. No Bragg peak were detected (up to film thickness=20nm). For $T_s=80^\circ\text{C}$, both Kiessig fringes and Bragg peaks of both phases are observed. Within our time resolution, as soon as they were observed, the peaks corresponding to the standing molecules had reached constant intensity (fig 3). The tilted phase peaks instead displayed a constantly increasing intensity during growth. The spacing associated with both these phases remained almost constant during the whole growth. For $T_s=120^\circ\text{C}$, the Bragg peaks intensity analysis (fig 4) showed that the standing phase appeared first and kept on growing slowly (possibly towards a saturation that was nevertheless not observed before interruption of the experiment) while the tilted phase appeared latter on and displayed a larger growth rate. Contrariwise to what was observed at 80°C , the peaks associated to both phases showed a position shift towards lower spacings during growth (fig. 5). It emerges from these observations that the first T6 islands are initially formed of molecules standing perpendicular to the substrate. Then a second phase appears (presumably of molecules located on top of a complete layer of standing molecules) which has a structure closer to the bulk one (the molecules being tilted by c.a. 25° away from the normal to the bc plane). At high enough temperatures both phases maybe formed together and keep on growing while a conversion process tends to tilt all the molecules, eventually reaching the bulk phase value of the tilt angle.

Besides these growth experiments we also performed some annealing tests during which we monitored the reflectivity of a film subjected to an increasing temperature. During this process we observed a continuous decrease of the Bragg peak intensities which was not recovered once we lowered the sample temperature. This strongly suggested an important T6 thermal desorption and a posteriori observation of the annealed films by atomic force microscopy (AFM) confirmed that the final sample coverage was extremely low. It is thus clear that, in order to build highly organized T6 thin layers, it is necessary to optimise the growth parameters (substrate temperature and deposition rate) rather than to rely on subsequent annealing.

Conclusions

This experiment has demonstrated the possibility to characterize in real time and in-situ the growth of organic thin films on technologically relevant substrates and has brought important informations concerning the molecular orientation in the very first molecular layers of T6 grown on SiOx. Further experiments will clarify the details of the kinetics of formation of these films as well as the influence of substrate free energy.

