

Development of a Compact System for In-situ X-ray Scattering Studies of Organic Thin Film Deposition

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Abstract. We have developed a compact vacuum deposition chamber for in-situ x-ray scattering studies of organic thin film growth. The system is based on a small cylindrical chamber that can be mounted on a standard four-circle diffractometer. Incident and scattered x-rays enter and exit the chamber through a curved Be foil window that covers 200 degrees, and is sealed to the body of the chamber. The sample is mounted on a support tube with heating and cooling from liquid nitrogen temperature to >100°C. Integral to the sample stage is a multi-wire feedthrough to facilitate in-situ electrical transport characterization of organic semiconductor thin films. This is one of the novel capabilities of the system. In addition, the sample stage is mounted on a rotary vacuum feedthrough, which is mechanically coupled to the “phi” stage of the diffractometer. An effusion cell, shutter, and quartz oscillator thickness monitor are also incorporated into the system, which is pumped by a small turbomolecular pump. The system thus configured is capable of access to full reciprocal space, within the limits of the Be window. Results of initial experiments performed at the 48-pole wiggler beamline A2, at the Cornell High Energy Synchrotron Source show that in-situ x-ray scattering is sensitive to the early stages of nucleation and growth of organic semiconductor thin films.

INTRODUCTION

X-ray scattering has recently become an important experimental method for the study of thin film growth kinetics. Advantages of the method stem from the fundamental properties of x-rays, which are highly penetrating and scatter weakly from materials. This is in contrast to electron-based probes such as Reflection High Energy Electron Diffraction, where the electrons interact very strongly with surfaces and also with residual gasses around the surface. Consequently, x-ray scattering can be the method of choice in a number of circumstances such as (i) when quantitative data is required, since x-ray scattering from surfaces and thin films is accurately kinematical in many cases, (ii) when an ambient background gas is present, since x-rays penetrate through gasses even at atmospheric pressure with little attenuation, and (iii) when studying delicate materials such as organic thin films, since x-ray produce less damage than electrons. A wide variety of instruments have been constructed in the past two decades. Here we concentrate on designs that are compact enough to be mounted on a standard four-circle diffractometer commonly used for x-ray diffraction experiments. Early designs focused on ultra-high vacuum chambers for surface crystallography experiments.¹⁻⁵ More recently, several groups have designed special-purpose small chambers for a variety of thin-film deposition experiments, including sputter deposition,^{6,7} and organic thin film deposition.^{8,9}

Here we describe a new system for in-situ x-ray scattering analysis of organic thin film growth with simultaneous electrical characterization. The philosophy of the design is to reproduce current practices in the field of organic semiconductor thin films for Organic Thin Film Transistors (OTFTs) and Organic Light Emitting Diodes (OLEDs). The current state-of-the art in this field is thermal evaporation of organic precursors in high vacuum (~10⁻⁶ Torr). Initial experiments with our system show that residual water vapor in the vacuum enclosure plays a role in organic thin film growth, and that water may be incorporated into devices fabricated by current techniques.

MECHANICAL DESIGN

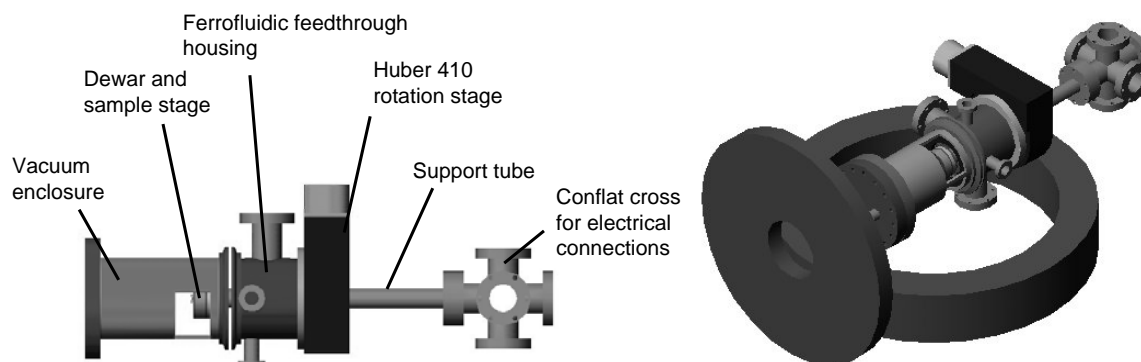


FIGURE 1. This diagram shows the major components of the system assembled onto the rotation stage (left), which is part of the x-ray diffractometer. The feedthrough hat and support tube enclosure are not shown in this diagram. Components of the chamber are shown assembled onto the diffractometer (right). The system is typically mounted on a 512 Eulerian cradle. Assembly takes less than one hour.

Figure 1 shows several of the the major components of the system. A 4" diameter vacuum enclosure surrounds the sample, and contains a 1.75" wide beryllium window. The Be window covers 200 degrees. The enclosure mates to the ferrofluidic feedthrough housing on one end via an o-ring seal, and mates to a 6" conflat flange on the other end. A custom conflat flange (not shown) containing the evaporation cell and shutter assembly are typically mounted on the conflat connection. The dewar is designed to contain liquid nitrogen, and is fed by tubes running the length of the support tube. A sample heater is embedded in the dewar itself. The sample stage is in intimate contact with the dewar, but electrically isolated, and contains three electrical connection to facilitate in-situ electrical characterization of three terminal devices such as Organic Field Effect Transistors. The system is designed to be mounted on a Huber 410 rotation stage, which is a standard part of the x-ray diffractometer. The support tube and conflat cross mate to rotary stage through the center hole of the Huber 410 stage. A 1.5" support tube surrounds the support tube and mechanically links the adapter plate and electrical feedthrough assembly. The Conflat cross contains liquid-nitrogen connections, heater wires, thermocouple feedthroughs, and electrical connections to sample.

The diagram on the right side of Figure 1 shows the system assembled onto a standard x-ray diffractometer (Huber Model 512 Eulerian Cradle). The body of the chamber can be mounted in any orientation, since an o-ring sealed connection with a clamp to compress the o-ring attaches it to the rest of the assembly. Typically it is mounted so that the incident and exit x-ray beam can enter and exit the chamber cleanly. The ferrofluidic feedthrough housing does not have a fixed position, and can also be rotated, for example, to make connection of the vacuum pump easier.

CAPABILITIES

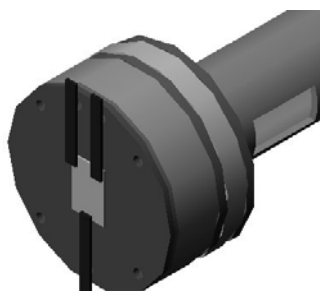


FIGURE 2. This diagram shows the sample with three electrical connections, the dewar assembly and support the tube.

The system has full 4-circle diffraction capability. Major scans of interest include specular reflectivity, rocking curve scans, and in-plane diffraction. The sample stage has unrestricted 360° azimuthal rotation (Fig. 1). Typically, the sample is heated to temperatures between room temperature and 100°C during thin film growth. Cooling is primarily to be used for temperature dependence of electrical properties (Fig. 3).

A Tungsten boat with internal baffles is used for evaporation. It can be operated in any orientation, which is a necessary feature since it is often operated in a downward-facing geometry. Temperature feedback is accomplished by a thermocouple spot welded to side of boat. Typical operation of the evaporation source is near 300°C for pentacene. A mechanical shutter is also installed between the sample and the evaporator. It is actuated by a rotary solenoid, and can be operated remotely. Finally, a thickness monitor is placed near the sample, but clear of the path of the x-ray beam to monitor deposited thickness.

EXPERIMENT

There has been great interest in organic semiconductor materials composed of molecules such as sexithiophene derivatives and pentacene for organic thin-film transistors (TFTs), due to their high field-effect mobilities, which approach that of amorphous silicon. It is thought that the high mobilities observed in these materials are due to intermolecular interactions which lead to larger grain sizes and fewer grain boundaries, facilitating charge transport.¹⁰⁻¹³ The biggest advantage of organic semiconductors is that they lend themselves to low-temperature processing, thereby enabling fabrication of electronic devices on a variety of substrates.

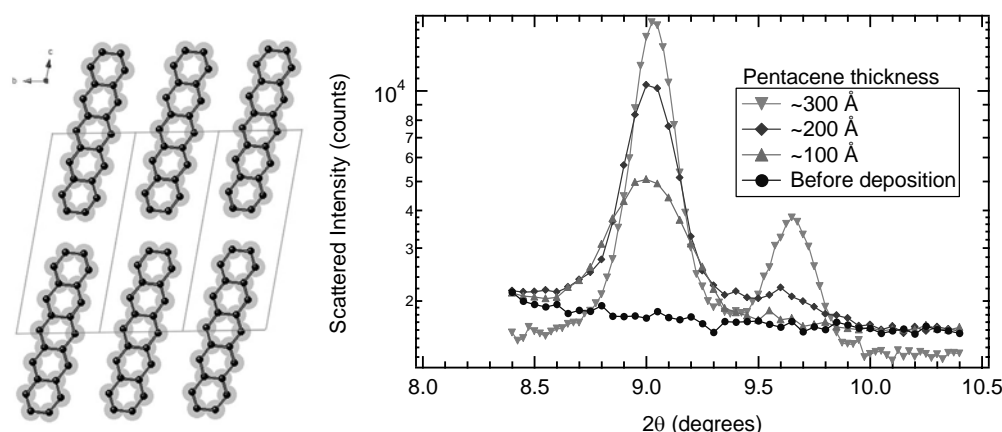


FIGURE 3. Crystal structure of pentacene (left). Evolution of the (002) reflection of pentacene (right) showing peaks from the thin film phase and the bulk phase. The x-ray wavelength is 1.24λ , and the sample was at room temperature during the deposition.

We have used our system extensively for growth of pentacene thin films (Fig. 3.) One of the most noticeable phenomena that we have studied is the change of layer spacing during growth. Typically, we observe a thin-film phase layer in contact with the substrate. Subsequent layers abruptly change to the bulk phase as the film growth proceeds. Fig. 3 shows the development of the (002) reflection as a function of deposited thickness. The substrate is Si(001) with 3000Å thermally grown SiO₂. An initial peak corresponding to the thin-film phase is visible at 100Å, and it narrows and increases in intensity as film thickness increases. A second reflection begins to develop at about 200Å and is clearly visible at 300Å.

Detailed characterization of reflectivity curves gives evidence for an adsorbed layer of water vapor on top of the SiO₂ layer. Preliminary analysis indicates that this layer is still present after deposition of pentacene. Further details will be presented in an upcoming publication

CONCLUSIONS

We have developed a system for in-situ characterization of film morphology under realistic conditions. Initial experiments show that in-situ characterization of organic thin films yield valuable information about the structure

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and morphology of organic semiconductor thin films. The role of water vapor in the growth has been under appreciated and will need to be addressed in future work. We also plan to combine in-situ electrical characterization with x-ray characterization in future work.

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REFERENCES

- ¹P. Zschack, J.B. Cohen, Y.W. Chung, J. Appl. Cryst. **21**, 466 (1989).
- ²I.K. Robinson, W.K. Waskiewicz, P.H. Fuoss, J.B. Stark and P.A. Bennet, Phys. Rev. B **33**, 7013 (1986).
- ³G.A. Held, J.L. Jordan-Sweet, P.M. Horn, A. Mak, R.J. Birgeneau, Phys. Rev. Lett. **59**, 2075 (1987).
- ⁴J.W. Chung, K. Evans-Lutterodt, E.D. Specht, R.J. Birgeneau, P.J. Estrup and A.R. Kortan, Phys. Rev. Lett. **59**, 2192 (1987).
- ⁵J.R. Dennison, S.K. Wang, P. Dai, T. Angot, H. Taub, S.N. Erlich, Rev. Sci. Instrum. **63** (8), 3835 (1992).
- ⁶A.P. Clemens, S. Brennan, Rev. Sci. Instrum. **63** (1), 1147 (1992).
- ⁷H. You, R.P. Chiarello, H.K. Kim and K.G. Vandervoort, Phys. Rev. Lett. **70**, 2900 (1993).
- ⁸P. Fenter, P. Eisenberger, P. Burrows, S.R. Forrest, and K.S. Liang, Physica B **221**, 145 (1996).
- ⁹K.A. Ritley, B. Krause, F. Schreiber and H. Dosch, Rev. Sci. Instrum. **72** (2), 1453 (2001).
- ¹⁰H.E. Katz, and Z. Bao, J. Phys. Chem. **104**, 671 (2000).
- ¹¹D.J. Grundlach, Y.Y. Lin, T.N. Jackson, S.F. Nelson and D.G. Schlom, IEEE Electron. Device. Lett. **18**, 87 (1997).
- ¹²F. Garnier, Acc. Chem. Res. **32**, 209 (1999).
- ¹³C.D. Dimitrakopoulos, A.R. Brown and A. Pomp, J. Appl. Phys. **80**, 2501 (1996).