

# Putting Color into Surface Diffraction

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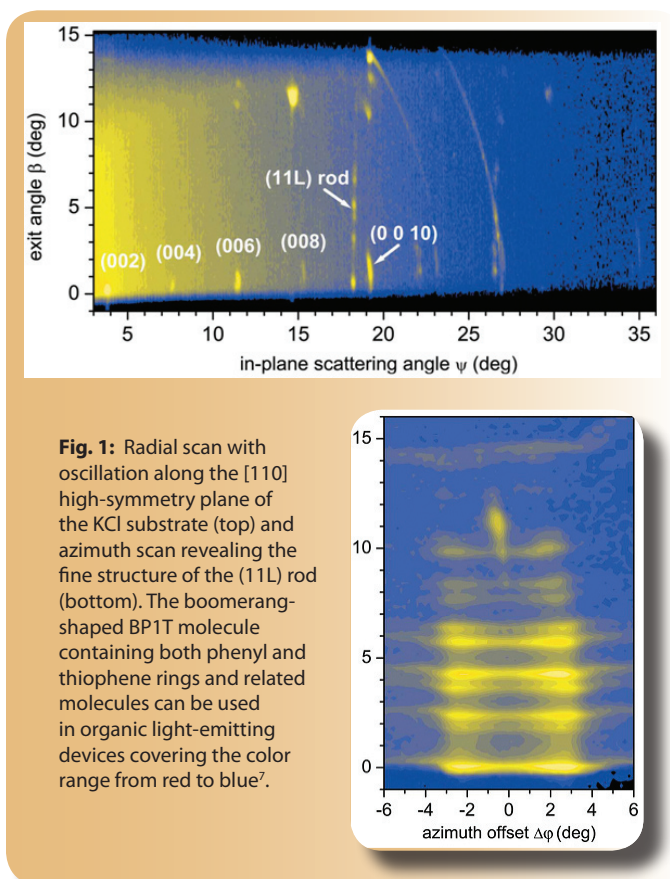
Surface X-Ray Diffraction (SXRD), also called Grazing-Incidence Diffraction (GID) is a well-established powerful tool for structure determination of surfaces<sup>1,2</sup>, monolayers<sup>3</sup>, and thin films<sup>4,5</sup>. Moreover, surface phase transitions<sup>1,2</sup> and time-dependent effects, such as growth kinetics<sup>6</sup>, have been studied in depth with this method. However, SXRD/GID also acquired a reputation of being highly esoteric with very refined representations of scattering data in unusual units.

Since molecular thin films have come into focus, be it for organic electronics device-grade films, self-organized functional coatings, or biophysical membranes, this spartan picture has begun to change. While in close-to-perfect inorganic structures all information is contained along the diffuse scattering rods perpendicular to the substrate surface, soft materials inherently have a larger amount of disorder. Hence, rather than just scanning the rods, now full reciprocal space maps (RSM) have become of interest, in order to determine structure and distinguish different types of disorder at the same time. Along with the reciprocal space maps has come the color.

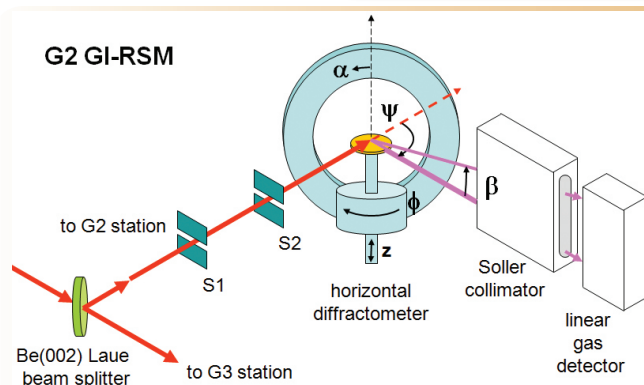
While we originally started out working in the conventional way of characterizing molecular films by hunting for molecular Bragg reflections along the symmetry directions of the substrate<sup>4</sup>, it soon became apparent that this was not the most efficient route to find all sufficiently strong film reflections, in order to collect as much structural information as obtainable. Moreover molecular films are often characterized by low-symmetry lattices such as monoclinic and triclinic, which complicates this search even more.

Hence we started combining the linear detection scheme from liquid surface diffraction<sup>3</sup> with the oscillation method from protein crystallography. The oscillation range could be set either narrow for proper integration of all reflections along a single scattering rod<sup>7</sup> or wide enough to cover the full irreducible range of rotation as given by substrate symmetry<sup>8</sup>. The latter "survey scans" provided the desired efficient method to identify all strong film reflections. In combination with azimuth scans around the surface normal at specific q-values to measure the scattering rods, all available information can be efficiently collected. We called our method GI-RSM<sup>7</sup>.

GI-RSM proved to be also an effective method for uniaxial powders. These are organic thin films that are grown on amorphous substrates such as native or thermal oxides of silicon wafers, glass, or indium-tin oxide (ITO) coatings. In such cases there often is a well-defined orientation of the molecular layers with respect to the surface, however, crystallites are oriented at random in the surface plane. The Bragg condition is met easily, where the ring-like Bragg reflections oriented parallel to the surface intercept the Ewald sphere. Hence 2D powders in grazing incidence geometry produce discrete spots in the scattering images, and the overlap problem of conventional powder diffraction is much reduced. The resulting diffraction patterns closely resemble fiber diffraction patterns.



**Fig. 1:** Radial scan with oscillation along the [110] high-symmetry plane of the KCl substrate (top) and azimuth scan revealing the fine structure of the (11L) rod (bottom). The boomerang-shaped BP1T molecule containing both phenyl and thiophene rings and related molecules can be used in organic light-emitting devices covering the color range from red to blue<sup>7</sup>.



**Fig. 2:** First incarnation of the GI-RSM set-up at G2, still using the horizontal four-circle diffractometer<sup>7</sup>. After upgrading the instrument to a six-axis psi-circle diffractometer<sup>9</sup> the detector arm can now also scan in the vertical direction extending the access to higher exit angles  $\beta$ , which was previously limited by the aperture of the linear detector.

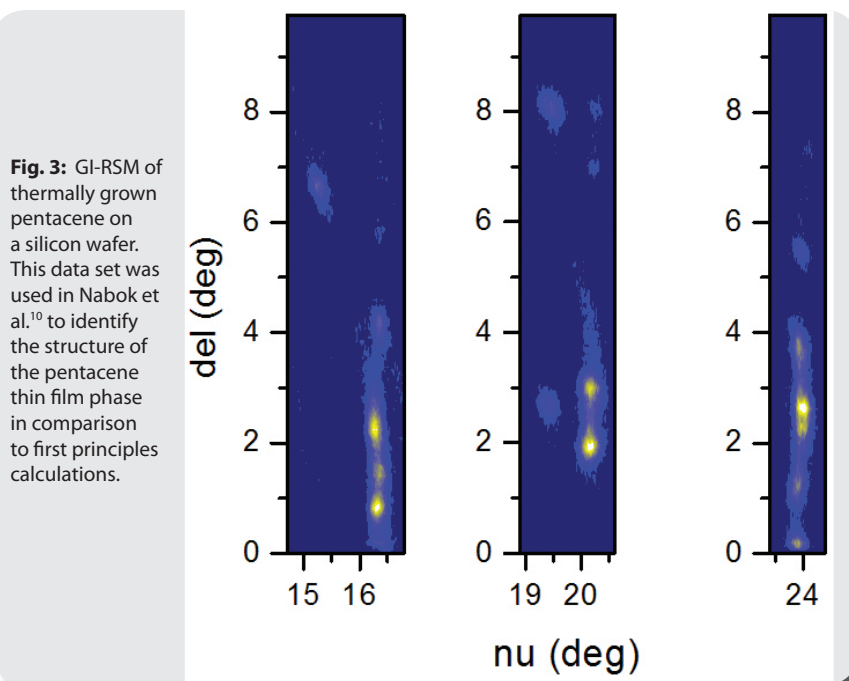
A first success for the Resel group was collecting enough information from a pentacene film to compare the structure of the thin film phase predicted by first principles methods with these low-resolution diffraction data<sup>10</sup>. By now we have refined data collection further with the new kappa diffractometer<sup>9</sup> so that angular ranges of up to 60° in  $\Psi$  and 50° in  $\beta$  can be collected by merging several 6-8° strips, collected with the linear detector<sup>11</sup>, at a time. An even more subtle kind of organization was found for Ru-bpy molecules deposited onto ITO in device-like samples. Ru bpy, a Ru<sup>++</sup>-bipyridine<sub>3</sub> complex with two PF<sub>6</sub><sup>-</sup> counterions, is known as an ionic conductor which produces efficient red light emission in organic light-emitting devices (OLED). In previous work it had been concluded that such Ru-bpy films were amorphous, as no discernable scattering was obtained with lab-based x-ray generators.

Using GI-RSM we found subtle broad ring-like scattering features, after we optimized the scattering geometry to suppress scattering from the substrate. We could correlate the weak powder rings with a known crystalline structure and concluded that Ru-bpy forms nanoscale domains of only a couple of lattice constants in diameter. In addition we traced back our observation, that occasionally films featured higher order, to water contamination in the glove box. This first proof of GI-RSM being able to reveal the medium range order in a nominally amorphous organic film was recognized in an inside cover of *Journal of Materials Chemistry*<sup>12</sup> and Daniel Blasini was awarded the CHESS Thesis Prize for this work and his other results at G2 station<sup>13</sup>.

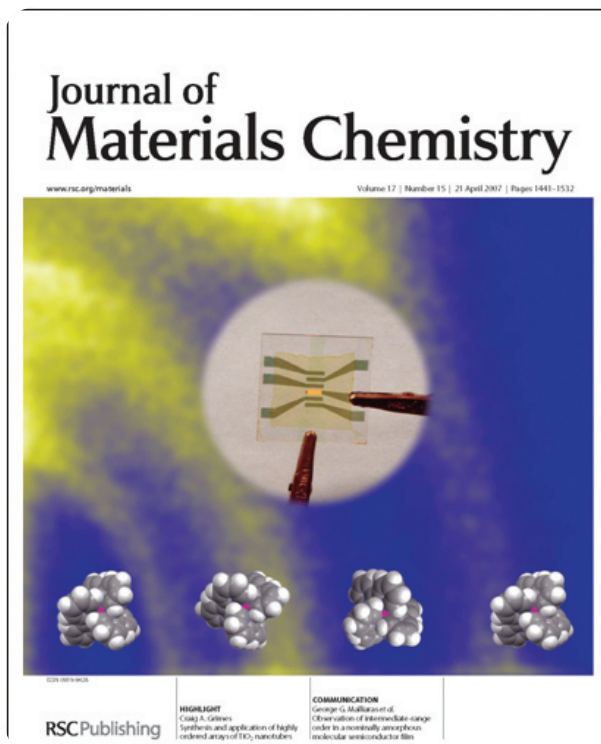
Molecular monolayers are the ultimate challenge in surface diffraction. The Allara group at Penn State has developed a wet-chemistry procedure of preparing thiol monolayers on GaAs surfaces. In Fourier-transform infrared (FTIR) spectra the thiols appeared well aligned, so the question was, whether these thiols would form well-ordered monolayers, as known for thiols on gold<sup>14</sup>.

Christine McGuinness' and coworkers' paper in *ACS Nano*<sup>15</sup> ended a ten year quest of optimizing and characterizing the order in thiol layers on GaAs(100). It turned out that thiols on GaAs(100) only form nanoscale domains, even under the best preparation conditions. These nanoscale domains show some preferential alignment along the [100] substrate azimuth, which we ascribed to alignment of thiol crystallites parallel to step edges. Moreover, the lattice spacing in the thiol domains shows a subtle variation as a function of the substrate azimuth. This in-depth study with about 30 samples became the most-cited paper in *ACS-Nano* in the first year of its introduction.

As the flux and stability of the beam at G-line has continuously improved, we have been increasingly facing the problem that the limited dynamic range of the ORDELA linear gas detector has become the bottleneck that limits the speed of data acquisition, since intense peaks need to be rescanned with attenuation. A couple of years ago, we started talking to Peter Siddons at NSLS about the possibility of obtaining one of his prototype diode array detectors. In such an advanced detector, each diode element samples a comparable solid angle like the corresponding MCA channel of the gas detector. However, as each element has its own electronics, it can handle a dynamic range from single photon counting to a couple of 10<sup>5</sup> counts/sec, while the gas detector shows signs of saturation already at 10<sup>3</sup> counts/sec/channel.



**Fig. 3:** GI-RSM of thermally grown pentacene on a silicon wafer. This data set was used in Nabok et al.<sup>10</sup> to identify the structure of the pentacene thin film phase in comparison to first principles calculations.



**Fig. 4:** Ru-bpy based-light emitting device and Ru bpy molecule depicted on top of the scattering map obtained at G2<sup>12</sup>.

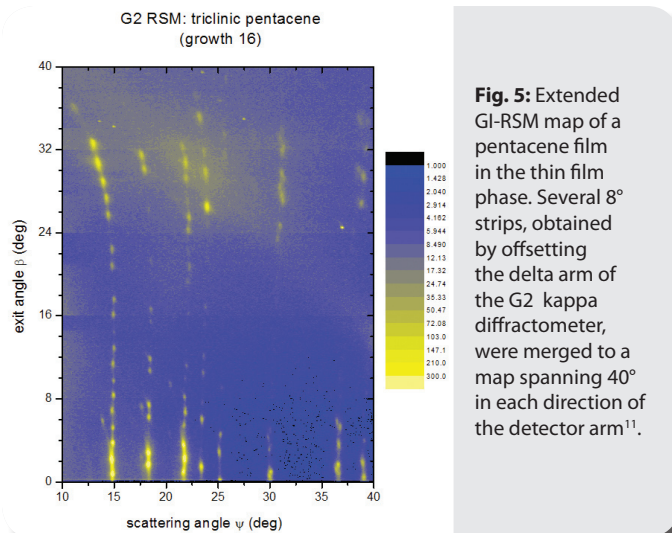
At the time of writing we have just obtained such a high performance diode array and it is currently being set up at G2 by Abruña student Michael Lowe and G2 scientist Arthur Woll. State-of-the-art extended GI-RSMs, such as the one shown in Fig. 5, can thus be scanned in future without beam attenuation or fear of saturation of the brightest peaks. The new detector should help us to overcome many of the restrictions imposed by the limited dynamic range of the linear gas detector, promising a bright future for the GI-RSM system at G2.

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**Fig. 5:** Extended GI-RSM map of a pentacene film in the thin film phase. Several 8° strips, obtained by offsetting the delta arm of the G2 kappa diffractometer, were merged to a map spanning 40° in each direction of the detector arm<sup>11</sup>.