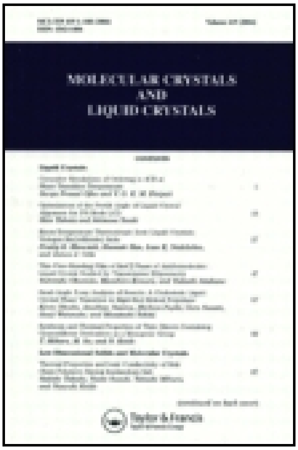

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# Structural Order and Photoelectric Properties of Organic Thin Films

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# Structural Order and Photoelectric Properties of Organic Thin Films

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Photoactive *organic* thin films are attracting rapidly growing attention. Model investigations are aiming at establishing a new era of electronics, based on molecular materials - with the potential of miniaturization down to the molecular level ("molecular electronics"). As a fundamental difficulty, however, electric, photoelectric and optoelectronic properties of organic thin film samples are often found to vary considerably with the preparation parameters. - Using vapor-deposited 3,4,9,10-perylene-tetracaboxylic- dianhydride (PTCDA) thin films and measuring the electron time-of-flight mobility we prove that, what appears as poor reproducibility, largely is a consequence of a wide scatter of structural parameters, such as the degree of cystallinity and orientational order. We find that the electron mobility - over orders of magnitude - is (anti-)correlated with the width of the X-ray rocking curve of the respective sample, reaching $3\times10^{-2}$ cm$^2$/Vs for our presently best one.

Keywords organic thin films; order; disorder; rocking width; electron mobility; PTCDA;

## INTRODUCTION

Different types of structural order/disorder occurring in thin films comprise azimuthal disorder, formation of multiple domains, small angle grain boundaries, texture, and polymorphism. *Azimuthal disorder* (on a scale $L$) can be detected either by methods that superimpose or average out directional properties over a certain area ($L^2$) such as e.g. low energy electron diffraction, LEED, (where $L$ is given by the electron beam diameter of ca. 1mm), optical double

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*present address: TRIKON GmbH, Ulm, Germany refraction and dichroism ($L \geq \lambda$), or by observing the orientational distribution of individual grains e.g. by transmission electron microscopy (TEM) in the imaging or in the diffraction mode. *Multiple domain formation* is usually found in conjunction with epitaxial growth if the substrate surface contains symmetry elements, offering several energetically equivalent orientations to grow. Therefore on a hexagonal surface, as e.g. that of cleaved graphite, up to 12 symmetry-equivalent domain orientations can be expected; optical and diffraction methods allow their detection.Information on *small angle grain boundaries*, i.e. on a microcrystalline sample with only small angular deviations of the individual grains from a common average orientation, can be obtained from X-ray rocking curve analysis, measuring the angular spread of a considered reciprocal lattice vector, cf. Figure 1, whereas *texture*, describing a certain degree of preferred orientation in a sample with near random grain orientations, can be inferred from a non-isotropic disribution of X-ray scattering power. A tendency towards *polymorphism* arises from the fact that the first few organic layers on a substrate often crystallize in a structure different from that of the usual bulk structure, an effect induced by details of the interactions with the substrate surface. These also determine different "wetting" behaviour, leading then to one or another type of growth modes (Frank – van der Merwe, Stranski – Krastanov, or Volmer – Weber). *Island growth,* typical of the latter, often leads to grain interfaces with stuctural or doping discontinuities, to pinhole formation in the layers or even to complete lack of connectivity; in addition, surface thickness may tend to be rather nonuniform; this can be checked to better than ± 1nm by the contrast ratio of small angle (Kiessig) X-ray interferences or, with high spacial resolution, by scanning atomic force microscopy (AFM).

There are a number of effects that these different types of disorder can have on the electric, photoelectric, optoelectronic, optical and other properties of a sample: structure and symmetry-determined anisotropic properties are averaged out; discontinuities of translational symmetry cause (additional) scattering, slowing down mobile excitations (electrons, excitons, phonons) and thus leading to increased transport resistance, or even full transport interruptions, and - in addition - may induce density of states at otherwise forbidden energies; structural changes and dopant aggregation at grain boundaries may lead to barrier formation and interface trapping. Alltogether, lifetimes of excited states are frequently reduced; spectral lines are broadened.

For whatever intended technical applications any possible improvement of structural order is thus highly desirable. In what follows an experimental example will be given.

## EXPERIMENTAL

For experiments devised to clarify the variability of structural order in vapor-deposited thin films and to elaborate its bearing on the photoelectrical parameters we chose the standard model substance PTCDA (3,4,9,10-perylene-tetracarboxylic-dianhydride; for the molecular structure see Figure 2). We report on a study of the different resistance against transportation exerted on photogenerated electrons in samples of different order, and measured as their effective mobility $\mu$ in a time-of-flight (TOF) type experimental setup.

Commercial PTCDA (Aldrich) was purified by a slow (1g/24h) multiple-temperature-step vacuum sublimation, followed by a slow temperature gradient (ca. 400K/m) sublimation in a stream of highly purified $N_2$ at 1 mbar. The central fractions were used. Before vacuum (HV: $10^{-6}$ mbar; UHV: $10^{-10}$ mbar) vapor deposition of PTCDA thin films the source material was preheated over night. Ca. 2 cm$^2$ layers, at a thickness between 230 and 480nm, were then deposited at a rate between 0.5 and 25 nm/min on different polycrystalline and single crystalline substrates, acting as one of the TOF-electrodes (Au on fused silica; In/Sn-oxide, "ITO", on glass; Si, covered with native oxide; and UHV-prepared bare single crystalline Si, which, however, was found to offer no advantage because arriving PTCDA molecules are immediately bound chemically in the first layer, a fact leading to polycrystalline films as well, rather than to an expected epitaxial ordering). Six segments of a semitransparent (ca. 15nm) gold cover electrode were finally overlaid by thermal evaporation and each was contacted (under air) by a tiny droplet of a liquid $In_{0.34}Ga_{0.66}$ alloy and a thin copper wire. Measurements were made under vacuum.

Charge carriers were pulse-excited near the gold electrode by strongly absorbed laser photons ($\sim 10^{11}$/10 mm$^2$-segment) ($\lambda$ = 337 nm, 0.9ns or $\lambda$ = 472 nm, 0.7 ns). Each drift current pulse j(t) (consisting of $\sim 10^8$ mobile electrons) was amplified by a broad-band amplifier, fed to a fast real time oscilloscope (Tektronix 7104 / 7A29 / 7B15), photographed single shot by a triggered CCD camera, and digitized to a j(t) diagram.

The time resolution of the eqipment was ca. 1 ns. At a typical (not greatly varied) drift field of 10 kV/cm, where signals were sufficiently above noise, a minimum useful drift time of ca. 4 ns limits the minimum allowable sample thickness d to 400 nm for detecting a mobility up to 1 cm$^2$/Vs, (or to 4nm for $\mu$ = $10^{-2}$cm$^2$/Vs; one should be aware, however, that for bulk photogeneration, even at maximum absorption ($\varepsilon = 3.8 \cdot 10^5$ cm$^{-1}$ at $\lambda$ = 472 nm), the Lambert–Beer $1/e$ light penetration depth (26 nm) may not be negligible in the evaluation).

## RESULTS AND DISCUSSION

Highest specific resistances of the 10 $mm^2$ TOF thin film sandwich samples ranged around $5\times10^{11}$ Ωcm, but most were lower and a number of samples displayed full through-contacts which we attributed to conductive bridges caused by pinholes; these could sometimes be burnt off by a voltage pulse. Charge carrier TOF pulses j(t) were obtained only for electron poling. These pulses did not show the ideal rectangular shape with a clear-cut arrival time kink, known from well purified single crystals. Dispersive transport was concluded therefore, and the curves were tentatively analyzed according to the Continuous-Time Random Walk model devised by Scher and Montroll [1]: A log j versus log t plot revealed a transition from a lower slope (1) to a larger slope (2) decay with a transition time $\tau$ depending on the applied electric field strength, thus excluding a pure deep trapping situation. Analysis of these slopes confirmed, as theoretically required by the model, that $j_1 \sim t^{-(1-\alpha)}$, $j_2 \sim t^{-(1+\alpha)}$, $0 < \alpha < 1$. Moreover, all measured TOF curves nicely coincided when drawn in relative units in a master plot, i.e. with each current relative to its value at time $\tau$, versus time in units of $\tau$, see Figure 2. This universality behaviour was taken as a justification to apply the model and to extract mobilities. All mobilities presented were so checked. (Notice that these are the *maximum* mobilities, connected with that class of carriers that find the fastest random walk routes).

Variations of structural order were achieved by using different substrates, a range of deposition rates and substrate temperatures between 173 and 423 K. It was found that the TOF electron mobilities obtained displayed a strong correlation (across orders of magnitude) with the structural order of the respective sample, as defined by the rocking width of the (102) Bragg-Brentano X-ray diffraction peak. PTCDA is known to tend to grow with its (102) plane preferentially parallel to the substrate surface on most substrates, no matter whether poly- or single - crystalline. Thus for a range of rocking widths of the (102) reflection decreasing from 22 deg to 3 deg (fwhm) the (room temperature) electron mobility increased from $7\times10^{-6}$ to $3\times10^{-2}$ $cm^2/Vs$, see Figure 3. Between 100 and 370 K these mobilities were slightly thermally activated ($E_{act} \simeq 20$ meV). More details on these TOF experiments in PTCDA films may be found in ref. [2].

Notice that the highest measured mobility was still associated with a rocking width of 3.4 deg. Better, (102) quasi-epitaxial ordering of PTCDA was observed on HOP- graphite and $MoS_2$(0001) and on GeS(010) single crystal surfaces with rocking widths of less than 0.3 deg. These highly ordered layers promise still much higher electron mobilities, as may be inferred from extrapolating Figure 1.

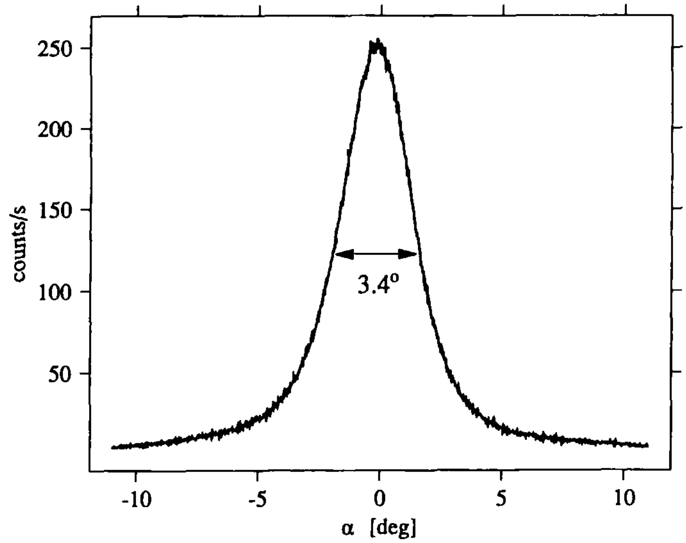

FIGURE 1 The X-ray rocking curve width of the (102) reflection of a highly ordered polycrystalline vapor-deposited PTCDA thin film is only 3.4 deg in this example.

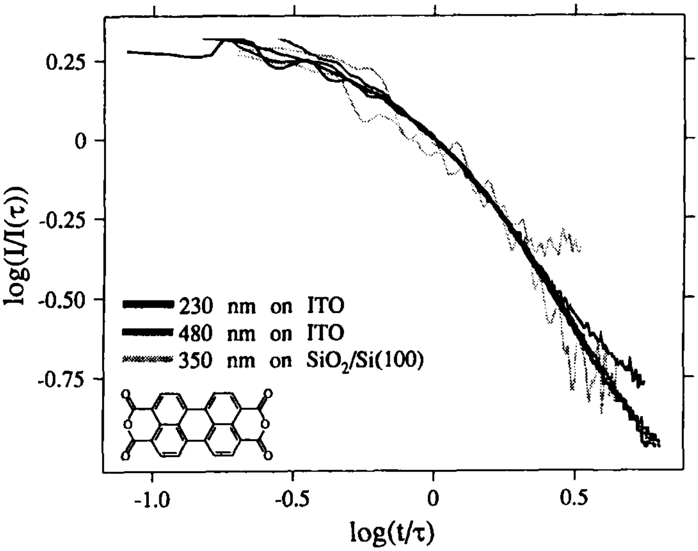

FIGURE 2 Normalized electron time-of-flight pulses obtained with different PTCDA vapor-deposited thin films coincide, as required by the Scher-Montroll model for dispersive transport. (Three samples at two different field strengths; τ covers a range from 8.9 to 628 ns.)

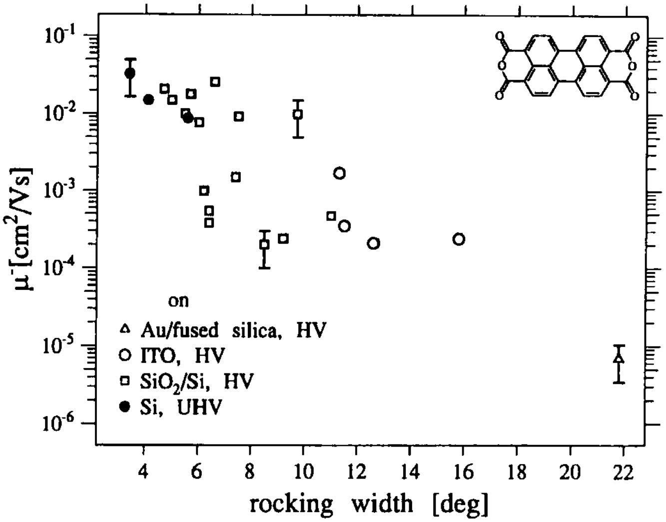

FIGURE 3 Electron mobilities (R.T.) in different samples of PTCDA thin films strongly (anti-) correlate with the X-ray rocking width, which is a measure of disorder of the respective thin film sample.

Unfortunately, however, we were not yet able to measure TOF mobilities with such samples so far because of severe through-contact formation during deposition of the Au cover electrode; this problem is likely to be caused by step edges formed during the preparation of these substrate surfaces by cleavage.

In summary, from these results and others to be found in literature [3] it is obvious that it makes sense to try to improve charge carrier transport properties of organic thin films by improving structural order. This will quite generally have considerable importance e.g. for increasing extractable power yield in photovoltaic cells, for reducing heat dissipation in electroluminescent organic thin film devices, and for speeding up organic thin film transistors.

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