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Heteroepitaxial growth of self-assembled highly ordered *para*-sexiphenyl films: A crystallographic study

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X-ray diffraction pole figure technique (XRD-PF), transmission electron diffraction (TED), and atomic force microscopy were used to characterize the crystalline structure of heteroepitaxial grown, self-assembled para-sexiphenyl (PSP) layers in detail. PSP was deposited by hot wall epitaxy on mica (001) substrates. The epitaxial growth was confirmed by XRD-PF as well as TED measurements. XRD-PF measurements reveal two crystallographic orientations of PSP parallel to the substrate, which are also cleavage planes of PSP. Both orientations—(11-1) and (11-2)—have very similar structural characteristics with respect to the substrate. Since in either orientations the interface lattices of PSP and mica are incommensurable, the observed growth mode can be referred to quasiepitaxy.

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Research on conjugated organic semiconductors is a rapidly expanding field within materials science due to the promising opportunities for applications in electronics and photonics.[1–6] Recent progress in the field of new organic devices (ambipolar thin film transistor, solid state laser, and solar cells of high efficiency) made from bulk molecular crystals such as pentacene or C_{60} has clearly demonstrated the need for further development of organic electronics based on the epitaxially grown, highly crystalline thin films with well-defined orientation of the molecules.[7] The present work focuses on crystalline films of the molecular material *para-sexiphenyl* [six phenyl moieties linearly attached (PSP)], which is a typical organic semiconductor showing intense blue photoluminescence and electroluminescence in the solid state.[3,8]

Thin films of PSP were already grown by physical vapor deposition or organic molecular beam epitaxy (OMBE).[9–12] It was shown that the substrate temperature during deposition, substrate type and the growth rate are important parameters for the preferred orientation of the crystallites relative to the substrate. Generally, the films grown by vapor deposition on ITO, glass, or GaAs consisted of randomly oriented islands (fiber textured), whose shapes and structures depend on the purity of the source material and on growth conditions.[10] In case of OMBE large islands of PSP (well-defined and oriented into two perpendicular directions, several micrometers long) were obtained on GaAs(001) substrates at similar growth conditions.[12] However, the epitaxial characterisations were performed without x-ray diffraction (XRD) proof, which prevents a more accurate determination of the crystallographic orientation.[12,13]

Recently, it was reported that highly ordered and anisotropic PSP films can be grown by hot wall epitaxy (HWE) on monocrystalline mica substrates.[14,15] Two essential prerequisites justify this preparation technique as well as the used substrate. At first, in contrast to commonly used deposition methods,[8–13] HWE is a semiclosed technique, in which the growth proceeds close to thermodynamic equilibrium.[16] Consequently, the large organic molecules can find energetically the most suitable arrangement before being incorporated into the crystal lattice. Second, mica is a layered material with well-defined smooth cleaved surface and weak

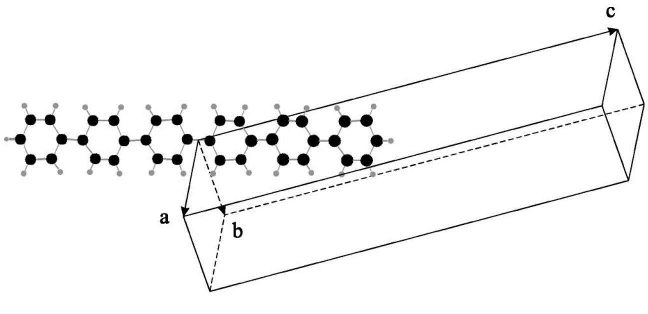


FIG. 1. Unit cell of crystalline PSP.

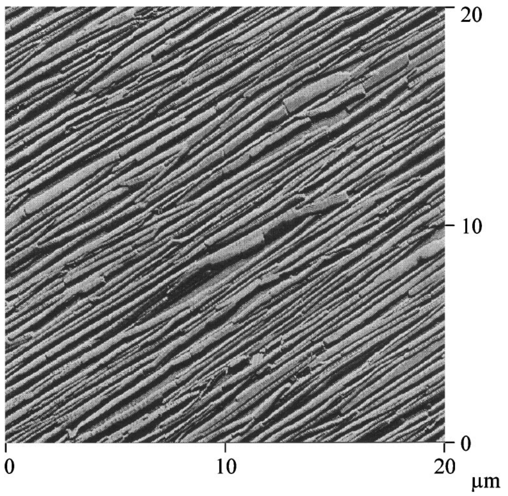
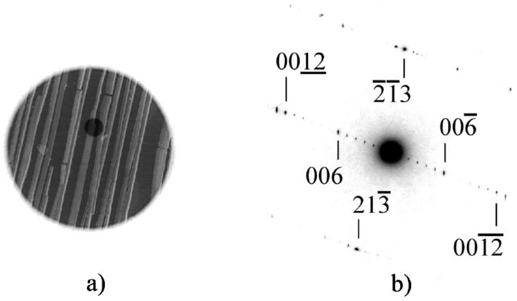


FIG. 2. 20×20 μm^2 AFM image of PSP on mica (001).

surface bonds, which are similar to van der Waals bonds in organic materials. Under HWE conditions these prerequisites result in highly anisotropically ordered structures of the deposited layers. The grown films were preinvestigated by XRD (Θ/2Θ scans) and optical measurements, which indicated that the PSP layers are highly crystalline.[14]

In this detailed study we combine various methods in order to characterize HWE-grown films of PSP: x-ray diffraction pole figure technique (XRD-PF), transmission electron diffraction (TED), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The XRD-PF is a nondestructive method, which enables a mapping of all crystallographic netplanes in volume of the film (in comparison to common Θ/2Θ scans) for accurate determination of the crystallographic orientations.[17,18] Another advantage is the possibility to investigate the grown films together with the substrate in contrast to TED measurements, which requires a removing of the film from the substrate.

PSP was purchased from Tokyo Chemical Industry, further purification was performed by threefold sublimation in vacuum. Thin films were grown in a HWE system, which has been used previously for the successful deposition of high quality crystalline molecular films.[14,19] Freshly cleaved (001) mica was used as substrate. The PSP material was evaporated at 240 °C and the substrate was held at 90 °C. During the deposition process the vacuum was of about 6×10^{-6} mbar. The investigated films were grown 60 min, which results in an average film thickness of about 120 nm. Further growth details can also be found in Refs. 14, 15 and 19. The film morphology was imaged by AFM using NanoScope IIIa Microscopes. Selected area TED measurements were employed with a Philips CM12 electron microscope. A Philips X'Pert system with an ATC3 texture cradle was utilized for the pole figure measurements performed in Schultz reflection geometry using Cr-K_α radiation and a secondary graphite monochromator. The software packages POWDER CELL 2.3[20] and STEREOGRAMM[21] were used for XRD data analysis.



a) b)

FIG. 3. (a) Transmission electron microscopy image of a PSP film in which the needlelike morphology is clearly visible. (b) Diffraction pattern taken from the darker spot of (a).

TABLE I. Calculated peak positions for different PSP and mica lattice planes.

PSP netplane	PSP 2Θ angle	mica netplane	mica 2Θ angle
±(1±1 −1)	29.04°	±(1±1 1)	30.88°
±(1±1 −2)	29.98°	±(1±1 −3)	34.29°
±(2±0 −3)	34.61°	±(0±2 3)	35.67°
±(2±1 −3)	42.40°	±(1±1 4)	41.87°
		±(1±1 −5)	42.98°

The used substrate was mica ($2M_1$ muscovite) which shows a monoclinic crystal structure with $a=5{,}20$ Å, $b=9{,}03$ Å, $c=20{,}11$ Å, $\beta=95{,}78°$.[22] PSP usually crystallizes in the β phase, which is monoclinic with the space group $P2_1/a$ and the lattice constants $a=8{,}09$ Å, $b=5{,}56$ Å, $c=26{,}24$ Å, $\beta=98{,}17°$.[23] Figure 1 shows the unit cell of bulk PSP. The long molecular axes of all molecules within bulk are oriented parallel to each other, whereas adjacent molecular planes are tilted about 66°, which form the typical herringbone structure of PSP.

Figure 2 shows an AFM image of a PSP sample prepared on mica by HWE, which reveal the typical nano-needle-like morphology.[14] Note that the imaged sample was used for XRD-PE investigation in this report. AFM line scans reveal typical needle widths, heights and lengths of about 800 nm, 130 nm, and more than 100 μm, respectively.

Several samples were investigated via TED whereby all

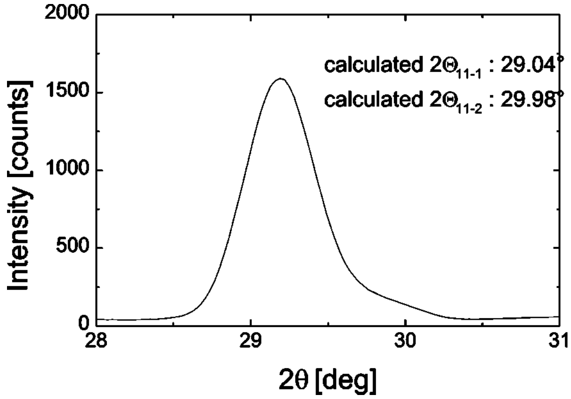


FIG. 4. Θ/2Θ scan of the 11-1 and the 11-2 reflection of PSP. The expected reflection positions of the β phase are inserted.

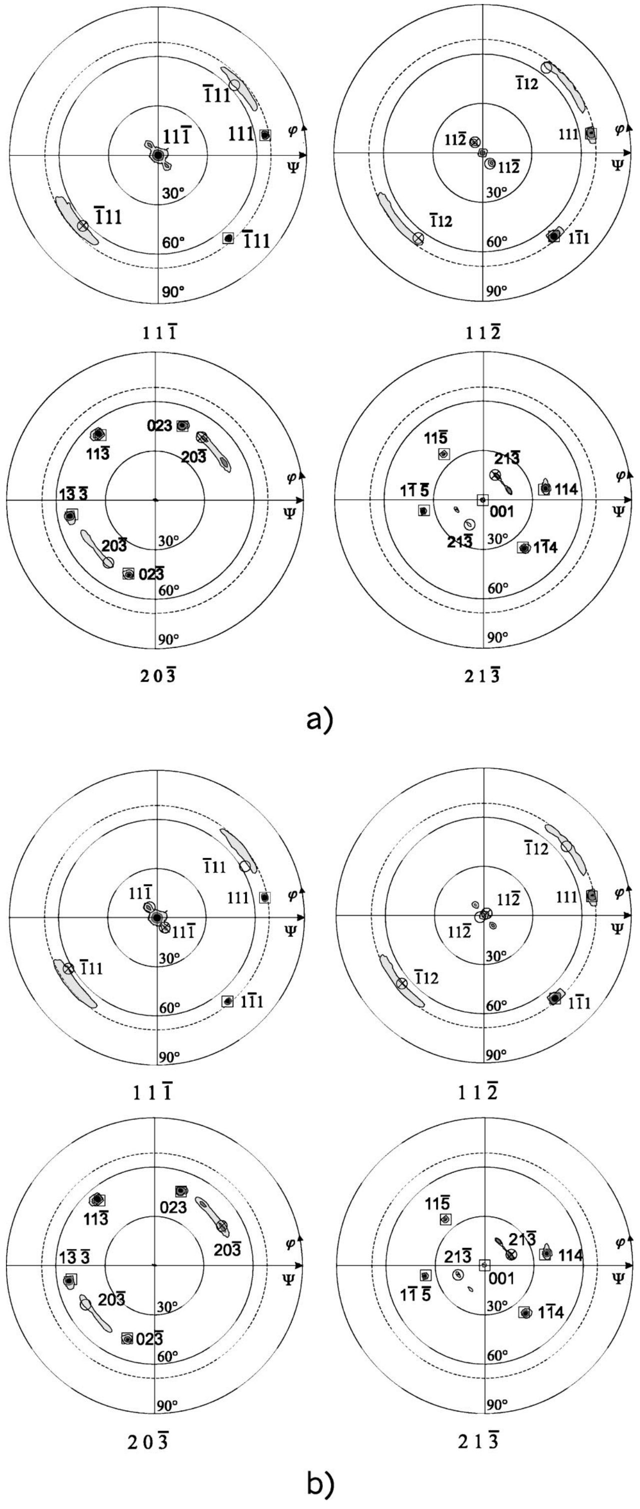


FIG. 5. XRD-PF measurements of PSP on mica (001) taken from the four strongest reflections of PSP, which are indicated below each figure. Every reflection within the pole figures can be explained by the (11-1) and (11-2) plane of PSP—(a) and (b), respectively. The identified mica reflections are indicated by squares. The dashed line indicates the measurement limit of $\Psi = 75°$. Different intensities represented by different gray scales where darker areas represent higher intensity. The intensity ranges are 11-1: 0–21 500 cps, 11-2: 0–10 500 cps, 20-3: 0–22 500 cps, and 21-3: 0–21 500 cps.

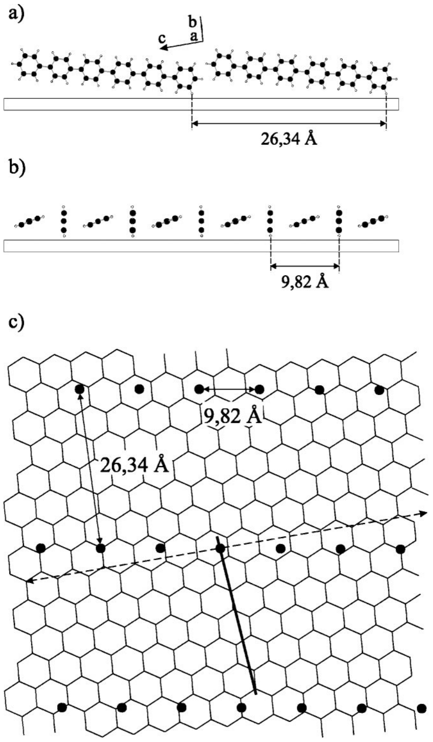


FIG. 6. Arrangement of PSP molecules on mica (001) for the (11-1) orientation of PSP: (a) side view; (b) parallel view; (c) top view of the contact point lattice of PSP on mica (001). The black line indicates one contacting molecule. Contact points are marked as black points and the hexagonal net represents the mica (001) surface. The dashed line indicates the needle direction determined by TED.

gave essentially the same results. A typical TED pattern is depicted in Fig. 3. The positions as well as the relative intensities of the diffraction pattern [Fig. 3(b)] are in excellent accordance with the crystal structure of PSP in the β phase.[23] Therefore, further analysis is based on this crystal structure.

Preliminary XRD measurements were performed in $\Theta/2\Theta$ mode. In accordance with our previous work[14] they revealed only two strong PSP reflections 11-1 and 11-2. Since the reflection maxima are very close together (see Table I) we actually observe one nonsymmetric peak in the $\Theta/2\Theta$ scan as shown in Fig. 4. To investigate the degree of ordering, also a rocking curve (not shown) was measured for the 11-1 reflection. The observed FWHM of 0.55° is close to the instrument resolution, which confirms a high crystalline quality of the films.

In order to get more detailed information about the epitaxial relationships between the PSP layer and the substrate, XRD-PF measurements were performed at the four strongest reflections of crystalline PSP: (11-1), (11-2), (20-3), and (21-3). The corresponding 2Θ angles of these reflections are given in Table I. Please note that in this case the planes with the Miller Indices $\pm(h \pm kl)$ have the same interplanar distance. Figures 5(a) and 5(b) show each four measured pole figures for the (11-1) and (11-2) plane of PSP parallel to the substrate surface, correspondingly. The obtained results are of unusual quality for epitaxial grown organic thin films in terms of reflection intensities and sharpness. Especially, it should be pointed out that pole figures in Fig. 5 are significantly different from those obtained from small molecule films fabricated by physical vapor depositions:[10,24–26] the fiber textures are missing here, which confirms the epitaxial character of HWE films. The detailed analysis reveals only two crystallographic planes of PSP parallel to the substrate surface: (11-1) and (11-2). Within both orientations, there are two antiparallel directions of the PSP crystallites. Moreover, the crystallographic (11-1) orientation is slightly preferred. The shown indexation is based on the calculated reflection positions of the β phase. The expected PSP reflection positions are marked as circles whereby crossed and uncrossed circles distinguish between the two antiparallel directions. Some mica reflections are also identified in the pole figures of PSP and indicated as squares in Fig. 5. The appearance of these very strong reflections is justified due to similar interplanar distances (see Table I) and the comparable widely open slits of the instrument. The simultaneous appearance of mica and PSP reflections enables an easy and accurate determination of the epitaxial relationships between the organic layer and the substrate: PSP(11-1)$\|$mica(001), PSP$[1\bar{2}\bar{1}]\|$mica$[\bar{3}40]$ and PSP(11-2)$\|$mica(001), PSP$[\bar{2}0\bar{1}]\|$mica$[\bar{3}10]$.

Additional measurements with a 2D-area detector reveal the PSP reflections as single spots, which confirms again the epitaxial character of the PSP films. Considering these results the elongated shapes of enhanced pole densities at higher ψ (Fig. 5) can be referred to the wide beam-geometry and the general reflection broadening at higher ψ angles. Particularly, in case of the (11-1) and (11-2) pole figures similar interplanar distances are responsible for additional elongation. Moreover, additional measurements done at high ψ angles with higher resolution reveal the broadened reflections as enhanced pole densities with clear maxima.

Based on the TED and XRD-PF studies we were able to determine the orientation of PSP molecules on the mica surface as schematically depicted in Fig. 6. Please note that both crystallographic orientations (11-1) and (11-2)$\|$mica(001) show a very similar alignment of the molecules relative to the substrate surface. Hence, we show only one of them—the (11-1) orientation. As demonstrated in Fig. 6(a) the long molecular axes are tilted by 5° with respect to the surface. This finding is also in good agreement with our previous optical studies.[14] Only the lowest aromatic rings of the molecules are in contact with the substrate surface, as visible in Fig. 6(a). This fact can be also clearly seen in Fig. 6(b), which shows the parallel view of the PSP molecules. It should be noted here that (11-1) plane is the cleavage plane of PSP. Since the contact molecules interact with the mica surface only at a single point, a contact point lattice can be generated on top of the mica grid as shown in Fig. 6(c). The dashed line indicates the needle direction determined by combined TEM and TED investigations with an accuracy of $\pm 5°$. The molecular axes [see bold line in Fig. 6(c)] are nearly perpendicular to the needle direction, which confirms previous optical results.[14]

As evident in Fig. 6(c) the point lattice of PSP and the hexagonal mica lattice are incommensurable. This type of growth can be referred as quasiepitaxy,[27] which is dominantly found for organic materials, in that intermolecular interactions are stronger than substrate-molecule interactions. The latest is in certain conflict with our previous growth studies[14,28] indicating an essential influence of the mica substrate on the growing PSP layer. In this context, we should point out that for the entire analyses the unstressed bulk structure of PSP was used. Therefore, additional studies are needed, which should refine proposed molecular arrangement. In particular, high resolution XRD measurements will be interesting in order to confirm the presence of elastic strain[29,30] within our films.

In conclusion, we have characterized thin PSP films grown by HWE on crystalline mica substrates. According to TED and XRD-PF measurements, the films are crystalline and highly ordered. The detailed analysis reveals two very similar crystallographic orientations of PSP: (11-1) and (11-2) planes parallel to the mica (001) substrates. The epitaxial character of the PSP film is clearly confirmed by all investigation methods used.

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, A. Kraft, and A. B. Holmes, Nature (London) **347**, 539 (1990); D. Braun, and A. J. Heeger, Appl. Phys. Lett. **58**, 1982 (1991); A. J. Heeger, Solid State Commun. **107**, 673 (1998); M. Granström, M. G. Harrison, and R. H. Fiend, in *Handbook of Oligo-and Polythiophenes*, edited by D. Fichou (Wiley-VCH, Weinheim, 1999).

[2] N. S. Sariciftci, D. Braun, C. Zhang, V. I. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl, Appl. Phys. Lett. **62**, 585 (1993); N. S. Sariciftci, and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers*, edited by H. S. Nalwa (Wiley-VCH, Weinheim, 1997); S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, Appl. Phys. Lett. **78**, 841 (2001).

[3] F. Meghdadi, S. Tasch, B. Winkler, W. Fischer, F. Stelzer, and G. Leising, Synth. Met. **85**, 1441 (1997); G. Leising, S. Tasch, and W. Graupner, in *Handbook of Conducting Polymers*, 2nd ed., edited by T. Skothem, R. Elsenbaumer, and J. Reynolds (Dekker, New York, 1997).

[4] M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Tompson, and S. R. Forrest, Appl. Phys. Lett. **75**, 4 (1999); J. Kido, and Y. Iizumi,

ibid. **73**, 2721 (1998); H. Yanagi and S. Okamoto, *ibid.* **71**, 2563 (1997).

[5] H. E. Katz, A. Dodabalapur, and Z. Bao, in *Handbook of Oligo- and Polythiophenes*, edited by D. Fichou (Wiley-VCH, Weinheim, 1999).

[6] C. W. Tang, Appl. Phys. Lett. **48**, 183 (1986); D. Wöhrle, and D. Meissner, Adv. Mater. **3**, 129 (1991); J. Rostalski and D. Meissner, Solar Energy Mater. Solar Cells **61**, 87–95 (2000).

[7] J. H. Schön, S. Berg, Ch. Kloc, and B. Batlogg, Science **287**, 1022 (2000); J. H. Schön, Ch. Kloc, A. Dodabalapur, and B. Batlogg, *ibid.* **289**, 599 (2000); J. H. Schön, Ch. Kloc, and B. Batlogg, Nature (London) **408**, 549 (2000); J. H. Schön, Ch. Kloc, E. Bucher, and B. Batlogg, *ibid.* **403**, 408 (2000).

[8] S. Tasch, C. Brandstätter, F. Meghdadi, G. Leising, G. Froyer, and L. Athouel, Adv. Mater. **9**, 33 (1997).

[9] H. Yanagi and S. Okamoto, Appl. Phys. Lett. **71**, 2563 (1997); H. Yanagi, T. Morikawa, S. Hotta, and Kiyoshi Yase, Adv. Mater. **13**, 313 (2001).

[10] R. Resel, N. Koch, F. Meghdadi, G. Leising, W. Unzog, and K. Reichmann, Thin Solid Films **305**, 232 (1997).

[11] R. Resel, G. Leising, Surf. Sci. **409**, 302 (1998).

[12] B. Müller, T. Kuhlmann, K. Lischka, H. Schwer, R. Resel, and G. Leising, Surf. Sci. **418**, 256 (1998).

[13] K. Erlacher, R. Resel, S. Hampel, T. Kuhlmann, K. Lischka, B. Müller, A. Thierry, B. Lotz, and G. Leising, Surf. Sci. **418**, 256 (1998).

[14] A. Andreev, G. Matt, C. J. Brabec, H. Sitter, D. Badt, H. Seyringer, and N. S. Sariciftci, Adv. Mater. **12**, 629 (2000).

[15] A. Andreev, G. Matt, H. Sitter, C. J. Brabec, D. Badt, H. Neugebauer, and N. S. Sariciftci, Synth. Met. **116**, 235 (2001).

[16] A. Lopez-Otero, Thin Solid Films **49**, 3 (1978).

[17] S. R. Forrest, M. L. Kaplan, and P. H. Schmidt, J. Appl. Phys. **56**, 543 (1984).

[18] S. R. Forrest, Chem. Rev. **97**, 1793 (1997).

[19] D. Stifter and H. Sitter, Appl. Phys. Lett. **66**, 679 (1995); D. Stifter and H. Sitter, J. Cryst. Growth **156**, 79 (1995); D. Stifter, H. Sitter, Thin Solid Films **280**, 83–85 (1996).

[20] W. Kraus and G. Nolze, J. Appl. Crystallogr. **29**, 301 (1996).

[21] S. Weber, J. Appl. Crystallogr. **29**, 306 (1996).

[22] S. W. Bailey, in *Crystal Structure of Clay Minerals and Their X-ray Identification*, edited by G. W. Brindley, and G. Brown, Mineral Society Monograph No. 5 (Mineral Society, London, 1980).

[23] K. N. Baker, A. V. Frantini, T. Resch, H. C. Knachel, W. W. Adams, E. P. Socci, and B. L. Farmer, Polymer **34**, 1571 (1993).

[24] B. Servet, S. Ries, M. Trotel, P. Alnot, G. Horowitz, and F. Garnier, Adv. Mater. **5**, 461 (1993).

[25] R. Resel, M. Ottmar, M. Hanack, J. Keckes, and G. Leising, J. Mater. Res. **15**, 934 (2000).

[26] S. Henke, K. H. Thürer, S. Geier, B. Rauschenbach, and B. Stritzker, Appl. Phys. A: Mater. Sci. Process. **60**, 383 (1995); S. Henke, K. H. Thürer, S. Geier, B. Rauschenbach, and B. Stritzker, in *Science and Technology of Fullerene Materials*, edited by P. Bernier *et al.*, MRS Symp. Proc. No. 359 (Materials Research Society, Pittsburgh, 1995), p. 399.

[27] S. R. Forrest, Y.-Z. Zhang, Phys. Rev. B **49**, 11 297 (1994); S. R. Forrest, P. E. Burrows, E. I. Haskal, and F. F. So, *ibid.* **49**, 11 309 (1994).

[28] A. Andreev, H. Sitter, C. J. Brabec, P. Hinterdorfer, G. Springholz, and N. S. Sariciftci, Synth. Met. **121**, 1379 (2001).

[29] J. Tersoff and R. M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).

[30] P. Fenter, P. E. Burrows, P. Eisenberger, and S. R. Forrest, J. Cryst. Growth **152**, 65 (1995); P. Fenter, F. Schreiber, L. Zhou, P. Eisenberger, and S. R. Forrest, Phys. Rev. B **56**, 3046 (1997).