

Preserving the crystal structure of organic semiconductors during cross-sectional specimen preparation for transmission electron microscopy using a focused ion beam

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Abstract

Transmission electron microscopy (TEM) analyses of cross-sectional lamellae prepared by a Ga⁺-focused ion beam are frequently applied in a variety of scientific disciplines where high-resolution information is required from a specific site of interest. Irradiation-sensitive Materials thereby require dedicated methods to facilitate an analysis of the specimen in its pristine state. Here, we present a method for preparing TEM lamellae of organic thin-film transistors (TFTs) that preserves morphology and crystal structure of beam-sensitive small-molecule organic semiconductor thin films as demonstrated for pentacene, DNTT and PhC₂-BQQDI. The two key measures are minimizing electron and ion irradiation of the organic layer using protective layers and optimized beam conditions, and performing the final lamella thinning at reduced temperature. Monte Carlo simulations can help to find the optimum beam settings, but channeling of electrons and ions, typically not considered in the simulations, can lead to an increased penetration depth and needs to be taken into account. As proof of concept for a successful TEM sample preparation workflow we demonstrate the edge-on growth of all investigated molecules with structural integrity. Furthermore, the zone axes for pentacene and DNTT and the existence of a previously unknown thin-film polymorph of the organic semiconductor PhC₂-BQQDI are identified.

Key words: organic semiconductor, molecular crystals, transmission electron microscopy, focused ion beam, beam damage, beam-sensitive materials

Introduction

Transmission electron microscopy (TEM) imaging and related spectroscopy techniques are indispensable tools to investigate structure and chemistry of materials at atomic resolution. Lamellae prepared with the help of scanning electron microscopy (SEM)/focused ion beam (FIB) dual-beam instruments thereby provide a means to perform these high-resolution investigations from a specifically selected region of interest [Giannuzzi and Stevie, 1999]. The vast majority of material-science samples are relatively insensitive to damage induced by the FIB and, for most specimens, the damage is limited to a thin amorphous layer at the surface. Nevertheless, a dedicated optimization of the preparation technique may be required to obtain the desired information from the specimen [Kato, 2004, Sato et al., 2020, Edwards et al., 2025]. For soft materials, e.g. from life sciences or biology, which more

strongly suffer from radiation damage, FIB preparation is often conducted at cryogenic temperatures (cryo-FIB) to protect the sample structure during preparation [Marko et al., 2007].

Small-molecule organic semiconductors, which are employed in organic-electronic applications such as transistors, are based on conjugated oligomers that form crystalline structures with low binding energies, mostly based on the van-der-Waals force [Klauk, 2010, Li et al., 2024]. These materials thereby combine the crystalline structure of typical material-science samples with the beam-sensitivity of soft materials. Radiolysis, *i.e.* the breaking of chemical bonds by ionizing radiation, is the dominant damage mechanism for organic materials [Egerton, 2019] and even the electron irradiation in SEM has been shown to cause damage to soft materials [Bassim et al., 2011]. Electron diffraction acquired from larger areas of thin-film specimens represents the most

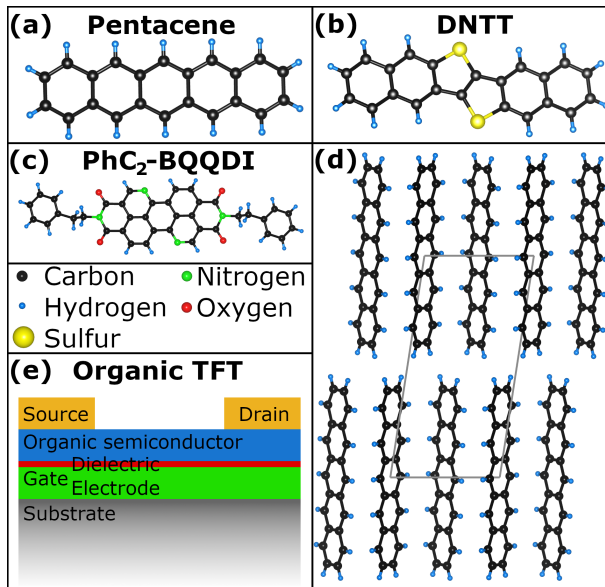


Fig. 1: Sketch of the three organic semiconductor molecules studied in this work: (a) pentacene [Schiefer et al., 2007], (b) DNTT [Yamamoto and Takimiya, 2007] and (c) PhC₂-BQQDI [Okamoto et al., 2020]. (d) Exemplary view along the 100 crystal direction of the pentacene molecular crystal (bulk phase). The gray lines indicate the unit cell. (e) Sketch of the layer system of a bottom-gate, top-contact organic TFT.

common TEM approach for studying organic semiconductors, as the required radiation dose can be strongly reduced, facilitating the investigation of their pristine crystalline structure [Martin et al., 2005, Minakata et al., 1992, Haas et al., 2011]. In contrast, the radiation to which the specimen is exposed during preparation and investigation of FIB-prepared cross-sectional lamellae is considerable, requiring a dedicated workflow of preparation and investigation. Consequently, most cross-sectional TEM images reported in literature exhibit a damaged, amorphous organic semiconductor layer [Sekitani et al., 2010, Peng et al., 2020, Wang et al., 2025] and only few examples demonstrating successful imaging of the molecular crystal exist [Murakami et al., 2009, Hettler et al., 2026].

In this work, we systematically investigated the TEM lamella preparation of organic semiconductors by FIB and propose a procedure that preserves the crystalline structure of organic semiconductor thin films and facilitates their TEM imaging. The key modifications of the standard routine are to minimize any irradiation of the organic semiconductor by electrons and ions and to perform the final FIB thinning of the lamella at reduced temperature. The method has been employed to image the crystal structure of three different organic semiconductors in functional thin-film transistors (TFTs), revealing, amongst others, the existence of a previously unknown thin-film polymorph of PhC₂-BQQDI.

Materials and Methods

Organic semiconductor molecules and transistors

Conjugated small molecules used as organic semiconductors commonly have a stick- or rod-like shape with one long axis. The investigations were conducted using organic TFTs based on three molecules, which are shown in Figure 1. Pentacene (C₂₂H₁₄) can

be seen as the standard reference material for p-channel small-molecule semiconductors and consists of five fused benzene rings (see sketch in Figure 1a). Pentacene crystallizes in a triclinic crystal (Figure 1d, Table 1) and exhibits polymorphism, [Schiefer et al., 2007] with the main phases being the thin-film and bulk phases. Table 1 details the crystal lattice parameters of the bulk phase.

Molecule	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$
Pentacene (bulk)	5.96	7.60	15.61	81.3	86.6	89.8
DNTT (bulk)	6.19	7.66	16.21	90	92.49	90
PhC ₂ -BQQDI (bulk)	7.72	5.04	35.99	90	92.2	90

Table 1. Crystallographic information of the studied pentacene [Schiefer et al., 2007], DNTT [Yamamoto and Takimiya, 2007] and PhC₂-BQQDI [Okamoto et al., 2020] bulk phases.

The second studied material here is dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT, C₂₂H₁₂S₂), [Yamamoto and Takimiya, 2007] which is another reference material for p-channel organic TFTs. In addition to the pure hydrocarbon structure of pentacene, it includes two sulfur atoms modifying the central benzene ring of pentacene (Figure 1b). The lattice parameters of the crystal structure of DNTT are only slightly larger than the ones for pentacene (Table 1) and the crystal exhibits a monoclinic structure. Like pentacene, also DNTT exhibits polymorphism, [Shioya et al., 2020, 2026] the values in Table 1 again represent the bulk phase.

Additionally, n-channel organic TFTs made of phenylalkyl substituted 3,4,9,10-benzo[de]isoquinolino[1,8-gh]-quinolinetetracarboxylic diimide (PhC₂-BQQDI) [Okamoto et al., 2020, Steffens et al., 2025] were studied in this work. A molecular structure is shown in Figure 1c and the lattice parameters of the monoclinic

	Step	Standard	Low-dose	Cooling
1	Coating	-	40 nm Pt	20 nm aC + 8 nm Au
2	Pt-FEBID	5 kV/1.6 nA	-	1 kV/1.6 nA
3	Pt-FIBID	30 kV/48 pA	-	16 kV/50 pA
4	Trench milling	30 kV/9 nA	16 kV/9 nA	16 kV/5 nA
5	Polishing prior lift out	30 kV/0.2 nA	16 kV/41 pA	16 kV/23 pA
6	Lift-out (Pt-FIBID)	30 kV/24 pA	16 kV/24 pA	16 kV/50 pA
7	Final thinning	30 kV/24 pA	16 kV/12 pA	16 kV/50 pA at -50°C & 5 kV/46 pA at -50°C
e ⁻ -beam settings		5 kV/1.6 nA	10 kV/50 pA	10 kV/25 pA

Table 2. Process steps and beam currents and acceleration voltages for TEM lamella preparation.

bulk phase are given in Table 1. The value of the c parameter is large as the unit cell comprises a stack of two molecules in [001] direction. To our knowledge, no polymorphism is known for PhC₂-BQQDI.

Organic TFTs fabricated in the inverted staggered (bottom-gate, top-contact) device architecture were prepared from all three molecules using the following recipe [Kraft et al., 2016, Steffens et al., 2025]: Initially, a 30 nm thick aluminum layer was deposited as gate electrode on a heavily doped silicon substrate by thermal evaporation. An oxygen plasma (30 sccm, 10 mTorr, 200 W) for 30 s was then employed to increase the thickness of the native aluminum oxide on the surface to 6 nm [Geiger et al., 2021]. Subsequent immersion into a 1 mM solution of *n*-tetradecylphosphonic acid in 2-propanol for a duration of 1 hour leads to the formation of a self-assembled monolayer (SAM) on the aluminum oxide surface, which is stabilized by heating to 80°C for 5 min. The organic semiconductor layer with nominal thickness of 50 nm is then deposited by thermal sublimation while keeping the substrate temperature at 60°C. Au source and drain contacts with a thickness of 35 nm were deposited in the final process step by thermal evaporation through a stencil mask. A sketch of the layer system is shown in Figure 1e.

TEM lamella preparation

TEM lamella preparations were initially conducted at room temperature using a Helios G4 (Thermo Fisher Scientific). In addition, a Helios 650 (Thermo Fisher Scientific) equipped with a Peltier Micro Heating and Cooling Stage (Kleindiek Nanotechnik GmbH) was used to prepare lamellae (partially) at -50°C. Both systems are equipped with a gas injection system (GIS), which was used for focused electron-beam and focused ion-beam induced deposition (FEBID/FIBID) of Pt.

TEM lamellae have been prepared using three approaches named *Standard*, *Low-dose* and *Cooling* throughout the manuscript. The employed beam voltages and currents are detailed in Table 2. It is noted that the voltages are important, but the currents were not studied systematically and should only be seen as a suggestion. The processes should work also for slight variations of these currents, for which the ion beam has a comparably small beam size. The general procedure consists of seven major steps: an optional additional coating prior to insertion into the dual-beam machine, Pt-FEBID and/or Pt-FIBID for protection of the lamella region during later FIB milling, trench milling, polishing prior to lift-out, lift-out and the final thinning of the lamella. Initial Pt or Au sputtering and amorphous carbon (aC) coating via carbon thread evaporation was done with a Leica ACE 600 machine. The thicknesses given for the coating layers were precisely measured

from the obtained cross section and can vary considerably from the nominally evaporated thickness. The results obtained from the used approaches are discussed in detail in the following section. The *Cooling* process was conducted with different FEBID/FIBID steps, which are specifically indicated for every analyzed lamella. Table 2 details the resulting optimum process. SEM imaging during the final thinning step was completely avoided and the thinning was followed only by FIB imaging from the top. The final thickness of each lamella was measured by FIB or by SEM imaging after TEM imaging (see Figure S1 in supplementary information (SI)) and varies between 60 and 200 nm. The thickness is again indicated and discussed for each analyzed lamella throughout the manuscript.

Transmission electron microscopy

TEM lamellae prepared at room temperature (*Standard* and *Low-dose* approaches) were analyzed with an image-corrected Titan³ (Thermo Fisher Scientific) equipped with a XF416(R) CMOS camera (TVIPS GmbH). For the TEM analyses of the pentacene and DNTT lamellae prepared using the *Cooling* process, a double-corrected Titan³ (Thermo Fisher Scientific) equipped with a Gatan K3 camera was employed for both TEM and high-angle annular dark-field (HAADF)-scanning (S)TEM imaging. Finally, a double-corrected Spectra Ultra with a 4k Ceta camera (Thermo Fisher Scientific) was used to analyze the PhC₂-BQQDI *Cooling* lamella. All TEM analyses were conducted at an electron energy of 300 keV and at room temperature.

Monte-Carlo simulations

Monte-Carlo simulations were conducted using the software package Casino v2.5.1.0 [Drouin et al., 2007] for electron irradiation and with the software SRIM (Stopping Range of Ions in Matter) [Ziegler et al., 2010] for ion irradiation. The layer system (from bottom to top) of the target was defined based on a pentacene TFT used for the *Cooling* process: Si substrate, 30 nm Al, 7 nm Al₂O₃, 40 nm pentacene, 35 nm Au source/drain contact, and 20 nm and 8 nm aC coating. The crystalline structure of the materials, and thus channeling effects, are not considered in the MC simulations. The Mott cross section was used for electron simulations.

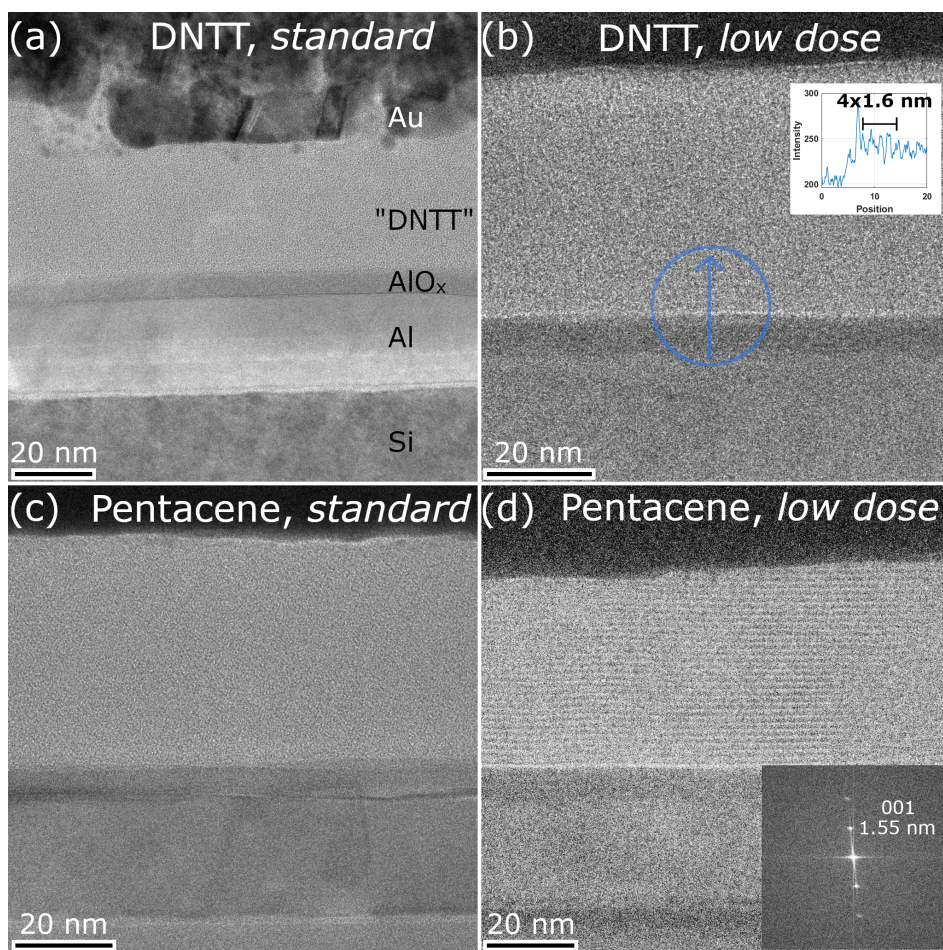


Fig. 2: TEM analyses of lamellae prepared at room temperature from organic TFTs with (a,b) DNTT and (c,d) pentacene as organic semiconductor. Lamellae analyzed in (a,c) were prepared using a *Standard* recipe. For *low-dose* lamellae analyzed in (b,d), electron-beam irradiation during preparation was reduced to a minimum and lower FIB currents and voltages were employed. (b) A minimum indication for a periodic stacking of the DNTT crystal can be found. The line profile (inset) reveals a periodicity of 1.6 nm, agreeing with the DNTT bulk phase. (d) For pentacene, the molecular stacking periodicity can be clearly revealed. Inset FFT (width of 4 nm^{-1}) shows the $[00l]$ reflections and the resulting $[001]$ periodicity calculates to 1.55 nm, coinciding with the bulk phase. Electron dose for acquisition of the TEM images was (b) $20 \text{ e}^{-}\text{\AA}^{-2}$ and (d) $7 \text{ e}^{-}\text{\AA}^{-2}$. Scale bars are 20 nm.

Results and Discussion

Standard lamella preparation

Figure 2a shows a TEM image of a cross section of an organic TFT with DNTT as organic semiconductor prepared with the *Standard* routine without limitation of neither electron nor ion dose. The lamella thickness is approximately 80 nm (Figure S1). The image reveals the layer system of the fabricated TFTs consisting of (from bottom to top) silicon substrate, aluminum gate electrode, aluminum oxide/SAM gate dielectric, the organic semiconductor layer and the Au top contact. Despite the fact that vacuum-deposited DNTT films grow in a polycrystalline morphology (e.g., see Figure 2 in [Kraft et al., 2016]) and despite the presence of the Pt-FEBID/FIBID protection layers, the organic semiconductor layer is found to be fully amorphized after lamella preparation, and no crystal structure can be seen. Figure 2c shows a similar image of an organic TFT with pentacene and, again, the organic crystal is fully amorphized, as seen in the previous work of

Sekitani et al. [2010]. The amorphization is observed for lamella thicknesses of 70 and 120 nm (Figure S1c). It is noted that thin films of the organic semiconductor 2,9-diphenyl-(DPh)-DNTT are sufficiently irradiation-resistant in order that its crystal structure is maintained during the *Standard* preparation routine as was shown recently [Hettler et al., 2026]. However, Figures 2a and c clearly show that the *Standard* TEM preparation process is not suitable to analyze the crystal structure of more beam-sensitive organic semiconductor thin films in organic TFTs.

Low-dose lamella preparation

In the *Low-dose* approach we minimized both types of irradiation. Therefore, both FEBID and FIBID of Pt, typically performed to protect the region of interest and to minimize the curtaining effect during lamella thinning, were fully avoided in this approach. In addition to the Au top layer, an additional 40 nm of Pt was sputtered on top of the sample to increase protection during FIB milling. Furthermore, imaging by electrons was reduced to

a minimum and the used current/voltage was reduced/increased to minimize the dose deposited in the organic thin film. The ion current for the final thinning step was reduced and the ion acceleration voltage was chosen to 16 kV. Detailed process parameters are given in Table 1.

Figure 2b and d show TEM images acquired from *Low-dose* lamellae prepared from DNTT and pentacene, respectively. The damage in the case of the DNTT lamella with a thickness of 200 nm is still very strong and only weak fringes can be seen directly at the top of the AlO_x gate dielectric (blue circle in Figure 2b), which indicate that the DNTT indeed could possess a crystalline structure in the organic TFTs. A line profile taken across the fringes reveals a fringe periodicity with 1.6 nm, agreeing with the c axis of the DNTT crystal structure (Table 1). In case of the pentacene thin film, a layer structure is clearly seen in the TEM image of a *Low-dose* lamella (Figure 2d). The periodicity can be determined to 1.55 nm, which agrees with the c axis parameter of the pentacene bulk phase. This confirms the results obtained in an earlier work, where pentacene thin films were analyzed in FIB-prepared TEM lamellae at room temperature [Murakami et al., 2009].

The results indicate that the damage to the organic semiconductor thin film can indeed be reduced by strongly reducing electron and ion irradiation and thereby making it possible to investigate the crystal structure. However, the TEM analyses are challenging as the fringe contrast is weak and vanishes quickly due to additional beam damage under the electron irradiation necessary for the TEM image acquisition. Despite offering the possibility to obtain information on the crystal structure, the amount of information is limited and the outcome comes with a high effort.

It is noted that the comparison of the TEM images of DNTT and pentacene does not allow us to conclude on the relative stability of the molecules. The total received electron and ion dose during specimen preparation was not measured and could be larger in case of DNTT lamella.

Monte-Carlo simulations

Monte-Carlo (MC) simulations were conducted to optimize the preparation and to find optimum electron and ion beam settings to avoid radiation damage. Damage during FIB specimen preparation can originate from electron irradiation through radiolysis processes [Bassim et al., 2011, Egerton, 2019] and from ion irradiation due to ion implantation, atomic displacement or sputtering processes. Irradiation occurs during imaging or FEBID/FIBID processes, where the irradiation has a vertical incidence on the substrate, *i.e.*, the irradiation has an angle of 90° to the surface. This is schematically depicted in Figure 3a for 5 keV electrons, the energy used during the Pt-FEBID/FIBID processes in the *Standard* process. The penetration volume is visualized by 20000 individual e^- trajectories obtained from a MC simulation. It is clearly seen that a considerable fraction of 5 keV electrons reach the organic semiconductor layer and can thus cause damage within this layer. Figure 3b shows the result of an additional MC simulation conducted for a reduced electron energy of 2 keV, for which a penetration into the organic semiconductor layer is completely avoided as all trajectories end in the protection layers or the Au source/drain layer. These results suggest that a reduction of the electron energy should lead to a complete prevention of damage during irradiation from the top. Such a reduction, however, results

in SEM images that give information only from the very surface, making it impossible to identify the location of the patterned Au source/drain contacts, from which the lamella is taken out (see Figure S2, SI). In case of electron irradiation, damage can also be decreased by an increase of the energy, which causes the electrons to largely transmit protection layers and the organic semiconductor layer. This is seen from the plot shown in Figure 3d, which shows the fraction of electron trajectories that end within the organic semiconductor layer and which can give an estimation of the damage caused in the organic semiconductor layer. A maximum of $>5\%$ is reached for 5 keV and the fraction drops below 1 % for energies larger than 10 keV. An increase of the electron energy thus should lead to a reduction of irradiation damage caused by SEM imaging, while maintaining a contrast that allows a clear identification of the patterned Au source/drain contacts (Figure S2).

Figure 3c shows the damage cascade including ion trajectories and recoil atoms for 30 keV Ga^+ ions vertically irradiating the layer system of the organic TFT. The penetration volume is visualized by 9999 individual ion trajectories from a MC simulation. This simulation thus suggests that no damage should occur in the organic semiconductor layer during a Pt-FIBID process conducted at 30 kV as all trajectories end in the layers above.

Additional damage is inflicted on the organic semiconductor during lamella thinning with the Ga^+ ion beam. Here, the irradiation is still vertical to the surface of the organic TFT but hits the side of the lamella under grazing, nearly parallel incidence. Similar to the top irradiation, a reduction of the energy will again cause a reduction of the penetration depth. However, MC simulations show that the penetration depth is in the order of several tens of nm, also for a reduced ion energy. In combination with the required small thickness of the lamellae of <200 nm to allow TEM investigation at high resolution, the penetration depth will always comprise a considerable part of the lamella. To preserve the structure of the organic crystal, it needs to be additionally protected during this final thinning by, *e.g.*, reducing the temperature.

Cooling lamella preparation

DNTT

Assuming that the largest amount of damage to the organic semiconductor layer is generated during the thinning of the lamella, only this final thinning process was conducted at a reduced temperature of -50°C using a cooling stage in the *Cooling* procedures. Similar as for the *Low-dose* approach, the lift-out process was done at room temperature and the Pt-FEBID and FIBID processes were varied to study their impact. In a first try, one half of a lamella prepared from an organic TFT with DNTT as organic semiconductor was coated by a FEBID process conducted at 5 keV while the second half was only protected by a Pt-FIBID process with 30 kV Ga^+ ions, as the MC simulations suggested that no ions should reach the organic semiconductor layer. Figure 4a shows a TEM image of the lamella region protected by the Pt-FIBID process only. It reveals that the DNTT layer is amorphized in the top part of the lamella, while lattice fringes can be seen in the lower part on top of the gate dielectric. However, these lattice fringes show a periodicity of 1 nm, which does not agree with the expected DNTT c lattice parameter. This result does not agree with the MC simulations (Figure 3) and

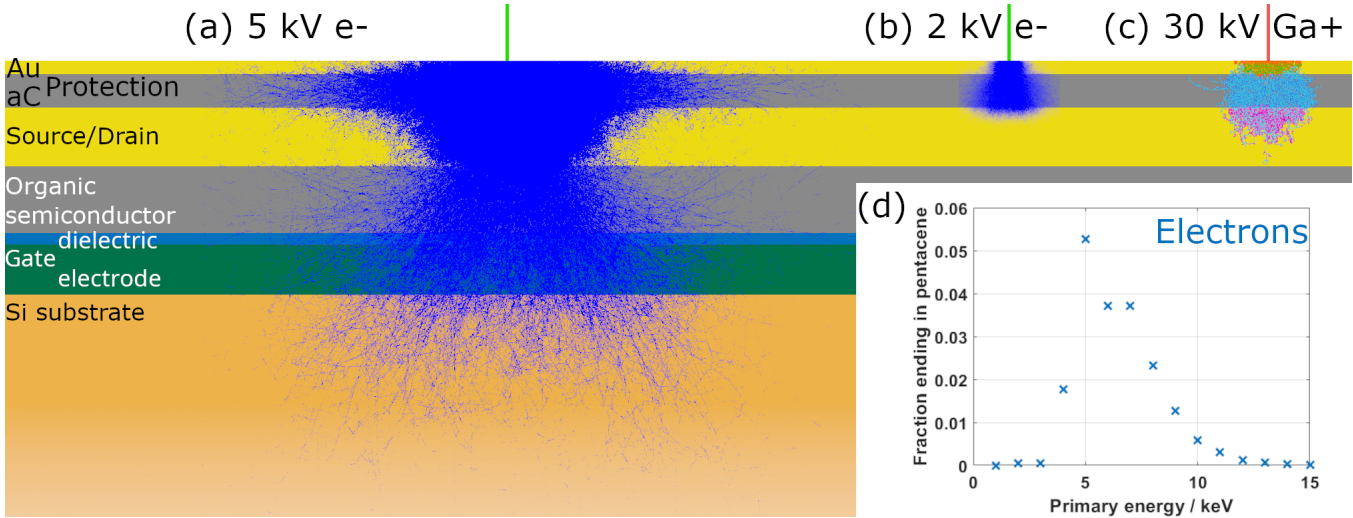


Fig. 3: (a-c) Plot of individual ray paths obtained from MC simulations revealing the penetration depth in an organic TFT with pentacene as organic semiconductor by top irradiation of (a,b) electrons with an energy of (a) 5 keV, (b) 2 keV and (c) visualization of damage cascade of Ga⁺ ions with an energy of 30 keV. (d) Fraction of electron trajectories ending in the pentacene layer in dependence of the electron energy.

indicates that the penetration depth of 30 keV Ga⁺ ions is larger than expected and causes a strong damage to the top part of the DNTT layer and even modifies the crystal structure of the lower part of the DNTT layer during the Pt-FIBID process. This increased penetration depth is attributed to channeling of the Ga⁺ ions in the crystalline Au layers [Kempshall et al., 2001, Giannuzzi and Michael, 2013]. If the ion incident direction agrees with a low-index crystallographic direction of the Au grain, the penetration depth is increased compared to the amorphous material assumed for MC simulations. In the region protected by the 5 keV FEBID layer, full amorphization is again observed (not shown), proving that low-energy electrons indeed cause strong damage to the molecular crystal.

In a second lamella prepared from a DNTT TFT, a FEBID process was avoided and the FIB voltage was reduced to 16 kV for the FIBID process of the Pt protection layer. Figures 4b-d show the results obtained by a TEM analysis of this *Cooling* lamella. The TEM image (Figure 4b) taken from a region with a thickness of 100 nm (Figure S1e) now reveals lattice fringes throughout the entire DNTT layer, confirming that the reduced energy of the Ga⁺ ions leads to a reduction of the penetration depth and avoids the damage inflicted during FIBID of Pt. As direct contact between the ions and the organic material cannot be avoided during lamella thinning, the cooling of the lamella in this final thinning step is crucial to preserve the crystal structure. The TEM image and a fast Fourier transform (FFT) calculated from the DNTT area only (Figure 4b and c) now allow a more accurate analysis of the crystal structure within the organic TFT. The FFT shows [00 $\bar{l}$] reflections (1.6 nm) with high intensity and also reveals [200] (0.3 nm) and [20 $\bar{l}$] reflections, making it possible to identify a [010] zone axis in the investigated area. The presence of these higher-order reflections confirms that the molecular crystal is well preserved during the *Cooling* process and Pt-FIBID with 16 kV Ga⁺ ions.

The vertically aligned [00 $\bar{l}$] direction demonstrates that the DNTT molecules grow in an edge-on configuration, *i.e.* they

are "standing" on the substrate, confirming results from X-ray diffraction [Shioya et al., 2026]. This configuration is also seen in the false-colored HAADF-STEM image taken from a thicker region of the lamella (200 nm, Figure S1e) and displayed in Figure 4d, which again reveals fringes with a periodicity of 1.6 nm, corresponding to the *c*-axis parameter of the DNTT crystal (Table 1). The presence of the sulfur (*Z*=16) atoms in the center of the DNTT molecule gives rise to stronger high-angle scattering compared to the hydrocarbon (*Z*=1 and 6) structure of the outer parts of the molecule and thus results in increased contrast of the central part in the HAADF-STEM image.

Pentacene

Figure 5 shows two TEM images and two respective FFTs calculated from the organic semiconductor layer of a pentacene-based organic TFT, which were obtained subsequently from the identical sample region of a *Cooling* lamella with a thickness of 200 nm (Figure S1d) and using only Pt-FIBID with 16 kV Ga⁺ ions during lamella preparation. The first image reveals horizontal fringes with strong intensity, which confirm the edge-on growth as the vertical direction corresponds to the [00 $\bar{l}$] direction of the pentacene crystal (Figure 5a,c). The corresponding FFT (Figure 5c) reveals additional [1 $\bar{1}$ $\bar{l}$] reflections suggesting an orientation close to the [110] crystal direction.

Figure 5b shows a second image obtained subsequently from the identical sample region, which similarly reveals continuous horizontal lattice fringes. However, the fringe intensity is reduced and several higher-order reflections disappear in the corresponding FFT (Figure 5d). This shows that the crystal structure is already considerably damaged after two TEM images.

Figure S3 (SI) shows a TEM image of the same lamella but obtained from a thinner region (60 nm, Figure S1e). The edge-on configuration is again revealed by horizontal fringes and corresponding spots in the FFT, but the lattice contrast is weaker compared to the thick region analyzed in Figure 5.

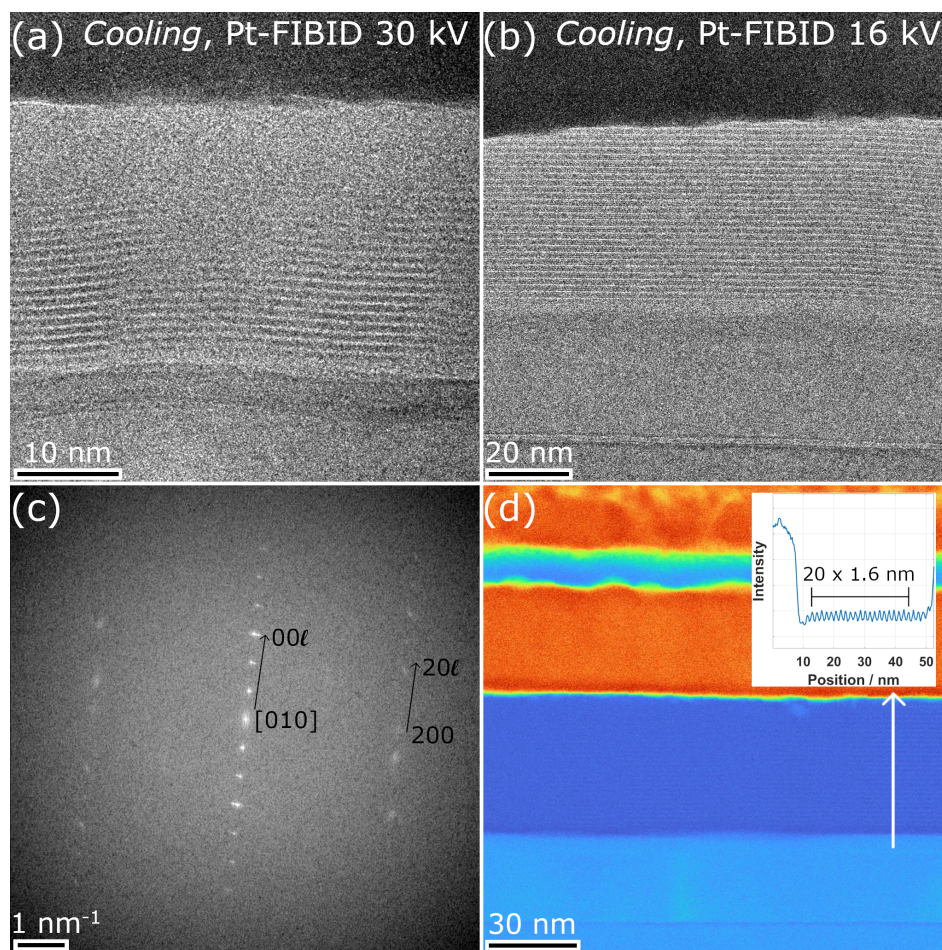


Fig. 4: TEM analysis of *Cooling* TEM lamellae thinned at -50°C from organic TFTs with DNTT as organic semiconductor. (a) TEM image of a lamella for which a FIB voltage of 30 kV was used for FIBID deposition revealing an amorphization in the top half of the organic semiconductor layer. (b) TEM image of a lamella where a FIB voltage of 16 kV was used for FIBID deposition. The crystal structure is preserved throughout the entire organic semiconductor layer. Electron dose for TEM image acquisition was $4.5\text{ e}^{-}\text{\AA}^{-2}$ (c) The FFT calculated selecting the DNTT layer only reveals strong $00l$ reflections and additionally weaker $20l$ reflections. (d) Color-coded HAADF-STEM image of the organic TFT system with line scan across the DNTT layer showing 001 periodicity. Scale bars are (a) 10 nm, (b) 20 nm, (c) 1 nm^{-1} and (d) 30 nm.

PhC₂-BQQDI

Figure 6 shows the TEM analysis of a *Cooling* lamella prepared from an organic TFT with PhC₂-BQQDI as organic semiconductor, employing both a Pt-FEBID process with 1 kV electrons and a Pt-FIBID process with 16 kV ions. The lamella thickness is only 60 nm (Figure S1f). The TEM image (Figure 6a) reveals the layer system of the organic TFT including the amorphous carbon and Au protection coatings. The organic semiconductor layer appears with horizontal fringes throughout the entire layer, confirming that a Pt-FEBID process with reduced electron energy of 1 keV does not cause damage to the molecular crystal, as predicted by the MC simulations discussed above.

A FFT calculated selecting only the organic semiconductor layer is shown in the inset image in Figure 6a. It reveals split $[00l]$ reflections suggesting the presence of two stacking periodicities of 1.8 and 2.1 nm. The reflection with smaller periodicity (1.8 nm) corresponds to half the value of the c parameter of the bulk

phase of PhC₂-BQQDI. The absence of the $[001]$ periodicity is explained by the vertical stack of two molecules within a single unit cell of PhC₂-BQQDI. A line scan taken across the organic semiconductor layer (arrow in Figure 6a) is shown in Figure 6b and confirms the presence of the two periodicities. The larger periodicity of 2.1 nm is found directly on top of the dielectric, while the smaller one, corresponding to the bulk phase, is found on top of it. This observation indicates the existence of a thin-film phase of PhC₂-BQQDI. Similar as for pentacene [Schiefer et al., 2007] and DNTT [Shioya et al., 2026], the periodicity of this thin-film phase is increased, which could be attributed to a more vertical arrangement of the molecules compared to the bulk phase. The fringes and corresponding spots in the FFT are weaker compared to the DNTT and pentacene images, which is attributed to the small thickness of the lamella (60 nm). Indeed, the visibility of a dark ring in the FFT, indicating the first zero of the phase-contrast

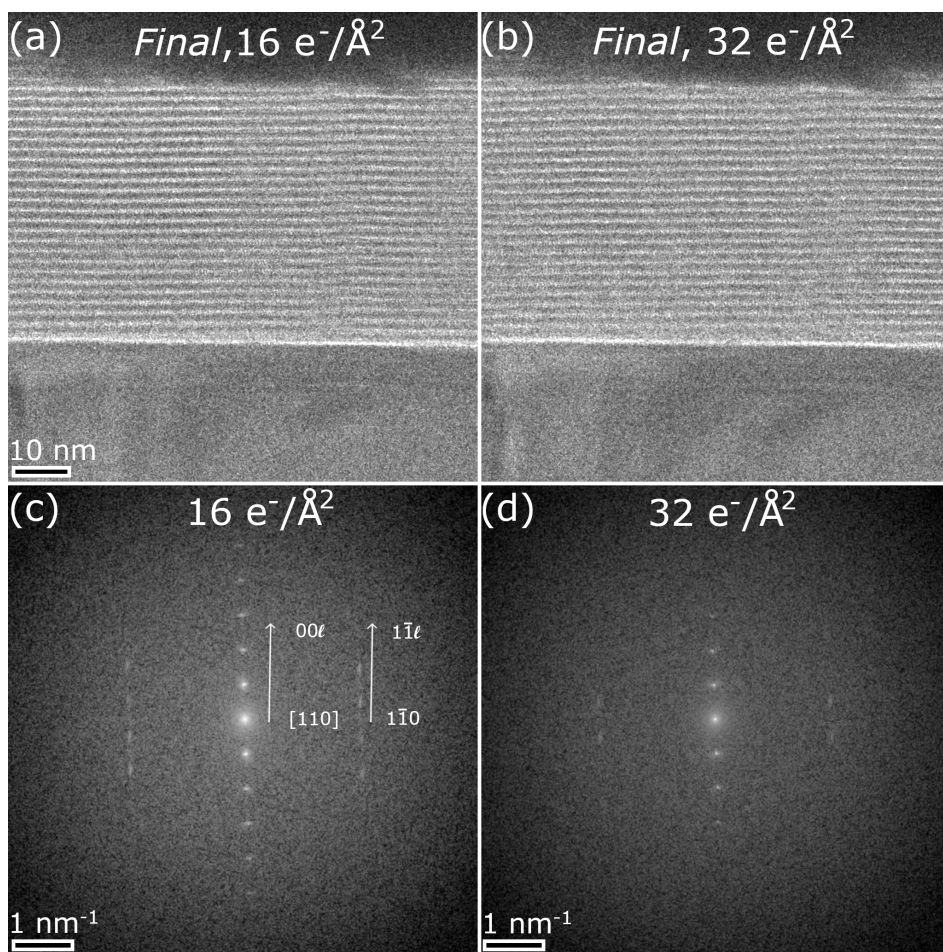


Fig. 5: TEM analysis of a *Cooling* TEM lamella thinned at -50°C from organic TFTs with pentacene as organic semiconductor. (a,b) Two subsequent TEM images of the identical sample region with the total dose given. (c,d) FFTs of the TEM images revealing an $[110]$ orientation of the pentacene crystal. Scale bars are (a,b) 10 nm, (c,d) 1 nm^{-1}

transfer function, reveals that amorphization at the surface of the lamella still takes place during thinning at a temperature of -50°C .

Discussion

The results shown above clearly demonstrate that both electron and ion irradiation in a SEM/FIB instrument can damage crystalline organic-semiconductor thin films. While damage by ion irradiation is not surprising, damage by low-energy electrons is somehow unexpected from a material-science point of view. However, the binding energies of the molecular crystal are dominated by weak van-der-Waals forces, which are apparently easily broken during low-energy electron irradiation and involved radiolysis processes. To our understanding, the generation of local electrical charges (secondary electrons) or plasmonic excitations during the irradiation leads to a rearrangement of the molecules causing an amorphization. It is noted that while the crystalline structure is clearly destroyed, the molecules will most probably remain intact to a large fraction. To avoid this amorphization, both types of irradiation must therefore be fully avoided by protection layers and optimum beam settings that can be estimated by MC simulations.

An alternative way to protect the crystalline structure during ion irradiation is cooling the specimen, which is strictly required during the final thinning for which the impact of ions on the crystal cannot be avoided. In this work, the specimen was cooled to -50°C , which was sufficient to protect the structure of the molecular crystals. A preparation at full cryo conditions was not tested. It could lead to a further improvement, however, it comes with higher effort and we have conducted cryo-TEM experiments on plan-view specimens that indicate that the strong cooling itself could damage the molecular crystal, which we attribute to the considerably large thermal expansion coefficients of these materials.

Electron irradiation is unavoidable during acquisition of the TEM images, which poses the fundamental limit of how much information can be obtained from the specimens. The results shown above indicate that the lamella thickness is a parameter that needs to be optimized when looking to extract the maximum information of cross-sectional lamellae. A compromise must be found between the presence of amorphized surfaces at low thicknesses and loss of resolution due to multiple scattering at higher thicknesses. The comparison of the results obtained

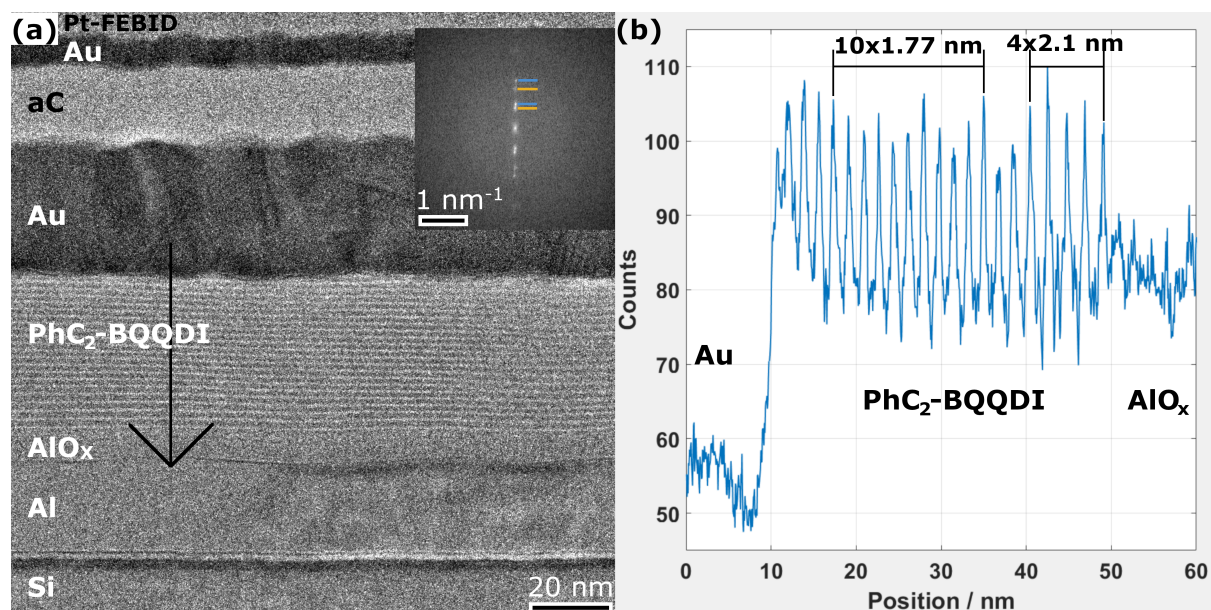


Fig. 6: TEM analysis of a *Cooling* lamella obtained from an organic TFT with PhC₂-BQQDI as organic semiconductor. (a) The TEM image reveals the layer system including the two additional protection layers and strong horizontal fringes throughout the entire organic semiconductor layer. The inset FFT reveals split [00 l] reflections, marked by blue and orange lines. Scale bars are 20 nm and 1 nm⁻¹. (b) Line profile across the organic semiconductor layer as indicated in (a) reveals two periodicities as indicated.

from the pentacene *Cooling* lamella with a thickness of 200 nm (Figure 5) and the PhC₂-BQQDI *Cooling* lamella with a thickness of 60 nm (Figure 6) shows that the optimum thickness will be larger than the ones typically pursued. This is attributed to the low atomic number of the elements forming the molecules and the resulting rather weak interaction with 300 keV electrons. The TEM experiments have been performed at room temperature, an improvement of the beam stability is expected by using cryo-TEM, however, as stated above, the cooling itself might generate defects that are not present in the original organic-semiconductor thin film.

Conclusions

The results show that the crystalline structure of organic-semiconductors thin films can be preserved during focused ion beam (FIB) lamella preparation by minimizing the electron and ion irradiation of the organic semiconductor layer in the scanning electron microscope/FIB dual-beam instrument and by performing the final thinning step of the lamella preparation at a reduced temperature of -50°C. Irradiation is minimized by additional coatings and optimized beam settings, which can be found through MC simulations that are helpful to find threshold values for ion and electron energy under which a penetration of the organic semiconductor layer for a given layer system of an organic electronic device, including protection layers, is avoided. However, the channeling effect can lead to an increased penetration depth as expected from MC simulations, and further reduction of the voltages might be required.

The TEM analyses reveal the growth in edge-on ("standing") configuration on top of the gate dielectric for all investigated molecules. The zone axis of DNTT and pentacene molecular crystals could be observed. The analysis of a lamella prepared

from PhC₂-BQQDI suggests the existence of a previously unknown thin-film phase. The results show that the lamella thickness is a parameter that needs to be optimized to maximize the obtainable information of the specimens. This work demonstrates that TEM analyses of cross-sectional lamellae can help to gain site-specific information from beam-sensitive organic semiconductors.

Competing interests

No competing interest is declared.

Author contributions statement

S.H. performed and analyzed the experiments and wrote the manuscript. U.Z. prepared the TFTs. H.K., M.P. and Y.E. reviewed the manuscript.

Acknowledgments

Funding by the German Research Foundation (DFG) through the collaborative research center CRC 1249 "N-Heteropolycycles as Functional Materials" (Project Number 281029004- SFB 1249, projects C01 and C12) is gratefully acknowledged. This work was partly carried out at the Laboratorio de Microscopías Avanzadas (LMA) at Universidad de Zaragoza. Support of L. Casado (LMA) with FIB preparation and SEM imaging is gratefully acknowledged.

References

L.A. Giannuzzi and F.A. Stevie. A review of focused ion beam milling techniques for tem specimen preparation. *Micron*,

- 30(3):197–204, June 1999. ISSN 0968-4328. doi: 10.1016/s0968-4328(99)00005-0.
- N. I. Kato. Reducing focused ion beam damage to transmission electron microscopy samples. *Journal of Electron Microscopy*, 53(5):451–458, October 2004. ISSN 1477-9986. doi: 10.1093/jmicro/dfh080.
- T. Sato, Y. Aizawa, H. Matsumoto, M. Kiyohara, C. Kamiya, and F. Von Cube. Low damage lamella preparation of metallic materials by fib processing with low acceleration voltage and a low incident angle ar ion milling finish. *Journal of Microscopy*, 279(3):234–241, February 2020. ISSN 1365-2818. doi: 10.1111/jmi.12878.
- Danny J. Edwards, Alan Schemer-Kohn, Matt Olszta, Ramprasad Prabhakaran, Yuanyuan Zhu, Jing Wang, Jacob Haag, Osman El Atwani, Timothy G. Lach, and Mychailo Toloczko. Understanding and removing fib artifacts in metallic tem samples using flash electropolishing. *Journal of Nuclear Materials*, 606:155618, February 2025. ISSN 0022-3115. doi: 10.1016/j.jnucmat.2025.155618.
- Michael Marko, Chyongere Hsieh, Richard Schalek, Joachim Frank, and Carmen Mannella. Focused-ion-beam thinning of frozen-hydrated biological specimens for cryo-electron microscopy. *Nature Methods*, 4(3):215–217, February 2007. ISSN 1548-7105. doi: 10.1038/nmeth1014.
- Hagen Klauk. Organic thin-film transistors. *Chemical Society Reviews*, 39(7):2643, 2010. ISSN 1460-4744. doi: 10.1039/b909902f.
- Fangyi Li, Jiayi Zhou, Jun Zhang, and Jiang Zhao. Research and progress on organic semiconductor power devices. *Materials*, 17(13):3362, July 2024. ISSN 1996-1944. doi: 10.3390/ma17133362.
- R.F. Egerton. Radiation damage to organic and inorganic specimens in the tem. *Micron*, 119:72–87, April 2019. ISSN 0968-4328. doi: 10.1016/j.micron.2019.01.005.
- N.D. Bassim, B.T. De Gregorio, A.L.D. Kilcoyne, K. Scott, T. Chou, S. Wirick, G. Cody, and R.M. Stroud. Minimizing damage during fib sample preparation of soft materials. *Journal of Microscopy*, 245(3):288–301, November 2011. ISSN 1365-2818. doi: 10.1111/j.1365-2818.2011.03570.x.
- David C. Martin, Jihua Chen, Junyan Yang, Lawrence F. Drummy, and Christian Kübel. High resolution electron microscopy of ordered polymers and organic molecular crystals: Recent developments and future possibilities. *Journal of Polymer Science Part B: Polymer Physics*, 43(14):1749–1778, June 2005. ISSN 1099-0488. doi: 10.1002/polb.20419.
- Takashi Minakata, Hideaki Imai, Masaru Ozaki, and Kentaro Saco. Structural studies on highly ordered and highly conductive thin films of pentacene. *Journal of Applied Physics*, 72(11):5220–5225, December 1992. ISSN 1089-7550. doi: 10.1063/1.352004.
- Benedikt Haas, Andreas Beyer, Wiebke Witte, Tobias Breuer, Gregor Witte, and Kerstin Volz. Application of transmission electron microscopy for microstructural characterization of perfluoropentacene thin films. *Journal of Applied Physics*, 110(7):073514, October 2011. ISSN 1089-7550. doi: 10.1063/1.3646549.
- Tsuyoshi Sekitani, Ute Zschieschang, Hagen Klauk, and Takao Someya. Flexible organic transistors and circuits with extreme bending stability. *Nature Materials*, 9(12):1015–1022, November 2010. ISSN 1476-4660. doi: 10.1038/nmat2896.
- Boyu Peng, Ke Cao, Albert Ho Yuen Lau, Ming Chen, Yang Lu, and Paddy K. L. Chan. Crystallized monolayer semiconductor for ohmic contact resistance, high intrinsic gain, and high current density. *Advanced Materials*, 32(34), 2020. ISSN 1521-4095. doi: 10.1002/adma.202002281.
- Jinwen Wang, Zheng Ren, Tingyi Yan, Ruofei Jia, Yanyan Cheng, Xiujuan Zhang, and Jiansheng Jie. Floating epitaxy and stitching growth of bilayer organic semiconductor single crystals on polymer dielectric toward high-performance and ultra-flexible transistors. *Advanced Materials*, December 2025. ISSN 1521-4095. doi: 10.1002/adma.202515477.
- Yosuke Murakami, Shigetaka Tomiya, Naoki Koshitani, Yoshihiro Kudo, Kotaro Satori, Masao Itabashi, Norihito Kobayashi, and Kazumasa Nomoto. Microstructural study of the polymorphic transformation in pentacene thin films. *Physical Review Letters*, 103(14):146102, October 2009. ISSN 1079-7114. doi: 10.1103/physrevlett.103.146102.
- Simon Hettler, Ute Zschieschang, Hagen Klauk, Martin Peterlechner, and Yolita M. Eggeler. Transmission electron microscopy analysis of the microstructure of nanocrystalline small-molecule semiconductors in functional organic thin-film transistors. *ACS Applied Materials & Interfaces*, 18(12):18073–18081, March 2026. ISSN 1944-8252. doi: 10.1021/acsami.6c01886.
- Stefan Schiefer, Martin Huth, Alexander Dobrinevski, and Bert Nickel. Determination of the crystal structure of substrate-induced pentacene polymorphs in fiber structured thin films. *Journal of the American Chemical Society*, 129(34):10316–10317, August 2007. ISSN 1520-5126. doi: 10.1021/ja0730516.
- T. Yamamoto and K. Takimiya. Facile synthesis of highly pi-extended heteroarenes, dinaphtho[2,3-b:2',3'-f]chalcogenopheno[3,2-b]chalcogenophenes, and their application to field-effect transistors. *Journal of the American Chemical Society*, 129(8):2224–2225, February 2007. ISSN 1520-5126. doi: 10.1021/ja068429z.
- Toshihiro Okamoto, Shohei Kumagai, Eiji Fukuzaki, Hiroyuki Ishii, Go Watanabe, Naoyuki Niitsu, Tatsuro Annaka, Masakazu Yamagishi, Yukio Tani, Hiroki Sugiura, Tetsuya Watanabe, Shun Watanabe, and Jun Takeya. Robust, high-performance n-type organic semiconductors. *Science Advances*, 6(18):eaaz0632, May 2020. ISSN 2375-2548. doi: 10.1126/sciadv.aaz0632.
- Nobutaka Shioya, Kazuo Eda, Takafumi Shimoaka, and Takeshi Hasegawa. Hidden thin-film phase of dinaphthothienothiophene revealed by high-resolution x-ray diffraction. *Applied Physics Express*, 13(9):095505, August 2020. ISSN 1882-0786. doi: 10.35848/1882-0786/abb061.
- Nobutaka Shioya, Fabian Gasser, Nina Strasser, Egbert Zojer, Roland Resel, Josef Simbrunner, and Takeshi Hasegawa. From monolayer to bulk: Thin-film-specific polymorphic transitions of a molecular semiconductor. *Chemistry of Materials*, 38(3):1527–1541, January 2026. ISSN 1520-5002. doi: 10.1021/acs.chemmater.5c03306.
- Sabrina Steffens, Tobias Wollandt, Karla Cordero-Solano, Robert Eichmann, Alexander Kochan, Xiuming Sun, Florian Letzkus, Joachim N. Burghartz, Sabine Ludwigs, Lutz H. Gade, and Hagen Klauk. Flexible n-channel organic transistors with low contact resistance. *ACS Applied Materials & Interfaces*, December 2025. ISSN 1944-8252. doi: 10.1021/acsami.5c17364.
- Ulrike Kraft, Kazuo Takimiya, Myeong Jin Kang, Reinhold Rödel, Florian Letzkus, Joachim N. Burghartz, Edwin Weber, and Hagen Klauk. Detailed analysis and contact

- properties of low-voltage organic thin-film transistors based on dinaphtho[2,3-b:2,3-f]thieno[3,2-b]thiophene (dnnt) and its didecyl and diphenyl derivatives. *Organic Electronics*, 35:33–40, August 2016. ISSN 1566-1199. doi: 10.1016/j.orgel.2016.04.038.
- Michael Geiger, Marion Hagel, Thomas Reindl, Jürgen Weis, R. Thomas Weitz, Helena Solodenko, Guido Schmitz, Ute Zschieschang, Hagen Klauk, and Rachana Acharya. Optimizing the plasma oxidation of aluminum gate electrodes for ultrathin gate oxides in organic transistors. *Scientific Reports*, 11(1):6382, March 2021. ISSN 2045-2322. doi: 10.1038/s41598-021-85517-7.
- Dominique Drouin, Alexandre Réal Couture, Dany Joly, Xavier Tastet, Vincent Aimez, and Raynald Gauvin. Casino v2.42—a fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users. *Scanning*, 29(3):92–101, April 2007. ISSN 1932-8745. doi: 10.1002/sca.20000.
- J.F. Ziegler, M.D. Ziegler, and J.P. Biersack. Srim – the stopping and range of ions in matter (2010). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 268(11–12):1818–1823, June 2010. ISSN 0168-583X. doi: 10.1016/j.nimb.2010.02.091.
- B. W. Kempshall, S. M. Schwarz, B. I. Prenitzer, L. A. Giannuzzi, R. B. Irwin, and F. A. Stevie. Ion channeling effects on the focused ion beam milling of cu. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 19(3):749–754, May 2001. ISSN 1520-8567. doi: 10.1116/1.1368670.
- L.A. Giannuzzi and J.R. Michael. Comparison of channeling contrast between ion and electron images. *Microscopy and Microanalysis*, 19(2):344–349, March 2013. ISSN 1435-8115. doi: 10.1017/s1431927612014286.