Influence of irradiation-induced disorder on the Peierls transition in TTF–TCNQ microdomains

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Abstract
The combined influence of electron irradiation-induced defects, substrate-induced strain and finite size effects on the electronic transport properties of individual micron-sized thin film growth domains of the organic charge transfer compound tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) have been studied. The TTF–TCNQ domains have been isolated and electrically contacted by focused ion beam etching and focused ion and electron-beam-induced deposition, respectively. This allowed us to measure the temperature-dependent resistivity and the current–voltage characteristics of individual domains. The dependence of the resistivity on temperature follows a variable-range hopping behaviour which shows a crossover of the exponents as the Peierls transition is approached. The low temperature behaviour is analysed within the segmented rod model of Fogler, Teber and Shklovskii which was developed for charge-ordered quasi one-dimensional electron crystals (Fogler et al 2004 Phys. Rev. B 69 035413). The effect of substrate-induced biaxial strain on the Peierls transition temperature is discussed with regard to its interplay with the defect-induced changes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
As early as in 1955, Peierls demonstrated that a one-dimensional metal with a partially filled electronic band is unstable against a periodic lattice distortion and undergoes a metal to insulator transition [2]. The ensuing periodic distortion of the electron gas results in the opening of a gap at the Fermi level. The formation of the gap at the Fermi level turns the material from metallic to semiconducting. This transition is referred to as the Peierls transition. The Peierls transition is associated with the implicit perfect nesting of the Fermi surface in one-dimensional metals. It has gained additional significance with regard to the study of electronic correlation effects in low-dimensional systems and the interplay of correlation and disorder.

Tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) is a quasi-one-dimensional organic metal which experiences a series of phase transitions at \( T_H = 54 \, \text{K} \), \( T_I = 49 \, \text{K} \) and \( T_L = 38 \, \text{K} \) [3–5], leading to a suppression of the metallic conductivity of the TTF and TCNQ chains and turning the material into a perfect insulator. The phase transition at 54 K is driven by a charge-density wave (CDW) Peierls instability in the TCNQ chains [6]. TTF–TCNQ consists of parallel segregated stacks of acceptor (TCNQ) and donor (TTF) molecules, where the stacks are aligned along the \( b \)-axis of the TTF–TCNQ. The overlap of \( \pi \)-orbitals arising along the stack direction, as is schematically shown in figure 1, causes a strongly anisotropic electrical conductivity.

The Peierls transition in TTF–TCNQ single crystals can be influenced by the presence of defects in the material and by hydrostatic pressure applied to the material [3, 8–11]. The study of transport properties of TTF–TCNQ single crystals was extended to TTF–TCNQ thin films [12–15]. There are several aspects regarding the electronic properties of this material...
which can be studied in thin films that are not accessible in single crystals, such as substrate-induced biaxial strain, which is hard to induce in bulk crystals [16], and the effect of disorder caused by electron-beam irradiation, because of the small penetration depth of electrons in the several keV energy range [17].

In this paper we study the dynamics of low-lying charge excitations in TTF–TCNQ domains with large defect densities induced by electron irradiation, both, above and below the Peierls transition temperature, which is hard to induce in bulk single crystals [18]. We argue that the data below 50 K can be explained in the framework of the segmented metal-rod model of Fogler, Teber and Shklovskii developed for a quasi one-dimensional electron crystal [1]. We speculate that the low-lying charge excitations above 50 K are mainly due to fluctuating CDWs, which are subject to the same segmentations as assumed in [1], albeit here an additional length scale enters, namely the average CDW-fluctuation correlation length. The possible influence of the substrate-induced strain on the Peierls phase transition temperature is discussed. First experiments on the fabrication of TTF–TCNQ domains using a different approach than presented here were recently reported in [19, 20].

2. Experimental methods

TTF–TCNQ domains (also called microcrystals in the following) were prepared by the physical vapour deposition method [21, 22] from as-supplied TTF–TCNQ powder (Fluka, purity ≥ 97.0%) at a background pressure of 8 × 10⁻⁸ mbar. The material was sublimated from a low-temperature evaporation cell using a quartz liner at a cell temperature of 88°C. The cell temperature was measured by a Ni–NiCr-thermocouple thermally coupled to the heated body of the evaporation cell by copper wool. The substrate was kept at room temperature. The distance between the substrate and the evaporation cell was 10 mm.

As-supplied chemically cleaned Si(1 0 0)/SiO₂(285 nm) substrates were used in the experiments. The pre-patterned Au(50 nm)/Cr(20 nm) contacts were formed on the substrate by a lithographical lift-off process and sputtering before the domain deposition. A shadow mask was used to define the region for TTF–TCNQ domain growth on the substrate between the metallic electrodes. One selected microcrystal on each substrate was contacted. The process of the domain formation is illustrated in figure 2. The size of a typical microcrystal used in the measurements varied within the range 1.5–3 μm in length, 110–550 nm in width and 10–110 nm in thickness.

Scanning electron microscopy (SEM) snapshots were done with a FEI xT Nova NanoLab 600 setup at a voltage of 5 kV, beam current of 1.6 nA and dwell time of 3 μs. Energy-dispersive x-ray spectroscopy (EDX) at 5 keV was employed in order to determine the chemical composition of the grown microdomains. The thickness of TTF–TCNQ domains was determined from atomic force microscopy (AFM) measurements performed with a Nanosurf easyScan 2 AFM in non-contact mode.

For electrical transport measurements the microcontacts between the TTF–TCNQ domain and the pre-patterned...
Au/Cr contacts were fabricated by the combination of focused-electron (FEBID) and ion-beam-induced deposition (FIBID) with trimethyl-methylcyclopentadienyl-platinum (MeCpPt(Me)₃) and tungsten hexacarbonyl (W(CO)₆) as precursors by means of electron-beam optical lithography using a Helios NanoLab 600. The electrical contacts on top of the TTF–TCNQ microcrystals were fabricated by FEBID and then extended by FIBID. The width of the contacts formed in the area of the domain was 100 nm and the thickness was 40 nm. The electron beam was operated at 5 kV and 1.6 nA. The focused ion beam was operated near the microcrystal at 40 nm. The electron beam was operated at 5 kV and 1.6 nA. The focused ion beam was operated near the microcrystal at 30 kV with a beam current of 10 pA. The microcontacts on the TTF–TCNQ domain were covered by a highly resistive Si(O)₃ passivation layer using neopentasilane (Si₅H₁₂) as precursor by means of FEBID. The thickness of the layer was about 10 nm.

The electrical conductivity measurements were carried out in a He cryostat with a variable temperature insert allowing cooling down of the sample from room temperature (300 K) to 4.2 K. Cooling–heating cycles of the sample were repeated several times and the conductivity showed no indication of either hysteretic behaviour or thermal-stress-induced damage formation in the domains. A four-probe scheme for the transport measurement was applied. The electrical transport properties were measured along the crystallographic b-axis of the TTF–TCNQ microcrystals. Temperature-dependent resistivity measurements were performed at fixed bias voltage of 0.2 V corresponding to an electric field of 800 V cm⁻¹. This rather large excitation level was needed to generate sufficient current. It is also related to the enhanced threshold voltage in the domains, as detailed in the next section. A fixed bias voltage was applied by a Keithley SourceMeter 2400 to the outer electrical contacts. The associated current was measured by an Agilent 34420A NanoVolt/Micro-Ohm meter. This measurement scheme allows one to eliminate the influence of the contact resistance. Possible Joule heating of the sample in the course of the current–voltage measurements was estimated from a finite elements simulation performed using COMSOL Multiphysics 3.2 simulation software for a sample temperature of 10 K.

3. Results

At first, the crystallographic orientation of the TTF–TCNQ microdomains grown on the Si(100)/SiO₂ substrate without gold contacts was determined by x-ray diffraction measurements. The measurements were performed in the same way as described in [15]. The crystallographic (ab)-plane of TTF–TCNQ microcrystals was found to be parallel to the substrate surface. The crystallographic b-axis is assumed to be parallel to the long axis of the TTF–TCNQ microcrystals, as was generally found to be the case in [13]. In further experiments the chemical composition of the microdomains was also determined. The composition TTF : TCNQ ≈ 1 : 1 was verified by selected area EDX on the crystallites. Figure 3 shows a typical example of a TTF–TCNQ domain (microcrystal) with fabricated contacts.

The length of the crystal in this example is 2.5 μm and corresponds to the crystallographic b-axis, the width is 530 nm and the thickness is 15 nm (parallel to c∗-axis). Each domain was irradiated with the electron beam. The density of the electron flux was about 250 As m⁻². The dose for the electron radiation in the experiments ranged from 1.3 to 2.4 GGY, as was determined by Monte-Carlo simulations using the Casino computer program [27]. The relatively high irradiation dose stems from the small volume of the irradiated sample. High irradiation doses result in the formation of defects in the TTF–TCNQ domains. The energy which is needed to introduce one defect in TTF–TCNQ single crystals is 21.2 keV, as reported in [28] for x-ray radiation. We assume the same radiation efficiency for electrons in our case. The energy absorbed in a typical domain allows one to estimate the defect densities to (0.62–1.13) × 10¹⁵ cm⁻³.

The room temperature electrical conductivity along the long axis of the microcrystal (the crystallographic b-axis of TTF–TCNQ) is in the range 10–30 Ωcm⁻¹. This value is more than one order of magnitude smaller than for high-quality TTF–TCNQ single crystals, which typically show σ_b ~ 500 (Ωcm)⁻¹ [29]. This reduced conductivity is caused by the electron-beam irradiation of the TTF–TCNQ domain.

The electrical resistivity of TTF–TCNQ domains fabricated with combined FEBID and FIBID processes shows a VRH behaviour starting from room temperature down to low temperatures [30]:

\[ R(T) = R_0 \exp \left( \frac{T_0}{T} \right)^m, \]

where \( T_0 \) and \( R_0 \) are constants and \( m \) is an exponent. In the experiment the exponent \( m \) varies for different irradiation doses and experiences a change at a temperature of about 50 K as is shown in figure 4. The activation temperature \( T_0 \) depends on the localization length \( \xi \) of the electronic wave functions relevant for the respective hopping processes. \( T_0 \propto 1/\xi^3 \).
Figure 3. (a) Exemplary SEM image of a TTF–TCNQ domain with contacts used for further analysis. The inset shows a zoomed-out SEM image of the TTF–TCNQ domain with FEBID/FIBID contacts together with the pre-patterned gold contacts. (b) AFM image of the TTF–TCNQ microcrystal with contacts. The thickness of the microcrystal in this example is about 15 nm. The AFM image was taken after the cryostat measurements. The voltage probes are marked by arrows.

Figure 4. Temperature dependence of the resistivity (squares) measured for two TTF–TCNQ domains irradiated by electron beam with (a) $1.3 \, \text{GGy}$, and (b) $2.4 \, \text{GGy}$ radiation dose, respectively. The exponents $m$ used in equation (1) are indicated in each plot. The applied voltage is $0.2 \, \text{V}$. The insets show the temperature dependence of the logarithmic derivative $d(\ln R) / d(1/T)^m$ with $m$ as indicated.

for $m = 1/4$ and $T_0 \propto 1/\xi$ for $m = 1/2$, to provide two prominent examples for Mott and Efros–Shklovskii behaviour, respectively. The strong dependence on the localization length in particular in the Mott regime causes very large activation temperatures in the case of small $\xi$-values.

The values of the exponents and the activation temperatures for the temperature ranges above and below 50 K are summarized in table 1. For reference purposes we analysed the behaviour of an epitaxial TTF–TCNQ thin film grown on NaCl(1 0 0) irradiated with a similar irradiation dose (about 1.4 GGy). The comparison of the temperature dependence of the logarithmic derivatives of the resistance for non-irradiated and irradiated TTF–TCNQ thin films is presented in figure 5. The logarithmic derivative of the resistivity is generally used to determine the Peierls transition temperature \cite{31}. The values of the exponent for the thin films are also included in table 1. It is important to note that the values for the exponents $m$ are to be taken with some caution. The respective fitting ranges, above and below about 50 K, are small. Nevertheless, the exponents given in table 1 created significantly better fits than other physically plausible choices taken from the set $m \in (1/4, 1/2, 2/5, 1/3, 1/4)$. Also, the crossover temperature of about 50 K is well-defined as this is the temperature where the fits for the high- and low-temperature data tended to deviate from the experimental values, respectively.

The manifestation of the Peierls phase transition in the TTF–TCNQ domains is smeared out in the resistivity-temperature dependence shown in figure 4. The absence of a minimum in the resistivity at about 54 K, i.e. the typical indication of the Peierls transition in TTF–TCNQ single crystals, is a result of the electron irradiation of the samples in the SEM, which induces defects in the TTF–TCNQ microcrystal. The thermo-activated behaviour of the resistivity generally found for TTF–TCNQ thin films \cite{15} also does not fit the resistivity-temperature dependence of the TTF–TCNQ domains. The irradiated TTF–TCNQ thin films still show Arrhenius behaviour (see figure 5). We are led to assume that the VRH behaviour is caused by an interplay of the high
concentration of defects in the domains which induce localized states near the Fermi level and the specific geometry of the individual domains.

For all cases presented in table 1 the transport regime changes at a temperature below 50 K. In order to explain the change of the VRH exponent the theoretical model suggested by Fogler, Teber and Shklovskii [1] for a quasi-one-dimensional electronic system was used. These authors studied a theoretical model of the influence of impurities on the low-temperature ohmic transport in one-dimensional chains and quasi-one-dimensional systems of many parallel chains. The theory predicts a non-monotonic dependence of the electronic resistivity on impurity concentration in quasi-one-dimensional systems like TTF–TCNQ. The electrons in [1] form a classical 1D Wigner crystal in the case of a single chain, or an array of such crystals in the 2D or 3D case. At temperatures below the phase transition the electronic charge distribution of an assumed Wigner crystal in the material is divided by impurities into metallic rods. Between the rods the electronic transport is performed via variable range hopping. The transport regime in the material is impurity dependent and also changes with temperature. Fogler et al introduce an average length of the segment of the chain which is not disturbed by impurities \( l = 1/(Na_z^2) \), where \( N \) is the defect concentration and \( a_z^2 \) is the area per chain. While in the theoretical model chains of the same type are considered, in the case of TTF–TCNQ two types of chains should be taken into account. The Peierls transition studied here refers to the TCNQ chains resulting in \( a_\perp \approx 10.4 \text{ Å} \) [32]. For each sample the average length of the segment was calculated and is given in table 1. For the non-irradiated epitaxial thin film sample the concentration of the defects was taken from our previous analysis on TTF–TCNQ thin films grown on various substrate materials [15]. The average length of the segment is responsible for the transport regime in the quasi-one-dimensional metal. According to Fogler et al [1] the hopping exponent \( m \) in table 1 can be parametrized as follows:

\[
m = \frac{\mu + 1}{\mu + d + 1},
\]

where \( d \) is the dimensionality and \( \mu = 0, 1, 2 \) depending on the respective hopping regime. For \( d = 3, \mu = 0 \) corresponds to \( m = 1/4 \) and Mott behaviour, \( \mu = 1 \) to \( m = 2/5 \), and \( \mu = 2 \) to \( m = 1/2 \) and Efros–Shklovskii VRH behaviour. When \( m = 1 \) the transport regime is thermo-activated.

The results for the exponents given in table 1 can be explained well by the framework of the metallic rods model formulated in [1]. For temperatures below 50 K the electrical transport of non-irradiated TTF–TCNQ thin films follows Mott’s conductivity law, while for irradiated thin films the average segment is shorter, therefore, the transport regime is changed and the value of the exponent equals 2/5. The individual TTF–TCNQ domains studied here were irradiated with comparable irradiation dose and the inevitable uncertainty in the \( l \) estimation does not allow for a clear statement concerning a crossover in the transport regime, which was possible in the case of irradiated and non-irradiated TTF–TCNQ thin films. The sample irradiated with 1.3 GGY shows Efros–Shklovskii behaviour and the sample irradiated with 2.4 GGY displays Mott behaviour at temperatures below 50 K. Both these regimes are probable for strongly irradiated quasi-one-dimensional electronic systems as follows from [1]. In any case the strong electron irradiation of the TTF–TCNQ domains does cause a complete suppression of the simple Arrhenius behaviour commonly observed in thin films. Also, the observed crossover of transport regimes stemming from the change of the VRH exponent \( m \) at temperatures of about 50 K for the measured TTF–TCNQ domains is ascribed to the presence of the slightly suppressed Peierls transition in the system, which is assumed to persist despite the increased defect concentration.

In order to get more information about CDW contributions below \( T_P \) (within the Fogler–Teber–Shklovskii scenario) and

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**Table 1.** Exponent \( m \) and parameter \( T_\theta \) (K) characterizing the electrical transport behaviour of TTF–TCNQ domains and thin films at temperature (1) \( T \geq 50 \text{ K} \) and (2) \( T < 50 \text{ K} \). The parameter \( l \) is used in the model [1] to characterize the average length of the segment of the chain which is not disturbed by impurities.

| Sample | Irradiation dose | Domain | Thin film |
|--------|------------------|--------|-----------|
|        | 1.3 GGY | 2.4 GGY | 0 GGY | 1.4 GGY |
| \( m; T_\theta \) (\( T < 50 \text{ K} \)) | 1/2; 1225 | 1/4; 399236 | 1/4; 8503056 | 2/5; 13995 |
| \( m; T_\theta \) (\( T > 50 \text{ K} \)) | 1/4; 130321 | 2/5; 15962 | 1; 137 | 1; 197 |
| \( l(\text{Å}) \) | 15 | 8 | 2.3 \times 10^3 | 13 |

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**Figure 5.** Normalized temperature-dependent resistance for (1) non-irradiated, and (2) irradiated TTF–TCNQ thin films. The inset shows the logarithmic derivative of the temperature-dependent resistance used to define the Peierls transition for (1) non-irradiated, and (2) irradiated TTF–TCNQ thin films. The irradiation dose was 1.4 GGY.

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above $T_F$ (via CDW fluctuations) we performed current–voltage $I(U)$ measurements and analysed these for possible threshold behaviour. Several $I(U)$ curves for one domain measured at different temperatures are collected in figure 6. The $I(U)$ curves exhibit a non-linear behaviour as the temperature is reduced to below about 100 K. The possible influence of Joule heating of the samples on the correctness of the current–voltage measurements was estimated by COMSOL simulations based on the resistance measurements on the TTF–TCNQ microdomains. Thermal conductivity data for TTF–TCNQ was taken from [33], for the Pt-EBID deposits from [34], and for the Si/SiO$_2$ substrate from the COMSOL physical property database. Convection and radiation losses were not taken into account, so that the calculated heat generation in the microcrystal represents an upper limit estimate. Contact resistances of typically a few Ohms were neglected. For a sample temperature of 10 K and a voltage of 2 V the upper limit estimation for the increase of the microdomain temperature was found to be $\Delta T = T_{\text{max}} - 10 = 0.22$ K (see the inset to figure 6). From this estimate it follows that microdomain heating during the transport measurements can be neglected and does not influence the behaviour of the current–voltage characteristics.

The measured $I(U)$ characteristics were used to obtain the threshold electric field for the TTF–TCNQ domain. In particular, figure 7 shows the differential resistance derived from the data presented in figure 6. The threshold electric field was defined from the dependence of the differential resistance on the electric field as the field where the differential resistance changes its behaviour from constant, corresponding to Ohm’s law, to a non-linear behaviour. The inset to figure 7 shows the temperature dependence of the threshold electric field for the two investigated samples. The obtained threshold electric field at 10 K (800 V cm$^{-1}$ and 8000 V cm$^{-1}$) is several orders of magnitude larger than commonly observed for TTF–TCNQ single crystals (10 V cm$^{-1}$ [35]) and for TTF–TCNQ thin films (3 V cm$^{-1}$ [36]). This increase in the threshold electric field is thought to be caused by two effects: (i) the relatively high concentration of defects in the domains [35], and (ii) the finite size of the sample, which has a severe influence on the threshold electric field in one-dimensional conductors as discussed in [37].

At this stage we assume that the persistence of the threshold voltage at temperatures substantially higher than the Peierls transition temperature (50 K) is attributed to the pinning of fluctuating CDW regions which are known to dominate the charge transport in bulk crystals even far above $T_F$. If this CDW-fluctuation contribution persists despite the large defect density, it would arguably be subjected to the same segmentation of the chains as assumed in the Fogler–Teber–Shklovskii model [1], albeit here an additional length scale enters, namely the average CDW-fluctuation correlation length.

As the final point in our analysis, we address an additional aspect which may be of relevance in developing a comprehensive understanding of the presented data. In [38] the influence of substrate-induced strain was studied on transport properties of the organic charge transfer salt $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. It was shown that by introducing either compressive or tensile strain the superconducting ground state of the material can be dramatically changed from superconducting to insulating. Thus, substrate-induced effects need also to be taken into account here. In our study we consider microscale TTF–TCNQ crystals deposited on top of a Si(1 0 0)/SiO$_2$ substrate. The Si/SiO$_2$ substrate has negligibly small thermal contraction [39] when compared with the thermal contraction of TTF–TCNQ [40]. Due to the difference of the thermal expansion properties of the substrate and the charge transfer complex a tensile biaxial strain is produced when the sample is cooled down. This does, of course, imply the assumption that the TTF–TCNQ microcrystal is fully clamped. A direct proof of clamping, as can in principle be provided by temperature-dependent x-ray diffraction experiments, is not feasible for individual
microcrystals. However, due to the very small thickness of the microcrystals and in view of our results obtained on thin films [15], a clamped state is highly likely.

A simple estimate [41] of this strain along the $a$ and $b$-axes of the TTF–TCNQ domain, with thermal expansion coefficients taken from [40] and elastic moduli from [42] at $T = 50$ K, yields the tensile strain and stress along the $a$-axis $\epsilon_a = 0.7\%$ and $\sigma_a^{\text{tens}} = 0.4 \text{ GPa}$, and along the $b$-axis $\epsilon_b = 2.3\%$ and $\sigma_b^{\text{tens}} = 1.3 \text{ GPa}$. TTF–TCNQ single crystals compressed by hydrostatic pressure of the same order of magnitude as calculated above experience a slight shift of the Peierls transition temperature of about $\pm 4 \text{ K}$ [3,8]. It is not appropriate to naively compare the possible effects of biaxial strain with results for hydrostatic pressure quantitatively. However, it may provide a qualitative idea about the range of changes of the Peierls transition temperature in the case of the biaxial strain as is expected to occur in the TTF–TCNQ microcrystals. The thermal tensile strain caused by the substrate-induced interaction decreases the overlap of the electronic wave function in TTF–TCNQ along the stack direction and one might rather expect an increase in the Peierls transition temperature. However, to our knowledge the influence of a biaxial strain on the Peierls transition temperature has not been studied by theoretical means so far. We are left with the qualitative statement that the strain effect is most likely not significant against the background of the change of the phase transition due to the induced defects. The performed analysis does not allow one to acquire the temperature dependence of electrical resistivity of pristine TTF–TCNQ micromdomains because the contact fabrication itself is accompanied with sample irradiation. Therefore, no measurements of non-irradiated domains were performed and the isolated influence of substrate-induced strain cannot be deduced directly by our approach. The Peierls transition temperature in TTF–TCNQ domains irradiated with electrons is attributed to the temperature where the exponent in the VRH behaviour changes, i.e. at about 50 K. The interplay of the disorder-induced reduction of $T_P$ and a possible increase of $T_P$ due to biaxial strain does not allow for a quantification of the strain effect.

4. Conclusion

In this paper the charge carrier dynamics in individual TTF–TCNQ domains fabricated by physical vapour deposition is discussed. For this purpose we have contacted individual domains of TTF–TCNQ microcrystals using a novel approach which includes focused-electron and ion-beam-induced deposition techniques. In TTF–TCNQ microdomains thin film specific aspects, such as substrate-induced strain, size effects and disorder-induced changes in the electronic structure, are combined. The results on TTF–TCNQ domains are compared with data obtained on epitaxial, as-grown TTF–TCNQ films of the two-domain type.

The contact fabrication process employed in the work is inevitably associated with defect incorporation which is caused by the electron irradiation of the organic microcrystals. As a consequence, the manifestation of the Peierls phase transition in the TTF–TCNQ domains is smeared out in the resistivity-temperature dependence. The relatively high defect concentration results in a variable range hopping behaviour of the resistivity instead of the commonly observed metallic or thermo-activated one. A non-linear behaviour in the current-voltage characteristics develops below about 100 K.

The properties of TTF–TCNQ domains differ dramatically from those of TTF–TCNQ single crystals and thin films. The influence of the substrate on the grown domains is appreciable. The development of tensile strain in the domain under cooling may lead to an increase in the Peierls transition temperature. In contrast to this, the Peierls transition temperature is reduced by defects. For the individual domains variable range hopping behaviour of a different kind above and below a temperature of about 50 K, corresponding to a slightly suppressed Peierls transition temperature, was observed. The data below 50 K can be explained in the framework of the segmented metal-rod model of Fogler, Teber and Shklovskii developed for a quasi-one-dimensional electron crystal [1]. The observed threshold voltage for TTF–TCNQ domains is assumed to correspond to the depinning of the charge-density wave below $T_P$, which persists as a fluctuating contribution at temperature above $T_P$ despite the relatively large defect concentration.

The approach followed in this work provides a new pathway to the isolation of individual TTF–TCNQ (or other organic charge transfer) domains for studying size effects and clamping. The electron-beam-induced effects are very useful for studying the influence of irradiation-induced defects. The combination of all of these aspects leads to additional complexities which cause us to conclude that (i) the combined action of finite size effects and disorder causes a crossover from Arrhenius-like to variable range hopping transport in TTF–TCNQ, (ii) the influence of biaxial strain has to be disentangled from the finite size and irradiation effects. It would be desirable to optimize the domain contact fabrication such that it can be performed without excessive defect formation.

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