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Strain induced on $(TMTSF)_2ReO_4$ microwires deposited on a silicon substrate

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Abstract. We present the successful recrystallisation of Bechgaard salts with the microwire shape using the drop casting method. The samples are deposited on a substrate with previously prepared patterns made by optical lithography. The physical properties of the microwires are shown. The excellent transport properties show that this technique provides a new method for the tuning of the physical properties of molecular conductors and the first step toward applications. The pressure effects of the substrate on the conduction are discussed.

PACS. 72.80.Le Polymers; organic compounds – 73.50.Dn Low-field transport and mobility; piezoresistance

1 Introduction

The realization of thin films is the key step toward applications through functional devices. In particular, organic materials are highly promising for cheap and large scale devices. For instance, the control of the evaporation of organic semiconductors allows synthesizing the well known organic semiconductors such as acenes or thiophenes in order to achieve field effect transistors with relatively high mobility competing with amorphous silicon[1]. On the other hand, another route toward organic electronics is obtained with charge transfer salts. In these compounds, the doping of the organic semiconducting matrix is no more controlled by a gate voltage but by a charge transfer between a p- or n-type organic molecule and an organic or inorganic counter anion. In this sense, this doping is much efficient as a charge transfer up to 1 is possible. This domain was developed in order to synthesize organic superconductors up to the highest temperature following

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the precursor idea of Little[2]. The discovery of organic superconductivity in 1979 in $(TMTSF)_2PF_6$ has raised a large research in this field (TMTSF = tetramethyl- tetraselenafulvalene) [3]. Unfortunately, up to now, the critical temperature remains below $14K$ under large pressure in $\beta' - (BEDT-TTF)_2ICl_2$ [4] or $11.8K$ at ambient pressure in $\kappa - (BEDT-TTF)_2Cu[N(CN)_2]Br$ [5] (BEDT-TTF=bis (ethylenedithio)- tetrathiafulvalene). These charge transfer (CT) salts present also a wide variety of other ground states such as charge density or spin density wave states or ferroelectricity [6]. Recently, a key step toward the manipulation of physical properties in charge transfer salts using a FET geometry has been obtained by manually depositing an ultra-small single crystal of $\kappa - (BEDT-TTF)_2Cu[N(CN)_2]Br$ on various substrates [7] following a first try in order to achieve nano-crystals using electrochemical electrocrystallization [8].

Herein, we present the realization of individual microwires of one of the Bechgaard salts, $(TMTSF)_2ReO_4$ using the drop-casting technique, which were deposited on a silicon substrate with lithographically made gold patterns. Electrical characterizations confirm the negative pressure induced by a silicon substrate and demonstrate the feasibility of this procedure in order to synthesize individual microwires on patterned substrates with various electrical properties.

2 Sample growth

We first prepared substrates made of a doped silicon wafer covered by 0.5μm thick thermally grown silicon oxide on which metallic patterns were deposited using standard optical lithography techniques. As shown in Fig. 1, the 3 μm wide thin gold fingers in the center of the pattern are made by the superposition of 1nm Cr followed by 2nm of gold. These fingers enlarge toward 150*150 μm^2 large gold pads on which 100nm thick gold was sputtered in a second step in order to make the contacts to the electrical measurement setup. $(TMTSF)_2ReO_4$ black needles were first synthesized using a standard electrocrystallization process and few of them were dissolved into about 1 cm^3 of solvent. Then, a droplet of this solution is deposited on a clean substrate at ambient temperature. The substrate is placed in a tightly closed box with silica gel inside and the substrate on the top of it. The box is reopened after evaporation of the solvent. Various results were obtained as a function of the solvent as shown in Table 1. Most of the time, pink platelets typical of neutral TMTSF crystals are obtained. Among the solvents, chlorobenzene which was successfully used to realize organic field effect transistors [9] on neutral TTF based semiconductors leads to wide pink films of neutral TMTSF crystals. From an optical point of view, the appearance of long and black needles is best achieved for only two tested solvents: acetonitrile and benzonitrile. Conductivity results with acetonitrile were already reported at room temperature [10]. The main drawback of acetonitrile is the numerous presence of residual droplets certainly due to the large solubility of water in this solvent and the growth of needles not necessarily sticked on the substrate. These two points are eliminated with benzonitrile which provides the best stick-

ing and the minimal amount of unwanted residues near the needles. A remarkable result is shown in Fig. 1 with another molecule, that is EDT-TTFCONHMe$_2$ where thin pink needles few mm long are fully sticked on the substrate. Such images are more rarely achieved using Bechgaard salts as the density of recrystallized needles is much smaller. Fig. 2 presents an electronic beam microscope image of recrystallized small needles of $(TMTSF)_2ReO_4$ on a microscope grid using the same drop-casting technique: the standard morphology of Bechgaard salts needles with the characteristic facets is recovered [11]. Finally, Electronic Diffraction Spectroscopy (EDS) performed on various needles has demonstrated the presence of selenium, phosphor and rhenium as expected. However, the size of the crystallites, their well-known sensitivity to irradiation and their low density on the substrate avoided us to perform standard X-ray diffraction measurements. Similar results (not shown) were obtained in other compounds of the $(TMTSF)_2X$ family.

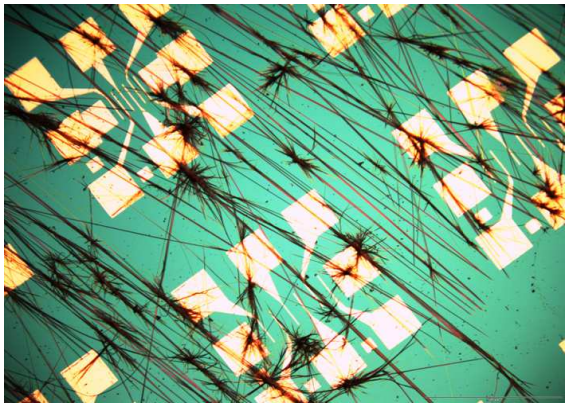

Fig. 1. Example of recrystallisation of neutral EDT-TTFCONHMe$_2$ molecule needles on a previously patterned silicon-silicon oxide substrate. Benzonitrile was used as the solvent. For scale, each gold square measures 150x150 μm^2

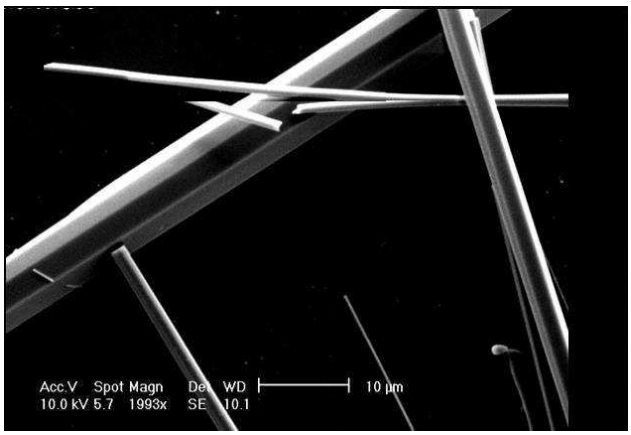

Fig. 2. Electronic microscope image of few recrystallized needles of $(TMTSF)_2ReO_4$

3 Electrical characterisations and discussion

The main purpose of this study is to present electrical characteristics which are crucial for possible applications and other physical characterisations. Fig. 3 presents the temperature evolution of the resistance of two needles (#1 and #2) recrystallized on the patterns as compared with a bulk crystal. The resistance is normalized to ambient temperature resistance and was measured by applying a low frequency 0.1μA current and the voltage was measured with a lock-in in a standard four-probe set-up. Microwires #1 and #2 are 1.2 and 0.85 μm wide respectively. As we were not able to measure directly the thickness without destruction of the microwires, we can estimate it from the room temperature resistance measured. As the resistivity of bulk $(TMTSF)_2ReO_4$ along the most conducting direction is about $1.45 m\Omega.cm$[12,13], and assuming that at room temperature, the microwires have the same conductivities as a bulk crystal, we obtain a thickness

Table 1. Influence of the solvent on the recrystallisation of Bechgaard salts. In the middle column, the existence or absence of neutral pink platelets of TMTSF is indicated. On the right column, the presence of needles of the Bechgarrd salt is indicated.

solvent	TMTSF	$(TMTSF)_2ReO_4$
heptan	no	no
1,1,1 trichloroethan	no	no
acetone	no	no
ethanol	few	no
chlorobenzene	large and thin	no
acetonitrile	few	large needles
benzonitrile	no	large needles

of 0.15 and 0.17 μm for microwires #1 and #2 respectively, which gives a thickness of about 10% of the width of the microwires which is typical for bulk crystals of the $(TMTSF)_2X$ family and is compatible with observations in Fig. 2. One also key parameter for the use of such microwires is the measurement of the contact resistance. As we are dealing with four point measurements, this quantity can be extracted. The meausred contact resistance is about 50kΩ with a contact area of 3.6 m^2. Extrapolating the contact area to the typical contact area in bulk crystals, $410^4 m^2$, it would give a contact resistance of about 4Ω which is of the same order of magnitude as the contacts made on bulk crystals. This value is also totally reproducible from one needle to another which was not the case for acetonitrile where strong fluctuations could be observed.

However, the resistivity curves of both microwires exhibit a behavior which is different from the bulk crystal. Upon cooling, the resistance of the microwires is always increasing and below about 180K, it increases faster which is related to the metal-insulator transition in the bulk crystal. X-ray diffraction has been made in bulk crystals of the $(TMTSF)_2X$ family under pressure and therefore the pressure effect of the substrate can be estimated. From the work of Gallois [14] on $(TMTSF)_2PF_6$, the decrease of the lattice parameter in a bulk sample from 300K down to 178K is equivalent to a change of the same lattice parameters of about 5.5 ± 0.5 kbar. The relative variation of the lattice parameter a between these two temperatures is 1.8% which is much larger than the thermal dilatation coefficient of both silicon and silicon oxide. As a result, assuming that the microwires are sticked on the substrate, the cooling of the microwires down to 180K is equivalent to an induced negative pressure of about 5.5 kbar on the organic sample at the silicon oxide-microwire interface. Going away from the silicon oxide substrate leads necessarily to a lower induced pressure. As a result, the induced pressure by the substrate in the microwire is certainly non uniform. As the resistivity in $(TMTSF)_2X$ salts is known to decrease under pressure at a typical rate of few % per kilobar, the substrate induced pressure may change the resitivity by a factor of about two with respect to the bulk value. This is in fair agreement with the experimental observation in Fig. 3. As a result, the resistance evolution of the microwires down to about 180K can be attributed to

the negative pressure effect of the substrate and an excellent sticking of the microwires on the substrate.

On the other hand, the phase diagram of $(TMTSF)_2ReO_4$ under hydrostatic pressure was first established by Parkin *et al.* [12] and Moret *et al.* [15]. The first order metal-insulator transition at 180K is due to an anion ordering with the wave vector $q = (1/2, 1/2, 1/2)$ [15] leading to the opening of a gap at the Fermi surface. From the evolution of the resistivity of our microwires, it is clear that this anion ordering transition is visible with an onset at about $T_{AO} \approx 185K$ tightly larger than 180K. Here, T_{AO} is determined as the temperature where the apparent linear extrapolation of the resistance at low and high temperatures intersect. This small increase of the anion ordering temperature can be directly correlated to the negative pressure effect induced by the substrate. Indeed, in bulk crystals, T_{AO} does not change drastically with hydrostatic pressure at the lowest pressures [12, 16]. The most striking feature is that both microwires present a much smaller increase of their resistivity as compared to the bulk crystal suggesting a smaller gap opened on the Fermi surface. We attribute this strong modification to the substrate again which avoids the characteristic behavior expected for a first order transition that is the change of the volume of the sample. As the needles are sticked on the substrate, the first order phase transition is transformed into a second order phase transition. As a result, the energy gap on the Fermi surface due to the anion ordering may be strongly modified. The activation energies extracted from the data of Fig. 3 in the insulating state for microwires

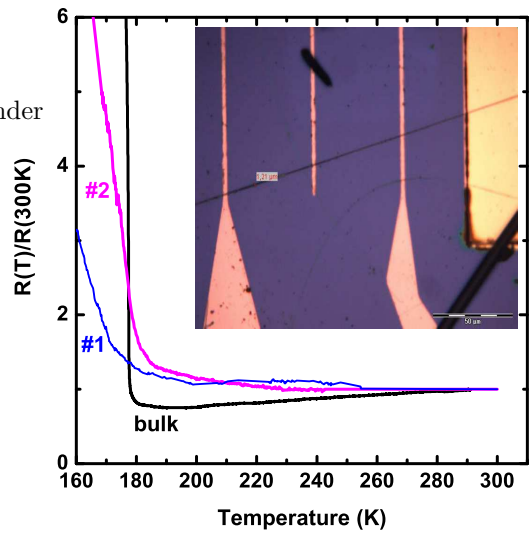

Fig. 3. Normalized resistance of two microwires #1 and #2 and a bulk crystal of $(TMTSF)_2ReO_4$ as a function of temperature. Inset: zoom on the microwire #1 on the substrate.

#1, #2 and the bulk crystal are 0.12 eV , 0.15eV and 0.2 eV respectively determined as the slope $\frac{d(lnR)}{dT}$ in the same temperature range $[140 - 170K]$. the bulk value is in agreement with previous resistivity determinations [12].

4 Conclusion

In conclusion, we have shown that organic microwires of $(TMTSF)_2ReO_4$ deposited on a silicon/silicon oxide substrate using the drop-casting technique support large strains which manifest on the resistivity of the microwires. In particular, the metal-insulator is modified and certainly leads to the transformation of the expected first order phase transition into a second order phase transition. In a more general way, our results indicate a strong influence of the substrate on the temperature dependence of the electri-

cal properties of organic materials deposited on an inorganic substrate. In particular, the physical properties of the organic field effect transistors may differ strongly at low temperature from the properties in bulk crystals due to inhomogeneous strains in the organic thin films. Our results also open a new field of investigation for charge transfer salts with the possibility to induce novel properties.

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