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Organic Superconducting Thin Films Generated at a Single Crystal−Solution Interface

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The growing interest in organized superconducting multilayers spans a number of areas. These include the basic studies of the crystal growth phenomena itself,[1] the studies of the dependence on the thin-film specific parameters of the electronic properties as compared to the corresponding (3D) bulk solids, i.e., the coherence length vs the size relationship, and more widely the role of surface defects and nanostructures on superconductivity,[2] and last the studies of the nanometer-scale devices which might result therefrom.[3] While various processes are being used to produce inorganic superconducting high-T_c films,[4] there is not yet access to organic superconducting films. We report herein that a solution-phase electrocrystallization-mediated process is one such possibility.

Electrocrystallization is currently used to prepare organic superconducting single crystals, although its detailed mechanism is not yet fully understood.[5] In this procedure, the electrodes provide highly pure oxidized (or reduced) forms of the organic components; they also allow some control over the resulting crystals by the modification of the current and potential parameters.[5] Remarkably, all the reported nucleations occur exclusively on the surface of the electrodes. Moreover, the surface structure of the electrodes[6] have been considered to interfere with the electrocrystallization process itself. A similar viewpoint led to the very interesting AFM study of the formation of ordered epitaxial layers of β-(ET)$_2$I$_3$ (ET = bis(ethylenedithiolo)tetrathiafulvalene) on a highly oriented pyrolytic graphite (HOPG) *electrode*.[7]

We have carried out the electrocrystallization of TMTSF$_2$ClO$_4$ superconductor[8] (TMTSF: tetramethyltetraselenafulvalene) at 40 °C[9] and, to our surprise, noticed the formation of a significant amount of single crystals *on the cell walls*, at remote positions from the platinum electrode.[8] Related to a higher solubility, this reflects an increased diffusion length of the oxidized species away from the electrode. Seeding of the cell under these conditions appears straightforward. We decided to introduce as a seed, into a solution containing TMTSF[10] and n-Bu$_4$N$^+$ClO$_4^-$ as an electrolyte, a single crystal of the isostructural[11] low-temperature narrow-gap semiconductor TMTSF$_2$PF$_6$[12] and to investigate the possible growth of superconducting TMTSF$_2$ClO$_4$ deposits on such an epitaxially matched substrate.

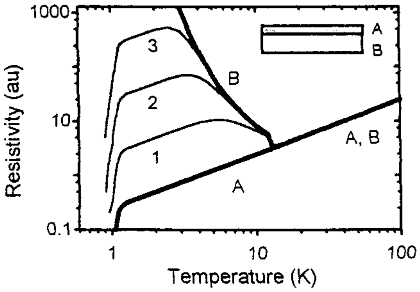

Figure 1. Calculated variations of the resistivities of two perfectly coupled ideal materials A (TMTSF$_2$ClO$_4$) (thickness xL) and B (TMTSF$_2$PF$_6$) (thickness $(1 - x)L$), as a function of temperature (see ref 13). A cross-section along the a direction is inserted; the considered thickness ratio for A (schematized in the c direction) is respectively 0.1, 0.01, and 0.001 for the curves 1, 2, and 3.

The results presently reported are related to the resistance measurements of such samples. At first, an ideal behavior for the resistivities of the latter, combining these two well-known molecular materials, was calculated (Figure 1) as a function of temperature.[13]

While an identical high-temperature regime was assumed for both (curves A and B), a transition (around 12 K) from a metallic to a spin density wave state (step on curve B) and finally an insulating state, involving an Arrhenius-type variation law (B) was considered for TMTSF$_2$PF$_6$. The resistivity of TMTSF$_2$ClO$_4$ (A) was assumed, on the other hand, to decrease continuously toward the superconducting transition (1.2 K) and go to zero (curve A). Coating TMTSF$_2$PF$_6$ with variable amounts of TMTSF$_2$ClO$_4$,[13] leads to a crossover regime, from 12 K to a low-temperature region, where the resistivity is scaled down by the superconductivity transition. In this crossover region, variable resistivity maxima were calculated and were found to depend on the TMTSF$_2$ClO$_4$ sample thickness (Figure 1, curves 1−3).

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[9] Electrocrystallization was carried out in dry and argon-purged deoxygenated dichloromethane solutions. TMTSF$_2$PF$_6$ seeds were prepared as usual[12] and were introduced in cells containing TMTSF (3×10^{-3} M) and nBu$_4$ClO$_4$ (0.2 M). The temperature of the tightly closed cell was maintained at 40 °C, and the oxidation completed (conversion <60%) with a low current density (2.5 mA cm^2).

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[11] The lattice parameters are as follows: (for TMTSF$_2$PF$_6$) a = 7.297 Å, b = 7.711 Å, c = 13.522 Å, α = 83.39°, β = 86.27°, γ = 71.01; and (for TMTSF$_2$ClO$_4$) a = 7.266 Å, b = 7.678 Å, c = 13.275, α = 84.58°, β = 86.73°, γ = 70.43°. See: Bechgaard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1 and references cited.

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[13] For any two perfectly coupled conducting materials A and B (a simple bilayer case is schematized in the Figure 1 insert), the current distribution inside the sample depends on the resistivities ρ of each of the components. Moreover, if A becomes a superconductor, then it will "short-cut" the poorly conducting layer B. The *overall conductivity* ρ^{-1} of two such materials A and B, with respectively xL and $(1 - x)L$ thickness, and ρ_A and ρ_B resistivities, is

$$\rho^{-1} = x\rho_A^{-1} + (1 - x)\rho_B^{-1}$$

Assuming (A) to be TMTSF$_2$ClO$_4$ and (B) TMTSF$_2$PF$_6$ and using this relation, the conductivity ρ^{-1} of a mixed sample was calculated as a function of temperature and x (the corresponding resistivity ρ, in arbitrary units, is plotted in the Figure 1; in the vicinity of the transitions the lines are estimated for convenience). Using now the standard four probe geometry (Figure 2, insert) involving contacts made on the surface of the needle-shaped crystal, the measured potential (and current) yield the longitudinal *resistance* variations (a product of the resistivity and a shape factor unmodified during the measurements) of the actual coupled conductors (Figure 2).

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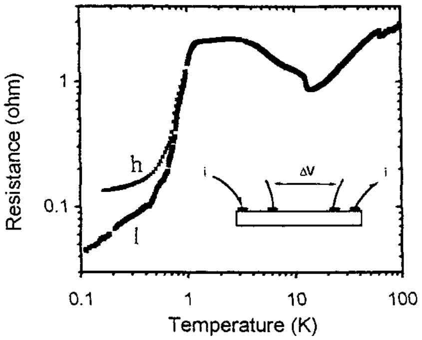

Figure 2. The measured variations (ac current and four-probe geometry using 15-μm silver paste glue) of the resistance of the $TMTSF_2ClO_4$ overlayers on a $TMTSF_2PF_6$ seed, as a function of the temperature. A cross section along the needle direction *a*, involving the four-probe geometry is inserted. The increase of the sample resistance in the 12−2 K region is related to the $TMTSF_2PF_6$ transition, and it allows an estimation of the overlayers thickness, whereas the decrease below 1.2 K is the signature of $TMTSF_2ClO_4$. Curves *h* and *l* correspond respectively to 100 and 4 μA intensities.

Upon completion of the electrocrystallization,[9] the seeding crystal was harvested, along with some "pure" $TMTSF_2ClO_4$ single crystals grown on the platinum electrodes, and its resistance was measured down to 0.1 K (Figure 2).

Interestingly, the measured variations were very close to the predicted simple schematic approach: the resistance of the sample decreases first to 12 K and, after increasing by nearly a factor of 2 from 12 to 2 K, a further decrease by more than 1 order of magnitude toward low temperatures is observed (Figure 2,curve *h*), lowering then the current density results in an even stronger decrease (a factor of 50 at the lowest temperature, curve *l*). These sharp resistivity decreases are clearly associated with the presence of superconducting $TMTSF_2ClO_4$ overlayers.[14] Moreover, considering the measured resistivity increase in the 12−2 K region as compared to the calculated behavior, the corresponding thickness might be estimated to be around 1/6 of the total sample thickness.[14]

The magnetoresistance of the sample was measured with the magnetic field oriented in the *c* direction (Figure 3). In the low-field range (Figure 3a) the resistivity of the normal state is rapidly restored with increasing field. This corresponds to the usual[16] H_{c2} critical field for the superconductivity of this material in the *c* direction: $\mu_0 H_{c2} = 0.17$ T. Above this field value (Figure 3b) the resistance increases, first smoothly to a saturation level, and then increases sharply above a threshold field, $\mu_0 H_t = 5$ T (Figure 3b). This behavior is the signature of the field-induced spin density waves (FI−SDW) state usually exhibited by this superconductor.[16] Therefore, this result highlights the formation of remarkably well ordered $TMTSF_2ClO_4$ layers, generated along the *c* direction.

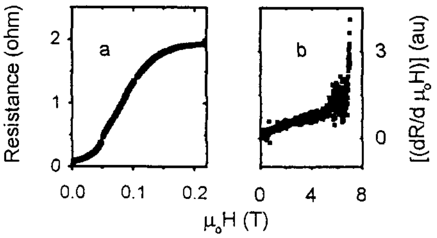

Figure 3. The variations as a function of the magnetic field of (a) the resistance of the sample of Figure 2 and (b) the derivation of the resistance above 0.2 T. H_{c2} critical field and H_t threshold field for the FI-SDW states are deduced from the graphs a and b, respectively.

The formation mechanism of the superconducting overlayers was probed[17] using a seed immersed in a cell containing a CH_2Cl_2 solution of TMTSF and the ClO_4 electrolyte maintained at 40 °C for a period of time corresponding to the electrocrystallization, with no applied current. In the absence of an electrochemical $TMTSF^{\bullet +}$ supply[18] the seed dissolved significantly. But, the remaining solid exhibited a conductivity very similar to the previous sample (Figure 2). This indicates the occurrence of a rather efficient, although unexpected, ion-exchange process which might account for the generation of the superconducting overlayers, as an alternative to epitaxy.

However, these results also raise several questions. The measured electrical resistances did not cancel out completely, and strong critical current effects were observed, at our lowest temperatures. Microbridges related to mechanical strain are excluded, because of the very close values of the thermal expansion parameters[19] of the $TMTSF_2ClO_4$ overlayers, as compared to $TMTSF_2PF_6$; however, an artifact related to silver-paste contact cracks on the sample could not be excluded. Alternatively, other nonsuperconducting barriers, specific to the formation of these overlayers might be considered. Further work directed at elucidating these aspects, and also ultimately studying the possible superconducting state of such surface-mediated nanostructures as a function of their size and topology is required.

In conclusion, the present results provide an easy and hopefully general way to generate organic superconductor thin films. The scope of the possible formation mechanisms (epitaxial or by ion exchange), the control over the width, the precise structure of the organic superconducting layers prepared here for the first time, as well as the study of their physical properties, are the subjects of future studies.

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(14) This estimated ratio implies a $TMTSF_2ClO_4$ thickness (not yet precisely determined) that is very large as compared to the coherence lengths, i.e., over several orders of magnitude larger than the latter in the *c* direction, where this coherence length value has been derived around the value of the lattice parameter (see ref 15). These coatings are therefore considered bulk superconductors.

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(17) We acknowledge a referee for suggesting this highly original and interesting experiment.

(18) The saturation levels required to avoid such dissolution could probably also easily be obtained by an alternate nonelectrochemical mean (i.e., a supply of $TMTSF_2ClO_4$).

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