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Metallic Polycrystalline Thin Films of the Single-Component Neutral Molecular Solid Ni(tmdt)$_2$

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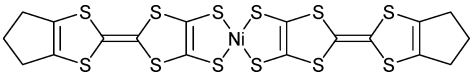
Intrinsically metallic molecular materials become in most cases activated semiconductors when prepared as thin films due to the formation of segregated domains (grains) separated by boundaries. The transport properties are thus determined by the morphology of the films. To date, only two examples of thin molecular organic films exhibiting metallic behavior down to liquid helium temperatures have been described, despite their polycrystalline character. The first one corresponds to θ-(BET-TTF)$_2$Br·3H$_2$O, BET-TTF = bis(ethylenethio)-tetrathiafulvalene, grown on polycarbonate substrates upon exposure to bromine vapor with room-temperature conductivities $\sigma_{RT} \approx 120$ S cm^{-1}.[1] The second example is TTF-[Ni(dmit)$_2$]$_2$, dmit = dithiolethionedithiolate, prepared as thin films on silicon wafers by electrocrystallization.[2] In this second case a reversible metal−insulator transition at 12 K has been observed.

There is tremendous interest in circumventing the extrinsic effects of grain boundaries to exploit the intrinsic physical properties of the pristine materials when targeting technological applications. However, the effect of grain boundaries is not always detrimental. In some cases the optical and magnetic properties are essentially preserved.[3]

In this study, we confirm that electrocrystallization[4] is the technique of choice to obtain truly metallic, organic thin films of single- and multicomponent materials, a necessary step toward the preparation of superconducting films.[5] Evidence of this statement is provided here with the single-component *neutral* molecular material Ni(tmdt)$_2$ (Scheme 1) grown on silicon substrates, tmdt

Scheme 1



= trimethylenetetrathiafulvalenedithiolate. Ni(tmdt)$_2$ has the honor to be the first synthesized single-component molecular metal, at least down to 0.6 K ($\sigma_{RT} \approx 400$ S cm^{-1}).[6] The possibility of obtaining such metals was predicted by theoretical work on the so-called two-band systems by showing that electron transfer could be induced internally between two types of bands of the same component and that transition metal bis(dithiolene) molecules could lead to single-component molecular metals.[7] Electrical conductivity in crystalline molecular materials is achieved by electron transfer, either by charge transfer or by doping, leading to partial filling of at least one band.

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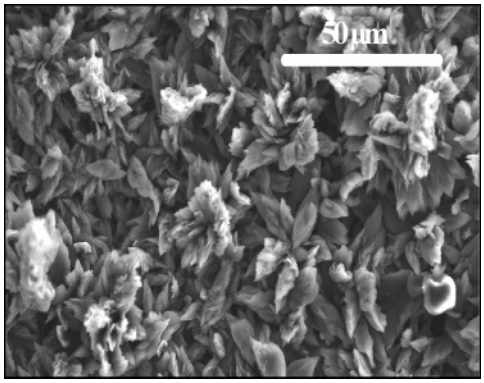

Figure 1. SEM image of a neutral thin film of Ni(tmdt)$_2$ (thickness ≈ 4 μm) grown on a passivated silicon wafer.

Thin Ni(tmdt)$_2$ films have been grown on silicon substrates (~2 × 1 cm^2) from an acetonitrile solution (40 mL) of (NMe$_4$)$_2$[Ni(tmdt)$_2$] (1.02 mmol L^{-1}) by the galvanostatic technique.[8] The dianionic precursor has been prepared as described elsewhere.[9] H-type and one-compartment cells have been used with the silicon wafer as the anode and a platinum wire as the counter electrode. The electrodeposition has been performed in a glovebox, with a current density of 2.5 μA cm^{-2} at 300 K during 5 days, due to the high air sensitivity of (NMe$_4$)$_2$[Ni(tmdt)$_2$].

The polycrystalline morphology of the films is evident from the SEM image shown in Figure 1. XRD patterns reveal that the deposits are composed of Ni(tmdt)$_2$ molecules and that they crystallize in the same crystallographic phase (triclinic) as single-crystal Ni(tmdt)$_2$ (see Supporting Information).[6]

Figure 2a shows the electrical behavior of the electrodeposited material measured with the standard four-probe method. The studied sample exhibits a clear metallic behavior down to 6 K. Taking into account the size and shape of the sample, we obtain $\sigma_{RT} \approx 100$ S cm^{-1} and $\sigma(6\text{ K}) \approx 135$ S cm^{-1}. As expected, because of grain boundary effects, σ_{RT} is clearly lower than the conductivity values found in single crystals (400 S cm^{-1} at 300 K). The contraction of the silicon substrate for decreasing temperatures (thermal expansion $\approx 2.6 \times 10^{-6}$ K^{-1}) improves the intergrain contacts favoring the electrical conductivity of the film. However, silicon exhibits a negative thermal expansion below ~80 K,[10] inducing the positive slope of the $\sigma(T)$ curve in the 75−105 K range. Below 75 K, the band-like metallic behavior of the film dominates over the substrate-induced semiconducting behavior. A similar effect has been observed for TTF[Ni(dmit)$_2$]$_2$ films.[2] Note that, despite the passivation procedure, a thin oxide layer remains on the silicon surface,

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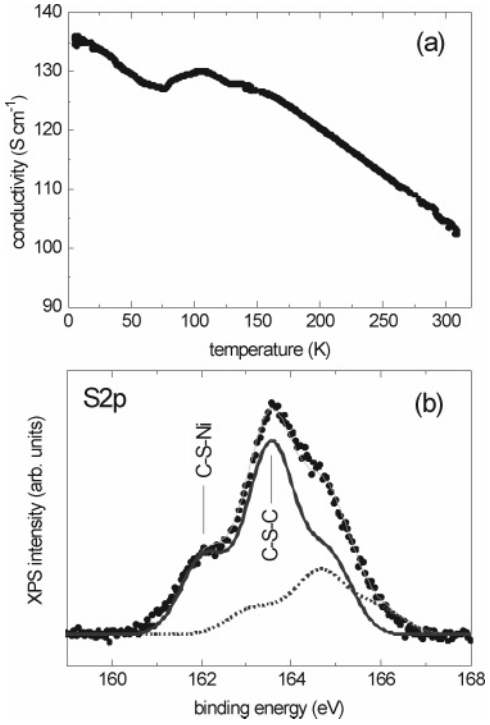

Figure 2. (a) Temperature dependence of the electrical conductivity and (b) room-temperature XPS spectra (black full dots) of a neutral thin Ni(tmdt)$_2$ film grown on a silicon wafer. The substrate shows a semiconductor behavior with $\sigma_{RT} \approx 10^{-3}$ S cm^{-1}. See Supporting Information for details on the fit in (b).

a fact that might explain the spread of the semiconducting-like temperature range.

The Raman spectra (see Supporting Information) show the characteristic C=C $a_g\nu_3$ mode of the TTF moiety at 1435 cm^{-1}. The position of this vibrational mode is very sensitive to the charge (1518 cm^{-1} for neutral TTF and 1420 cm^{-1} for TTF$^+$), suggesting a charge transfer of about 0.8−0.9 in Ni(tmdt)$_2$.[11]

Figure 2b shows a high-resolution XPS spectrum of the S2p line. The experimental line shape (full dots) can be satisfactorily decomposed in two equivalent contributions (continuous and discontinuous dark gray lines). Each contribution has two components, the more intense one corresponding to C−S−C bonding and the less intense one to C−S−Ni. Both components are shifted by 1.5 eV and each one contains two lines, $2p_{3/2}$ and $2p_{1/2}$, separated by 1.2 eV (see Supporting Information). The intensity ratio of the components, 2:1, is imposed by the chemical composition of the Ni(tmdt)$_2$ molecule (see Scheme 1). From this constraint it follows that the experimental data cannot be fitted to a single contribution. The presence of more than one contribution indicates the presence of molecules in different charge states.

This effect has been also observed when comparing XPS S2p spectra of neutral BEDT-TTF, BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene, with those of the Fabre salt (TMTTF)$_2$PF$_6$, TMTTF = tetramethyltetrathiafulvalene, both containing a TTF central motif.[12] Neutral BEDT-TTF shows a single component, C−S−C, with a binding energy of the $2p_{3/2}$ line of 163.2 eV. In the case of (TMTTF)$_2$PF$_6$ two equally intense components separated by ∼1 eV are observed. The lower (higher)-energy line corresponds to the neutral (charged) state. Both dynamical configurations TMTTF^0 and TMTTF^{+1} can be observed with XPS because photoemission is an intrinsically rapid process (∼10^{-15} s). Analogous S2p spectra have been obtained for TTF-TCNQ single crystals, with two components separated by ca. 1 eV.[13]

Summarizing, the most intense contribution of Ni(tmdt)$_2$ to the S2p feature (continuous line) corresponds to molecules in the neutral state, whereas the less intense one (discontinuous line) corresponds to charged species. Surface charging effects can be excluded, since the films are metallic. The fit does not improve when using a single contribution with a Doniach−Sunjić line shape,[14] which models the effect of screening by the conduction electrons of the holes generated during the photoemission process.

In conclusion, we present here the first example of a thin film of the single-component neutral molecular metal Ni(tmdt)$_2$ preserving its intrinsic metallic behavior. The versatile and well-known electrocrystallization technique appears to be the most convenient technique to prepare metallic films of molecular organic materials.

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Supporting Information Available: Raman spectrum, XRD pattern, and details of the fit of the S2p spectrum of thin Ni(tmdt)$_2$ films. This material is available free of charge via the Internet at http://pubs.acs.org.

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