Charge-transfer induced surface conductivity for a copper based inorganic-organic hybrid

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Inorganic-organic hybrids are receiving increasing attention as they offer the opportunity to combine the robust properties of inorganic materials with the versatility of organic compounds. We have studied the electric properties of an inorganic-organic hybrid with the chemical formula: CuCl4(C6H5CH2CH2NH3)2. This material is a ferromagnetic insulator that can easily be processed from solution. We show that the surface conductivity of the hybrid can be increased by five orders of magnitude by covering the surface with an organic electron donor. This constitutes a novel method to dope perovskite-based materials and study their charge transport properties. © 2009 American Institute of Physics. [doi:10.1063/1.3254328]

Conventional electronics is based on inorganic materials because of their robust electric and magnetic properties. However, the usage of inorganic materials is restricted by expensive processing and fabrication processes. Organic materials are less robust, but enable inexpensive fabrication by means of spin coating and printing. Moreover, organics are flexible and their properties can be tuned by making small changes in the chemical composition. Inorganic-organic hybrid materials combine the robustness of inorganics with the processability of organics.1,2 For example, Kagan et al.3 showed that SnLi(C6H5CH2CH2NH3)2 enables the fabrication of field effect transistors (FETs) by spin coating. The mobility approaches 1 cm2/V s but the material is unfortunately toxic and sensitive to air which makes it less suitable for applications.

We have studied the electric properties of an inorganic-organic hybrid with the chemical formula: CuCl4(C6H5CH2CH2NH3)2. This hybrid is air stable, non-toxic and has a similar crystal structure4 to the material studied by Kagan et al.3 The inorganic component consists of two-dimensional perovskitelike sheets that exhibit long range ferromagnetic order below 13 K.5,6 We have investigated the electronic transport in single crystals of this copper-based hybrid and its response to interface doping with an organic electron donor, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) contacts were evaporated using a shadow-mask, with a gap of 90 μm between the current contacts and a gap of 30 μm between the voltage contacts. The area between the voltage contacts was 1.6 square. Platinum wires and silver paste were used to connect the contacts to the probes, preventing damage to the soft crystal. In order to dope the crystals, two methods were used. First, FETs were fabricated either by laminating the crystal onto prefabricated doped silicon with a silicon dioxide dielectric or by evaporating dielectric parylene films on top of the crystals.11–13 Second, a layer of electrically insulating, electron donating TTF (600 nm thick) was evaporated on top of the crystal. In this case gold contacts were used to prevent re-evaporation of the TTF-TCNQ. The temperature dependent resistance measurements were performed using a Janis cryogenic probe station sourcing a constant current (Keithley Instruments 236 electrometer), and measuring the voltage (Hewlett-Packard 3458 multimeter).

The crystal structure of the copper based inorganic-organic hybrid agrees with reports in the literature.4 It consists of two-dimensional sheets of corner sharing CuCl6 octahedra (see Fig. 1). The Jahn–Teller active Cu2+ d9 ion causes a cooperative distortion of the octahedra, which are elongated in one in-plane direction while the other in-plane and the out-of-plane Cu–Cl distances have almost the same length. This introduces an antiferrodistortive arrangement of neighboring octahedra, which is responsible for the ferromagnetic interactions. Between the inorganic copper chloride sheets, two layers of organic molecules are present. They are connected to the inorganic backbone via Coulomb interactions and hydrogen bonds. These organic molecules are not expected to contribute to the conductivity as they exhibit no π–π stacking.

Current-voltage (I-V) measurements on the undoped and doped CuCl4(C6H5CH2CH2NH3)2 hybrid are compared in Fig. 2. All measurements were performed in the a-b plane of

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CuCl₄-hybrid crystal introduces charge transfer at the TTF-molecule, more mobile charge carriers than in FETs. Similarly, the thin TCNQ crystal can generate up to two orders of magnitude of charge transfer at the interface between a TTF and a Coulomb interaction. The organic rings are perpendicular to each other and the organic molecules are connected to the inorganic part by hydrogen bonds and are 2 nm apart and separated by two layers of organic molecules. The organic molecules are perpendicular to the interface that increases the conductance by five orders of magnitude. The temperature dependence of the resistivity is caused by a phase transition in the hybrid.

The doped hybrid interface displays a sheet resistivity of \(1 \times 10^7\) \(\Omega/\text{sq}\), which is at least five orders of magnitude lower than the undoped hybrid. Alves \textit{et al.}\textsuperscript{11–13} already showed that charge transfer at the interface between a TTF and a TCNQ crystal can generate up to two orders of magnitude more mobile charge carriers than in FETs. Similarly, the thin film of the electron donating TTF on top of the CuCl₄-hybrid crystal introduces charge transfer at the TTF-hybrid interface that increases the conductance by five orders of magnitude. The temperature dependence of the four-point resistivity measurements follows Arrhenius behavior (Fig. 3), from which an activation energy of approximately 0.17 eV was calculated.

The carrier density at a charge-transfer interface can be estimated by comparing the measured interface sheet resistivity with the sheet resistivity of the material in the FET geometry, in which the amount of carriers can be determined.\textsuperscript{9} Unfortunately, the FETs of the copper hybrid did not show any gate effect. In order to obtain a rough estimate of the carrier density and the mobility, we use the 0.17 eV above 240 K. This transition is related to a phase transition in the hybrid, which is also observed in the heat capacity and the dielectric constant of the undoped material. The origin of the transition is still under investigation and will be reported elsewhere. Nevertheless, the observation of this phase transition in the resistivity is evidence that the charge transport is associated with the hybrid-TTF interface and not restricted to the TFF-layer.

The resistivity of undoped CuCl₄(C₆H₅CH₂CH₂NH₃)₂ is of the order of 1 \(\Omega/\text{sq}\), which is many orders of magnitudes higher than that of the structurally similar SnI₄(C₆H₅CH₂CH₂NH₃)₂, which was previously studied by Kagan \textit{et al.}\textsuperscript{2} The origin of the high resistivity in the undoped copper based hybrid is twofold. First, the Cu⁺ and Cl⁻ ions are relatively small and the bonds in the inorganic layer are more ionic than in the SnI₄-hybrid. In such an ionic bond the carriers are localized and the conductivity is low. Second, the copper ion is Jahn–Teller active, which results in an antiferrodistortive orbital ordering of the half filled d(\(x^2−y^2\)) like d-orbitals.\textsuperscript{14} This orthogonal arrangement blocks the transport of charge carriers and reduces the conductivity even more. The organic molecules are not expected to contribute to the conductivity as \(\pi−\pi\) stacking is absent.

The electron-rich TTF donates electrons into the inorganic sheets at the interface of the hybrid crystal. These electrons will result in the coexistence of Cu²⁺ and Cu⁺ in the perovskite layer. This mixed valence increases the conductivity. Moreover, the Cu⁺ ion has a d\(^{10}\) configuration and is not Jahn–Teller active. Therefore, the doping removes the charge carrier blockade of the antiferrodistortive arrangement of the d(\(x^2−x^2\)) and d(\(z^2−y^2\)) type orbitals, as has been extensively studied for perovskite-based layered Cu- and Mn-oxides.\textsuperscript{15} The doping results in a higher conductivity, because it both introduces extra carriers and promotes greater delocalization. Due to the electron doping the magnetic moment at the TTF-hybrid interface is partially canceled.\textsuperscript{16} It is presently unclear how this effect influences the overall ferromagnetic state.

The carrier density at a charge-transfer interface can be estimated by comparing the measured interface sheet resistivity with the sheet resistivity of the material in the FET geometry, in which the amount of carriers can be determined.\textsuperscript{9} Unfortunately, the FETs of the copper hybrid did not show any gate effect. In order to obtain a rough estimate of the carrier density and the mobility, we use the
previously reported carrier density at the TTF-TCNQ interface as an upper limit, which Alves et al.\(^8\) estimated to be approximately \(5 \times 10^{14}\) carriers \(\text{cm}^{-2}\). Our hybrid is a poorer electron acceptor than TCNQ, but this value of \(5 \times 10^{14}\) carriers \(\text{cm}^{-2}\) can, nevertheless, be used as an upper limit for the TTF-hybrid system. This doping level corresponds to one extra electron per copper atom at the TTF-hybrid interface (assuming that the carriers remain at the surface CuCl\(_4\) layer, following the arguments of Alves et al.). From the number of charge carriers and the sheet resistivity of the doped TTF-hybrid interface \(\frac{1}{10^7} \text{Ω/sq}\) we calculate a lower limit for the mobility of \(1 \times 10^{-3}\) cm\(^2\)/Vs.

In summary, the pure hybrid CuCl\(_4\)(C\(_6\)H\(_5\)CH\(_2\)CH\(_2\)NH\(_3\))\(_2\) is ferromagnetic insulator. The crystal interface can be doped by evaporating a layer of the electron donor TTF on top. At the doped interface the conductance is enhanced by at least five orders of magnitude and the activation energy is low, 0.17 eV. The undoped hybrid exhibits a phase transition near 240 K, which can be observed in the resistivity at the hybrid-TTF interface, providing evidence that the charge transfer is present and that the charge transport takes place at this interface.

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