When TTF Met TCNQ

John R. Kirtley and Jochen Mannhart

Just as the boundary between land and water produces some of the most striking landscapes on earth, the boundary between two materials can give rise to outstanding phenomena in electronics. The *pn*-junction in semiconductors and two dimensional electron gases (2-DEG) causing the Quantum Hall Effects are but just two examples. On page xxx of this issue, Alves *et al.* show [1] that single interfaces, purposely created between different organic materials, can generate electronic phases that cannot be produced in one mixed layer alone. The principle, crystal lamination, is strikingly simple. The authors bring two crystals of TTF (tetrathiofulvalene) and TCNQ (7,7,8,8,-tetracyanoquinodimethan) into direct, mechanical contact (see Figure 1). What a remarkable experiment this is: First, it is striking that stable and reproducible conducting layers can be obtained by mechanically pressing two single crystals together. Second, both TTF and TCNQ are insulating, and yet they generate a conducting layer with a high carrier density which even exceeds 10^{14} cm^{-2}. In addition, the carriers are created with no impurities intentionally included in the interface.

As in metals, the resistance of the conducting sheets decreases monotonically as the temperature is lowered – a stunning behavior for a TTF-TCNQ-based system, because bulk TTF-TCNQ is insulating below 38 K. This insulating ground state is caused by the one-dimensional structure of the TTF and TCNQ molecules, which induces two so-called Peierls transitions, one each for TTF and for TCNQ, to the insulating state [2]. The Peierls transitions herald themselves with pronounced resistance steps upon cooling. No trace of such a step is observed for the interface, however, thereby revealing that the interface conductance is not related to the bulk conductivity. The lack of Peierls transitions makes it appear unlikely that the two types of molecule are diffusing into each other, and suggests that the metallic conduction arises from charge transfer between the TTF and TCNQ molecules that meet at the interface between the two bulk crystals.

The mechanism underlying the generation of the conducting layer in this system is strikingly different from that of GaAs-$Al_xGa_{1-x}As$ heterojunctions [3] (Figure 2). In the latter, carriers donated by dopant atoms close to the interface are caught in a potential well induced by the difference of the semiconducting gaps between the two materials. The well is so narrow that the quantization of the electron states in the direction of the layer thickness causes a two-dimensional quantum mechanical behavior of the electron gases. This two-dimensional nature provides, for example, the basis for the Quantum Hall Effects notable in these systems.

It is proposed in Alves *et al.* that in their TTF-TCNQ interfaces electrons transfer from the highest occupied orbital (HOMO) in the TTF molecules to the lowest unoccupied orbital (LUMO) in TCNQ molecules. Because the interaction between neighboring TTF or TCNQ molecules is minute, the authors argue that only the molecules at the interface take part in this transfer. If this interpretation was correct, the conductance in TTF-TCNQ contacts results from two layers with equal but opposite amounts of charge. The layers are separated by less than 2 nm, the intermolecular spacing [4]. It therefore seems reasonable that the conducting sheets at the TTF-TCNQ interfaces are even spatially smaller than the 2-DEG electronic wave functions in GaAs-$Al_xGa_{1-x}As$ heterojunctions, characterized by a typical value of 5 nm [5]. The heat is on to prove the existence of 2-DEGs at interfaces of organics, such as TTF-TCNQ contacts.

The results have exciting implications. This simple process, which can presumably be used for a wide variety of organic semiconductors, produces conductivity in a very thin layer with no intentional dopants. The estimated interface carrier density of 5×10^{14} cm^{-2} is ten times larger than in the $LaAlO_3/SrTiO_3$ system [6], and may therefore exhibit magnetism [7] or interface superconductivity [8]. Although the interface resistance is currently too large for device applications, high-quality transistor characteristics have already been demonstrated by Alves *et al*. The authors also raise the possibility to fabricate an excitonic insulator, in which electrons and holes form pairs, causing an insulating state that is reminiscent of the BCS superconducting state. This excitonic insulator was proposed 40 years ago [9], but has not been observed experimentally. Most importantly, however, new classes of organic electronic systems, states that cannot be achieved in conventional bulk materials, can be prepared with this technique.

J.R. Kirtley is a Humboldt fellow at the Center for Electronic Correlations and Magnetism of the University of Augsburg. J. Mannhart is at the Center

for Electronic Correlations and Magnetism of the University of Augsburg.

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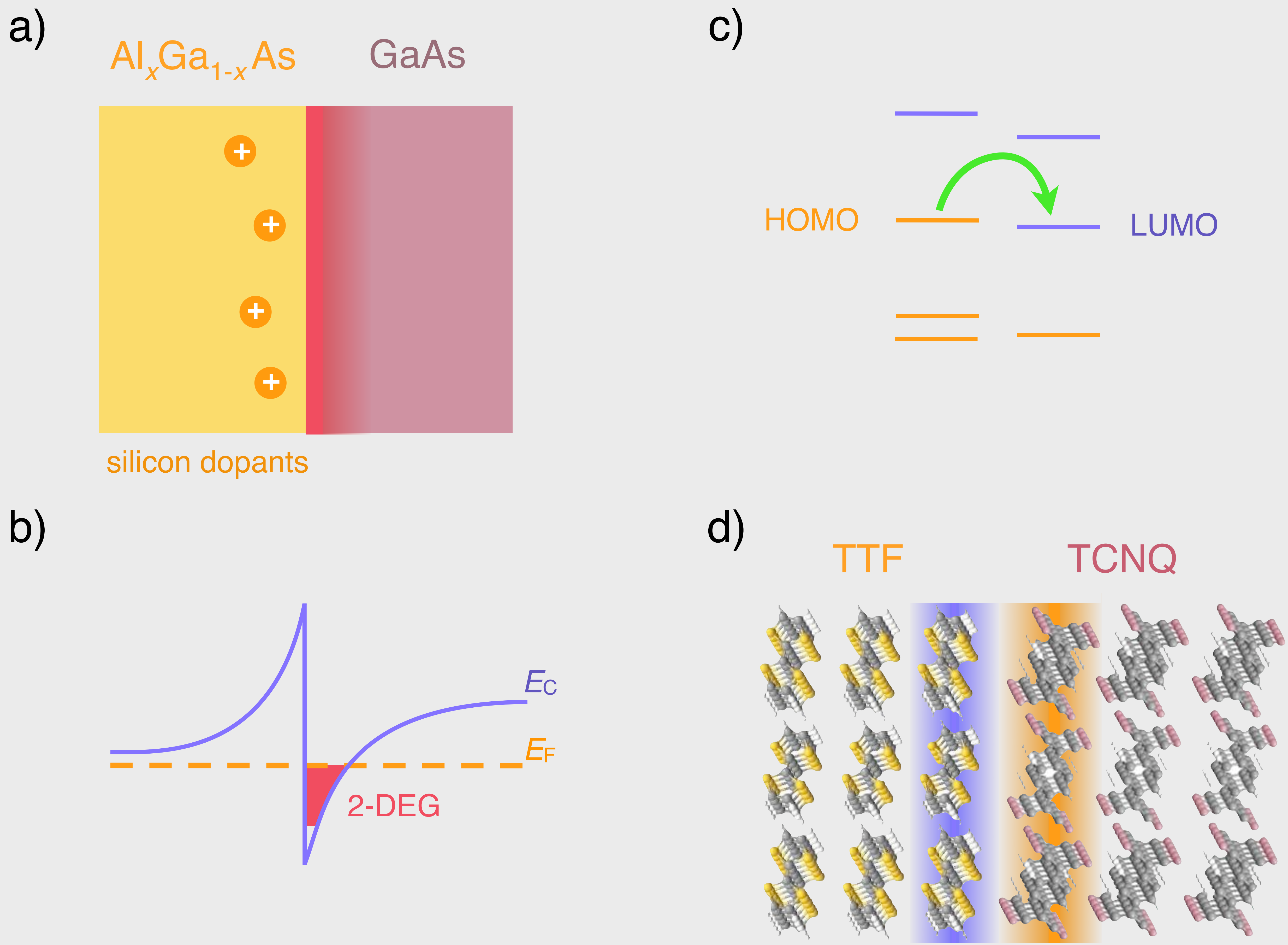
Figure Captions:

1. Optical micrograph of single crystals of TTF (dark orange) and TCNQ (light yellow) single crystals. The crystals shown are ~1-3 mm long and with a thickness of several microns thicker than the crystals used in the crystal-lamination experiments (photo courtesy of A.F. Morpurgo).

2. Formation mechanisms of conducting layers at the interface of a GaAs-$Al_xGa_{1-x}As$ heterojunction and a TTF-TCNQ interface. In the former (a) silicon atoms near the interface donate electrons which are caught as a two-dimensional electron gas (2-DEG) in a potential well formed at the heterojunction (b). In the proposed mechanism for TTF-TCNQ contacts, electrons are transferred from the highest occupied molecular orbital (HOMO) of the TTF to the lowest unoccupied molecular orbital (LUMO) of the TCNQ (c), forming a conducting double-layer of positive and negative charge (d).

Fig. 1



a)
$Al_xGa_{1-x}As$
GaAs
silicon dopants
b)
E_C
E_F
2-DEG
c)
HOMO
LUMO
d)
TTF
TCNQ

Fig. 2