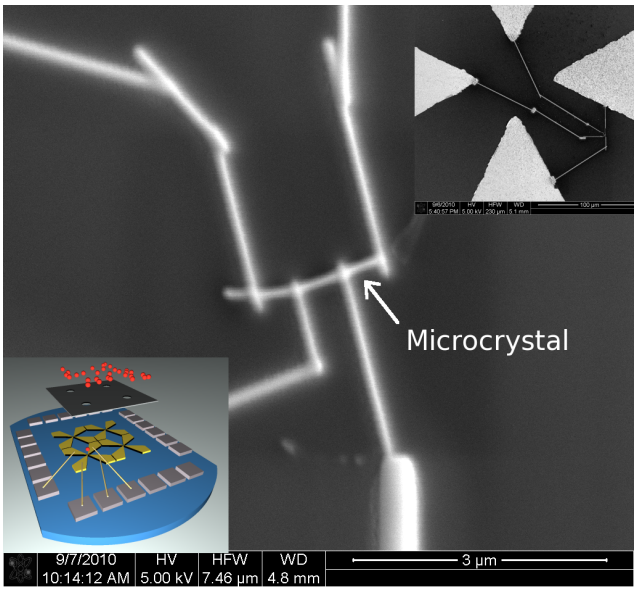
Project B9 - Thin film and microcrystal investigations on organic charge-transfer systems

In this project electronically correlated organic charge-transfer systems (CTS) of the radical-ion salt type are studied with emphasis on using thin-film specific aspects for tuning phase transitions, in particular of the charge density wave and para-to-ferroelectric type.

In the first funding period one focus has been on the systematic search for new CTS using a selection of new donor (D) and acceptor (A) molecules by both, thin film preparation techniques and crystal growth from solution. Several new CTS have been obtained in close collaboration with projects B8 (Aeschlimann/Schönhense) and B10 (Müllen). The physical properties of a subset of these new CTS are now further elucidated with a view on finding new materials of the mixed-stack type that show a temperature- or pressure-driven neutral-ionic (NI) phase transition, i.e. a transition between two different charge states on the D and A lattice sites. Charge-transfer materials showing a NI phase transition illustrate the competition between a lattice phonon driven second order Peierls transition and molecular (local) vibrations that favor a first order transition. The results obtained in this regard are summarized for the new CTS TMP-(F_4)TCNQ (TMP: tetramethoxypyrene) in Refs. 1 and 2 which show a mixed stack lattice structure and an insulating ground state with moderate to strong anisotropy in the conductivity. A detailed understanding of these materials has been obtained by additional band structure calculations performed in project B2 (Jeschke/Valenti).



SEM micrograph of TTF-TCNQ microcrystal contacted by focused electron beam induced deposition (FEBID). Lower left inset: Schematic drawing of TTF-TCNQ evaporation through shadow mask onto the area of pre-defined electrical contact pads. Upper right inset: Zoomed-out SEM image of mircocrystal electrically connected to macroscopic contact pads.

In a second focus of the first funding period specific thin-film related aspects have been studied with regard to the charge density wave transitions in the archtypical one-dimensional organic metal TTF-TCNQ. These aspects are the influence of biaxial strain induced by the elastic coupling of TTF-TCNQ thin films to the substrate (clamping) and of growth-related defects onto the Peierls transition, as well as the influence of electron irradiation induced defects on the dynamics of the charge density wave in TTF-TCNQ thin films and individual micro crystals (see also Fig. 1) [3,4].

In the second funding period the main focus will be on studying the paraelectric (PE) to ferroelectric (FE) phase transition in the NI-system TTF-CA (CA: chloranil) which is also associated with the formation of a dimerized, one-dimensional, antiferromagnetic spin chain (FE/AFM-multiferroicum). Bulk TTF-CA shows a first order phase transition into the FE phase at T_C=81 K. With moderate hydrostatic pressure this transition can be shifted to room temperature (at about 6 kbar). We prepare thin films of TTF-CA in the thickness range below 100nm and to utilize substrate-induced clamping effects to create biaxial tensile or compressive strain. This results in a strong shift of the Curie temperature. We also developed a new concept for monitoring the PE-FE phase transition which is highly suitable for studying the FE- and PE-domain boundary dynamics. This approach relies on our direct nanostructure writing techniques, such as FEBID. First results of this work, comprising the thin film growth and the new monitoring concept, will be published in 2014.

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