Environmental and In Situ SEM/TEM

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In situ characterization of Ag-TCNQ nanowires

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Unique properties, such as reversible field-induced electric switching behavior and high densities of charge carriers are found in one-dimensional nanostructures of metal-tetracyanoquinodimethane (M-TCNQ). Consequently, increasing research interests has been generated for their potential application in functional nano-scaled electric devices [1,2,3]. In spite of the very promising performance and inexpensive and convenient synthesis procedure [4], studies about M-TCNQ nanowires, especially for the individual one, like its electric states during phase transition and field emission property have rarely been reported.

In the case of Ag-TCNQ, reversible phase transition was induced by an electric field along the TCNQ π stacking direction. The switching took place within around tens of nanoseconds, and the on-off ratio was reported to be as high as 10^4 [5]. An assumption for the mechanism points out that, a partial neutral species of Ag and TCNQ form during the transition, provide additional conduction channels and increase the material conductivity substantially [6]. However, no direct evidence for the existence of neutral Ag or TCNQ in the nanowires after the phase transition has been reported yet. Moreover, for the probability as a field emitter, investigations in the literatures mainly focus on film or arrays of the Ag-TCNQ nanowires. Typical parameters extracted from these reports, such as onset voltage, field enhancement factor and work function, are quite different among these work [7,8].

We have investigated the structures and electric properties of individual Ag-TCNQ nanowires by (in situ) TEM. Procedure for sample preparation in our study follows the previous report in the literature [1]. Figure 1a-b show typical TEM images of the nanowires at different magnifications. The diffraction pattern in Figure 1c is obtained from a bundle of Ag-TCNQ nanowires. All the spots fit well with the orthorhombic Ag-TCNQ phase II structure [9], and a consistent growth along [100] direction can be determined for these nanowires.

In situ electric measurements were performed using an STM-TEM holder from Nanofactory Instruments AB in combination with the aberration-corrected Titan^3 80-300 microscope at the University of Erlangen-Nürnberg. Figure 2a shows the experiment setup. TEM copper grid (with nanowires grown directly onto it) and W tip (commercially available from Bruker) serve as the two electrodes. Contacts are made when an Ag-TCNQ nanowire suspends in between. During the measurement, we are able to stimulate the phase transition of individual nanowires with an external electric field along the tube axis, and track simultaneously any accompanied changes in the sample structure and electric state. Also, effects of electron beam irradiation on sample are taken into consideration. Figure 2b shows the I-V behavior of an individual nanowire with beam centered and shifted away. Significant increase in conductivity is noticed, as the incident electrons helping overcome the Schottky barriers formed at the electrode/nanowire interfaces.
Both experimental and theoretical results will be discussed in this presentation.[10]

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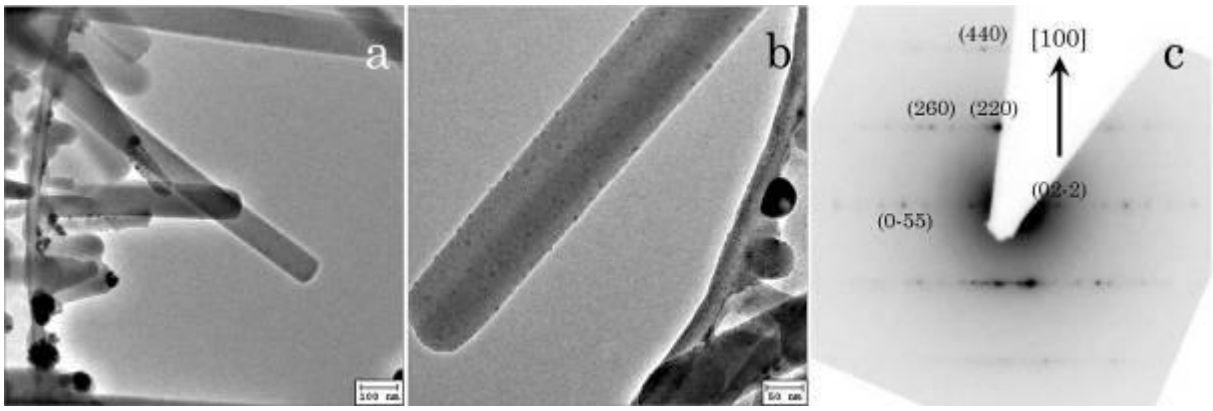

Figure 1. (a-b) TEM images of Ag-TCNQ samples at different magnifications. (c) Diffraction pattern from a bundle of Ag-TCNQ nanowires, reflecting a consistent growth along [100] direction, and indexed by the Ag-TCNQ phase II structure.

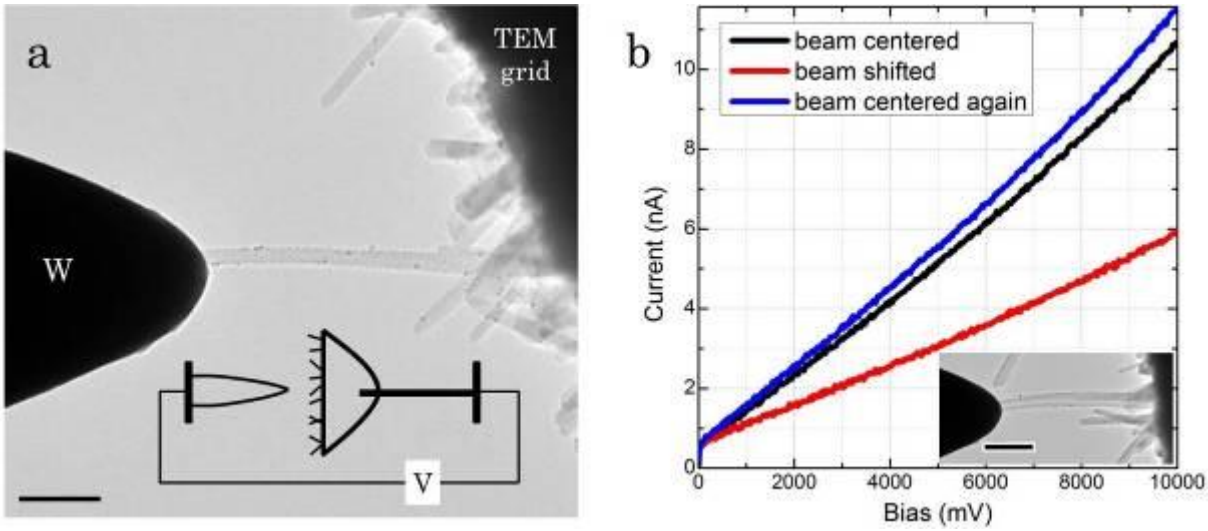

Figure 2. (a) TEM image showing the experiment setup for in-situ measurement, left W electrode, right Ag-TCNQ nanowires protruding from the TEM grid, and one of them contacting the W electrode. Inset is a schematic diagram of the experiment setup. (b) I-V measurements from a single Ag-TCNQ nanowire with electron beam centered and shifted away. Scale bars are 500 nm.