

Investigation of copper-7,7',8,8'-tetracyanoquinodimethane as memory material for resistive switching memories

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Abstract - Copper-7,7',8,8'-tetracyanoquinodimethane (CuTCNQ), is a promising material for memory applications because it can reversibly switch from a high resistance state to a low resistance state by applying external voltage. In this study, CuTCNQ was prepared from the reaction between metallic copper and hot TCNQ gas at low pressure to form nanowires-based memory arrays. Since local variations of structure, microstructure and composition of CuTCNQ may affect the reliability of the future memory device, it is of primary interest to investigate them by transmission electron microscopy. In this work, reference powders of TCNQ and CuTCNQ are first studied, and then followed by TEM experiments on CuTCNQ material integrated in via structures.

1. Introduction

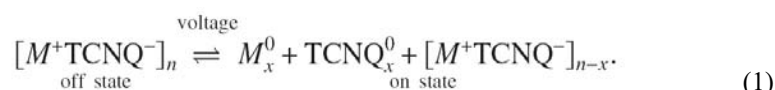
In 1979, Potember *et al.* reported first the electrical field-induced resistive switching in CuTCNQ material [1]. Since then, a significant number of papers dealing with the elaboration methods and general switching characteristics of this metal-organic complex have been published. In contrast, the integration of CuTCNQ material within a microelectronic architecture is recent and opens new possibilities to form low-voltage high-density non-volatile memories [2-3].

The microstructure, structure and thickness of the CuTCNQ films strongly depend on the elaboration method. For instance, Kever *et al.* have produced amorphous films of CuTCNQ by co-deposition of copper and TCNQ while Potember *et al.* formed crystallized CuTCNQ. It has also been demonstrated that crystallized CuTCNQ can exhibit two different crystallographic phases, so-called phase I and phase II (*cf.* Table 1). Besides, although both phases crystallize in a monoclinic symmetry, grains of phase I crystallize with a needle-like morphology while grains of phase II exhibit a platelet-shaped morphology [4].

	Phase I	Phase II
Symmetry	monoclinic	monoclinic
Space group	Pn	P2/n
a, b, c (in Å)	3.888, 11.266, 11.266	5.334, 5.331, 18.875
β (in deg.)	90.00(3)	94.04

Table 1 – Summary of the crystallographic data of CuTCNQ

The switching phenomenon in the case of organic semiconductors such as CuTCNQ is thought to originate in the reversible charge transfer ability of the CuTCNQ complex according to the following reaction [5]:



where M is a metallic donor (*e.g.* Cu) and the TCNQ molecule the acceptor. This charge transfer as origin of the memory effect is largely supported by the fact that the electric field-induced resistive switching of CuTCNQ is not related to the crystalline nature of the material since both crystallized and amorphous CuTCNQ materials exhibit switching phenomena.

First, we will focus our attention on transmission electron microscopy (TEM) study of reference samples, *i.e.* TCNQ powders and CuTCNQ nanowires prepared from the reaction of metallic copper with hot TCNQ gas. Beside, since the solid-gas reaction enables the growth of CuTCNQ nanowires into via structures, TEM experiments were performed on memory arrays in parallel with electrical testing.

2. Second section

TEM experiments on TCNQ powders showed that the samples are electron beam-sensitive, in agreement with previous experiments conducted by Koshino *et al.* on pure TCNQ [6]. In this paper, they addressed the radiation damage issue in the case of TCNQ and F₄TCNQ; indeed, they demonstrated that TCNQ undergoes electron beam-induced crystal degradation and in the case of high doses a mass loss (nitrogen sublimation) with a possible "polymerization" of the structure by cross-linking bonds. In our case, low dose TEM observations on TCNQ were possible as seen in Figure 1. The electron diffraction (ED) patterns are unambiguously indexed in the TCNQ crystallographic structure described by Long *et al.* [7].

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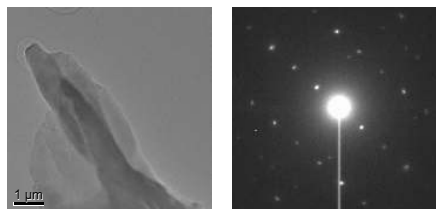


Figure 1 – On the left hand side, low magnification TEM image of TCNQ. On the right, corresponding electron diffraction pattern with a [010] zone axis.

Figure 2-a1 shows the nanowire morphology of the CuTCNQ powders prepared by solid-gas reaction. The diameter of wires is fairly constant, ~ 100 nm, while the length of the wires varies from one to several microns. TEM observations in normal conditions led to the amorphization of CuTCNQ after one or two minutes of study. However, short time/low dose experiments led to diffraction patterns with distances compatible with the CuTCNQ structures [4] (Figs. 2-a2 and 2-a3).

TEM/HREM experiments were performed on CuTCNQ nanowires grown in via structures. Figure 2b presents a TEM cross section of the whole stack with CuTCNQ nanowires with typical diameter of 150 nm on the top of the structure. The TEM sample preparation by Focused Ion Beam FIB was first optimized to improve the quality of images of via structures especially due to the low contrast between CuTCNQ and surrounding SiO₂. The first ED results showed that the CuTCNQ material is amorphous in disagreement with previous x-ray diffraction experiments. It is thought that the sample preparation and/or electron observation may cause such an amorphization. Besides, it has been observed huge reaction between the CuTCNQ nanowires and Pt protective layer during FIB preparation. Pt nanoregions of 2-3 nm were formed on the top of CuTCNQ nanowires, Fig. 2-c.

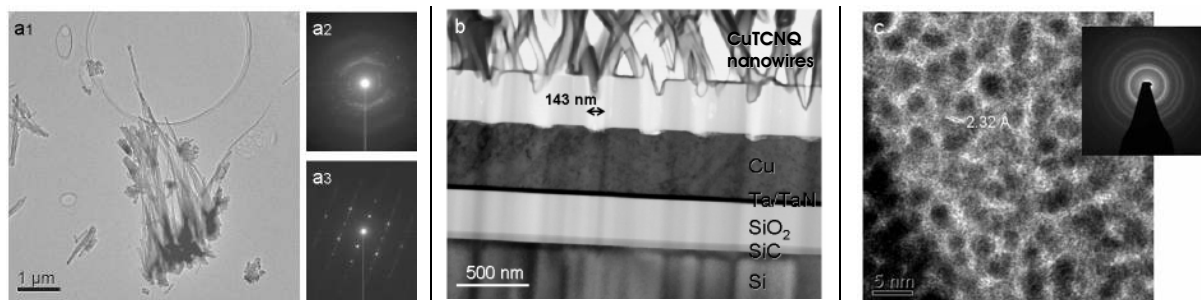


Figure 2 – (a1) TEM image of CuTCNQ nanowires with typical electron diffraction patterns (a2, a3). (b) TEM image of CuTCNQ in via structures. (c) High resolution TEM image in via with in inset the corresponding ED pattern showing the presence of nanosized Pt particles.

3. Conclusion

In the frame of the future generations of memory (*i.e.* resistive switching), CuTCNQ nanowires prepared by solid-gas reaction have to be investigated to anticipate the possible failure mechanisms due to the integration of this material. To do so, TEM is used to gain local information on CuTCNQ microstructure, structure and local composition. Preliminary experiments showed that FIB sample preparation causes the amorphization of CuTCNQ with diffusion of the Pt top protective layer into CuTCNQ nanowires. Besides, as for TCNQ, CuTCNQ undergoes irreversible irradiation damages during the TEM observations. Thus, new sample preparations will be explored in order to obtain artifact free samples. Low dose TEM observations with the use of a cryo-sample holder will be undertaken in order to minimize the irradiation damages.

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4. References

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