

Organic CuTCNQ non-volatile memories for integration in the CMOS backend-of-line: Preparation from gas/solid reaction and downscaling to an area of $0.25 \mu\text{m}^2$

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Abstract

CuTCNQ is an organic semiconductor charge transfer material that allows the realization of non-volatile cross-bar memory arrays with conductivity switching. In this work, we present a simple preparation method of this organic memory material, compatible with industrial processing and downsizing of the memory cells. CuTCNQ nanowires were prepared on Cu by a solid–gas phase corrosion reaction between the metal and hot TCNQ gas at low pressure. Surface coverage increased with reaction time and temperature. Cu/CuTCNQ/Al cross-point cell arrays with memory areas of 0.01 mm^2 exhibited I – V curves with ON/OFF current ratios of about 10. Further downscaling of the CuTCNQ nanowire memory elements was successful on top of $0.25 \mu\text{m}^2$ copper-filled vias. Corresponding memories achieved ON/OFF current ratio of about 100. This is, to our knowledge, the first report on downscaling of organic memories to this size. © 2006 Elsevier Ltd. All rights reserved.

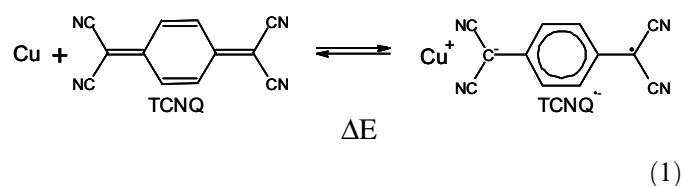
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1. Introduction

Downscaling of actual non-volatile memory technology (Flash) becomes more and more challenging due to physical limitations and increasing processing complexity. Use of resistive-switching materials (Oxide Resistive RAM [1], phase change memory [2], programmable metallization cell [3], ...) combined with nanotechnology is a solution for further scaling. Organic semiconductors are currently investigated as alternative to inorganic (metal-oxide) resistive-switching material for future memory generations.

Films of CuTCNQ, an organometallic semiconductor prepared by corrosion reaction of metallic copper by 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, Eq. (1)), have been referred to as a prototype of a molecular electronic device since the discovery of their bistable reproducible and nanosecond electrical switching (Eq. (2)) by Potember in 1979 [4].



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"OFF" state "ON" state

Most published procedures of CuTCNQ film preparation were based on Potember's original method consisting in a reaction of TCNQ dissolved in acetonitrile with metallic copper [4]. This technique, referred as "spontaneous electrolysis", can be considered as a localized corrosion–crystallization process [5] in which metallic copper is oxidized into Cu^+ cations and TCNQ reduced into TCNQ^- radical anions before precipitating together bluish-black film at the copper surface. Morphology and thickness of the CuTCNQ films prepared from solution [6–9] – as well as from molten TCNQ [10] – can be altered to a high extent by changing experimental conditions [11,12]. In addition to these "wet" methods, CuTCNQ films can also be prepared by "dry" procedures – vapor deposition of TCNQ on Cu [13], alternate vapor deposition of multilayers [7,13,14], and thermal codeposition of TCNQ and Cu [15,16]. Direct vapor deposition of the organometallic semiconductor itself having been reported unsuccessful because of its thermal decomposition at the temperature of evaporation [16]. Strong layer non-uniformity hamper device uniformity and prevent decent yield when integration is done on top of CMOS. Therefore we investigate methods improving layer uniformity.

In this contribution we present a "dry" procedure of CuTCNQ film preparation consisting in corrosion of a Cu substrate by TCNQ vapor at reduced pressure, and report on the downsizing of CuTCNQ memories and electrical conductivity switching of memory elements grown on top of $0.25 \mu\text{m}^2$ copper-filled vias.

2. Experimental

Cu/CuTCNQ/Al cross-bar memory arrays (Fig. 1) with nominal areas of 0.04, 0.02 and 0.01 mm^2 were prepared as described previously [17], using a reaction between Cu and hot TCNQ vapor instead of the *n*-butyronitrile based

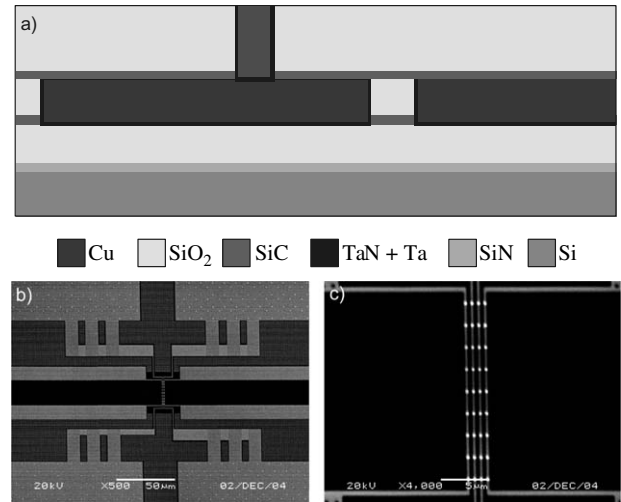


Fig. 2. Test structure for integration in the CMOS backend-of-line (a) cross-section (scheme), (b, c) SEM micrographs: (b) structure with bonding pads (500 \times magnification) and (c) central part with copper-filled vias (white circles) and copper interconnect lines (gray, beneath the SiO_2 layer) to the bonding pads.

"wet" method. The reaction was carried out by a procedure similar as reported for the preparation of AgTCNQ nanowires [18] on silver covered silicon substrates.

Test structures with $0.25 \mu\text{m}^2$ copper-filled vias (Fig. 2, IMEC P-line) were covered by CuTCNQ according to this procedure. Top contacts (Al, 100 nm thickness) were vapor deposited and lithographically patterned.

Electrical measurements were performed under ambient conditions with an Agilent 4156C Precision Semiconductor Parameter Analyzer, using a load resistor in series to the memory element in order to prevent switching to a permanent ON state (Fig. 3). Current–voltage characteristics were recorded by applying the signal to the Al top electrode and the ground to the Cu bottom electrode. CuTCNQ films and memories were characterized by optical microscopy (Olympus AX70) and scanning electron microscopy (Jeol JSV5600LV).

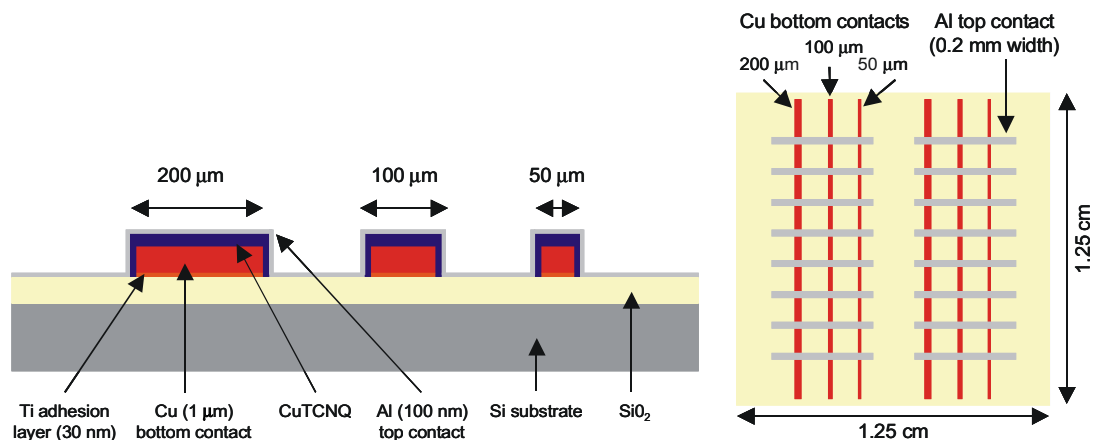


Fig. 1. Section view (left) and top view (right) of the CuTCNQ cross-point cell arrays.

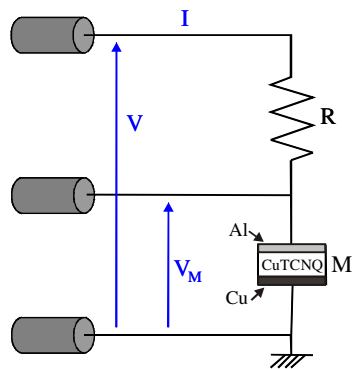


Fig. 3. Measurement setup with variable load resistor (R).

3. Results and discussion

3.1. Cross-bar memory elements from Cu microlines

CuTCNQ films produced by the method described above appeared – with naked eye and by optical microscopy with low magnification ($\leq 20\times$) – as bluish-black, very similar to films prepared by “spontaneous electrolysis” in nitrile solvents (Fig. 4a) [17]. Higher magnification however allows observing a dense layer of needle-like crystals (Fig. 4b).

Scanning electron microscopy (Fig. 5) revealed that the CuTCNQ layer is composed of disordered nanowires and large void areas. Typical nanowires are several micrometers long and have diameters between 150 and 200 nm which decreases at the end below about 40 nm.

Electrical measurements of Cu/CuTCNQ/Al cross-bar memory arrays obtained from these materials showed excellent conductivity switching with an ON/OFF current

ratio of about 10. Starting with a positive voltage applied to the Al top electrode, CuTCNQ organic memories were first in OFF state. After reaching a sufficient negative voltage the memories switched to a high conductive ON state, in which they remained until a sufficient positive voltage was applied in order to switch them back to a low conductivity OFF state (Fig. 6). This behavior is similar to the one described for CuTCNQ memories prepared from a saturated TCNQ solution in hot *n*-butyronitrile [17] and previous reports indicating that the nature of the electric contacts likely play an essential role in the bipolar memory effect [6].

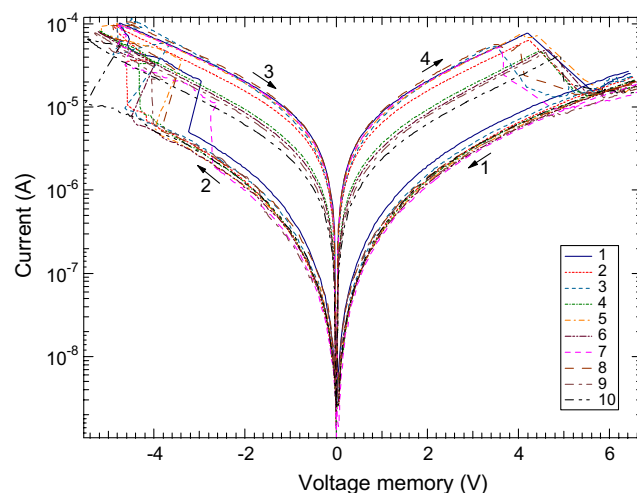


Fig. 6. $\log|I|$ – V curves of a CuTCNQ memory element ($50\ \mu\text{m} \times 200\ \mu\text{m}$, $R = 22\ \text{k}\Omega$) prepared by reaction of Cu microlines with hot TCNQ vapor.

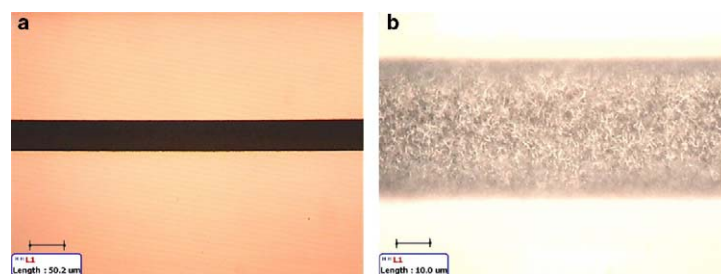


Fig. 4. Optical micrographs of CuTCNQ grown by reaction of vapor phase TCNQ on $50\ \mu\text{m}$ width Cu lines. (a) $20\times$ objective and (b) $100\times$ objective.

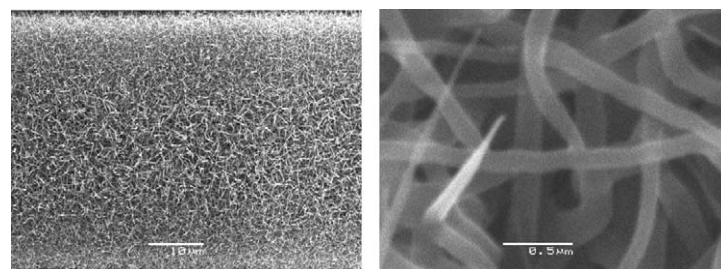


Fig. 5. SEM micrographs of CuTCNQ film prepared on $50\ \mu\text{m}$ width Cu line by reaction with TCNQ gas (left: $2000\times$ magnification and right: $50,000\times$).

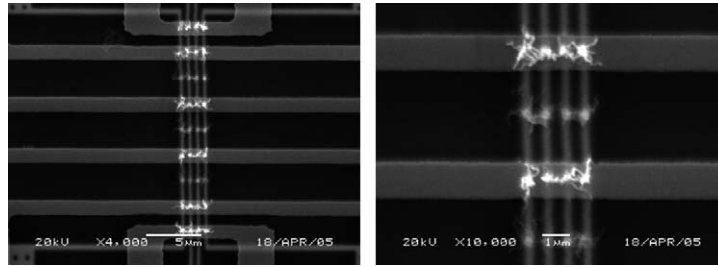


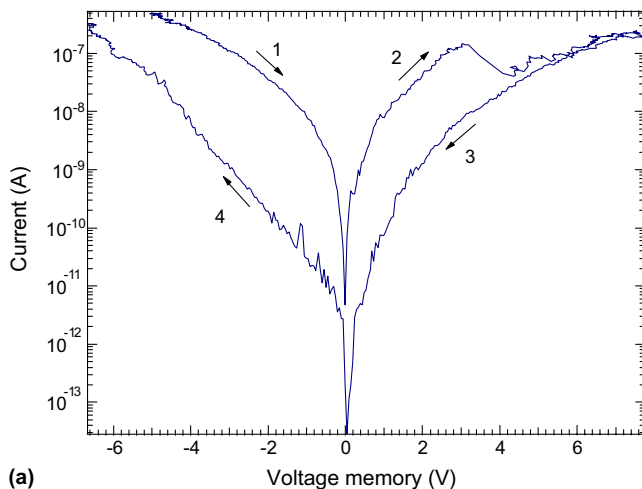
Fig. 7. SEM micrograph of the test structure of Fig. 2a after CuTCNQ growth and deposition of Al top contacts. 4000 \times (left) and 10,000 \times (right) magnification.

3.2. Integration in the CMOS backend-of-line

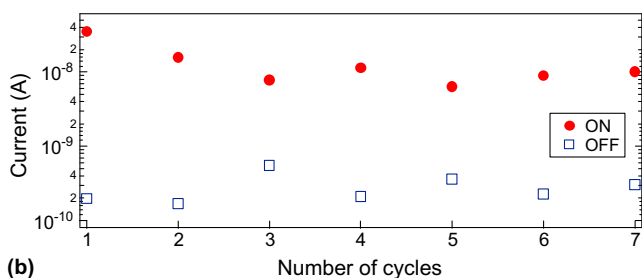
CuTCNQ nanowires were grown from vapor phase TCNQ on top of Cu-filled vias of the test structures shown in Fig. 2. Since downscaling results in an increase of the mass transfer rate (due to additional contribution by radial diffusion), reaction time and temperature were decreased in order to limit growth of CuTCNQ in the space between the memory elements. Top contacts were made by thermal deposition of a thin aluminium layer (100 nm) under high vacuum, followed by photolithographic patterning and etching. SEM micrographs of the cell arrays (Fig. 7) show

that the organic memory material is well covered by the Al top electrodes. Four probe measurements of the electrical resistance on both ends of the top Al electrode (100–200 Ω), as well as on the bonding pads connected to the Cu bottom electrode (10–20 Ω), showed that the voltage drop is negligible at the currents reached during resistive switching of the memory.

Current–voltage curves of Cu/CuTCNQ nanowire/Al memory elements on top of 0.25 μm^2 vias presented conductivity switching with ON/OFF current ratio of about 150 (Fig. 8a). Switching was reproducible several times for prototypes of this kind of memories. Although the ON/OFF current ratios of the consecutive cycles were a little lower than observed during the first write-erase cycle, a clear distinction between the ON and OFF state was always possible at a reading voltage of -2 V (Fig. 8b).



(a)



(b)

Fig. 8. (a) $\log|I|$ – V curve of a CuTCNQ memory element on top of a 0.25 μm^2 copper-filled vias, $R = 10$ M Ω) shown in Fig. 7. (b) ON and OFF reading currents (at a memory voltage of -2 V) recorded during repetitive cycling.

4. Conclusions

CuTCNQ nanowires were prepared by a procedure consisting in reaction of hot TCNQ vapor under low pressure with Cu metal, and used as organic memory material in Cu/CuTCNQ/Al cross-bar memory arrays. Pad-size devices with effective cell areas down to 0.01 mm^2 exhibited conductivity switching with ON/OFF current ratio of 10. Downscaling of the memory cell area was achieved to 0.25 μm^2 copper-filled vias. Results of first prototypes show several write-erase cycles with an ON/OFF current ratio around 100. Work is currently underway to optimize CuTCNQ growth for improving the endurance of the device.

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