Electrodeposition of copper tetracyanoquinodimethane for bipolar resistive switching non-volatile memories

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Electrodeposition experiments of the charge-transfer complex copper tetracyanoquinodimethane (CuTCNQ) (where TCNQ denotes 7,7',8,8'-tetracyanoquinodimethane) on noble metal electrodes (M=Pt and Au) were optimized in order to produce suitable layers for bipolar resistive switching cross-bar M/CuTCNQ/Al memory cells. Corresponding memories exhibited up to more than 10 000 consecutive write/erase cycles, with very stable on and off reading currents and an on/off current ratio of 10. CuTCNQ electrodeposition techniques were furthermore optimized for growing the material in 250 nm diameter contact holes of complementary metal oxide semiconductor dies with tungsten bottom contacts.

Keywords: electrodeposition; copper tetracyanoquinodimethane; non-volatile memories; bipolar switching; template growth; 7,7',8,8'-tetracyanoquinodimethane

1. Introduction

Resistive electrical switching non-volatile memories are currently being investigated for use in future mass storage devices. Various kinds of materials exhibit this behaviour, such as for example inorganic compounds like sulphides, oxides and chalcogenide glasses (Terabe et al. 2002; Seo et al. 2004; Choi et al. 2005; Kaeriyama et al. 2005; Kozicki et al. 2005; Lin et al. 2007; Tsunoda et al. 2007), as well as organic materials (Potember et al. 1979; Bandyopadhyay & Pal 2003; Ma et al. 2003; Bozano et al. 2005; Caironi et al. 2006; Cölle et al. 2006; Joo et al. 2006; Weitz et al. 2006; Choi et al. 2007; Paul 2007; Verbakel et al. 2007; Erlbacher et al. 2008).

Aiming at the integration of emerging memory materials in nanometre-sized contact holes in complementary metal oxide semiconductor (CMOS) wafers, in 2004 IMEC started to investigate the charge-transfer complex
Figure 1. (a) Schematic side view of a Cu CMOS wafer with vias; (b) scanning electron microscopy (SEM) top view of a Cu CMOS die with 250 nm vias after extensive exposure to a TCNQ solution in CH$_3$CN.

copper tetracyanoquinodimethane (CuTCNQ) (where TCNQ denotes 7,7',8,8’-tetracyanoquinodimethane) as a potential candidate. This material, known since 1979 to display resistive electrical switching (Potember et al. 1979) in Cu/CuTCNQ/Al memory cells, is typically prepared by a spontaneous oxidation–reduction reaction of metallic Cu with neutral TCNQ in acetonitrile (CH$_3$CN, ACN) solution (Potember et al. 1979) or in the gas phase (Müller et al. 2006a) (where s, l and g denote, respectively, the solid, liquid and gas phase):

$$\text{Cu}^{(s)} + \text{TCNQ}^{(l,g)} \rightarrow \text{Cu}^{+} \text{TCNQ}^{-}^{(s)}.$$  (1.1)

This reaction allows the material to be grown directly from the bottom of nanometre-sized contact holes (vias) of Cu CMOS wafers (figure 1a) (Müller et al. 2006b; Santamaría-Prado 2006). A drawback, however, is that the Cu metal of the bottom contact is consumed during the growth process. For integration of CuTCNQ in vias of Cu CMOS wafers, this uncontrolled corrosion could lead to inhomogeneity in CuTCNQ layer thicknesses as well as to damage of the Cu interconnect lines (figure 1b). Other, well-established deposition methods of organic materials that could avoid this issue cannot be applied to CuTCNQ. Spin coating is impossible because of the low solubility of the organic salt (its solubility in the ‘good’ solvent ACN, calculated from the solubility product (Harris et al. 2005), is only 0.037 ± 0.013 mg ml$^{-1}$). Vapour deposition of CuTCNQ is also not possible because the material decomposes under high vacuum before evaporation (Tamada & Omichi 1994). Finally, coevaporation of Cu and TCNQ or alternate deposition of thin layers of both reagents can lead to smooth CuTCNQ films (Oyamada et al. 2003; Kever et al. 2006), although perfect matching of the 1:1 stoichiometry between Cu and TCNQ is challenging, and integration in vias might be difficult. In this paper, we report on electrodeposition of CuTCNQ for non-volatile memory applications, a method that can be considered as the liquid-phase analogue of coevaporation. Electrodeposition has the following advantages inherent to electrochemical methods: (i) it can, in principle, be applied to grow CuTCNQ on all kinds of conductive substrates, (ii) no significant amount of CuTCNQ is deposited on insulating layers, and (iii) the quantity of electrodeposited material can be controlled by the electrical charge.
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2. Principle of copper tetracyanoquinodimethane electrodeposition

Deposition of conductive organic charge-transfer complexes like CuTCNQ can be performed by electrocrystallization, ‘a process involving electrochemical conversion of a reagent into an ionic species capable of forming a precipitate via condensation with a second reagent at the working electrode’ (Ward 1989). For depositing CuTCNQ, the required ionic species are the Cu$^{+}$ cation and the TCNQ$^{-}$ anion. Electrocrystallization of CuTCNQ occurs when the product of the local concentrations of both species at the electrode/solution interface exceeds a constant $K_s$ called the solubility product:

$$[\text{Cu}^+] \times [\text{TCNQ}^-] > K_s. \quad (2.1)$$

When this condition is fulfilled, the solution is (locally) supersaturated and electrodeposition of CuTCNQ at the electrode can occur. Shields (1985) already electrocrystallized CuTCNQ on a Cu electrode in 1985 by electrolysing a TCNQ solution in ACN between two Cu electrodes. Under these experimental conditions, Cu is oxidized to Cu$^+$ cations (coordinated by ACN; Irangu & Jordan 2003; Weitz et al. 2007) at the anode and TCNQ is reduced to TCNQ$^-$ at the cathode. In the presence of the electric field both ions migrate to the oppositely charged electrode where the local concentrations exceed the solubility product and lead to ‘hair-like dendritic’ CuTCNQ deposition (Shields 1985). More recently, researchers of Bond’s group electrodeposited CuTCNQ on Au, Pt and carbon (Harris et al. 2005), as well as indium tin oxide and boron-doped diamond substrates (O’Mullane et al. 2006), from a solution containing Cu(CH$_3$CN)$_4$PF$_6$, TCNQ and $n$-(C$_4$H$_9$)$_4$N$^+$PF$_6^-$ as supporting electrolyte. In their process, a constant potential was applied to the substrate, which is the working electrode in a conventional three-electrode cell (Bard & Faulkner 2001). By polarizing this electrode so negatively that TCNQ is reduced to TCNQ$^-$, but Cu$^+$ is not reduced to metallic Cu, the local Cu$^+$ and TCNQ$^-$ concentrations exceed the solubility product of CuTCNQ, resulting in electrodeposition of the charge-transfer complex. Initial electrocrystallization experiments lead to the growth of well-spaced large dendritic-type crystals, formed by rapid CuTCNQ growth at preferred sites (defects) of the surface (Harris et al. 2005; O’Mullane et al. 2006). Later, the same group reported that CuTCNQ electrodeposition can occur by two slightly different mechanisms, the first leading to the above-mentioned dendritic growth, and the second, performed at a slightly more negative potential (or at a higher current density), giving rise to an extensive coating of small crystals on all sections of the electrode, but not within the diffusion field of the initially formed larger dendritic crystals (Harris et al. 2006). As the presence of conductive areas uncovered by CuTCNQ will probably give rise to short circuits in corresponding metal/CuTCNQ/metal memory elements (by direct contact between the top and bottom contacts), the two CuTCNQ growth processes are not directly suited for memory cells.

Our method for CuTCNQ electrodeposition was inspired by a prior work published by Shields (1985) and Neufeld et al. (2003). The latter prepared CuTCNQ by the electrochemical reduction of (solid) TCNQ microparticles adherent to a glassy carbon electrode in contact with aqueous CuSO$_4$ electrolyte. In order to prepare a solution for CuTCNQ electrodeposition comprising all
required constituents, we replaced water by ACN (a good solvent for TCNQ) and CuSO₄ by copper(II) trifluoromethanesulphonate (an ACN-soluble Cu²⁺ salt). As Cu²⁺ cations are generally less reactive towards oxygen and water than are Cu⁺ cations, their use should increase the stability of the solution. Furthermore, a small quantity of supporting electrolyte \((n\text{-C}_4\text{H}_9)_4\text{N}^+\text{PF}_6^-\) was added to the medium in order to assure electrical conductivity. For this composition, CuTCNQ electrodeposition, depicted in figure 2, can be summarized by the following equation, in which \(\text{org}\) represents the organic liquid phase (ACN):

\[
\text{TCNQ}^{\text{(org)}} + \text{Cu}^{2+\text{(org)}} + 2e^- \rightleftharpoons \text{Cu}^+\text{TCNQ}^{\text{−(s)}}. \tag{2.2}
\]

3. Experimental details

Typical electrodeposition experiments were carried out in unstirred ACN containing 4 mM copper(II) trifluoromethanesulphonate, 4 mM TCNQ and 4 mM \((n\text{-C}_4\text{H}_9)_4\text{N}^+\text{PF}_6^-\), using a two-electrode cell configuration (Bard & Faulkner 2001a). Electrodeposition was realized with a Princeton Applied Research potentiostat/galvanostat (Model 273) under manual control, allowing the experiments to be stopped for a given electrical charge (typically 100–400 mC). Substrates \((1.25 \times 1.25 \text{ cm Si/100 nm SiO}_2 \text{ with 10 interconnected 200 \text{ μm wide, 10 mm long and 100 nm thick Au or Pt lines})} were polarized negatively towards a platinum-covered silicon die \((1.25 \times 1.25 \text{ cm})\) serving as a counterelectrode. After CuTCNQ electrodeposition, Al top contacts \((200 \text{ μm width, 100 nm thickness})\) were evaporated through a shadow mask perpendicular to the CuTCNQ-covered noble metal lines in order to obtain cross-bar memory arrays. Electrical characterization of the memory cells was performed by a Keithley 2602 source-measure unit controlled via a Labview program. Memory elements were probed by voltage scans from 0 V to a lower limit \(V_-\), then to an upper limit \(V_+\) and finally back to 0 V. The signal was applied to the Al top contact; the noble metal bottom contact served as ground. During all the experiments (carried out in ambient), the memories were protected by a load resistor against overcurrent, and both
4. Results and discussion

(a) Influence of CuTCNQ electrodeposition conditions on the layer morphology and resistive electrical switching properties of the memories

The optimal voltage range for electrodeposition of CuTCNQ on the noble metal substrates was determined by constant voltage experiments. Electrodeposition of dark-blue CuTCNQ layers occurred at voltages of around $-3$ to $-4$ V for the solution composition mentioned in §3. SEM micrographs revealed that the layer was composed of large dendritic crystals embedded in a much more compact film of submicrometre-sized crystals (figure 3).

Corresponding Pt/CuTCNQ/Al and Au/CuTCNQ/Al cross-bar memory cells exhibited CuTCNQ typical non-volatile memory behaviour. At the beginning of the voltage scan (0 V), the memories were in a low-conductivity off state. By scanning towards the negative limit ($V_-$), they switched to a high-conductivity on state in which they remained until a sufficiently positive voltage was applied during the scan towards the positive limit ($V_+$). This cycling could typically be repeated 10 to 1000 times before the memory remained permanently in either the on or the off state. No influence of the nature (and workfunction) of the bottom electrode metal (Pt and Au) on the electrical switching properties of the memory cells could be observed. This is in agreement with the present view of the switching mechanism in which the switching process itself occurs in a native aluminium oxide layer at the interface between the CuTCNQ and the Al top contact (Billen et al. 2007; Müller et al. 2008).

In order to improve the quality of the CuTCNQ layer, we considered optimizing the voltage signal applied during the electrodeposition step. It is well known from potential step (‘chronoamperometric’) experiments in electrochemistry (Cottrell 1903; Bard & Faulkner 2001b) that a concentration
gradient develops at the electrode/solution interface as a function of the time: the local concentrations of the reagents Cu$^{2+}$ and TCNQ decrease from their bulk values to macroscopically zero at the interface. Figure 4 depicts the theoretical concentration profiles for a species (with a diffusion coefficient of $1 \times 10^{-5}$ cm$^2$ s$^{-1}$, which is of the same order of magnitude as those of Cu$^{2+}$ and TCNQ in ACN at room temperature) during the first second of a potential step experiment (Bard & Faulkner 2001b). As shown, the diffusion layer extends more and more into the solution as a function of the time, so that after 1 s the concentration at 1 µm distance from the electrode is less than 2 per cent of the bulk concentration.

For electocrystallization experiments of conductive crystals like CuTCNQ (CuTCNQ phase I has a room-temperature conductivity of 0.25 S·cm$^{-1}$; Heintz et al. 1999), this signifies that the tips of the crystals initially grown at the electrode are always in the presence of higher reagent concentrations than in the presence of new nucleation sites at the electrode/solution interface. Therefore, the growth of existing crystals is favoured with respect to nucleation, as already reported by Harris et al. (2006) for electrodeposition of CuTCNQ from a Cu$^+$ and TCNQ-containing ACN solution.

In order to avoid this preferential growth of the first crystals and improve the homogeneity of CuTCNQ layers, we investigated electrodeposition under pulsed voltage conditions. The signal applied by the potentiostat consisted of short voltage pulses interrupted by rest periods at open circuit potential. Compared with constant voltage electrodeposition, the rest periods allow replenishment of the electrode/solution interface by diffusion of Cu$^{2+}$ and TCNQ$^-$ ions from the bulk towards the electrode before applying the next voltage pulse. As large concentration gradients were expected to provoke the preferential growth of initially formed CuTCNQ crystals, pulsed voltage electrodeposition should lead to improved layer homogeneity. Corresponding experiments were performed with sequences of 100 ms short voltage pulses (the shortest pulse length available with the PAR273 potentiostat) at $-4$ V, separated by rest periods of, respectively, 100, 200 and 300 ms. SEM micrographs of the electrodeposited CuTCNQ layers confirmed that this method allows us to grow several micrometres thick CuTCNQ films with improved homogeneity compared with constant voltage electrodeposition (figure 5). The most compact CuTCNQ layers were obtained...
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Figure 5. SEM (a–c) top and (d–f) side views of CuTCNQ electrodeposited by voltage pulses on Pt lines. Plating pulse: 100 ms; rest periods: (a,d) 100 ms, (b,e) 200 ms, (c,f) 300 ms.

For sequences with both 100 ms voltage pulses and rest periods (figure 5a); longer rest periods (figure 5b,c) lead to an increased number of voids within the layer. Partial redissolution of CuTCNQ during the rest periods might be the origin of these voids.

Extensive electrical cycling of the memory elements prepared from electrodeposited CuTCNQ with 100 ms pulse and rest period length showed good resistive switching properties, with an endurance of up to more than $10^4$ write/erase cycles (figure 6a,b) within 57 h of continuous operation. During these cycles, the typical on/off current ratio was 10, and the threshold voltages (defined as the voltage at which the highest change in conductivity was recorded) remained quite stable (figure 6b,c).

Although the thickness of electrodeposited CuTCNQ layers (several micrometres) was much higher than that of coevaporated CuTCNQ (typically 50–300 nm) (Oyamada et al. 2003; Kever et al. 2006), the required threshold voltages did not seem to scale with it. This is in agreement with papers reporting that bipolar resistive electrical switching does not occur in the bulk of the charge-transfer complex, but at the CuTCNQ/Al interface (Oyamada et al. 2003; Billen et al. 2007; Kever et al. 2007; Hefczyc et al. 2008). According to our current view, the switching process involves bridging of an ion-permeable ‘switching layer’ (for example, within pores of the native aluminium oxide at the CuTCNQ/Al interface) by conductive copper channels, resulting from electrochemical reduction of Cu$^+$ ions provided by the solid ionic conductor CuTCNQ (Billen et al. 2007; Müller et al. 2008). Further studies are required in order to elucidate whether the enhanced switching properties of electrodeposited CuTCNQ-based memory cells are related to an improvement in the Cu$^+$ ion transport within the material or in the switching layer at the CuTCNQ/Al interface.
Figure 6. (a) Log $|I|$–$V$ curves for an Au/CuTCNQ/Al memory: solid line, cycle 1; dashed line, cycle 5000; dotted line, cycle 10 000. (b) On and off currents at $-1$ V across the memory element: filled circles, on; open squares, off. (c) Threshold voltages as a function of the cycles: open squares, on $\rightarrow$ off; closed circles, off $\rightarrow$ on.

Figure 7. SEM top view of CMOS dies with W bottom contact and 250 nm via size (a) before and (b, c) after CuTCNQ electrodeposition under (b) pulsed and (c) constant voltage.

(b) Electrodeposition of CuTCNQ in sub-micrometre sized contact holes

Electrodeposition of CuTCNQ in 250 nm diameter vias (330 nm height) was investigated on blanket W dies (figure 7a) of similar structure as depicted in figure 1a. Under pulsed voltage conditions, CuTCNQ particles were deposited outside the vias (figure 7b). This might be attributed to the diffusion of
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electrogenerated Cu\(^+\) and TCNQ\(^-\) from the W electrode at the bottom of the vias to the outside of the contact hole during the rest periods. Performing electrodeposition under constant voltage (−3 V) resulted in good filling of the vias with CuTCNQ as depicted in figure 7c. Compared with the growth of CuTCNQ nanowires in vias of Cu CMOS wafers (Müller et al. 2006b), the electrodeposition of CuTCNQ seems to produce a more homogeneous filling with much less void space within the vias.

As electrodeposition of CuTCNQ by this method avoids corrosion of the bottom contact metal, the procedure might be very useful for future integration experiments of CuTCNQ and related charge-transfer complexes in CMOS wafers.

5. Summary

Compact CuTCNQ layers of several micrometres thickness were prepared by pulsed voltage electrodeposition of the material on Au and Pt lines. Corresponding cross-bar memory cells with evaporated Al top contacts achieved more than 10 000 write/erase cycles within 57 h of continuous operation with very stable on and off reading currents and threshold voltages. Furthermore, CuTCNQ electrodeposition in 250 nm vias of CMOS dies with W bottom contact was achieved. The scientific and technological challenge now consists in optimizing and combining both parts with the goal to produce high-endurance CuTCNQ-based memory cells integrated in submicrometre vias.

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References


