Direct electroplating of copper on tantalum from ionic liquids in high vacuum: origin of the tantalum oxide layer

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In this paper, it is shown that high vacuum conditions are not sufficient to completely remove water and oxygen from the ionic liquid 1-ethyl-3-methylimidazolium chloride. Complete removal of water demands heating above 150 °C under reduced pressure, as proven by Nuclear Reaction Analysis (NRA). Dissolved oxygen gas can only be removed by the use of an oxygen scavenger such as hydroquinone, despite the fact that calculations show that oxygen should be removed completely by the applied vacuum conditions. After applying a strict drying procedure and scavenging of molecular oxygen, it was possible to deposit copper directly on tantalum without the presence of an intervening oxide layer.

1 Introduction

Ionic liquids are solvents that entirely consist of ions. They are interesting electrolytes for electrodeposition of reactive metals because of their wide electrochemical window and their intrinsic electric conductivity.1–3 All ionic liquids, even the most hydrophobic ones, readily absorb water from the air4,5 as they are composed of ions and hence are polar. This absorbed water has a strong influence on the viscosity and it will reduce the electrochemical window of the ionic liquid.5–12 Therefore, ionic liquids that are used for electrochemical studies need to be carefully dried. A typical drying procedure is to heat the ionic liquid in vacuo, with or without stirring. Heating of ionic liquids in vacuo is also effective for degassing. An alternative method for drying ionic liquids is by electrolytic decomposition of dissolved water.13 In many cases, these drying and degassing procedures are not sufficient to lower the concentrations of dissolved water and oxygen gas to levels at which they no longer influence the electrochemical properties of reactive species.

We recently showed that electrodeposition can be performed under high vacuum conditions (4 × 10⁻⁶ mbar) from ionic liquids because of their negligible vapor pressure.14 Electrochemical vacuum deposition (EVD) was used for the electrodeposition of copper on a tantalum electrode. The rationale for using such conditions was to avoid the presence of water and oxygen gas that could lead to passivation of the tantalum substrate.

Despite the low pressures involved, the copper–tantalum interface showed a 4–5 nm thick layer of tantalum oxide. In this paper we present the results of the research towards the origin of this oxide layer. The possibility of direct deposition of copper, the contact material, on a tantalum barrier is of great importance for the microelectronics industry i.e. in state-of-the-art wafer technology, a barrier layer of Ta/TaN prevents the diffusion of copper into the silicon dioxide or dielectric and eventually into the silicon.15–17 Presently, the copper layer is fabricated via a two-step process. First, a copper seed layer is grown by Physical Vapor Deposition (PVD) and this layer protects the underlying tantalum against oxidation. On top of this seed layer, copper is deposited electrochemically from an aqueous copper(II) sulfate solution until the desired thickness is reached. For through-silicon-vias (TSV), the fabrication of the copper seed layers through vapor techniques is troublesome because of the high aspect ratio, resulting in an uneven distribution of the vapor deposited copper. This leads to further difficulties in the subsequent electrodeposition from aqueous solution. Hence, direct copper electrodeposition without the need of a seed layer can result in a major advancement.

We investigated the origin of the oxygen atoms that cause the formation of the tantalum oxide layer, during the electrodeposition in high vacuum. Different sources of oxygen are considered: residual water, residual oxygen gas, or oxygen from oxygen-containing species in solution. It will be shown how Nuclear Reaction Analysis (NRA) can be used to detect tiny amounts of oxygen atoms on a tantalum electrode.

2 Experimental

1-Ethyl-3-methylimidazolium chloride (99.5%), [C₃mim]Cl, was purchased from IoLiTec. Cu(Tf₂N)₂ was prepared by dissolving an excess of CuO (99%) in an 80% aqueous...
solution of H(Tf₂N) (bought from IoLiTec, 99%). The remaining CuO was filtered off and the water evaporated under reduced pressure. Before use, appropriate amounts of Cu(Tf₂N)₂ and the liquid ion were mixed and dried in vacuo (6 × 10⁻⁶ mbar) at 120 °C. H₂¹⁸O (97%) was purchased from Isotec™. Electrochemical experiments were conducted using a EG&G Princeton Applied Research potentio-stat/galvanostat. The electrochemical cell (5 cm³) was a home-made copper crucible which also served as a counter electrode. By using a copper crucible, the equilibrium of the comproportionation reaction Cu + Cu²⁺ ⇌ 2 Cu⁺ was maintained. The crucible was placed in the vacuum chamber and the pressure was reduced below 4 × 10⁻⁶ mbar. A polyimide Thermofoil heater was used to maintain the temperature at 90 °C. The working electrodes were cut from silicon wafers covered with SiO₂ − 10 nm TaN − 40 nm Ta − 150 nm Cu. These electrodes were pretreated by rinsing with acetone, immersing in a 1:1 mixture of demineralized water and HCl, and finally rinsed with demineralized water and ethanol and dried. Before the actual deposition experiment, the copper top layer was electrochemically stripped at +0.1 V for 400 s. This caused the tantalum layer to be exposed to the solution. Next, copper was deposited again at a deposition potential of −2.0 V. All potentials mentioned are relative to a copper pseudo-reference electrode.

Thin lamellas for transmission electron microscopy (TEM) investigations were prepared via a NOVA 200 (FEI) dual beam system combining a focused ion beam (FIB) and a scanning electron microscope (SEM). Lamellas were prepared in standard lift out geometry and were subsequently transferred with a micromanipulator (Omniprobe) to TEM grids (Omniprobe). To prevent lamella bending, a window milling technique was applied during the pre-thinning procedure, followed by a low energy cleaning step at 5 kV and 70 pA at an angle of 5° on both sides to reduce amorphized surface layers. All TEM investigations were performed at 200 kV on a Tecnai T20 FEI/STEM, equipped with a Gatan Quantum EELS spectrometer. For imaging, bright field phase contrast techniques were applied, whereas for the chemical analysis, the system was set up in scanning TEM mode, employing a beam diameter of approximately 0.5 nm, a beam convergence of about 10 mrad and a collection angle of 15 mrad.

In order to assess the oxygen content in the ionic liquid, Nuclear Reaction Analysis (NRA) was applied. To this end, we relied on the ¹⁸O(p,γ)¹⁹N nuclear reaction which exhibits a sharp resonance at a proton energy of 629 keV. In order to avoid any possible effects from surface contamination, a beam energy of 730 keV was selected. Due to this higher energy, the ¹⁸O concentration was probed at a depth of approximately 3 μm. The samples were measured in the Ion and Molecular Beam Laboratory using a tandem Pelletron S5DH-2 accelerator by NEC. The emitted x particles were detected with a Canberra PIPS (Passivated Implanted Planar Silicon) detector at an angle of 24° away from the incident beam.

3 Results and discussion

1-Ethyl-3-methylimidazolium chloride, [C₂mim]Cl, was selected as the ionic liquid for copper deposition because chloride-based ionic liquids are good solvents for electroplating additives. These additives were necessary for obtaining a satisfactory morphology of the deposit. Many ionic liquids with the bis(trifluoromethylsulfonyl)imide anion ([Tf₂N]⁻) are poor solvents for these additives, which are often ionic compounds that need to be dissociated in order to dissolve. Ionic liquids with chlorine anions are better suited for this task due to the complex forming ability of the chloride ions. As source of copper, Cu(Tf₂N)₂ was used. The advantage of using Cu(Tf₂N)₂ compared to CuCl₂ is that the [C₂mim]Cl–Cu(Tf₂N)₂ liquid is less viscous than the [C₂mim]Cl–CuCl₂ liquid.

In our previous attempts to deposit copper directly on a tantalum substrate, an oxide layer was always found at the Cu–Ta interface. This oxide layer must originate from either of the following sources: (1) oxygen gas dissolved in the electrodeposition bath, (2) water that, despite the drying procedure, remains in solution, (3) oxygen atoms of the solvent, for instance the oxygen atoms of the [Tf₂N]⁻ anion.

The presence of oxygen gas in ionic liquids under high vacuum conditions was refuted on theoretical grounds. In an earlier paper, the amount of oxygen gas that can react with the substrate was calculated based on Fick’s second law of diffusion. In this calculation, the partial pressure pO₂ of O₂ over the ionic liquid was used to find an estimate of the bulk concentration of O₂ in the ionic liquid. This relationship is given by the Henry coefficient Hₐ₁:

\[ p_{O₂} = H_{O₂} X_{O₂} \]  

where \( X_{O₂} \) is the molar fraction of O₂ in the ionic liquid. This calculation was made for 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMP][Tf₂N]) because the Henry coefficient was not available for [C₂mim]Cl. Fig. 1 shows the amount of O₂ that can be transported by diffusion to the electrode and that can consequently convert the tantalum metal into tantalum oxide. This amount is given by integrating the flux \( J \) found by Fick’s diffusion law (with \( D_{O₂} \) the diffusivity

![Fig. 1](http://pubs.rsc.org/en/content/articlelanding/2012/cp/c2cp41786c#!content/abstract)
for $O_2^{-20}$ and $c_{O_2}$ the concentration of $O_2$, calculated from $x_{O_2}$):\[
\int_0^t J(\tau) d\tau = 2c_{O_2} \frac{D_{O_2}}{\pi} (2) \]

The available amount is about eight orders of magnitude smaller than the amount that is required for the formation of one monolayer of tantalum(\textit{v})oxide (see right vertical axis). This calculation therefore indicates that the influence of residual oxygen gas in the ionic liquid on the oxidation of the tantalum layer should be negligible.

A second possible source of oxygen is water. Normally, the amount of water in ionic liquids is determined by Karl Fischer titration. However, the remaining amounts of water in the ionic liquid (<1 ppm) are below the detection limit of the coulometric Karl Fischer technique. Therefore we selected a more sensitive characterization technique for measurement of the water content of the ionic liquid, i.e. Nuclear Reaction Analysis (NRA), taking advantage of the nuclear reaction $^{18}O(p,\alpha)^{15}N$. In this method, an $^{18}$O-containing surface layer is irradiated with a 730 keV proton beam. A proton that collides with a $^{18}$O nucleus will induce a reaction to a $^{15}$N nucleus along with emission of an alpha particle. Hence, the number of emitted alpha particles is a direct measure of the number of $^{18}$O atoms present in the surface layer of the substrate. The strength of this approach is (1) its high sensitivity, which allows us to detect minute amounts of oxygen, and (2) the fact that the reaction only occurs for the $^{18}$O isotope whereas it is blind to $^{16}$O. To detect whether the oxidation of the tantalum substrate is caused by remaining traces of water, the ionic liquid solution was spiked with $^{18}$O-enriched water. The natural abundance of $^{18}$O is 0.21%, whereas the added water contained 97% of $^{18}$O. This radioanalytical technique has been used by other authors to track the ion transport mechanism in the growth of oxide films with $^{18}$O as a tracer,\textsuperscript{21,22} to study the source of oxygen during anodic oxidation,\textsuperscript{23} or the growth laws of oxide films.\textsuperscript{22,24} More details on the detection of small quantities of isotopes of oxygen (but also nitrogen and fluorine) are given in the literature.\textsuperscript{18,25} The flowsheet for the NRA experiments is given in Fig. 2. First, a solution of 0.5 mol dm$^{-3}$ of $\text{Cu(Tf}_2\text{N)}_2$ in $[\text{C}_2\text{mim}]\text{Cl}$ was prepared. This mixture was heated to 120 °C in low vacuum ($6 \times 10^{-2}$ mbar) to remove the bulk water and crystal water of the copper salt. Next, 10 vol% of $H_2^{18}O$ was added to this mixture, so that almost all water in solution is enriched in the $^{18}$O isotope. Thereafter it was stirred for several days in a glass flask with copper foil to transform $Cu^{2+}$ into $Cu^{+}$, by a comproportionation reaction, because $Cu^{+}$ ions are more stable than $Cu^{2+}$ ions in the ionic liquid $[\text{C}_2\text{mim}]\text{Cl}$. A first series of electrochemical experiments was done in this solution (undried solution). Subsequently, this solution was put in high vacuum ($< 4 \times 10^{-6}$ mbar) at 90 °C overnight. This temperature was chosen as it was the standard temperature for the electrochemical experiments. The second run of electrochemical experiments was performed using this solution (standard drying procedure). For a third run, the solution was heated overnight to 150 °C (adjusted drying procedure). The number of detected $\alpha$ particles is given in Fig. 3. Every data point is the average of at least three measurements. The experimental error range of one individual measurement is given by

\[
\text{error} = \frac{\#\text{counts}}{1 \pm \sqrt{\#\text{counts}}} (3) \]

The plotted experimental error is the average of the experimental errors, divided by $\sqrt{n}$, in which $n$ is the number of experiments performed.

The undried sample showed a high number of counts: 149 ± 7. This was to be expected because the solution contained 10 vol% of $H_2^{18}O$ so that the tantalum could easily be oxidized as soon as it was exposed to the solution. When the solution was subjected to the standard drying procedure (120 °C at low vacuum ($6 \times 10^{-2}$ mbar) for 8 hours), the number of NRA counts of the electrodeposits decreased significantly to 39 ± 4, yet it was still higher than the $^{18}$O background (27 ± 2 counts). The background signal originates from the $^{18}$O present in the underlying thermal SiO$_2$ layer of the wafer pieces. This clearly indicates that not all water was removed from solution, although bulk water would have evaporated under these circumstances (the vapor pressure of water at 90 °C is 701 mbar\textsuperscript{26}), the water that remained in solution no longer acts as having the properties of bulk water. It is assumed that all water molecules interact with the ions of the ionic liquid. It has been reported

![Fig. 2 Drying procedure and sampling.](image-url)

![Fig. 3 Number of counts as a function of drying procedure. See also Fig. 2 for an explanation of the drying procedures.](image-url)
earlier\textsuperscript{12,27} that for low concentrations, water is in a special state: the hydrogen bonds are perturbed or even broken by the strong electric field of the ions, whereas free water is present only when the water concentration is higher than 50 mol\%. When the temperature was increased to 150 °C, the measured NRA counts dropped to 30 ± 3, which is within the error equal to the background signal, and one can conclude that the concentration of water in the ionic liquid was undetectably low. The consequences of these results cannot be underestimated. It means that if one wants to use materials that are highly water sensitive, such as tantalum substrates, in ionic liquids, a strict drying procedure is indispensable. Simply drying in low vacuum ($\geq 10^{-1}$ mbar) and/or only moderately heating is not sufficient to achieve a truly dry ionic liquid.

From the results of the previous paragraph, it was known under which conditions water could be removed. The next step in preventing oxidation of the copper-tantalum interface was to avoid oxidation by one of the constituents of the electrodeposition bath. In order to do this, oxygen-containing [Tf$_2$N]$^-$ anions were replaced by chloride as counter ions for Cu$^{2+}$ and Cu$^+$, and Janus Green B (JGB, Fig. 4) was selected as an additive to improve the morphology. Adding JGB gave smooth copper deposits without open grain boundaries. Such open grain boundaries can result in post-deposition oxidation of the Cu-Ta interface so that it becomes impossible to determine the origin of the oxide layer. Moreover, despite all these efforts, TEM analysis still showed the presence of an oxide layer between the copper layer and the tantalum substrate (Fig. 5).

For the characterization of the oxide interface two approaches have been considered. First, a quantitative compositional EELS (electron energy loss spectroscopy) analysis was carried out, employing experimentally determined inner-shell ionization cross-sections from standards. For this, cross-sections were measured from a pre-fabricated Ta$_2$O$_5$ thin-film that was characterized by EDX and electron diffraction. In a second step these EELS spectra were converted $via$ a differential oscillator strength to the angular conditions used for the investigation of the unknown oxide. Several EELS spectra from the interface have been recorded and the oxygen K-edge and tantalum M$_{45}$-edges were analyzed by stripping of an oxide layer between the copper and tantalum layers and is indicated by an arrow.

The intensity variations within the first ~40 eV of the oxygen edge with multiple scattering calculations. For this purpose the FEFF package from the University of Washington\textsuperscript{28} was fed with different crystallographic data for phases like Ta$_2$O, TaO, TaO$_2$ and Ta$_2$O$_5$ and then compared with the experimental spectra. As illustrated in Fig. 6, a different chemical composition leads to different spectral shapes, ranging from single peaks (Ta$_2$O and TaO) to doublet peaks like in TaO$_2$ or Ta$_2$O$_5$. The first category could be clearly excluded, whereas the main difference between the former and the latter is the change in the $\frac{M_1}{M_2}$ ratio. The overall fine structure fits best to the Ta$_2$O$_5$ reference, giving further evidence for the existence of a fully oxidized tantalum barrier.

So far, water and oxygen-containing constituents of the solution were ruled out experimentally as possible oxidizing agents causing the passivation of the tantalum substrate. Focus was therefore placed again on O$_2$, as it was only eliminated based upon theoretical grounds, but not on experimental ones. One way to remove very small amounts of O$_2$ is by using an oxygen scavenger such as hydroquinone.\textsuperscript{29} Hydroquinone is known to react with molecular oxygen according to the reaction:

$$\text{Hydroquinone} + \frac{1}{2} \text{O}_2 \rightarrow \text{benzoquinone} + \text{H}_2\text{O} \quad (4)$$

Therefore, hydroquinone was added to the electrodeposition bath at a concentration of 0.01 mol dm$^{-3}$ and was allowed...
to react with oxygen gas for three days. This was followed by the adjusted drying procedure (vide supra) to remove the water that formed by reaction (4). A TEM investigation of the copper layer, deposited on tantalum, showed that about 70% of the Cu–Ta interface still contains an oxide layer, but for about 30% of the substrate, there was direct contact between copper and tantalum, without an intervening layer of tantalum oxide (Fig. 7).

4 Conclusions

It was shown that the high vacuum conditions are not sufficient to completely remove water and oxygen from the ionic liquid 1-ethyl-3-methylimidazolium chloride. Complete removal of water demands heating at 150 °C, while oxygen gas can only be removed by the use of an oxygen scavenger such as hydroquinone. When these conditions are met, it is possible to deposit copper directly on tantalum without the presence of an intervening oxide layer. This could be a breakthrough in the plating of copper for microelectronic devices.

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References


Fig. 6 (a) Simulated FEFF spectra for TaO₂, TaO, Ta₂O₅ and Ta₂O₃, (b) experimental EEL spectra.

Fig. 7 TEM cross section of a copper layer deposited on a tantalum electrode at –2.0 V vs Cu, after scavenging oxygen with hydroquinone. There is no oxide layer, but direct contact between Cu and Ta, as indicated by the arrows.