

Autolab Application Note EC11

Investigation of intermediates in the electrodeposition of copper using the Autolab RRDE

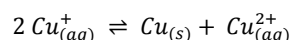
Keywords

Plating, Copper deposition, Chloride, Rotating Ring Disc Electrode

Summary

Copper is arguably one of the most technologically relevant metals, especially for the semi-conductor industry. Since 1997, metallic copper is used as interconnect in the production of processors. The deposition process used in this industry is known as the dual-damascene process and it involves the electrodeposition of copper from an acidic cupric, in the presence of additives.

One of the crucial additives in these copper plating baths is chloride, which is known to play an important role in the disproportionation reaction:



The cuprous ion is known to be unstable in normal acidic solution and it disproportionates in metallic copper and cupric ions. In the presence of chloride however, the disproportionation reaction equilibrium is shifted and the cuprous ions are stabilized.

It is now known that the Cu^+ intermediate is required in order for the other additives (brightener, suppressor, leveler) used in the dual-damascene process to operate as intended. It is therefore important to know if the Cu^+ intermediate is formed during the electrodeposition of copper.

This application note illustrates the use of the Autolab rotating ring disc electrode (RRDE) for the study of electrodeposition of copper and the detection of the Cu^+ intermediate.

Experimental conditions

An Autolab PGSTAT204 fitted with a BA, dual-mode bipotentiostat module was used in combination with the Autolab RRDE.

The measurements were carried out in a three electrode cell. The cell used in the experiments was a Metrohm 6.1415.350 vessel, with a volume of 400 mL. The large volume is required in order to establish a stable and reproducible hydrodynamic flow during the measurements.

The reference electrode was a double junction $Ag/AgCl$ (3 M KCl) reference electrode (Metrohm 6.0726.107). The counter electrode was a platinum sheet. Both the reference electrode and the counter electrode were located slightly above the bottom part of the ring disc electrode in order to reduce possible interferences with the hydrodynamic flow.

The RRDE electrode consisted of a 5 mm platinum disc with a concentric platinum ring. The gap between the two electrodes was 375 μm and the collection efficiency was 24.9 %.

Prior to the measurement, the electrolyte was purged with N_2 to minimize any interference due to the existence of dissolved oxygen in the solution.

Two different copper solutions were used:

- 1 mM $CuCl_2$ in 0.5 M KCl
- 1 mM $CuSO_4$ in 0.5 M Na_2SO_4

Experimental results in KCl solution

Figure 1 shows a typical measurement obtained at 500 RPM in the Cl^- containing solution.

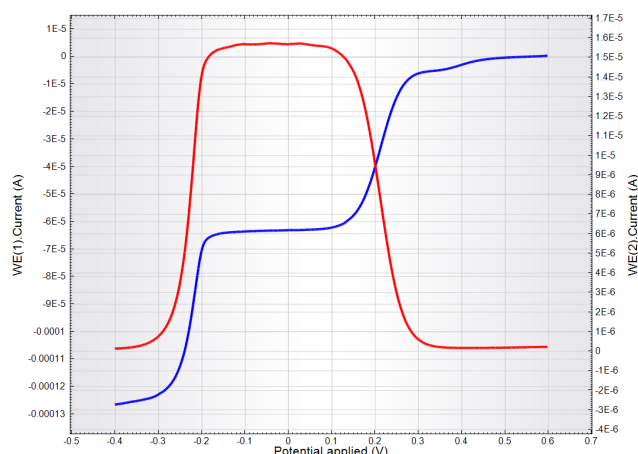


Figure 1 – Ring (red curve) and disc (blue curve) measurement carried out at 500 RPM in the Cl^- containing solution. Ring potential: 0.6 V vs Ag/AgCl. Scan rate: 10 mV/s.

The blue curve corresponds to the current measured on the disc and the red curve corresponds to the current measured on the ring. Since the ring is polarized at a fixed potential of 0.6 V vs Ag/AgCl, the oxidation current measured on the ring can be ascribed to the oxidation of the Cu^+ intermediate formed on disc. Indeed, the appearance of the Cu^+ intermediate matches the onset of the reduction of Cu^{2+} , at about 0.3 V vs Ag/AgCl.

Additionally, at around -0.2 V, the disc current transitions from a mass-transport limiting current plateau to a second plateau at more negative potentials. This transition corresponds to the second reduction step leading to the formation of copper. Since the Cu^+ intermediate is consumed in this second reduction, it can no longer be detected on the ring and the ring current falls back to the background value observed at the beginning of the measurement.

Figure 1 and 2 also show two well separated electron transfers, consistent with a two electrode reduction of Cu^{2+} to metallic copper.

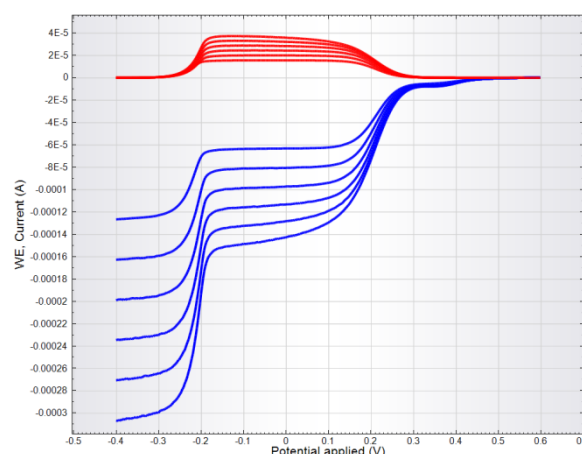


Figure 2 – Ring (red curves) and disc (blue curves) measurements carried out at rotation rates from 500 RPM to 3000 RPM in the Cl^- containing solution. Ring potential: 0.6 V vs Ag/AgCl. Scan rate: 10 mV/s.

Experimental results in Na_2SO_4 solution

Figure 3 and 4 show the results obtained when the same measurements were carried out in 0.5 M Na_2SO_4 (chloride free solution) containing 1 mM $CuSO_4$. Looking at the current recorded from the disc, it can be clearly seen the one step reduction of Cu^{2+} with the onset of the Cu underpotential deposition (UPD) around 0.2 V. The only feature present on the ring current is much less pronounced compared with the ring current measured in Cl^- containing solution (see also Figure 5) and it is most probably due to a very small amount of Cu^+ intermediate formation during the Cu UPD.

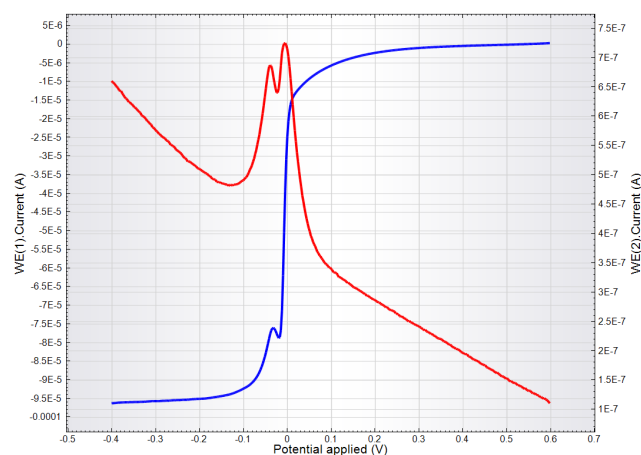
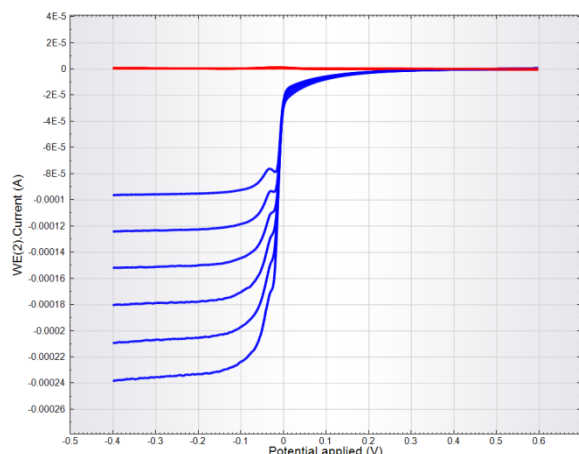


Figure 3 - Ring (red curve) and disc (blue curve) measurement carried out at 500 RPM in the Cl^- free solution. Ring potential: 0.6 V vs Ag/AgCl. Scan rate: 10 mV/s.



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Figure 4 – Ring (red curves) and disc (blue curves) measurements carried out of rotation rates from 500 RPM to 3000 RPM in the Cl^- free solution. Ring potential: 0.6 V vs Ag/AgCl. Scan rate: 10 mV/s.

This confirms the fact that in Cl^- free solutions, the Cu deposition is a single step process.

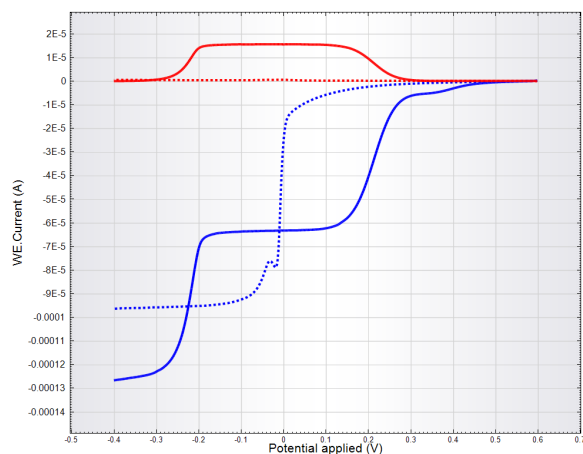


Figure 5 – direct comparison between the currents obtained for both disk (blue) and ring (red) in Cl^- containing (solid lines) and Cl^- free (dotted lines) solutions. Ring potential: 0.6 V vs Ag/AgCl. Scan rate: 10 mV/s.

Conclusions

In this application note, the Autolab RRDE system was used to distinguish between two different reaction mechanisms of copper deposition on Pt, depending on the electrolyte used: Cl^- free and Cl^- containing electrolytes. The Cu^+ intermediate was detected on the ring when a Cl^- containing electrolyte was used while in Cl^- free electrolytes, the current on the ring due to the existence of Cu^+ was almost not existent and it was due only to the Cu underpotential deposition.