Electrodeposition of Copper from Deep Eutectic Solvents by Using Pulse Current

Xiaomeng Su, Dr Todd Green, Prof Sudipta Roy
Department of Chemical and Process Engineering, University of Strathclyde, Glasgow

Abstract

Cu electroplating is of great significance in various industries and traditionally the process was performed in aqueous solution. However, such electrolyte suffers a number of drawbacks including poor deposit quality for some metals and environmental concerns. Deep eutectic solvents (DES) can serve as the alternative and overcome those limitations. In addition, the Cu deposit quality and metal properties can also be improved by applying pulse current instead of conventional direct current. This research aims to explore how the effects of pulse plating parameters including pulse on-time and duty cycle on the morphology and microstructure of Cu deposit as well as current efficiencies in DES electrolyte.

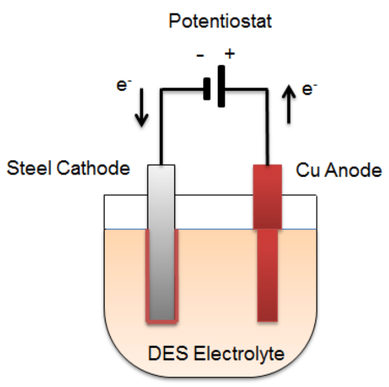
Electrochemical Reactions

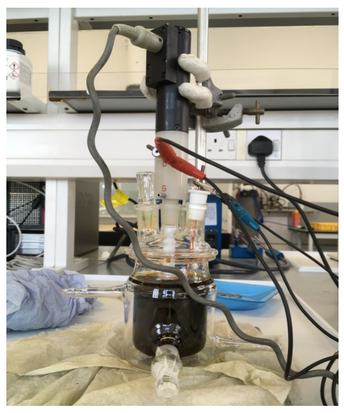
Cu electrodeposition is performed in a electrochemical cell which is composed by power supply, cathode, anode and electrolyte. Cu is dissolved on the anode and plated on the cathode. Electrolyte conducts the movement of ions and forms a complete circuit with anode, cathode and power supply.

Anode reaction: $Cu^0 + 2Cl^- \rightarrow Cu^{I}Cl_2^- + e^-$

Cathode reaction: $Cu^{II}Cl_4^{2-} + e^- \rightarrow Cu^{I}Cl_2^- + 2Cl^-$

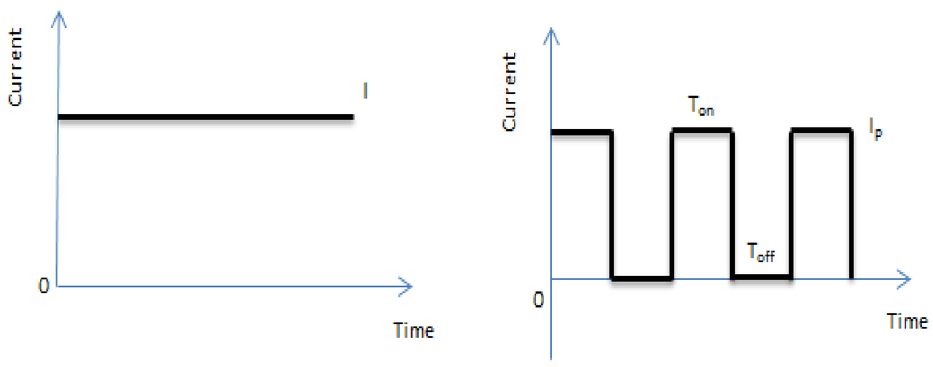
$Cu^{I}Cl_2^- + e^- \rightarrow Cu^0 + 2Cl^-$





Pulse Current

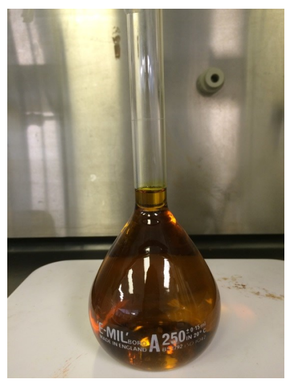
Cu electroplating can either be applied by direct current (DC) or pulse current (PC). In DC plating a fixed unidirectional current is applied throughout the process. In PC plating the current changes in a periodically sequence between on and off. Compared to DC, PC can achieve finer grain morphology and smaller deposit grain size. In addition, PC reduces the usage of additives, which have been widely used in DC condition.

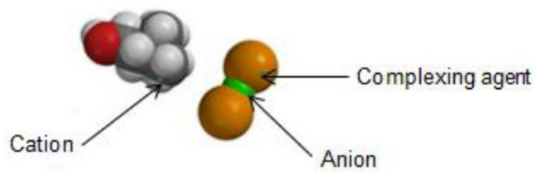


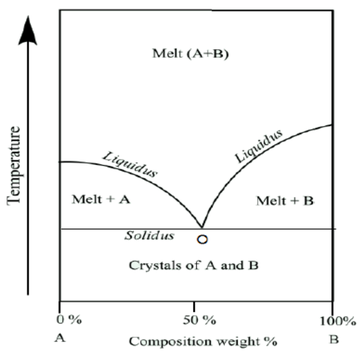
Direct Current **Pulse Current**

Deep Eutectic Solvents Electrolyte

DES is a sort of low temperature molten salt with melting point below 100°C. It is composed of only cations and anions. DES have large electrochemical windows to plate metals which aqueous solution can not or plate with poor deposit quality. They are also more benign to human health and environment. In this research the Cu ethaline melt DES is used as electrolyte since they are low cost and easy to prepare.

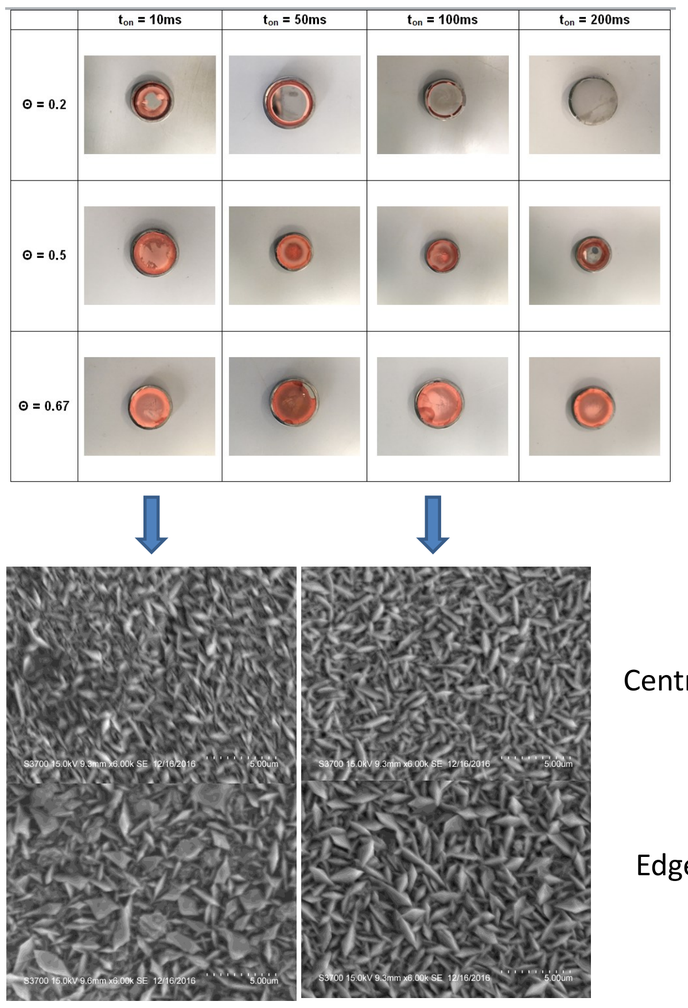


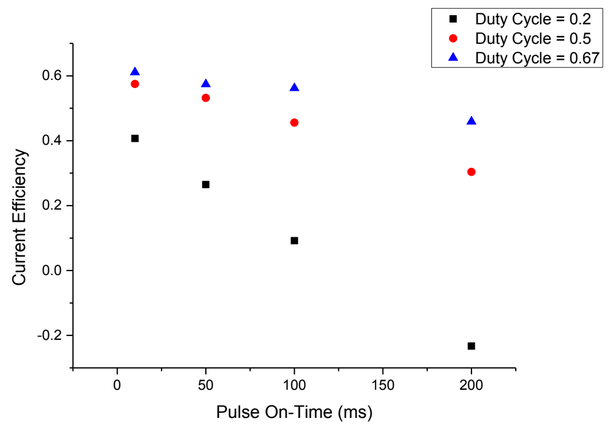


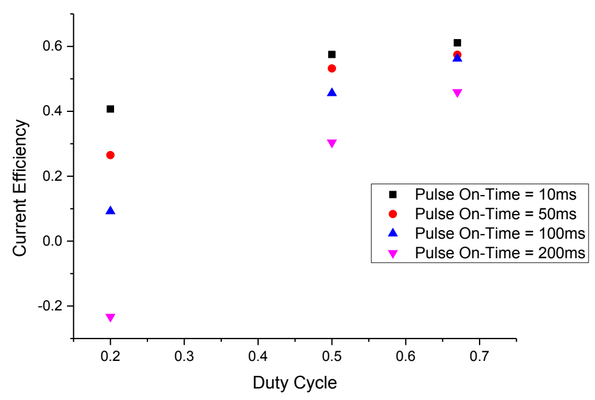


Results & Conclusions

Four groups of pulse on-time (t_{on} = 10ms, 50ms, 100ms and 200ms) and three groups of duty cycle (θ = 0.2, 0.5 and 0.67) conditions were tested in the pulse plating experiments. It was found that under the same θ, more Cu was stripped from the substrate surface with a falling current efficiency when t_{on} increased. When t_{on} was fixed, more Cu was plated on the substrate surface and the current efficiency increased. The SEM analysis showed the grain size of Cu deposit on the electrode edge was larger than the one on the electrode centre. It was hypothesized that Cu was dissolved into solution during the pulse off time and needed to be investigated further







Contact

Xiaomeng Su
Department of Chemical and Process Engineering
University of Strathclyde
Email: xiaomeng.su@strath.ac.uk

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