Modulation of Copper(I) oxide reduction/oxidation in Atmospheric Pressure Plasma Jet

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Abstract

We describe the controlled reduction of copper(I) oxide films to metallic copper in a non-thermal, atmospheric pressure, helium plasma jet. Thin layers (≈ 0.1 μm) of Cu_2O are electrochemically deposited onto Pt electrodes and placed in capacitively coupled helium plasma doped with H_2, O_2 and CH_4 gases. *Ex-situ* Raman spectroscopy was used to probe the effect of plasma treatment on the deposited copper oxide layer. We show that application of a static bias voltage to the Pt substrate during plasma exposure can control the rate of reduction of the copper(I) oxide film. We propose that the reduction process is mediated by plasma electrons and controlling the electron flux to the surface can be used as a means to modulate the reduction process.

Key Words: Copper(I) oxide; reduction; atmospheric pressure; plasma jet; gaseous electrode.

Introduction

All chemical reactions involve a change in the electron arrangement or distribution within molecules. As electrochemists, we are interested in stimulating electron attachment and detachment processes to control chemical change. Conventionally, we make electrons available via an electrically conducting solid in contact with a liquid phase containing a reactive species. Of course, there are exceptions to this picture, e.g. liquid/liquid interfaces. Perhaps a less obvious sources of electrons are gaseous plasmas. Gases have typically been ignored due to their feeble electrical conductivity. However, with the advent of new accessible approaches to form stable plasmas, these electrically conducting gases are attracting some significant interest as exotic electrochemical environments.

The defining property of plasmas is the presence of mobile electrons and cations, making them electrically conducting and candidates as both electrolytes or electrodes. Hickling Vennekamp, and Ogumi outlined the use of non-thermal plasma as an electrolyte for metal surface oxidation [1-6]. Our work extended this idea by using a flame plasma as an electrolyte to support redox reactions at an electrode surface probed using voltammetry [7-11]. Richmonds, Brettholle and Meiss demonstrated that the presence of free electrons made them analogous to electrodes, by positioning a plasma discharge in contact to a liquid electrolyte they demonstrated charge-transfer processes at the plasma/liquid interface [12-15]. Plasma reduction of copper oxide layers has been described in H_2/He plasma in vacuum by Sawada *et al*. [16] and Sabat *et al*. [17], also Inui *et al*. showed CuO and Cu_2O reduction in H_2/Ar atmospheric pressure plasma [18]. In all these studies the reduction was associated to the hydrogen radicals present in the doped plasma. However, we postulate here that plasma derived electrons do indeed reduce the copper oxide.

Here we describe the control of redox properties of a Cu_2O coating on an electrode held in a helium atmospheric plasma jet, by modulating the bias voltage applied to the copper coated

electrode. We compare the extent of reduction of Cu_2O in the presence of hydrogen, methane and oxygen as additive gases, while the electrode is biased positive and negative versus the plasma potential. We show, using *ex situ* Raman, that the oxidation state of copper is dependent more on the polarity of the bias voltage applied rather than on the additive gas.

Experimental

Atmospheric pressure, capacitively coupled plasma (CCP) was generated in a quartz tube of 7.5mm ID, 9.0 mm OD. Helium (CP Grade, BOC Gases, UK) plus dopant gases O_2, H_2 and CH_4 (BOC Gases, UK) were fed through mass flow controllers (Brooks Instruments, UK), as shown in Fig 1 a. The flow rates were 0.004 and 2.000 L min^{-1} for the dopant and helium gases respectively, providing a mixing ratio of 0.2 % v/v for all experiments in doped plasma. The temperature of the effluent gas was measured to be 85 °C, at approximately 1 W dissipated power. Radio Frequency (RF) power was generated by a 50W 13.56 MHz RF generator (Coaxial Power Systems, UK), matched to the plasma load via a manual matching network and then fed to the RF electrodes through a 1:1 current Balun.

An in house constructed two electrode assembly with a central platinum (99.99 %, Advent Materials) disc (0.5 mm diameter) and an outer copper ring, shown in Fig. 1 b. The electrode assembly was placed axially into the plasma jet, 2 mm behind the leading edge of the grounded RF electrode, centred within the quartz tube. The outer copper electrode was grounded and the coated Pt electrode was biased to ± 210V (Model 2450 Source Measure Unit, Keithley, UK) during plasma exposure. The experiments were run under positive bias, negative bias and floating potential conditions. In all experiments the Cu_2O coated electrode was exposed to the plasma for 180 s, and analysed using Raman immediately after. A bias voltage was applied between the coated platinum electrode and the outer copper ring electrode in a clean helium plasma. A secondary discharge was established within the plasma, the current was electron

current limited due to the large counter electrode, reaching a saturation value of 90 µA. A double Langmuir probe was used to determine electron density and temperature. Tungsten rods (0.5 mm diameter) were placed within a double bore alumina tube, 1 mm apart. The assembly was then placed in a stainless steel, 4.0 mm diameter, 1.5 mm thick grounded tube to minimize RF interference. The Langmuir probe sweep range was -30 to 30 V.

The Pt electrode was coated with thin films of Cu_2O electrochemically deposited onto the polished Pt electrode surface as described in ref [19]. The electrodeposition solution comprised of 0.4 M $CuSO_4·H_2O$ and 3M Lactic Acid (>85%, Sigma-Aldrich, UK), the pH of the plating solution was altered to pH 12 by addition of 5 M NaOH solution. The Cu_2O layer was grown potentiostatically (PGSTAT100, Autolab, Windsor Scientific, UK) at -0.5V vs. Ag/AgCl reference electrode using a large area copper counter electrode. The total charge transferred was -135 µC over 300 seconds at 40 °C. The resulting film was light blue in colour due to second order interference, suggesting a film thickness of approximately 0.1 µm [20].

Raman spectra were taken with a Raman microscope (InVia, Renishaw, UK), using a 514.2 nm Argon laser as the excitation source. Care was taken to work with low power in order to avoid re-oxidation of the Cu surfaces during measurements. After spectra collection, the surface of the electrode was dampened with deionised water (18 MΩ Millipore, Gradient system) and the Argon laser was used to locally heat the surface and re-oxidize the reduced copper thin film.

Results and Discussion

The Raman spectra of the copper coating, before exposure to the plasma shows the typical spectra for Cu_2O are shown in Figure 2 a. After exposure to a clean helium plasma the Raman signal for the copper oxide remains unchanged, when the bias voltage was negative. However, when the bias voltage was reversed to positive, the signal from the copper oxide almost entirely

disappears, suggesting that the oxide has been reduced to elemental copper. The corresponding images of the coating are shown in Figure 2e and f. We confirm that ablation is minimum by reoxidation of the copper surface by localised heating of with focused 512nm laser under aerated DI water. Reoxidation was shown to restore the pale blue copper oxide thin film and signal in the Raman spectra, Figure 2 g.

Exposure of the copper coating to the helium plasma doped with 0.2 % v/v hydrogen, methane or oxygen are shown in figure 2 b, c, and d, respectively. As with the clean plasma Raman spectra corresponding to negative and positive bias applied to the copper oxide coated electrode. The final redox state of the coating was shown to be highly dependent on the polarity of the bias voltage; not the nature of the dopant gas. Perhaps surprisingly, despite the presence of the reducing gases hydrogen and methane in the plasma, there was virtually no change in the Raman spectra when the electrode was polarised negative. Furthermore, in the presence of oxygen in the plasma yielded very similar results. Reduction of Cu_2O only occurs significantly when the coating was positively charged with respect to the copper ring electrode. This indicates that the reducing agent in this system is the plasma electrons. It is highly unlikely that the reduction is caused by negative ions, there will be very low concentrations of stable negative ions in this collision dominated plasma. The only species with a high enough electronegativity to sustain stable negative ion would be oxygen atoms. Except for the plasma jet with added oxygen, the other plasmas will contain insignificant amount of oxygen. Any oxygen would be drawn from entrainment effects when the jet meets the atmosphere, and this would not provide enough oxygen to ionise.

The plasma used here was at atmospheric pressure; therefore, the electron mean free path was short approx. 700 nm and the collision density was very high compared to the equivalent process in vacuum plasma processing systems. This plasma is highly non-equilibrium, in that the plasma electron temperature is much higher than the neutral or cation temperature. The

helium excitation temperature was calculated using the Boltzmann plot method [21] on the He 668, 706 and 728 nm lines, giving approximately 1200 ± 150 K with all dopant species. Double Langmuir probe measurements yielded a value of 2.0 ± 0.2 eV (or 23,200 K) for electron temperature and electron densities on the order of 4.0 ± 1.0 x10^{10} cm^{-3} for all the dopants except for O_2 which had a measured electron density of 1.0 ± 0.2 x10^{10} cm^{-3}. The lower level of ionisation in oxygen doped plasma reflects the high electronegativity of oxygen producing a significant concentration of negative ions, compared to undoped and methane or hydrogen doped plasma. The corresponding emission spectra for doped helium plasma and clean helium plasma as shown in figure 3. The emission lines for helium (706.5 nm, 667.8 nm, 587.6 nm) are weak compared to the lines for other components such as OH (309 nm), O (777.4 nm) and emission from additives (Fulcher-α-bands for hydrogen around 600 nm, CH and C_2 bands in the presence of methane between 300 and 400 nm, etc.) and fragments of additives.

The modulation of reduction activity by the bias polarity suggests that the reduction was not due to any neutral species in the plasma, otherwise the reduction or modulation of the reduction would occur independently of the bias voltage polarity. In turn, positive ionic species are also not responsible for the reduction, otherwise the reduction would be observed under positive bias.

This observed difference in reduction rate as a function of voltage biasing, can be rationalised by considering the electric field effect on the plasma composition close to the copper oxide coating. The physical flow rate of the plasma feed gases was 2.0 L min^{-1}, the electrical Reynolds number calculated based on the flow rate and electron temperature values is approx. 0.1, smaller than the critical Reynolds number of 1, indicating a stationary plasma where electron and ion collection processes are dominated by diffusion or migration but not bulk flow of gas. When the surface of the copper oxide is positively biased, electrons are accelerated

towards the surface increasing the flux of electrons. On negative biasing the coating remains predominantly oxide clearly preventing any reduction from the plasma.

This difference in reduction activity between the positive and negative bias strongly suggests that the reduction mechanism is mediated by plasma electrons. There may be some other reduction process involving perhaps some of the neutrals, but this appears to be insignificant under these conditions. Furthermore, reduction occurs when the substrate is unbiased, floating or grounded however, at a much-reduced rate, data not shown.

Conclusion

In this study we describe the reduction of copper oxide to copper using a helium plasma produced using a dielectric barrier discharge. The significant conclusions are:

- The reduction of a copper oxide coating in a helium DBD plasma is mediated by plasma electrons.

- A voltage bias applied to the coating via the underlying platinum electrode can control the rate of the reduction of copper(I) oxide.

- The addition of hydrogen, methane or oxygen does not affect the reduction rate of the copper oxide.

- The neutral components of the plasma show little reduction activity

The ability to pattern surfaces with control of the surface redox state opens new technological opportunities for post deposition modification of coatings. This and other papers demonstrate that the plasma mediated chemistry is a rich area of research, with significant promise of uncovering very interesting new strands of surface chemistry.

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Figures
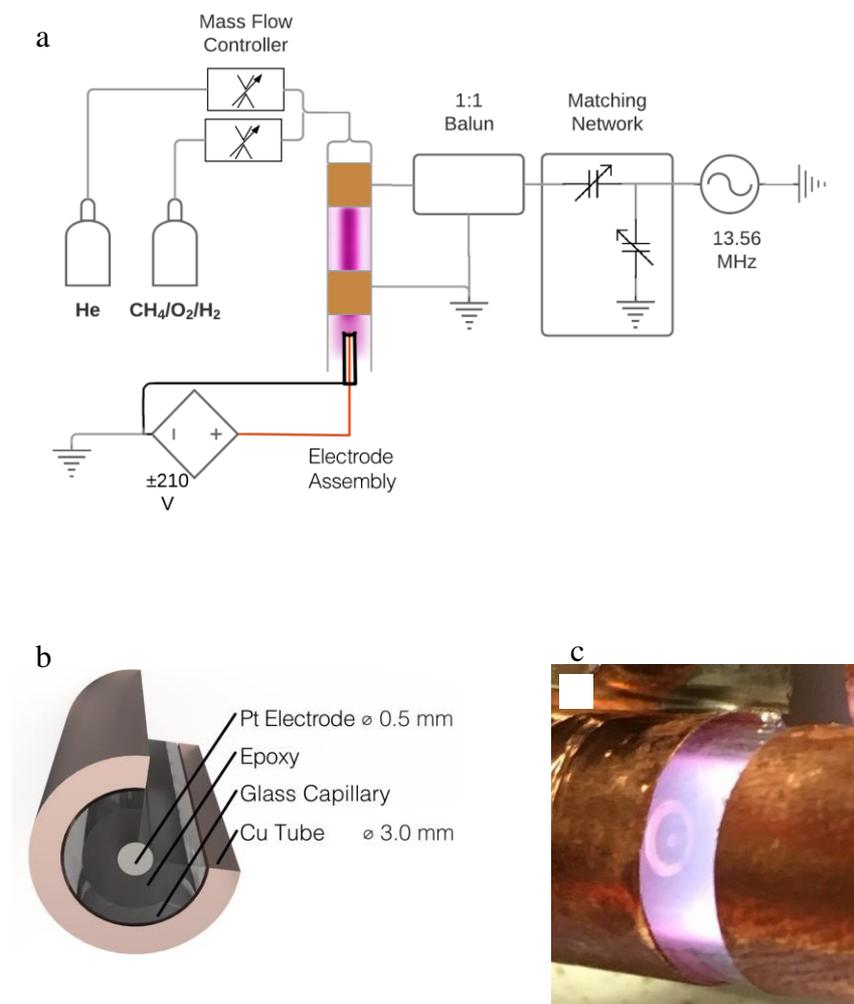
Figure 1. (a) Schematic diagram showing the gas flow system, plasma cavity within the quartz tube showing the two tubular silver plated copper electrodes separated by 2.6 mm and power supply for the plasma generation and electrode biasing. (b) schematic of the electrode assembly composed of 0.5 mm diameter platinum working electrode and outer copper ring electrode. (c) The electrode positioned in the plasma jet.
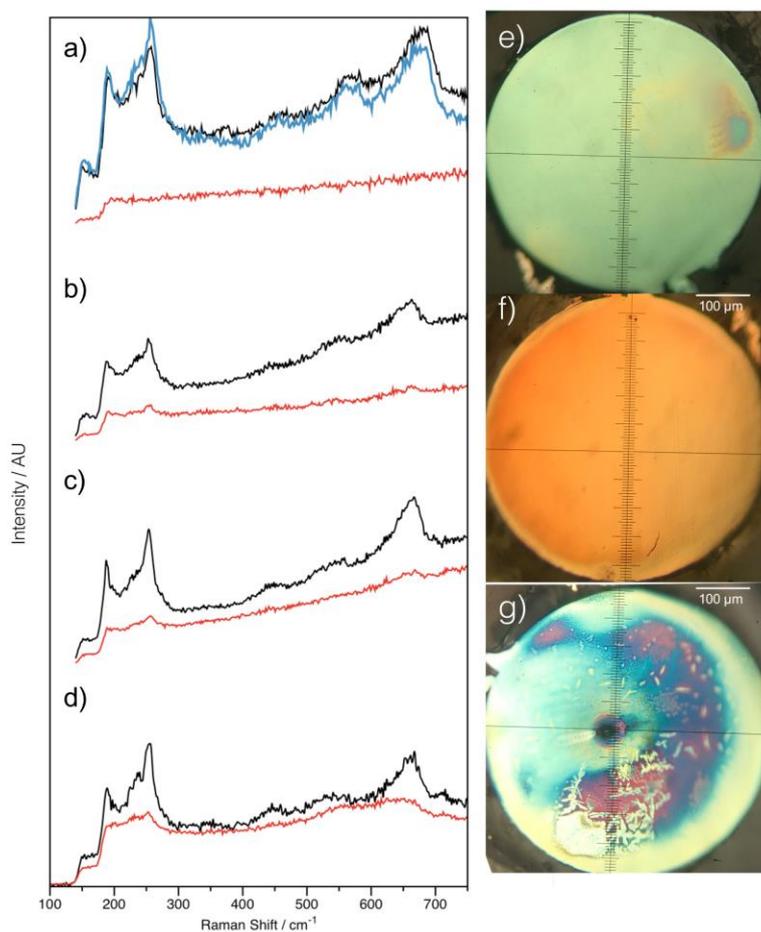
Figure 2. Raman spectra of the coating (a) before exposure to an undoped plasma (blue line) and exposed biased negative (black line) and positive (red line), (b), (c) and (d) are the Raman spectra for the coating exposed to the plasma containing 0.2 % v/v H_2, CH_4 and O_2, respectively. Images of the coated platinum electrode with the copper oxide deposit (e), after exposure to the plasma with a positive bias applied (f) and after reoxidation of the reduced coating (g).
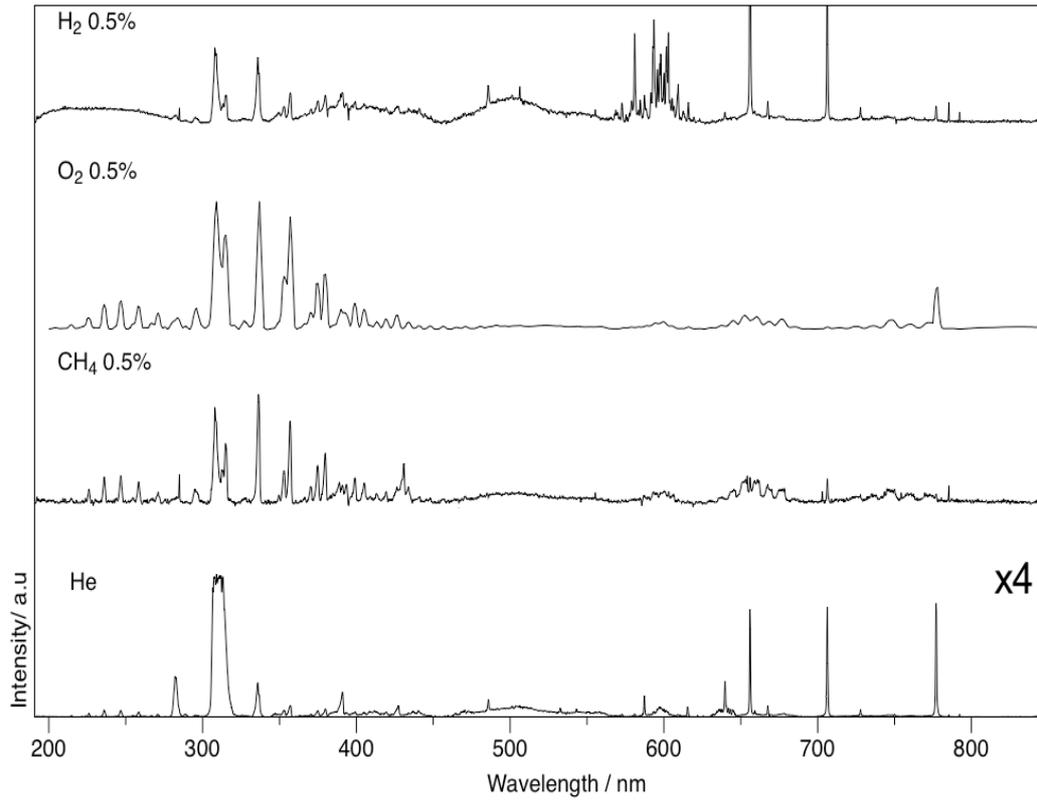
Figure 3. Showing the emission spectra of the plasma doped with hydrogen, oxygen, and methane and undoped helium plasma. The spectra were collected using the plasma between the electrodes through the quartz tube.