Low temperature plasma deoxidation of copper surfaces

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Abstract

In this study, the application of a dielectric barrierer discharge plasma for metal deoxidation was shown on differently oxidized copper surfaces in an Ar/H_2 atmosphere at 100 hPa and room temperature. Plasma treatments with a discharge voltage of 11 kV and a frequency of 8.8 kHz yielded an almost complete deoxidation of samples with native Cu_2O layers and samples with pre-oxidized CuO layers, both within minutes of the Ar/H_2 plasma treatment.

1. Introduction

Metals are commonly contaminated with surface oxide layers, which limit the performance of materials in different industrial applications like coating or welding. Therefore, the implementation of a technique, which can provide a deoxidation effect to a metal surface without a morphology modification, is of big interest. Up to date, a large number of studies have been focused on the development of hydrogen plasma deoxidation techniques, which operate at pressures below 1 hPa. Such methods usually require long times for deoxidation and additional heating, which generally raises the costs of techniques [1]. In contrast, promising results of deoxidation performance were shown for dielectric barrier discharge (DBD) plasmas [2]. The relative simplicity of the plasma setup, the ability of operating at atmospheric pressure as well as the lack of studies and additional information about the deoxidation effect motivate this work on DBD plasma deoxidation.

2. Methodology

2.1. Materials and sample preparation

In the present study, copper foils (99.9 %; Mateck GmbH, Germany) with a size of 10×10 mm^2 were used as a starting material. In order to provide two differently oxidized surfaces, samples were prepared in two different ways. One copper sample was highly-polished and exposed to air for around one hour, resulting in the formation of a ~2 nm-thick Cu_2O native oxide layer [3]. Another sample was pre-oxidized with a DBD plasma in air at 100 hPa and 20 °C for around 1 minute, yielding a formation of a >10 nm-thick CuO oxide layer. Afterwards, the morphology of the samples was analysed with the confocal laser scanning microscope (CLSM) and transferred into a ultrahigh vacuum (UHV) system, where X-ray photoelectron spectroscopy (XPS) analysis and plasma treatments were carried out.

2.2. DBD plasma system

Plasma treatments were performed in the reactor, which is directly connected to the UHV system for XPS analysis. The high voltage (HV) electrode was produced from a quartz tube with a wall thickness of around 2 mm, which was filled with brass powder [4]. The stage with samples was used as a grounded counter-electrode. DBD plasma treatments were performed within a discharge gap of 2 mm, at a discharge voltage of 11 kV and a frequency of 8.8 kHz. A pre-commercial HV power supply (Plasma Green GmbH, Germany) was used for the plasma treatments. The images of the DBD plasma system are provided in the published dataset [5].

2.3. Deoxidation process

Plasma deoxidation of copper samples was carried out in an Ar/H_2 gas (98 %/2 %; Westfalen AG, Germany) at 100 hPa and 20 °C. The surfaces were treated at several steps. After each treatment step, the reactor was evacuated to the ~10^{-7} hPa and samples were transferred into the UHV for XPS measurements.

2.4. Analysis

The chemical structure and stoichiometry of surfaces before and after the treatment was analysed at 20 °C in an UHV chamber using XPS with an Al K_α X-ray source. The morphology of surfaces before and after the treatment was characterized via CLSM using Color 3D laser Microscope VK-X200K (Keyence Corporation, USA) in the presence of ambient air. Additionally, reactive species within the Ar/H_2 plasma were identified using an AvaSpec–ULS2048CL–EVO optical emission spectrometer (OES) (Avantes, Netherlands). More detailed explanation of the analysis methods including the parameters and software is provided in the published dataset [5].

3. Results and discussion

3.1. Treatment of a polished surface

Figure 1a shows the stoichiometry of a copper surface during the experiment, which was calculated using the XPS spectra. The highly polished sample was characterized before the plasma treatment showing copper, oxygen and carbon species in the amounts of 27 at.%, 35 at.% and 37 at.%, respectively. The contaminations were assigned to native layers of cuprous oxide Cu_2O and adventitious carbon. A sharp increase of copper amount to the value of 67 at.% was observed already after 10 seconds of treatment, whereas the contribution of oxygen and carbon species was reduced to 9 at.% and 23 at.%, respectively. The changes in the structure of the copper Cu $L_3M_{45}M_{45}$ Auger line (c.f. Figure 1b) indicates that the main amount of the Cu_2O was reduced to Cu after around 10 seconds. An almost fully deoxidized copper film was obtained after around 50 seconds of treatment, yielding a stoichiometry of 83 at.% of copper, 3 at.% of oxygen and 13 at.% of carbon. Therefore, the O/Cu ratio of 1.24 before the treatment decreased to 0.03 after the final step.

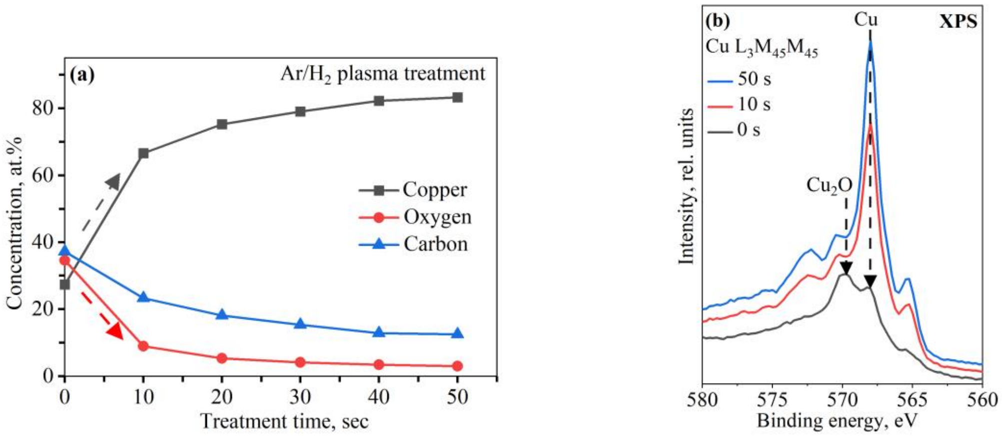

Figure 1: (a) Stoichiometry of a copper sample as a function of treatment time; (b) Cu $L_3M_{45}M_{45}$ Auger line of a sample before treatment (black line) and after 10 s (red line) and 50 s (blue line) of plasma treatment

3.2. Treatment of a pre-oxidized surface

Figure 2a shows the stoichiometry of a copper sample with a composition after an initial air plasma oxidation of 28 at.% copper, 50 at.% oxygen, 20 at.% carbon and 2 at.% nitrogen. The obtained >10 nm thick oxidized layer mainly consisted of CuO, which was fully reduced to Cu_2O and Cu after around 1 minute of Ar/H_2 plasma treatment (c.f. Figure 2b). An almost deoxidized surface was obtained after 3 minutes of the Ar/H2 plasma treatment, yielding a stoichiometry of 77 at.% Cu, 10 at.% O, 13 at.% C and 0 at.% N as well as a O/Cu ratio of 0.14.

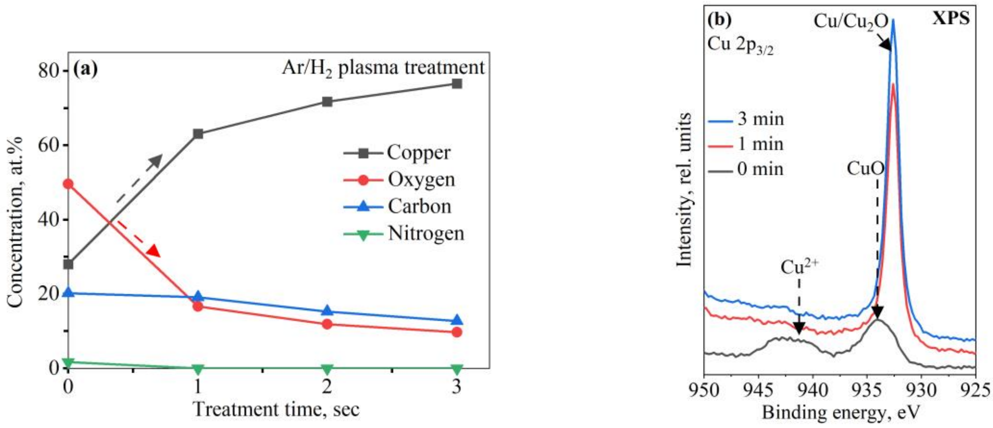

Figure 2: (a) Stoichiometry of an air plasma-oxidized sample as a function of treatment time; (b) Cu $2p_{3/2}$ spectra of a sample before treatment (black line) and after 1 min (red line) and 3 min (blue line) of treatment

3.3. Characterization of morphology and analysis of reactive species

CLSM measurements showed that the Ar/H_2 plasma did not change the surface structure, particularly yielding similar values of roughness before and after the treatment. OES spectra revealed the presence of atomic hydrogen radicals H_α in the reaction zone, which is the likely source of the deoxidation effect of the Ar/H_2 plasma.

Additional spectra as well as all data including the XPS analysis files, the CLSM figures and the OES spectra are provided in the published dataset [5].

4. Conclusions

The treatment of differently oxidized Cu surfaces using an Ar/H_2 DBD plasma was studied at 100 hPa and 20°C. The Cu_2O native oxide was almost fully removed after ca. 50 s of treatment, yielding a deoxidized Cu surface. In contrast, a pre-oxidized sample with >10 nm thick CuO layers were almost deoxidized after 3 minutes, showing that CuO was completely reduced to Cu/Cu_2O after around 1 minute of treatment. Additionally, the results revealed an unaffected surface morphology and the presence of H_α radicals in the plasma as likely origin of the deoxidation effect.

5. Acknowledgements

The project was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 394563137 – SFB1368.

6. References

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