Tuning surface morphology and stoichiometry by microplasma generated reactive oxygen species and short pulsed laser irradiation

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Abstract: Copper surfaces were treated simultaneously using reactive oxygen species from a micro-atmospheric plasma jet and laser irradiation, with the densities of O, O_3, $O_2(a^1\Delta_g)$ and $O_2(b^1\Delta_g^+)$ measured to understand the plasma's influence. The treated surfaces were analyzed using a Scanning Electron Microscope to study nanostructure formation and X-ray Photoelectron Spectroscopy to determine the composition of the resulting copper oxides.

1. Introduction

New catalyst materials are heavily researched to enable alternative green or more efficient production methods for various chemicals. The morphology of catalytically active surfaces and their chemical composition play an important role in optimizing their performance. [1]

The focus for the catalyst optimization is the CO_2 electrolysis to produce high value hydrocarbons (C_{2+}). For this application, copper (Cu) or more precisely its oxides e.g. CuO, have shown to be very effective. [1,2]

We investigate the modifications induced by a combined laser and plasma treatment. While the short pulsed laser is able to generate nanocale structures like Laser Induced Periodic Surface Structures (LIPSS) and Pulsed Laser Induced Dewetting (PLID) nanoparticles, the plasma provides reactive species to the surface which change its chemical composition.

2. Experimental setup

Laser irradiation was performed using a frequency-doubled Nd:YAG laser (532 nm) focused on the sample inside a vacuum chamber. Plasma treatment was applied using a COST Reference Micro Plasma Jet [4], operated with a helium (He)–oxygen (O_2) gas mixture to generate reactive oxygen species. The plasma jet and laser beam were precisely aligned to target the same spot on the sample. All experiments were conducted in a controlled helium–oxygen atmosphere to minimize contamination from ambient air. Investigated surfaces were either thin copper layers deposited on silicon (Si) wafers through High Impuls Magnetron Sputtering (HiPIMS) or bulk copper from a 0.1 mm thick foil.

3. Investiagation of reactive species

The reactive oxygen species atomic oxygen, ozone, $O_2(a^1\Delta_g)$ and $O_2(b^1\Delta_g^+)$ were measured by absorption and emission spectroscopy. For increased signal to noise ratio, we used a bigger absorption/emission volume which required the use of a gas flow cell. A plug-flow simulation and a 2D fluid simulation were used to understand the gas flow dynamics within the cell.

Comparing the simulations to the experiment revealed a strong dependence of the $O_2(a^1\Delta_g)$ density on the gas flow dynamics within the cell, while ozone was slightly overestimated by the simulation outside the plasma region. The $O_2(b^1\Delta_g^+)$ density followed simulated results closely.

4. Chemical composition analysis

The change in chemical composition of the copper samples was investigated by comparing the Auger spectra obtained by X-ray Photoelectron Spectroscopy (XPS).

As shown in Fig 1, there is no difference between laser treated and untreated surfaces. A combined treatment of laser and plasma can increase the production of CuO while reducing the amount of metallic Cu and Cu_2O. The ratio of the copper oxides can therefore be tuned by the treatment time with the plasma.

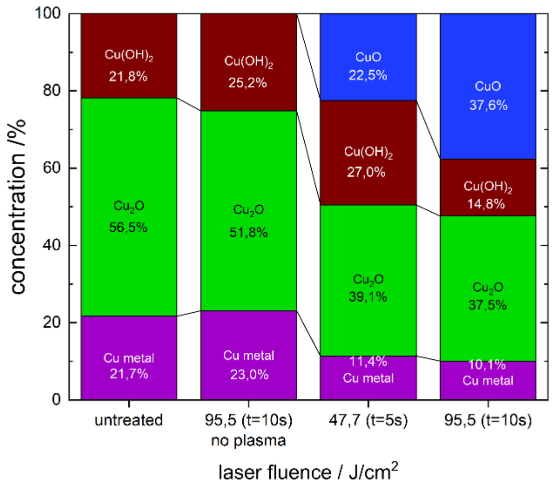

Fig 1: Copper oxide concentration depending on the combined laser plasma treatment time. [4]

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References

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