# Self-organisation of sub-µm surface structures stimulated by microplasma generated reactive species and short-pulsed laser irradiation

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**Abstract:** Thin copper layers were treated with reactive oxygen species of a micro atmospheric plasma jet and laser irradiation. The treated surfaces were examined using a Scanning Electron Microscope regarding the formation of nanostructures as well as X-ray Photoelectron Spectroscopy to deduce the composition of formed copper oxides through the treatment. The combined laser plasma treatment achieved a controllable nanoparticle generation and could change the Cu(II) concentration from 0% for untreated samples to 20%.

**Keywords:** plasma jet, catalysis, copper, nanoparticles, thin layers, laser, atomic oxygen

## 1. Motivation

The efficiency of a catalyst is heavily influenced by its surface characteristics. Identified as most important were the morphology of the surface or its nanostructure and the chemical composition [1].

We investigate the combined application of reactive species produced by a micro-scaled atmospheric plasma jet and the electric fields and energy input of pulsed laser irradiation. This can lead to a very effective functionalisation of catalytic surfaces via complex laser-plasma-surface interactions. The focus for the catalyst optimization is the $CO_2$ electrolysis to produce high value hydrocarbons, such as methan ($CH_4$). For this application, copper (Cu) or more precisely its oxides e.g. CuO, have shown to be very effective. [2,3]

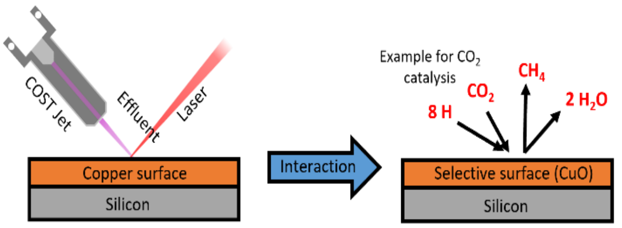


Fig. 1: Schematic of catalytically enhanced $CO_2$ electrolysis.

## 2. Experimental setup

For the laser irradiation a frequency-doubled Nd:YAG (532nm) is used, which is focused on the sample in a vacuum chamber. The plasma treatment is provided by a COST Reference Micro Plasma Jet [4]. The plasma jet is operated with a helium (He) - oxygen ($O_2$) admixture to produce reactive oxygen species. Both, plasma jet and laser spot are aligned to the same spot on the sample. All experiments are conducted under a helium-oxygen atmosphere to reduce sample pollution through contact with ambient air. The treated surfaces are thin copper layers deposited on silicon (Si) wafers through High Impuls Magnetron Sputtering (HiPIMS). This procedure was most successful in preventing ablation of the copper through laser irradiation.

## 3. Surface nanostructuring mechanism

Pulsed laser treatment of copper forms mainly Pulsed Laser Induced Dewetting Structures (PLIDS). An absorbed laser pulse heats the copper layer until it melts and creates a dewetting of the copper on the silicon wafer. After the laser pulse, copper solidifies almost instantly. Through irradiation with multiple laser pulses "droplets" are formed due to the surface tension of the liquified metal. In theory, after the formation of the nanoparticles this state remains constant even after longer laser irradiation time.

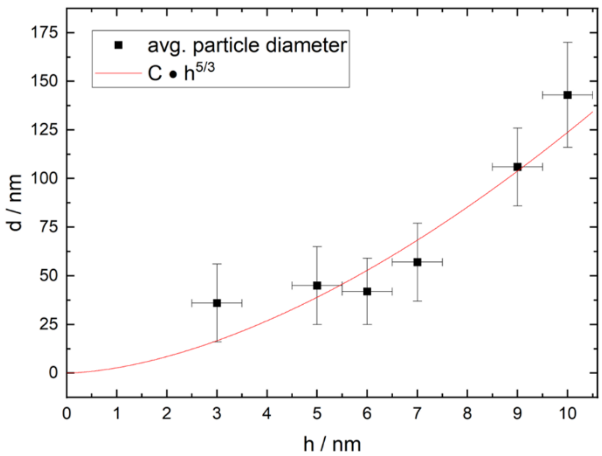


Fig. 2: PLIDS diameter depending on the copper layer thickness.

Scanning Electron Microscope (SEM) images allow to analyse the size distribution of the generated particles. The diameter of the spherical nanoscale particles can be controlled through the copper layer thickness and modelled via (1), which is obtained through Thin Film Hydrodynamic (TFH) instability [5] as shown in Fig 2.

$$D = \left(\frac{24\,\pi^3\,\gamma}{A\,f(\theta)}\right)^{1/3} h^{5/3} = C\,h^{5/3} \qquad (1)$$

## 4. Reactive species densities and plasma treatment

To understand the influence of the plasma treatment on the chemical composition of the surface, it is important to know which reactive species are produced inside the COST plasma jet. For this, the transport to the surface as well as their densities are key parameters. One interesting reactive species is atomic oxygen (O) whose absolute density was measured using Two Photon Absorption Laser Induced Fluorescence (TALIF). Outside the plasma in its effluent the atomic oxygen density shows an asymptotic decay. The introduction of a surface into the effluent path slows this decay and produces a pronounced density maximum in front of the surface, mainly due to stagnation effects in the gas flow (see Fig. 3).

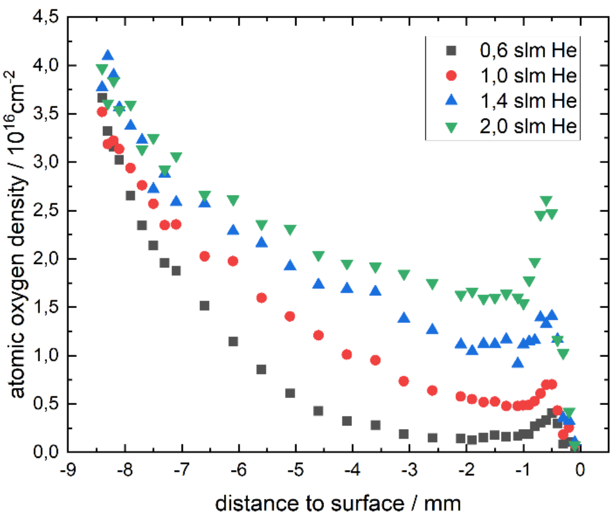


Fig 3: Atomic oxygen density in the effluent of the plasma jet near a copper surface.

The simultaneous application of plasma treatment and laser irradiation introduces a complication. High gas flows inhibit the formation of PLIDS on the sample. As such, although high gas flows would be ideal for high reactive species densities, lower gas flows must be employed for stable nanostructuring of the surface, thus introducing a trade-off. This can be achieved by either reducing the gas flow rate or increasing the jet distance to the sample (see Fig. 4).

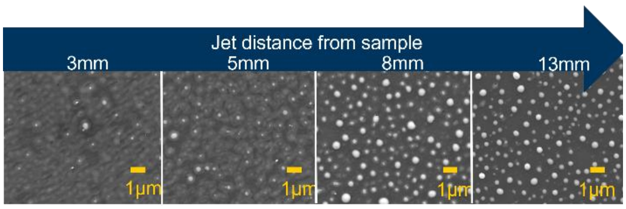


Fig. 4: PLIDS formation influenced by jet distance variation.

## 5. Chemical composition analysis

To investigate the chemical composition regarding the produced copper oxides X-ray Photoelectron Spectroscopy (XPS) was used. Samples that were treated simultaneously with plasma and laser showed a clear distinction in their Cu 2p spectra when compared to untreated samples. The oxygen shake-up peak as well as the change in shape of the Cu $2p_{3/2}$ peak can be attributed to an increase in the concentration of Cu(II) species like CuO or $Cu(OH)_2$. Unfortunately, Cu 2p spectra only allow a qualitative analysis regarding the ratio of different copper oxides because differentiating between the different oxides is very difficult. Instead, the Auger spectra are used. These allow a distinction between the copper oxides because of their characteristic shape [6]. The composition of the Auger spectrum consisting of different oxides also allows for an estimation of their ratio. (see Fig. 5). To do this, the copper oxide Auger reference spectra are fitted as a superposition to the Auger spectrum of the treated sample. Their fitted areas can then be used to calculate the ratio between the different oxides.

Preliminary results show that the combined application of both plasma and laser treatment is able to change the Cu(II) species concentration from 0% for untreated samples to 20% on treated ones while simultaneously forming self-organising nanostructures.

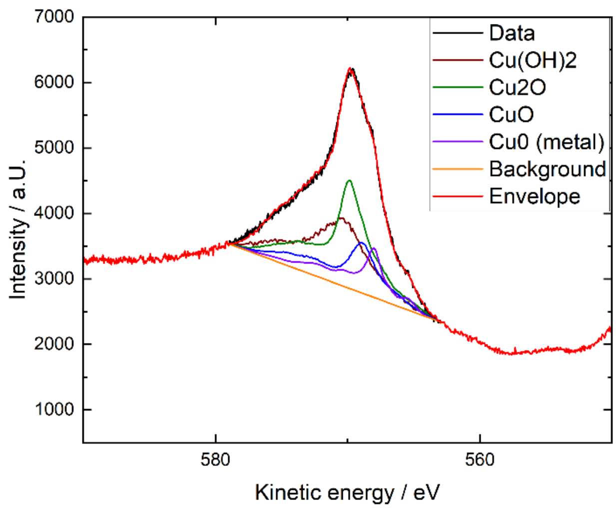


Fig: 5: Auger spectrum of a treated copper surface and its composing oxides.

## 6. Acknowledgement


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## 7. References


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