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Influence of nanosecond pulsed plasmas in water on copper surfaces and on nanoparticle formation

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Abstract: Discharges in liquid, so called in-liquid plasmas, enable a variety of applications. For instance, they can be used to induce nanoparticle formation both in the treated liquid and on a surface in contact with the liquid. A surface in direct contact with the treated liquid can be modified by the reactive species created in the plasma. The changes of the surface can be monitored by Fourier-Transformed Infrared Spectroscopy (FTIR).

Keywords: in-liquid plasmas, nanoparticle formation, FTIR, TEM

1. Introduction

Plasmas in liquids, when ignited by voltage pulses with fast rise times and nanosecond pulse lengths applied to a small electrode wire, yield a high degree of dissociation of the liquid, a high mass transport and efficient reaction rates. Through the plasma treatment a variety of reactive species, e.g. solvated electrons, hydroxide (OH^-) and hydrogen peroxide (H_2O_2) species can be created from the liquid medium (distilled water in this work). These species can react with surfaces placed in the liquid, possibly inducing surface changes with useful applications.

In this work, in-liquid plasma treatment is used to modify a copper surface. Copper oxide nanocubes possess catalytic properties and, for instance, are being used in the electrochemical reduction of CO_2. The activity of the nanocubes decreases over time with use. Therefore a method to re-activate these catalytic properties is needed. By the in-liquid plasma treatment, the reactive species in the liquid such as H_2O_2 might induce an oxidation of copper and the growth of such copper oxide nanoparticles.

In previous experiments with the setup used in this work, it has been found that the electrode degrades over time, dissolving the electrode material into the liquid. In this work, tungsten is used as an electrode material due to its high melting point, leading to its high durability during the experiments. It has been found by Lukes et al. [1] that the electrode material of an in-liquid plasma has an influence on the concentration of H_2O_2 in the treated liquid. As a result the choice of electrode material might affect the modification of the treated surface. Therefore another focus of this project is to investigate the production of nanoparticles from the electrode material.

2. Experimental Setup

The plasma is ignited in a chamber made from polymethyl methacrylate (PMMA), with a volume of 25 ml. As a medium, distilled water with a conductivity of <1 µS/cm is used. The discharge is ignited using a pin-to-pin electrode configuration where the tip of the driven electrode consists of a tungsten wire with a diameter of 50 µm. A sketch of the chamber can be seen in Fig.1.

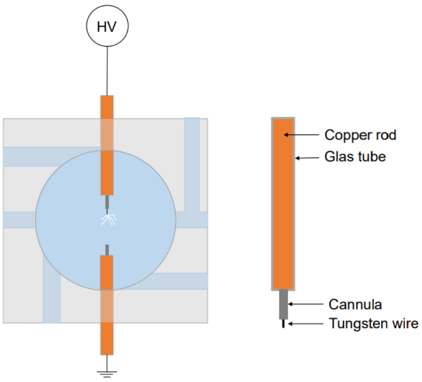

Fig. 1. reactor setup and electrode configuration [K. Laake]

The back wall of the reactor consists of a substrate holder where the surface that is to be treated can be mounted. The substrate consists of a wafer made from either silicon or silicon dioxide, coated on the side exposed to the liquid with a copper layer with a thickness of approximately 10 nm. The distance between substrate and electrode is 1 cm.

Additionally the chamber contains three fused silica broadband windows that allow for line-of-sight camera measurements of the electrodes.

The surface modification is monitored using Fourier-Transformed Infrared Spectroscopy (FTIR). A sketch of the setup is presented in Figure 2. The IR beam is directed at the backside of the waver and is detected under a 45° angle.

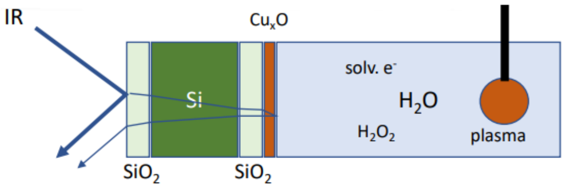

Fig. 2. sketch of FTIR measurement setup

The wavenumber range of interest is the fingerprint region of the spectrum ranging from 340 cm^{-1} to 1500 cm^{-1}.

The electrodes are being monitored by shadowgraphy images taken before and after plasma treatment.

Additionally a Scanning Electron Microscope (SEM) is used to investigate the surface structure of the electrodes before and after use and Transmission Electron

Microscopy (TEM) is used to inspect the particles in the treated liquid in cooperation with the Center for Solvation Science (ZEMOS) at the Ruhr-University Bochum.

3. Preliminary results

The results of the FTIR surface monitoring can be seen in Figure 3.

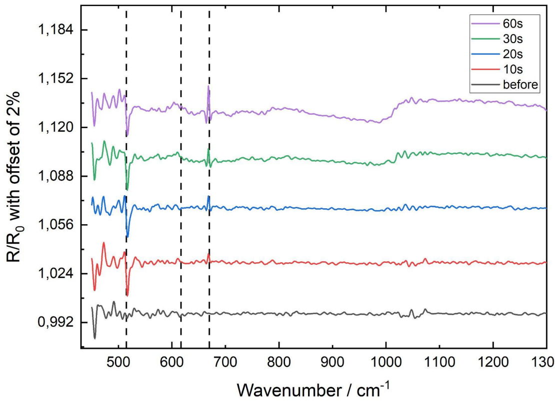

Fig. 3. FTIR spectra of a 10 nm Cu layer on a SiO$_2$ wafer before and after 10, 20, 30 and 60s of plasma treatment. The peak at 670 cm^{-1} is caused by CO$_2$ in the beam path, the peaks at 515 cm^{-1} and 617 cm^{-1} are attributed to CuO and Cu$_2$O, respectively.

The FTIR spectra show a rise of the absorption line at 670 cm^{-1}. This peak is caused by CO$_2$ in the beam path and is not of interest in this work. The peaks at 515 cm^{-1} and 617 cm^{-1} are attributed to cupric oxide (CuO) and cuprous oxide (Cu$_2$O), respectively. Their development suggests that the amount of CuO increases on the surface, whereas the Cu$_2$O decreases slightly. The plasma treatment causes an oxidation of the surface, possibly converting the cuprous oxide into cupric oxide. The broad increase of transmission between 1000 cm^{-1} and 1300 cm^{-1} is most likely caused by the SiO$_2$ wafer.

The spectra are compared with a measurement of a Cu coated Si wafer in Figure 4:

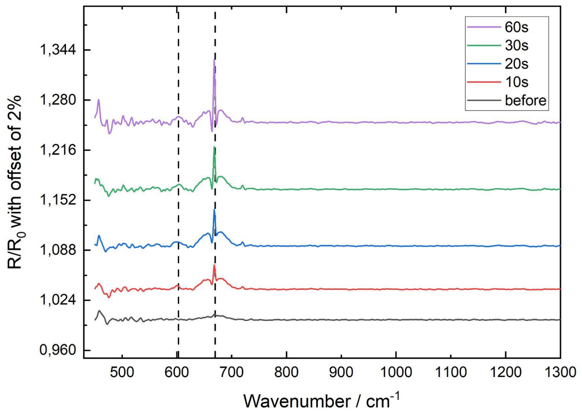

Fig. 4. FTIR spectra of a 10 nm Cu layer on a Si wafer before and after 10, 20, 30 and 60s of plasma treatment. The peak at 670 cm^{-1} is again caused by CO$_2$.

In Figure 4 the rise of the line at 670 cm^{-1} of the CO$_2$ is again recorded. The signal caused by the SiO$_2$ is not visible, which is to be expected. The peak at 515 cm^{-1} caused by CuO is not visible as well. At 604 cm^{-1} a slight increase is recorded that could be attributed to CuO according to Balik et al. [2]. This indicates a decrease of CuO caused by the plasma treatment. The change at a wavenumber of 617 cm^{-1} (Cu$_2$O) is also not visible when the Si wafer is used. The spectra suggest that the plasma treatment reduced the copper oxide on the surface. Apparently the reactivity of the copper surface in the in-liquid plasma system is affected by the difference between SiO$_2$ or Si as substrate. An important difference is the lack of charge build up at the copper surface in the experiment using a Si layer only. One could speculate that the solvated electrons react differently on an insulation and a conductive nm sized metal target.

The erosion of the electrodes of in-liquid plasmas is assumed to be mainly caused by current heating. First SEM images of the electrode tips before and after use have shown that through the plasma treatment, protrusions on the surface are created. The images are comparable with findings of Lukes et al. [3] and suggest a rapid heating and cooling of the metal, during which electrode material can get ejected into the liquid.

In Figure 5 a TEM image of the particles found in the treated water is shown:

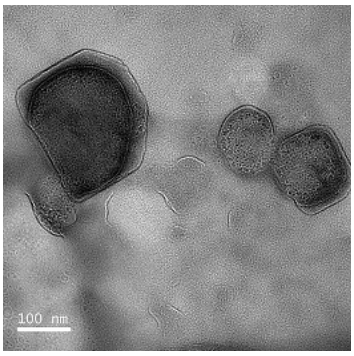

Fig. 5. TEM image of the particles found in the plasma treated liquid, produced at a voltage of 26kV at 100 Hz after 70 minutes. [P. Cignoni, E. Jüngling]

First TEM measurements show that particles in the size range of 100 nm can be found in the liquid. An inspection of the power densities reveals a value of ~50 GW/cm² at a Voltage of 20kV, which is typical for conventional laser ablation systems used for nanoparticle synthesis. In laser ablation, high energy laser pulses focused on a small area are used to remove particles from a surface, creating a plasma in the process. One could speculate that in-liquid plasmas can be used to produce nanoparticles in a similar fashion if the size of the particles can be controlled, making plasma-induced ablation another possible method for nanoparticle synthesis.

4. References

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