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# REMOVAL OF SURFACE IMPURITIES FROM QCM SUBSTRATES WITH THE LOW-PRESSURE OXYGEN-PLASMA TREATMENT

## ODSTRANJEVANJE POVRŠINSKIH NEČISTOČ S QCM-PODLAG Z OBDELAVO V NIZKOTLAČNI KISIKOVI PLAZMI

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A novel method for cleaning quartz crystals used in QCM is presented. Crystals were covered with a thin film of impurities containing protein fibrinogen, sodium stearate and sodium chloride. Samples were exposed to the oxygen plasma created by an electrodeless radiofrequency discharge in the H-mode. The oxygen pressure was fixed to 10 Pa, the nominal power of the RF-generator was 200 W, the reflected power was about 24 W, and the treatment times were up to 40 s. The plasma was characterized with optical emission spectroscopy. During the treatment of the samples the spectral features indicating a removal of impurities appeared in the optical spectra. The temporal evolution of characteristic optical features allowed for a real-time monitoring of the cleaning procedure. All the spectral features have been normalized to the temporal evolution of the atomic oxygen line at 615 nm. The CO features appeared in the first few seconds of the plasma treatment indicating a preferential removal of organic components. The Na atomic line at 589 nm became measurable after a few seconds of the plasma treatment, increasing for about 10 s and decreasing thereafter until it became very low after about 35 s. The results clearly indicate the applicability of oxygen plasma for a rapid removal of impurities from the surface of quartz crystals. Organic impurities are removed in a very short time due to an extremely high affinity of oxidation, while inorganic impurities can be removed only with a prolonged treatment when the thermal effects become important.

Keywords: protein fibrinogen, oxygen plasma, surface cleaning, etching

V članku predstavljamo novo metodo čiščenja QCM-podlag iz kremenovega kristala. Kristale smo prekrili s tanko plastjo nečistoč, ki so vsebovale protein fibrinogen, natrijev stearat in natrijev klorid. Vzorce smo izpostavili kisikovi plazmi, ustvarjeni z brezelektrodno radiofrekvenčno razelektritvijo v H-načinu. Obdelovali smo jih pri konstantnem tlaku 10 Pa, časi obdelave so bili do 40 s, moč RF-generatorja je bila 200 W, odbita moč pa okoli 24 W. Značilnosti plazme smo merili z optično emisijsko spektroskopijo. Med obdelavo vzorcev so se na optičnem spektru pojavile emisijske spektralne črte, ki jasno nakazujejo odstranjevanje nečistoč. Časovni potek teh črt nam je omogočil spremljanje postopka čiščenja v realnem času. Vse emisijske črte smo normalizirali s časovnim potekom kisikove atomske črte pri 615 nm. V prvih nekaj sekundah so se v spektrih pojavile emisijske črte molekule CO, kar nakazuje odstranjevanje organskih komponent. Intenziteta natrijeve emisijske črte pri 589 nm postane merljiva po nekaj sekundah plazemske obdelave, se veča približno 10 s, doseže maksimum in se nato manjša, dokler ne doseže nizkih vrednosti pri 35 s. Rezultati jasno prikazujejo uporabnost kisikove plazme pri hitrem odstranjevanju nečistoč s površin kremenovih kristalov. Organske nečistoče očistimo v zelo kratkem času zaradi visoke afinitete oksidacije, medtem ko anorganske nečistoče lahko odstranimo le z daljšimi obdelavami, ko termični efekti postanejo pomembni.

Ključne besede: protein fibrinogen, kisikova plazma, čiščenje površin, jedkanje

## 1 INTRODUCTION

Quartz crystal microbalance (QCM) is one of the most accurate devices for determining thin-film thickness.[1–6] The method is based on measuring the resonance frequency of the oscillating crystals, depending on the mass of the material deposited on the quartz crystal.[7] Quartz crystals are rarely used several times if the deposited material is not removed properly, making this technique rather expensive. In the vacuum practice crystals are often cleaned and reused in order to reduce costs. Several techniques for removing the surface impurities have been applied and most of them use wet chemical cleaning. Not only is this technology unfriendly to the environment, it often does not ensure an atomically clean surface. One can use different solvents for removing specific impurities such as organic solvents for removing organic materials and acids or bases for removing inorganic impurities. The latter may destroy the samples if not used properly. In many practical applications hundreds of samples should be measured and the cleaning of crystals may represent a major concern especially because the atomic cleanliness of a surface is not always guaranteed. In order to overcome this problem we have developed an alternative technique for removing the surface impurities that is based on an application of highly aggressive oxygen plasma.[8]

## 2 EXPERIMENTAL WORK

Commercially available QCM crystals have been used for the experiments. The crystals were covered with about a 100-nm thick film containing a mixture of fibrinogen, sodium citrate and sodium chloride. A commercially available lyophilized mixture of these materials

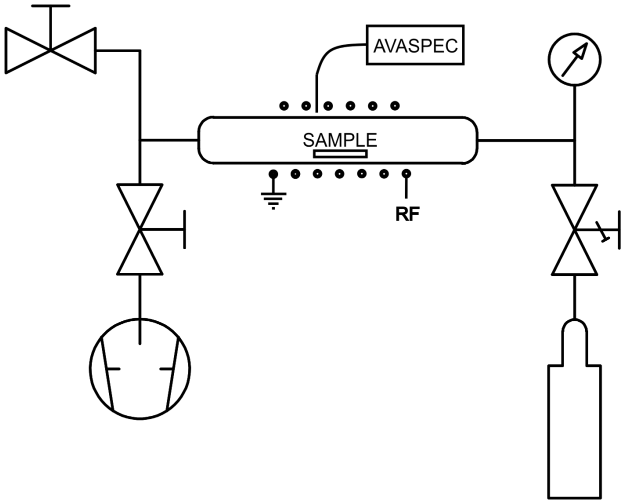


**Figure 1:** Schematic of the experimental set-up
**Slika 1:** Shema eksperimentalne postavitve

(Fibrinogen, Fraction I, type III from human plasma) was purchased from Sigma-Aldrich, dissolved in MiliQ water in order to obtain a 0.1 % solution, applied on a quartz crystal and distributed evenly by spinning it at 500 r/min. The samples were mounted into a vacuum system presented schematically in **Figure 1**. The system is pumped with a two-stage rotary pump with the nominal pumping speed of 80 $m^3 h^{-1}$. Commercially available oxygen is leaked into the system on the other side, so the oxygen pressure during continuous pumping is 10 Pa. The pressure is measured with a precise pressure gauge MKS Baratron 722A. Plasma was excited inside a glass tube with a diameter of 4 cm. A copper coil was connected to an RF-generator via a matching network. The generator operated at the standard frequency of 13.56 MHz and the nominal power variable up to 1000 W. During the current experiment the applied power was 200 W and the reflected power was 24 W, so the plasma was well matched with the generator. Luminous plasma was concentrated within the coil indicating almost a pure H-mode of the electrical discharge.

The plasma was characterized with optical emission spectroscopy. We used a spectrometer AVASPEC 3648 and the integration time was fixed to 50 ms. Such an integration time, rather unusual for a characterization of luminous plasma in the H-mode, was applied in order to let the major peaks oversaturate and detect the minor peaks and bands.

## 3 RESULTS

A typical spectrum of gaseous plasma at the absence of any sample is presented in **Figure 2**, while a spectrum of plasma during the treatment of a quartz crystal contaminated with a film of impurities is shown in **Figure 3**. Both spectra show oversaturated major atomic lines, but the spectral features corresponding to the etching of

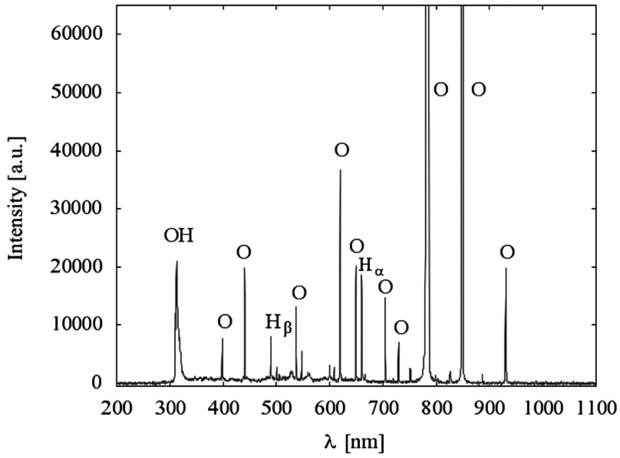


**Figure 2:** Typical optical spectrum of oxygen plasma at the absence of a sample
**Slika 2:** Značilni optični spekter kisikove plazme brez vzorca

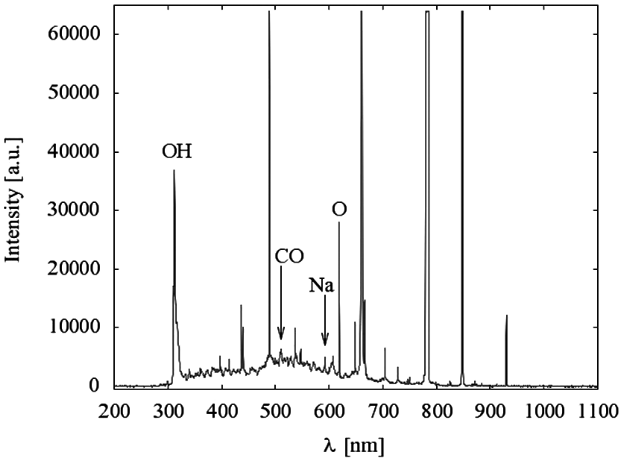


**Figure 3:** Typical optical spectrum of oxygen plasma at the presence of a sample
**Slika 3:** Značilni optični spekter kisikove plazme pri obdelavi vzorca

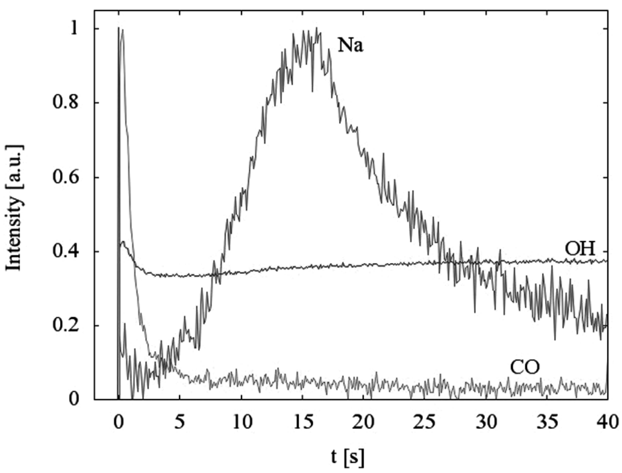


**Figure 4:** Temporal evolution of specific spectral features during the plasma cleaning of the quartz crystal contaminated with a 100-nm thick film of impurities
**Slika 4:** Časovni potek določenih emisijskih spektralnih črt med plazemskim čiščenjem kremenovega kristala z naneseno debelo plastjo nečistoč 100 nm

surface impurities are clearly visible in **Figure 3**. Selected spectral features during the plasma treatment of a sample are presented in **Figure 4**. These spectral features have been normalized to the temporal evolution of the atomic oxygen line at 615 nm.

## 4 DISCUSSION

Optical spectra of oxygen plasma during the treatment of quartz crystals, contaminated with surface impurities, have been collected continuously for 40 s. A spectrum without a sample was also measured and it is presented in **Figure 2**. As expected, neutral oxygen-atom atomic lines prevail. The absence of any molecular bands just indicates a well-known characteristic of plasma, created by the RF-discharge in the H-mode – an almost 100 % dissociation rate. Such a very high dissociation rate is due to a very low coefficient for a heterogeneous surface recombination of O-atoms on the glass surface as well as the absence of three body collisions at 10 Pa that could otherwise allow for a gas-phase recombination. Plasma is therefore almost 100 % dissociated and many oxygen atoms are probably found in the excited states that are metastable. Such atoms are chemically extremely reactive and will interact with organic as well as some inorganic impurities even at room temperature. Well pronounced spectral features peaking at 309 nm correspond to OH radicals. This peak is due to the presence of water vapour in our vacuum system that has never been baked. Water molecules dissociate to OH and H radicals in a rather powerful discharge. The spectral features presented in **Figure 3** are different. Not only are the hydrogen atomic lines corresponding to Balmer series much higher, but other features are observed as well. The most significant one is the broad continuum that has been assigned to various transitions of CO radicals.[9,10] Also, the Na atomic line at 589 nm is clearly visible. The existence of these two features indicates a substantial etching of the surface impurities deposited on quartz crystals.

The time evolution of some spectral features is shown in **Figure 4**. Let us first discuss the extremely sharp peak of the OH radical found just after turning on the discharge. As mentioned earlier, our system was frequently vented and never baked so that the surfaces are covered with adsorbed water molecules. As soon as the discharge is turned on the molecules desorb and quickly dissociate in gaseous plasma and are excited by the inelastic collisions with free electrons. Since the amount of water molecules on the surfaces is rather low, practically all the molecules desorb in a very short time. This is the reason of the sharp peak observed in **Figure 4**. For the next few seconds the intensity of the OH peak slowly decreases until it becomes constant. Such a decrease cannot be attributed to the desorption of water molecules from the discharge tube, as it is probably due to the oxidation of organic impurities containing hydrogen. This hypothesis is sound with the behaviour of the CO peak. This peak appears immediately after turning on the discharge. Since it is absent in the plasma created in an empty tube, it can be attributed to the oxidation of organic materials. The fact that the peak appears only in the first few seconds of the plasma treatment indicates a rapid oxidation of organic impurities. Such a rapid oxidation is probably due to a rather high density of excited oxygen atoms in plasma. As mentioned earlier such metastable atoms are chemically extremely reactive. The sodium peak is also presented in **Figure 4**. The temporal evolution of this peak is completely different from the OH and CO peaks. The sodium peak becomes measurably high after about 5 s and its intensity is the highest after about 15 s. Oxygen plasma is obviously aggressive enough to react also with this sort of impurities.

## 5 CONCLUSIONS

A novel method for cleaning quartz crystals was presented. The method is ecologically benign since it does not produce any wastes. The method allows for a rapid removal of organic impurities since about a thick film 100 nm of fibrinogen with stearates is effectively removed in a few seconds. As expected, inorganic impurities such as sodium chloride are more resistant and it, therefore, takes a longer time to remove them. It is worth mentioning that oxygen plasma does not interact with silicon dioxide so that the properties of quartz crystals are preserved.

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