Hydrogen plasma cleaning of gold plasmonic nanostructures for better reproducibility of SERS spectra

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SERS is often used for the detection of self-assembled monolayers that attach to the gold surface of plasmonic nanostructures via gold-sulfur bonds. Oxygen plasma is typically used to remove such monolayers in order to clean and reuse the plasmonic nanostructures for further SERS measurements. In this paper, we show that oxygen plasma increases the SERS background signal and its variability. We found that hydrogen plasma cleaning leads to much more reproducible SERS spectra, thus providing a better alternative to oxygen plasma cleaning of SERS substrates.

Introduction

Surface-enhanced Raman spectroscopy (SERS) enables sensitive and selective detection of a molecule by acquiring a molecule-specific Raman signal that is enhanced in the proximity of a plasmonic nanostructure. Due to its sensitivity, SERS is often used for the detection of self-assembled monolayers (SAM) that attach to the gold surface of plasmonic nanostructures via gold-sulfur bonds. To clean and reuse such plasmonic nanostructures for SERS measurements, an oxygen plasma is normally used to remove the SAM. X-ray photoelectron spectroscopy, scanning tunneling microscopy, ellipsometry, and contact angle measurements were used to show that oxygen plasma cleaning contaminates the gold surface with oxidized sulfur species [1]. Hydrogen plasma has, therefore, been proposed as an alternative removal method of the SAM on gold nanostructures, as it produces a sulfur-free gold surface [1].

Methodology

Here, we examine the effects of oxygen and hydrogen plasma removal of the SAM from the gold nanostructures on SERS spectra. We perform these experiments on gold nanodomes, SERS substrates that provide high SERS enhancements and are easy to fabricate [2]. To make the SAM, we use the peptide CALNNF$_{CN}$SF$_{CN}$GGGGVRGNFSF, where the peptide sequence is written from the N-terminus to the C-terminus [3]. A peptide is a biological molecule found in nature, which consists of several amino acids linked with peptide bonds. Each amino acid is represented with one letter in the peptide sequence. In this particular peptide, the SERS peaks originate from the aromatic amino acids phenylalanine (F) and cyano-phenylalanine (F$_{CN}$). We observe the SERS peak of F at 1003 cm^{-1}, and the peak of F$_{CN}$ at 1180 cm^{-1}. The possible contaminants on the gold surface after plasma cleaning do not provide distinguishable SERS peaks but rather influence the SERS background signal.

We examined three different samples. In the first sample, a newly fabricated SERS substrate was labeled with the SAM. In the second and third sample, we labeled the SERS substrate with the SAM, then cleaned it for 2 minutes with hydrogen and oxygen plasma respectively, and relabeled the substrate with the same SAM. To assess the effects of oxygen and hydrogen plasma cleaning of the gold SERS substrates, we recorded the SERS spectra of the peptide and calculated the integrated counts of the SERS background signal.

Results and Discussion

In Figure 1, we show the SERS spectra of the three different samples. Figure 1(a) shows the background-subtracted SERS spectra acquired with identical acquisition conditions, namely identical laser power, laser spot size and integration time. The SERS peaks of the samples cleaned with hydrogen plasma have prominently lower SERS peak intensities compared to the other two samples. In addition, we plot the normalized SERS spectra of the three samples in Figure 1(b), where the spectra are normalized on their respective highest peak intensities. We see that the SERS background of the samples cleaned with oxygen plasma is much more prominent, so that even the higher SERS peaks are not easily distinguishable from the SERS background.

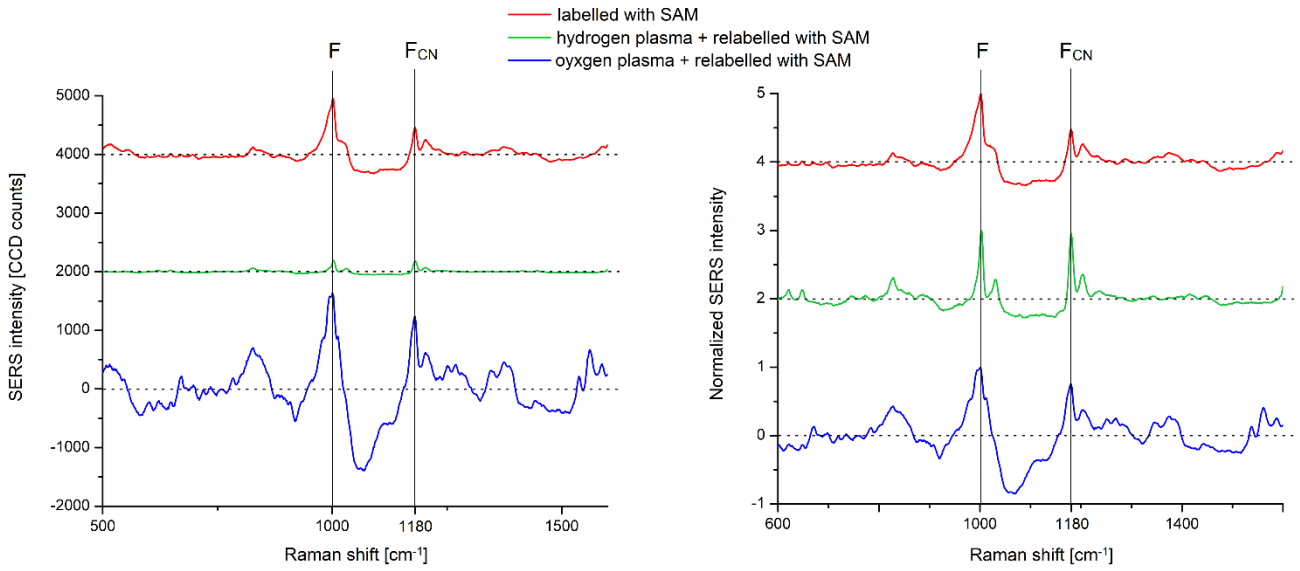

Figure 1. SERS spectra of the samples labeled with the SAM (red), cleaned with hydrogen plasma and then relabeled with the SAM (green) or cleaned with oxygen plasma and relabeled with the SAM (blue). (a) Background-subtracted SERS spectra acquired with identical acquisition conditions. (b) SERS spectra from (a), normalized on their respective highest peak intensities. The dashed horizontal lines represent the zero line of each spectrum, whereas the full vertical lines mark the SERS peaks of the aromatic amino acids.

We then integrated the SERS background signal counts for the Raman shifts in the range from 500 to 1500 cm^{-1} to evaluate the effects of oxygen and hydrogen plasma cleaning of the gold SERS substrates, as shown in Figure 2. We notice that reusing the SERS substrates after cleaning them with oxygen plasma increases their SERS background signal, and even more prominently, increases the variability of the background signal. On the other hand, hydrogen plasma cleaning offers a much more reproducible SERS

background, which can be of crucial importance when subtracting the SERS background to detect (weaker) SERS peaks.

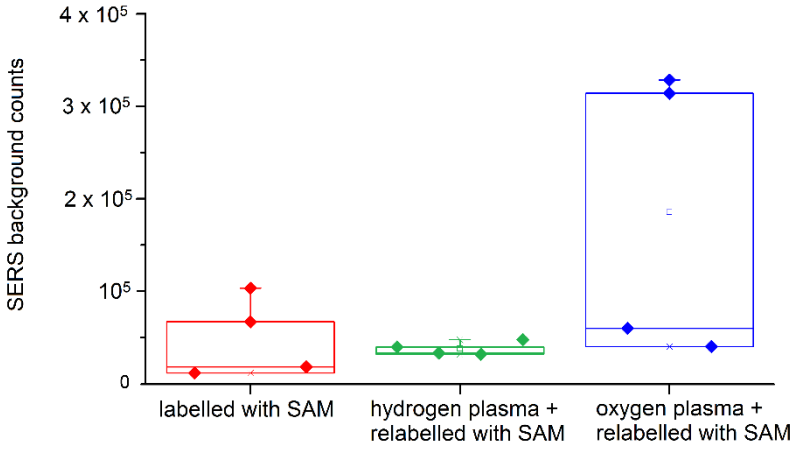

Figure 2. SERS background counts integrated between 500 and 1500 cm^{-1} for the samples labeled with the SAM (red), cleaned with hydrogen plasma and then relabeled with the SAM (green) or cleaned with oxygen plasma and relabeled with the SAM (blue). The points represent the averaged values on individual samples, whereas the box plot represents the statistical distribution of the points.

Next, we examined the F/F_{CN} peak intensities for the three different samples (Figure 3). As explained above, the remaining contaminants will only affect the SERS background and will not result in SERS peaks. However, to quantify the SERS peaks of the Raman analytes of interest, we rely on the accurate subtraction of the SERS background. Since SERS background reproducibility is negatively affected by the oxygen plasma cleaning, the background subtraction therefore becomes more unreliable, additionally resulting in an increased variability of the quantification of the SERS peaks of the Raman analytes of interest, in our case the peptide.

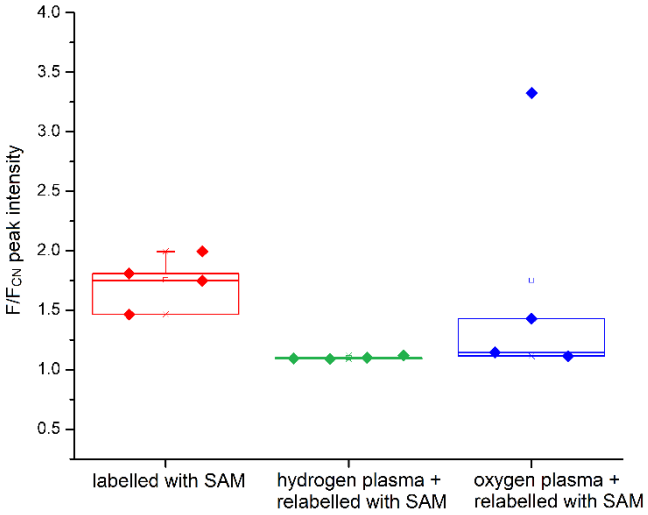

Figure 3. F/F_{CN} peak intensities for the samples labeled with the SAM (red), cleaned with hydrogen plasma and then relabeled with the SAM (green) or cleaned with oxygen plasma and relabeled with the SAM (blue). The points represent the averaged values on individual samples, whereas the box plot represents the statistical distribution of the points.

We show scanning electron microscopy images of the three different samples in Figure 4. From Figure 4(c), it is clear that hydrogen plasma cleaning can have a negative influence on the gold nanodome SERS substrate. Indeed, we notice the appearance of the circular defects on the gold nanodomes fabricated on a silicon nitride wafer. We have not found a record of similar defects in literature, but we assume that the defects are specific for the silicon nitride and the gold that we used to fabricate the gold nanodomes. With the optimization of the hydrogen plasma parameters, specifically the plasma power, it is possible however to avoid the formation of the circular defects.

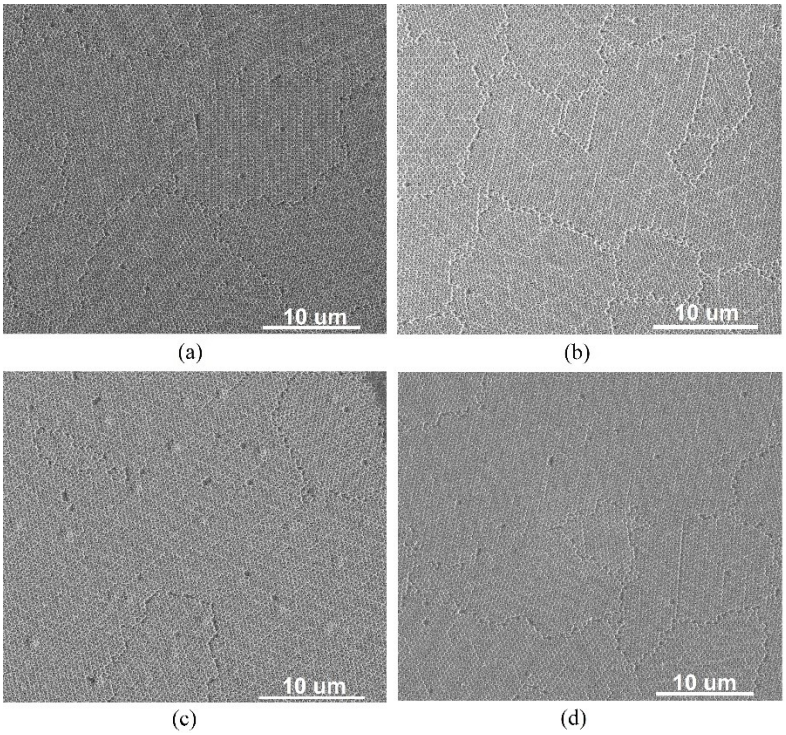

Figure 4. Scanning electron microscopy (SEM) images of the samples labeled with the SAM (a), cleaned with oxygen plasma and then relabeled with the SAM (b) or cleaned with hydrogen plasma with different plasma powers and relabeled with the SAM (c, d).

Conclusions

We have demonstrated that hydrogen plasma cleaning of the self-assembled monolayers from gold nanostructures results in more reproducible SERS background spectra than when oxygen plasma cleaning is used. Consequently, the SERS peak characterization of our Raman analytes of interest is more reliable due to the more reproducible background subtraction. We furthermore discovered that using hydrogen plasma to clean our gold nanodomes on silicon nitride can introduce some additional surface defects, which can however be avoided by optimizing the parameters of the hydrogen plasma process.

References

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