Surface Preparation of Gold Nanostructures on Glass by Ultraviolet Ozone and Oxygen Plasma
for Thermal Atomic Layer Deposition of Al₂O₃

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Abstract

Thin film deposition to create robust plasmonic nanomaterials is a growing area of research. Plasmonic nanomaterials have tunable optical properties and can be used as substrates for surface-enhanced spectroscopies. Due to the surface sensitivity and the dependence of the near-field behavior on structural details, degradation from cleaning or spectroscopic interrogation causes plasmonic nanostructures to lose distinctive localized surface plasmon resonances or exhibit diminished optical near-field enhancements over time. To decrease degradation, conformal thin films of alumina are deposited on nanostructured substrates using atomic layer deposition. While film growth on homogenous surfaces has been studied extensively, atomic layer deposition-based film growth on heterogeneous nanostructured surfaces is not well characterized. In this report, we have evaluated the impact of oxygen plasma and ultraviolet ozone pre-treatments on Au nanoparticle substrates for thin film growth by monitoring changes in plasmonic response and nanostructure morphology. We have found that ultraviolet ozone is more effective than oxygen plasma for cleaning gold nanostructured surfaces, which is in contrast to bulk films of the same material. Our results show that oxygen plasma treatment negatively impacts the nanostructure and alumina coating based on both scanning electron microscopy analysis of morphology and changes in the plasmonic response.

Keywords: alumina, atomic layer deposition, substrate cleaning, gold nanostructures, UV ozone, oxygen plasma, localized surface plasmon resonance

1. Introduction

At the nanoscale, materials exhibit different electrical, conductive, optical, and mechanical properties. One example of a nanoscale optical phenomenon is the localized surface plasmon resonance (LSPR) response of metal nanoparticles. In the presence of electromagnetic (EM) waves, coherent oscillations of electrons in metal nanoparticles lead to wavelength selective absorption and scattering of light as well as locally enhanced EM fields around the particles [1]. The LSPR response is highly dependent on the structural properties and dielectric environment of the nanoparticles and this behavior has formed the basis for using metal nanoparticles in sensing and spectroscopy applications [2-6]. Due to the strong dependence on structural characteristics, plasmonic nanoparticles can lose distinctive LSPR responses and EM fields enhancements may diminish over time due to structural degradation from functionalization or cleaning procedures. In addition, exposure of the metal nanostructures to high-energy femtosecond lasers also often leads to deformation or melting of metal nanostructures, especially when plasmons are induced leading to focusing of the incident intensity due to plasmonic antenna effects [7]. Degradation of the surface of nanoparticles limits shelf life (i.e. storage under N₂, etc.), especially due to oxidation processes of materials such as silver and adsorption of molecules from the surrounding environment leading to changes in surface properties over very short time periods. In order to inhibit or avoid surface degradation and structural damage, incorporation of ultra-thin protective coatings to cover complex, high aspect ratio structures over large surface areas has been investigated [7-9].

One approach to introduce a thin protective coating is atomic layer deposition (ALD) of alumina (Al₂O₃). In ALD of alumina, a sub-nanometer conformal thin film is deposited by self-

terminating reactions of trimethylaluminum (TMA) and water via a well-understood mechanism [10-13]. ALD-based film deposition is an especially good approach for protecting plasmonic nanostructures because the near field enhancements decay rapidly, on the order of a few nanometers to tens of nanometers from the surface. The physical robustness of Al_2O_3 protected metal nanostructures has been documented for femtosecond laser excitation [7] and for thermal cleaning treatments up to 400 °C [9]. These studies have shown that Al_2O_3 protected structures retain morphology and plasmonic properties under harsh experimental and cleaning conditions. While these alumina ALD studies are done on nanostructured surfaces, there is yet no research into the quality of the alumina film covering the nanostructures, unlike in alumina film coverage of continuous metal films on substrates which has been studied more extensively [14, 15].

On most continuous metal surfaces, an Al_2O_3 film forms via island growth, nucleating at a few defect sites from which the islands grow together after several deposition cycles to eventually form a film [10]. This type of growth can lead to pinhole defects and irregular surfaces and is especially problematic for fabricated gold nanoparticles. After a few minutes of exposure to air, gold becomes hydrophobic due to surface adsorption of species in the environment [16, 17], which can negatively impact alumina deposition. One approach to establish defect-free alumina films is through control of the TMA nucleation by increasing the hydrophilicity of the gold substrate using surface cleaning techniques. However, surface modification is more challenging for a heterogeneous surface such as metal nanostructures supported on a substrate because of the presence of different materials (i.e., the nanostructures and the underlying substrate). With increasing interest in thin film deposition on heterogeneous nanostructured surfaces, it is important to take into account the unique properties the nanoscale regime offers.

Modification of the metal nanoparticle structure leads to changes in the LSPR response, which ultimately impacts any application based on tailoring the optical properties through control of structural features. Sub-nanometer controlled deposition of a reproducible, defect-free ultrathin film is necessary, especially when the desired application depends on accessing the exponentially decaying EM near-field. Ideally, the surface preparation needs to leave the underlying nanostructure undamaged while also yielding a defect free, ultra-thin film.

Two surface preparation techniques, oxygen plasma and ultraviolet-ozone (UVO), are used extensively in fabrication to remove hydrocarbon contaminants from bulk Au and Si surfaces [14, 18-20] and from nanostructured surfaces [21-23]. Both techniques generate hydrophilic surfaces, which is ideal for Al_2O_3 deposition. However, the comparative impact of these techniques on nanostructured surfaces with different materials exposed (e.g., gold and SiO_2) has yet to be examined to the same extent as has been observed for uniform Au films or silicon surfaces. Recently, reports have indicated that oxygen plasma can be destructive to Au nanoparticles (AuNPs) [24, 25] but others have argued that the plasma does not alter the AuNP surface or damage only happens under very aggressive conditions [21]. In the case of UVO cleaning of surfaces, early studies were conducted for continuous planar metal films, but the assessment of the impact of UVO cleaning has not been extended to nanostructured surfaces.

In this report, fabricated plasmonic Au nanodisks (AuNDs) on glass were used as the model heterogeneous nanostructured substrate to investigate the effects of oxygen plasma compared to UVO treatment as a surface preparation process for Al_2O_3 thin film deposition. Due to the surface sensitivity of the LSPR response of AuNDs, any changes of the structure (shape changes,

etching effects, etc.) as well as the local environment of the structure (the alumina film), can be monitored with UV/vis spectroscopy. Our studies demonstrate that when oxygen plasma cleaning procedures used for bulk metal films and glass or silicon substrates are applied to nanostructures, the process significantly alters the surface of gold nanostructures, as observed by changes in the LSPR response based on transmission UV-vis spectroscopy measurements and structure morphology from scanning electron microscopy analysis. Subsequently, damaging of the nanostructures impacts the nucleation of the Al_2O_3 film and nanostructure stability.

2. Experimental Details

2.1. Fabrication

Nanosphere template lithography coupled with ion beam milling was used to fabricate gold nanodisks (AuNDs) and has been described elsewhere [26-28]. Briefly, using an electron-beam evaporator (Denton SJ20C Vacuum USA, Moorestown, NJ), a 35 nm gold film as measured by a quartz crystal microbalance (XPC2 Inficon, East Syracuse, NY) was deposited ($1 \text{ \AA/s}$; normal to the substrate surface) under high vacuum ($1.3 \times 10^{-7} \text{ Pa}$ or $1.0 \times 10^{-6} \text{ mTorr}$) onto 1 in. x 1 in. glass slides. A 0.01 % w/v solution of $220 \pm 17.6 \text{ nm}$ polystyrene beads (Polysciences, Inc.) was spin cast (900 rpm, 35 sec) on the Au films. An argon ion milling system (PlasmaLab 80 Plus, Oxford Instruments) was used to remove the Au film at a power of 100 W and flow rate of 10 sccm. The polystyrene spheres serve as templates by shielding portions of the Au from the ion beam milling, producing nanodisks. The polystyrene beads were then removed by lift-off using transparent tape, and the samples were stored under nitrogen.

2.2. Atomic layer deposition

A Cambridge NanoTech Fiji F200 Plasma (Cambridge, MA) ALD reactor was used to grow an Al_2O_3 film on the AuNDs and glass substrate. TMA and water were pulsed alternately in a nitrogen carrier stream using a growth temperature of 33 °C and base pressure of 1.33 Pa (1.6×10^{-6} mTorr). The process occurred in four steps: (1) 0.06 sec pulse of water, (2) 60 second purge with nitrogen, (3) 0.06 second pulse of TMA, (4) 10 second purge with nitrogen.

2.3. Cleaning treatments

AuNDs and alumina-coated AuNDs (Al_2O_3 -AuNDs) were exposed for 10 minutes with either UVO (Jelight 342, Irvine CA) or oxygen plasma (PlasmaLab 80 Plus, Oxford Instruments) at 10 sccm, 75 W and a base pressure of 3.33 Pa (25 mTorr). The commercial UVO system produces 28 mW/cm^2 at 5 mm (operating distance from lamp) at ambient pressure. An exhaust assembly with blower attachment was used to maintain a positive flow of media through the system.

2.4. Characterization

The optical properties of the AuNDs were characterized by transmission UV-vis spectroscopy. Extinction spectra were collected with a Perkin-Elmer Lambda 750 UV/vis spectrophotometer with 100 % angular controlled s-polarized light. The λ_{max} was determined using Spectrum software and the center of gravity function with all unaltered, as-fabricated disk samples. Scanning electron microscopy (SEM) (FEI NovaNano 630 equipped with a Helix detector) was used to analyze film deposition and structural changes of bare and alumina coated AuNDs.

2.5. Contact angle measurements

Images of 10 μL drops of Nanopure deionized water were collected with a c525 Logitech webcam. Contact angle measurements were made with the ImageJ Contact Angle package.

3. Results and Discussion

We investigated the utilization of UV ozone (UVO) and oxygen plasma for surface preparation of a heterogeneous nanostructured surface comprised of gold nanodisks (AuNDs) supported on glass for ALD-based alumina film growth. Oxygen plasma for cleaning is generated by converting oxygen gas into monatomic oxygen and oxygen ions and radicals by radiofrequencies at low pressure. The ions and radicals react with hydrocarbons, either C-C or C-H bonds, to form H_2O , CO, and CO_2 which are then pumped out of the system. The high kinetic energy of the ions can lead to sputter-etching of surfaces when they collide, but this is typically considered a more minor secondary process. For UVO cleaning, atmospheric air is exposed to UV light to form reactive species. Molecular oxygen dissociates into oxygen anions at 184.9 nm and these anions can then form ozone by reacting with O_2 . Ozone absorbs radiation at 253.7 nm and forms $3[\text{O}]^\cdot$. These ions react with hydrocarbons and generate volatile molecules that subsequently desorb from the surface.

We studied the impact of UVO and oxygen plasma cleaning on the nanostructures and ALD film growth by electron microscopy analysis of the AuNDs and by monitoring the plasmonic response of the AuNDs. Two sets of AuNDs were cleaned with either UVO or oxygen plasma and these were compared to a control set that was left untreated prior to each of two Al_2O_3 depositions. The optical properties of the three sets ($n=9$ samples per set) of 35-nm-thick AuNDs were collected by extinction spectroscopy at three different time points: after fabrication (λ_{max}),

after the initial cleaning and Al_2O_3 deposition (λ_{ALD1}), and after the second cleaning and Al_2O_3 deposition (λ_{ALD2}). Each Al_2O_3 deposition was prefaced with the designated cleaning treatment. The time between the fabrication of the AuNDs and the initial cleaning and deposition was 24 hours. The initial Al_2O_3 deposition was 200 AB cycles, which ideally would deposit an 18 nm-thick Al_2O_3 film. After optical analysis with UV/vis spectroscopy, all samples were kept in sealed storage jars for one month to model shelf storage. After the one month storage, samples were cleaned as described (untreated, oxygen plasma, or UVO) and a second Al_2O_3 deposition of 50 AB cycles was performed which would ideally deposit a 4.5 nm-thick Al_2O_3 film. This second deposition evaluates the effectiveness of the cleaning techniques to prepare an aged Al_2O_3 -coated Au nanostructured surface for an additional film deposition via ALD.

3.1. Hydrophobicity of treated films

While the hydrophobicity of UVO and oxygen plasma treatments has been studied, we qualitatively evaluated Au films and nanostructured substrates to compare with the trends reported in literature based on the cleaning techniques used here[17]. An evaporated Au film was stored in a sealed jar for 24 hours. After this time period, the film had a contact angle of 94° ; after treatment with UVO (10 min.) the surface was completely wetted by a 10 μL drop of deionized water. A separate film that was fabricated at the same time, under the same conditions, was treated with an oxygen plasma (10 min.) and had a water contact angle of 10° , suggesting a slightly more hydrophobic surface than the surface treated with UVO. It is important to note that the contact angle measurement was carried out 4 hours after oxygen plasma treatment.

AuND samples stored for 24 hours had water contact angles of 49° , showing that the nanostructured surface became more hydrophobic during that time, though not as significantly as the Au films. After UVO treatment, the AuNDs supported on glass were completely wetted by 10 μL drop of deionized water. After oxygen plasma exposure (4 hour delay between exposure and measurement) the contact angle was 17° . The oxygen plasma treatment on the heterogeneous AuNDs was less effective than the oxygen plasma treatment on the Au film as evidenced by the larger contact angle. This difference highlights the fact that these cleaning treatments do not necessarily lead to the same outcomes for bulk films and heterogeneous surfaces and the different physical properties of these surfaces need to be accounted for when fabricating thin films over nanostructured substrates.

3.2. LSPR based characterization of film formation and nanostructure changes

The LSPR response of the AuNDs depends on the local materials (Au nanostructures and Al_2O_3) and the response is used to gain an understanding of surface changes by monitoring shifts in the LSPR peak using UV/vis spectroscopy. Angstrom scale depositions of alumina can be detected by monitoring changes in the λ_{max} due to the sensitivity of the LSPR to the addition of the material on the surface of the nanostructures [29, 30]. Specifically, AuNDs are sensitive to a change in refractive index (RI). As alumina (RI = 1.63) is deposited, there is a red shift in the λ_{max} and if alumina is removed from the AuND surface, there is a blue-shift in the LSPR response. LSPR can also be used to probe changes to the underlying nanoparticle structure because the LSPR is highly dependent on metal nanostructure shape parameters (diameter, height, shape). If the structure is made smaller by etching, the LSPR response blue shifts; as a general rule, smaller particles are blue shifted with respect to larger particles of the same

geometry. Therefore, LSPR response of the AuNDs is used to probe film formation with high sensitivity as well as nanostructure fidelity. The initial λ_{max} of the unaltered AuNDs ranged from 952-980 nm. Figure 1 shows SEM images of the final Al_2O_3 -AuNDs and spectra of representative samples immediately after fabrication (solid line), after 200 AB cycles of Al_2O_3 deposition (dashed line), and after 50 AB cycles of Al_2O_3 addition (dotted line). The average LSPR peak shift for the first 200 AB depositions is summarized in Table 1 as $\Delta\lambda_{\text{ALD1-max}}$ and the peak shift after the second alumina deposition of 50 AB cycles is summarized as $\Delta\lambda_{\text{ALD2-ALD1}}$.

The freshly prepared AuNDs supported formation of an alumina film. The untreated AuNDs (spectra Figure 1D) exhibited an average $\Delta\lambda_{\text{ALD1-max}}$ of 80.8 ± 2.4 nm for the first Al_2O_3 film deposition (Table 1). After the AuNDs were stored for one month, we attempted to form a second alumina film. After 50 AB cycles of Al_2O_3 deposition, the untreated AuNDs had an average LSPR shift of $\Delta\lambda_{\text{ALD2-ALD1}}$ of 0.3 ± 3.3 nm ($n=8$ samples). This suggests that the Al_2O_3 surface of the untreated samples did not maintain a clean surface capable of ideal Al_2O_3 nucleation and growth after one month of storage.

Oxygen plasma treated AuNDs (Figure 1E) had a $\Delta\lambda_{\text{ALD1-max}}$ of 59.2 ± 4.1 nm. The red shift indicates that material was deposited on the AuNDs, but less than the untreated or UVO treated AuNDs. After one month of storage, a second cleaning process and 50 AB cycles of alumina deposition, the LSPR response blue-shifted with a $\Delta\lambda_{\text{ALD2-ALD1}}$ of -49 ± 9 nm. Based on the blue shifted LSPR response, we suspected that the Al_2O_3 surface of the oxygen treated samples did

not support Al_2O_3 nucleation and Au or Al_2O_3 was likely removed during exposure to the oxygen plasma. The reason for this conclusion will be discussed in more detail below.

UVO treated AuNDs (Figure 1F) had a $\Delta\lambda_{\text{ALD1-max}}$ of 82.0 ± 2.3 nm after the first cleaning treatment and alumina film growth. After the one month of storage, a second cleaning treatment and 50 AB cycles of Al_2O_3 deposition, the UVO treated AuNDs exhibited a $\Delta\lambda_{\text{ALD2-ALD1}}$ of 11.2 ± 1 nm. Thus, the UVO treatment of the AuNDs led to alumina film formation after both cleaning treatments, even after storage of Al_2O_3 -coated AuNDs. Compared to the untreated and oxygen-plasma cleaned AuNDs, the UVO treatment led to consistent Al_2O_3 film nucleation and consistent, reproducible growth.

The untreated laboratory stored AuNDs and the UVO cleaned AuNDs exhibited similar LSPR responses, 81 and 82 nm red shifts, respectively, after the addition of Al_2O_3 in the first deposition. The similar response for untreated (Figure 1A and D) and UVO treated (Figure 1C and F) AuNDs suggests that the difference in surface reactivity for Al_2O_3 nucleation between “fresh” AuNDs (untreated) and UVO treated AuNDs is minimal. The 60 nm LSPR shift of the AuNDs after the first oxygen plasma treatment and alumina film growth indicates that (Figure 1B and E) the nucleation and film growth was inhibited relative to the untreated and UVO treated AuNDs. Significantly, the aged Al_2O_3 -AuNDs could only support additional Al_2O_3 film growth when treated with UVO without damaging the underlying structure. Similar to the loss of hydrophilicity that a metal or Si film or structured surface would experience upon introduction to the atmosphere and consequential buildup up hydrocarbons and debris [14, 18, 19, 25, 31, 32], the hydrophilic alumina surface becomes hydrophobic over time. Once the surface is

hydrophobic to some extent, the deposition of alumina is impeded and is increasingly island-like and less conformal.[33]. By cleaning the aged Al_2O_3 -AuNDs with UVO, the debris is removed and the $-\text{OH}$ terminated or hydrophilic properties of the Al_2O_3 film are renewed or “re-activated.”

We undertook an additional study to determine the cause of the smaller initial LSPR red shift (60 nm) of the oxygen plasma treated AuNDs after the initial alumina deposition and the blue shift (-49 ± 9 nm) of the oxygen plasma treated Al_2O_3 -AuNDs following the second alumina deposition. After fabrication and LSPR characterization (i.e. determination of the LSPR λ_{max}), AuNDs were treated with UVO or oxygen plasma and the LSPR peak position (λ_{cleaned}) was determined with UV/visible spectroscopy without an additional alumina deposition. In order to have the most freshly cleaned AuNDs for alumina deposition for the study described above, we did not characterize the LSPR response of those AuNDs immediately after cleaning, before alumina deposition. In this study, measurement of the LSPR response (λ_{cleaned}) after cleaning, but before the addition of alumina, probes the effect of the cleaning treatment on the Au nanostructures. Table 2 presents a summary of the results. The oxygen treated AuNDs had a blue-shifted $\Delta\lambda_{\text{cleaned.} - \text{max}}$ of -20 ± 6 nm and the UVO treated AuNDs exhibited a red-shifted $\Delta\lambda_{\text{cleaned.} - \text{max}}$ of 1 ± 2 nm after the cleaning procedure. The blue shift of the LSPR response after the cleaning treatment provides evidence that the oxygen plasma etches the AuNDs. This 20 nm blue shift corresponds well to the difference between the LSPR responses measured for oxygen plasma and UVO treated AuNDs discussed above ($\Delta\lambda_{\text{ALD1-max}}$, 59.2 ± 4.1 nm and 82.0 ± 2.3 nm, respectively). It may be that Au is removed from the surface by a secondary sputtering process during the oxygen plasma exposure, but Al_2O_3 nucleates and forms a film to the same extent as is

formed on the UVO treated samples. The combination of these two processes would lead to a smaller $\Delta\lambda_{\text{max}}$ compared to AuNDs that have not been etched before alumina film growth. However, this does not explain the origin of the substantial blue shifted $\Delta\lambda_{\text{ALD2-ALD1}}$ of -49 ± 9 nm for the oxygen treated Al_2O_3 -AuNDs that was observed after the second alumina deposition.

In order to probe if the oxygen plasma treatment was also etching the alumina film, we fabricated Al_2O_3 -coated AuNDs and monitored the LSPR response after exposure to oxygen plasma. An alumina film was formed on AuNDs using a 50 AB cycle ALD process (~ 5 nm Al_2O_3) immediately after an initial oxygen plasma treatment to insure the cleanest AuNDs for Al_2O_3 deposition. After the initial LSPR (λ_{max}) of the Al_2O_3 -AuNDs was determined with UV/visible spectroscopy, two sets ($n=9$ per set) of AuNDs were treated with either UVO or oxygen plasma and the λ_{cleaned} was determined. The oxygen plasma treated Al_2O_3 -AuNDs exhibited a LSPR shift of -48 ± 7 nm and the UVO treated Al_2O_3 -AuNDs had a LSPR shift of 6 ± 6 nm (see Table 2). The large blue shift for the oxygen plasma treated AuNDs indicates that both Al_2O_3 as well as possibly Au are etched during treatment. The size of the observed blue shift (-48 nm) agrees well with the shift observed in the AuND cleaning experiments discussed above. The total blue shifting of the LSPR response of -20 nm after oxygen treatment of uncoated AuNDs and -48 nm after treatment of alumina-coated AuNDs accounts for the approximately 70 nm difference between UVO and oxygen plasma treated AuNDs in the cleaning experiments (see Table 1) after the two treatment/ALD deposition processes.

3.3. SEM characterization of film formation

The observations of the LSPR response as related to both etching and alumina deposition are supported by the SEM images shown in Figure 1. The individual nanodisk in each image shown is representative of the entire sample set and the high uniformity of nanodisk structures is well known [27, 34]. The diameter of UVO treated Al_2O_3 -AuND (n=50 AuNDs) averaged 309 ± 15 nm, untreated (n=56 AuNDs) averaged 307 ± 14 nm, and oxygen treated (n=36 AuNDs) averaged 255 ± 18 nm. These size differences are consistent with the LSPR shifts and the standard deviations are within that of the native polystyrene template (see section 2.1). The UVO treated AuNDs supported alumina film growth during both deposition cycles ($\Delta\lambda_{\text{total}}$ of 93 ± 2 nm) and had the largest diameter. The oxygen treated AuNDs had the smallest $\Delta\lambda_{\text{total}}$ of 11 ± 12 nm and also the smallest diameter of the final Al_2O_3 -AuNDs. A qualitative inspection of the SEM images shows that UVO and untreated Al_2O_3 -AuNDs (Figure 1A and C, respectively) have similar, uniform Al_2O_3 film growth. The AuNDs are clearly seen beneath the Al_2O_3 film, which has a smooth and sharply contrasted edge as shown by the outer ring in the SEM images. In comparison, the oxygen plasma treated Al_2O_3 -AuND (Figure 1B) does have a coating of Al_2O_3 , but the film forms a less uniform layer around the AuND. The film appears to have an almost serrated-edge outer ring that lacks the sharp contrast of the other alumina-coated AuNDs; this suggests incomplete nucleation and film growth or a roughened AuND. While literature reports that oxygen plasma does not damage gold surfaces[14], the oxygen plasma pretreated Al_2O_3 -AuND shows signs of deterioration of the underlying AuND which is consistent with a blue-shifted LSPR response (as discussed in section 3.2).

The serrated-edge structures shown in the SEM images and the size discrepancy between UVO and oxygen plasma treated samples qualitatively show that the oxygen plasma samples had less

Al_2O_3 growth and the underlying AuND was etched, creating a smaller nanostructure with more surface roughness. Damage to the nanostructures highlights the importance of investigating nanostructure properties and stability compared to bulk films of the same material under the same surface preparation conditions.

There is extensive research showing that oxygen plasma and UVO both have utility in removing hydrocarbons from Au films and silicon substrates. Berman and Krim [14] showed that oxygen plasma can be used in radio-frequency microelectromechanical system (RF-MEMS) applications to clean gold films without increasing surface roughness. In a direct comparison of UVO and oxygen plasma, a monolayer of tridecafluorotris(dimethylamino)silane or FOTAS, was chemically bonded to a MEMS device and then treated with either UVO or oxygen plasma[18]. Using Time-of-Flight secondary ion mass spectrometry (ToF-SIMS), it was determined that oxygen plasma was a more effective cleaning method for occluded areas of silicon surfaces[18]. However, the vast majority of studies comparing UVO and oxygen plasma treatments were based on investigations using bulk films. The study that is most relevant for substrates supporting micro- and nano-structures is presented by Raiber et al. The authors discuss the use of self-assembled monolayers (SAMs) as a resist in lithographic techniques to produce micrometer-sized Au-structured films. The fabrication method uses an oxygen plasma to remove the SAMs in a post-etching process. The authors did not report damage to the resulting microstructures. However, this may be because the Au films used in the fabrication were quite thick (40-200 nm) and were large in terms of their lateral dimensions (i.e., well beyond nanoscale or even microscale features). Our study indicates that the sensitivity of nanoscale structures to morphology necessitates consideration of whether or not a surface treatment process used for

bulk films can be transferred without consequences to heterogeneous nanostructured surfaces, even processes as simple as surface cleaning and preparation.

Our studies also provide evidence that surface treatments can impact robust alumina coatings. We observed that oxygen plasma treatment of alumina-coated AuNDs resulted in blue-shifted LSPR responses (section 3.2) and produced nanostructures with roughened edges (Figure 1B), indicating the alumina coating was etched to some extent. In contrast, UVO treated AuNDs had consistent Al_2O_3 growth and UVO treatment re-activated old Al_2O_3 -AuND after short-term storage (one month) without damaging the structures.

4. Conclusions

We have observed that oxygen plasma exposure, though a successful cleaning method for bulk Au films and silicon surfaces, has detrimental effects on heterogeneous surfaces composed of Au nanostructures supported on glass. For bare AuNDs and Al_2O_3 -AuNDs on glass substrates, oxygen plasma etches both the Au and the Al_2O_3 . We have also shown that an Al_2O_3 -coated device can have a long shelf with the use of a simple cleaning technique, making the development of these devices practical. UVO treatment of AuNDs prior to Al_2O_3 deposition generates uniform growth and re-activates aged and “dirty” Au and Al_2O_3 surfaces. This adds to early work by King [16], which demonstrated that UVO treatments result in a rapid loss of surface bound hydrocarbons and oxycarbons. By treating the AuNDs with UVO, the surface reactivity is more homogeneous, which leads to uniform nucleation in the ALD process. This is an important finding as defect-free films are a key component of nanostructure protection and fabrication optimization.

In summary, there have been conflicting reports on the impact of oxygen plasma on nanoparticles, but our findings support other observations that oxygen plasma treatments are detrimental to nanoparticles [24, 25]. Moreover, we propose the use of UVO to clean heterogeneous Au nanoparticle surfaces with the additional benefit of being a superior technique for preparation of thin film deposition when a hydrophilic surface is required, as in the case of atomic layer deposition of alumina.

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REFERENCES

- [1] K.A. Willets, R.P. Van Duyne, Localized surface plasmon resonance spectroscopy and sensing, *Ann. Rev. Phys. Chem.* 58 (2007) 267-297.
- [2] C.E. Talley, J.B. Jackson, C. Oubre, N.K. Grady, C.W. Hollars, S.M. Lane, T.R. Huser, P. Nordlander, N.J. Halas, Surface-enhanced raman scattering from individual Au nanoparticles and nanoparticle dimer substrates, *Nano Lett.* 5 (2005) 1569-1574.
- [3] R.F. Aroca, R.A. Alvarez-Puebla, N. Pieczonka, S. Sanchez-Cortez, J.V. Garcia-Ramos, Surface-enhanced Raman scattering on colloidal nanostructures, *Adv. Colloid Interface Sci.* 116 (2005) 45-61.
- [4] H. Aouani, M. Rahmani, H. Šípová, V. Torres, K. Hegnerová, M. Beruete, J. Homola, M. Hong, M. Navarro-Cía, S.A. Maier, Plasmonic nanoantennas for multispectral surface-enhanced spectroscopies, *J. Phys. Chem. C* 117 (2013) 18620-18626.
- [5] P. Johansson, H. Xu, M. Käll, Surface-enhanced Raman scattering and fluorescence near metal nanoparticles, *Phys. Rev. B* 72 (2005) 035427.
- [6] Z. Zhang, T. Imae, Study of surface-enhanced infrared spectroscopy: 2. Large enhancement achieved through metal-molecule-metal sandwich configurations, *J. Colloid Interface Sci.* 233 (2001) 107-111.
- [7] J. Sung, K.M. Kosuda, J. Zhao, J.W. Elam, K.G. Spears, R.P. Van Duyne, Stability of silver nanoparticles fabricated by nanosphere lithography and atomic layer deposition to femtosecond laser excitation, *J. Phys. Chem. C* 112 (2008) 5707-5714.
- [8] J. He, C.-y. Huang, N. Dai, D.-m. Zhu, Study of surface plasmon resonance of Au nanoparticles coated with dielectric layers, *SPIE*, 2011, pp. 81910N-81910N-81917.
- [9] S.M. Mahurin, J. John, M.J. Sepaniak, S. Dai, A reusable surface-enhanced Raman scattering (sers) substrate prepared by atomic layer deposition of alumina on a multi-layer gold and silver film, *Appl. Spectrosc.* 65 (2011) 417-422.
- [10] S.M. George, Atomic layer deposition: An overview, *Chem. Rev.* 110 (2010) 111-131.
- [11] A.C. Dillon, A.W. Ott, J.D. Way, S.M. George, Surface chemistry of Al_2O_3 deposition using $\text{Al}(\text{CH}_3)_3$ and H_2O in a binary reaction sequence, *Surf. Sci.* 322 (1995) 230-242.
- [12] K. Devloo-Casier, K.F. Ludwig, C. Detavernier, J. Dendooven, In situ synchrotron based x-ray techniques as monitoring tools for atomic layer deposition, *J. Vac. Sci. Technol. A* 32 (2014) 14.
- [13] R.L. Puurunen, Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process, *J. Appl. Phys.*, 97 (2005) 121301-121301-121352.
- [14] D. Berman, J. Krim, Impact of oxygen and argon plasma exposure on the roughness of gold film surfaces, *Thin Solid Films* 520 (2012) 6201-6206.
- [15] Y. Zhang, J.A. Bertrand, R. Yang, S.M. George, Y.C. Lee, Electroplating to visualize defects in Al_2O_3 thin films grown using atomic layer deposition, *Thin Solid Films*, 517 (2009) 3269-3272.
- [16] D.E. King, Oxidation of gold by ultraviolet light and ozone at 25 °c, *J. Vac. Sci. Technol. A*, 13 (1995) 6.
- [17] G.L. Gaines Jr, On the water wettability of gold, *J. Colloid Interface Sci.*, 79 (1981) 295.
- [18] D.A. Hook, J.A. Olhausen, J. Krim, M.T. Dugger, Evaluation of oxygen plasma and UV ozone methods for cleaning of occluded areas in MEMS devices, *J. Microelectromech. Syst.* 19 (2010) 1292-1298.
- [19] Y.-S. Lin, A surface analysis on oxygen plasma-cleaned gold pattern-plated substrates for wire bondability, *Surf. Coat. Technol.* 173 (2003) 47-57.

- [20] K. Raiber, A. Terfort, C. Benndorf, N. Krings, H.-H. Strehblow, Removal of self-assembled monolayers of alkanethiolates on gold by plasma cleaning, *Surface Science* 595 (2005) 56-63.
- [21] J. Gun, D. Rizkov, O. Lev, M.H. Abouzar, A. Poghossian, M.J. Schoening, Oxygen plasma-treated gold nanoparticle-based field-effect devices as transducer structures for bio-chemical sensing, *Microchim. Acta* 164 (2009) 395-404.
- [22] J. Llorca, A. Casanovas, M. Dominguez, I. Casanova, I. Angurell, M. Seco, O. Rossell, Plasma-activated core-shell gold nanoparticle films with enhanced catalytic properties, *J. Nanoparticle Res.* 10 (2008) 537-542.
- [23] A. Fahmi, A. D'Aleo, R.M. Williams, L. De Cola, N. Gindy, F. Voegtle, Converting self-assembled gold nanoparticle/dendrimer nanodroplets into horseshoe-like nanostructures by thermal annealing, *Langmuir* 23 (2007) 7831-7835.
- [24] K. Winkler, T. Wojciechowski, M. Liszewska, E. Gorecka, M. Fialkowski, Morphological changes of gold nanoparticles due to adsorption onto silicon substrate and oxygen plasma treatment, *RSC Advances* 4 (2014) 12729-12736.
- [25] D. Hohertz, S.F. Romanuik, B.L. Gray, K.L. Kavanagh, Recycling gold nanohole arrays, *J. Vacuum Sci. Technol. A* 32 (2014) 031403.
- [26] C.L. Haynes, R.P. Van Duyne, Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics, *J. Phys. Chem. B* 105 (2001) 5599-5611.
- [27] Y.B. Zheng, B.K. Juluri, B. Kiraly, T.J. Huang, Ordered Au nanodisk and nanohole arrays: Fabrication and applications, *J. Nanotechnol. Eng. Med.* 1 (2010) 031011.
- [28] P. Hanarp, M. Käll, D.S. Sutherland, Optical properties of short range ordered arrays of nanometer gold disks prepared by colloidal lithography, *J. Phys. Chem. B* 107 (2003) 5768-5772.
- [29] A.V. Whitney, J.W. Elam, S. Zou, A.V. Zinovev, P.C. Stair, G.C. Schatz, R.P. Van Duyne, Localized surface plasmon resonance nanosensor: A high-resolution distance-dependence study using atomic layer deposition, *J. Phys. Chem.* 109 (2005) 20522-20528.
- [30] F. Mazzotta, T.W. Johnson, A.B. Dahlin, J. Shaver, S.-H. Oh, F. Höök, Influence of the evanescent field decay length on the sensitivity of plasmonic nanodisks and nanoholes, *ACS Photonics* 2 (2015) 256-262.
- [31] J.C. Peter, S. Naoko, J.B. Anders, F.P. Jose, Stability of reference masses: Vii. Cleaning methods in air and vacuum applied to a platinum mass standard similar to the international and national kilogram prototypes, *Metrologia* 50 (2013) 532.
- [32] T. Smith, The hydrophilic nature of a clean gold surface, *Journal of Colloid and Interface Science*, 75 (1980) 51-55.
- [33] N.P. Kobayashi, C.L. Donley, S.-Y. Wang, R.S. Williams, Atomic layer deposition of aluminum oxide on hydrophobic and hydrophilic surfaces, *J. Cryst. Growth* 299 (2007) 218-222.
- [34] B.K. Juluri, N. Chaturvedi, Q. Hao, M. Lu, D. Velegol, L. Jensen, T.J. Huang, Scalable manufacturing of plasmonic nanodisk dimers and cusp nanostructures using salting-out quenching method and colloidal lithography, *ACS Nano* 5 (2011) 5838-5847.

Table Captions and Tables

Table 1. LSPR $\lambda_{\max}$ shift of all AuNDs (n = 9) after cleaning treatment and Al₂O₃ deposition, with the exception of the untreated $\Delta\lambda_{\text{ALD2-ALD1}}$ where n=8.

	$\Delta\lambda_{\text{ALD1} - \max} \text{ (nm)}$			$\Delta\lambda_{\text{ALD2-ALD1}} \text{ (nm)}$			$\Delta\lambda_{\text{Total}} \text{ (nm)}$		
Cleaning Procedure	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ
Untreated	81	$\pm$	2	0.3	$\pm$	3.3	78	$\pm$	12
Oxygen plasma	60	$\pm$	4	-49	$\pm$	9	11	$\pm$	12
UVO	82	$\pm$	2	11	$\pm$	1	93	$\pm$	2

Table 2. LSPR shift ($\Delta\lambda_{\text{cleaned}} \cdot \lambda_{\max}$) of all AuNDs (n = 9) and Al₂O₃-AuNDs (n=9) after specified cleaning treatment.

	AuND			Al ₂ O ₃ -AuND		
	$\Delta\lambda_{\text{cleaned} - \max} \text{ (nm)}$			$\Delta\lambda_{\text{cleaned} - \max} \text{ (nm)}$		
Cleaning Procedure	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ
Untreated	-6	$\pm$	4	2.3		
Oxygen plasma	-20	$\pm$	6	-48	$\pm$	7
UVO	1	$\pm$	2	6	$\pm$	6

Figure Captions:

Figure 1. LEFT: SEM of AuNDs on SiO₂ after 250 AB cycles to create a an Al₂O₃ film; (A) untreated sample with no cleaning process before Al₂O₃ deposition; (B) oxygen plasma treated before Al₂O₃ deposition; (C) UVO treated before Al₂O₃ deposition. Scale bar is 500 nm.

RIGHT: Spectra of AuNDs immediately after fabrication (solid line), after 200 AB cycles of Al₂O₃ deposition (dashed line), and after an additional 50 AB cycles of Al₂O₃ (dotted line); (D) untreated sample with no cleaning process before Al₂O₃ depositions; (E) oxygen plasma treated before each Al₂O₃ deposition; (F) UVO treated before each Al₂O₃ deposition.

Table 2. LSPR $\lambda_{\max}$ shift of all AuNDs (n = 9) after cleaning treatment and Al₂O₃ deposition, with the exception of the untreated $\Delta\lambda_{\text{ALD2-ALD1}}$ where n=8.

	$\Delta\lambda_{\text{ALD} - \text{max}}$ (nm)			$\Delta\lambda_{\text{ALD2} - \text{ALD1}}$ (nm)			$\Delta\lambda_{\text{Total}}$ (nm)		
Cleaning Procedure	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ
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Table 2. LSPR shift ($\Delta\lambda_{\text{cleaned-max}}$) of all AuNDs (n = 9) and Al₂O₃-AuNDs (n=9) after specified cleaning treatment.

Cleaning Procedure	AuND			Al ₂ O ₃ -AuND		
	$\Delta\lambda_{\text{cleaned - max}}$ (nm)			$\Delta\lambda_{\text{cleaned - max}}$ (nm)		
	$\bar{\lambda}$	$\pm$	σ	$\bar{\lambda}$	$\pm$	σ
Untreated	-6	$\pm$	4	2.3		
Oxygen plasma	-20	$\pm$	6	-48	$\pm$	7
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Figure 2. LEFT: SEM of AuNDs on SiO₂ after 250 AB cycles to create an Al₂O₃ film; (A) untreated sample with no cleaning process before Al₂O₃ deposition; (B) oxygen plasma treated before Al₂O₃ deposition; (C) UVO treated before Al₂O₃ deposition. Scale bar is 500 nm. RIGHT: Spectra of AuNDs immediately after fabrication (solid line), after 200 AB cycles of Al₂O₃ deposition (dashed line), and after an additional 50 AB cycles of Al₂O₃ (dotted line); (D) untreated sample with no cleaning process before Al₂O₃ depositions; (E) oxygen plasma treated before each Al₂O₃ deposition; (F) UVO treated before each Al₂O₃ deposition.