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Surface preparation of gold nanostructures on glass by ultraviolet ozone and oxygen plasma for thermal atomic layer deposition of Al_2O_3

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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.

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 field 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 N_2, 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 (Al_2O_3). 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].

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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. Subnanometer 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 Å/s; normal to the substrate surface) under high vacuum (1.3×10^{-7} Pa or 1.0×10^{-6} mTorr) onto 1 in. × 1 in. glass slides. A 0.01% w/v solution of 220 ± 17.6 nm polystyrene beads (Polysciences, Inc.) was spin cast (900 rpm, 35 s) 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 s pulse of water, (2) 60 s purge with nitrogen, (3) 0.06 s pulse of TMA, (4) 10 s purge with nitrogen.

2.3. Cleaning treatments

AuNDs and alumina-coated AuNDs (Al_2O_3-AuNDs) were exposed for 10 min 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 $3[O]^-$. These ions react with hydrocarbons and generate volatile molecules that subsequently desorb from the surface.