Postdeposition UV-Ozone Treatment: An Enabling Technique to Enhance the Direct Adhesion of Gold Thin Films to Oxidized Silicon

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ABSTRACT: We found that continuous films of gold (Au) on oxidized silicon (SiO$_2$) substrates, upon treatment with ultraviolet (UV)-ozone, exhibit strong adhesion to the SiO$_2$ support. Importantly, the enhancement is independent of micro- or nanostructuring of such nanometer-thick films. Deposition of a second Au layer on top of the pretreated Au layer makes the adhesion stable for at least 5 months in environmental air. Using this treatment method enables us to large-scale fabricate various SiO$_2$-supported Au structures at various thicknesses with dimensions spanning from a few hundreds of nanometers to a few micrometers, without the use of additional adhesion layers. We explain the observed adhesion improvement as polarization-induced increased strength of Au-$\delta$-Si-$\delta$+ bonds at the Au-SiO$_2$ interface due to the formation of a gold oxide monolayer on the Au surface by the UV-ozone treatment. Our simple and enabling method thus provides opportunities for patterning Au micro/nanostructures on SiO$_2$ substrates without an intermediate metallic adhesion layer, which is critical for biosensing and nanophotonic applications.

KEYWORDS: UV-ozone treatment, adhesion enhancement, gold thin films, gold oxide, oxidized silicon substrates

Micro/nanostructures made of Au supported on fused-silica or oxidized silicon (SiO$_2$) substrates have attracted much interest in recent years due to their wide range of potential applications such as chemical and biological sensors, optical devices, localized surface plasmon resonance spectroscopy, and surface-enhanced Raman spectroscopy (SERS). However, fabrication of such structures has been considered challenging due to the inherently poor adhesion of Au to SiO$_2$. Generally, an additional metallic adhesion layer, for example, titanium (Ti) or chromium (Cr), is used to improve the adhesion of the Au films. However, it is reported that such adhesion metals deteriorate the optical and electrical properties of pure Au. Various other methods have been explored to enhance the adhesion of Au on substrates such as plasma treatment of the substrates with different gases, postirradiation of deposited Au films with high energetic ion beam, and spin-casting of organic layers. Treating the substrate with a plasma before the Au deposition, e.g., Ar/H$_2$O plasma, or Ar plasma, or SF$_6$/O$_2$ plasma, can increase the surface wettability and/or the surface roughness in nanoscale of the substrates, thus improving the Au adhesion. Although being easy to operate, the plasma treatment method is mostly used for polymer substrates, e.g., poly(methyl methacrylate) (PMMA) and polyethylene (PE), as their surface properties can be easily modified by the plasma. Irradiating the deposited Au films with high energetic ion beams, e.g., 0.1 MeV Kr ion beam or 15 MeV Cl$^+$ ion beam, can also result in a good adhesion, which is attributed to an increase in the wetting of...
the gold at the substrate interface. However, this method requires a complex treatment process and a dedicated system. Spin-casting of organic layers, e.g., amino- and mercaptosilanes17 or silk protein,18 used as an adhesion layer provides an opportunity to pattern ultrathin and ultrasmooth Au layers well-adhered to the substrates, but in this case an additional layer is required.

In this paper, we report a method to significantly enhance the adhesion of deposited Au films to SiO2 substrates, by using a postdeposition UV-ozone treatment. The paper is structured into three sections. In the first section, we describe how postdeposition treatment of SiO2-supported Au films with UV-ozone results in an exceptional increase in their adhesion strength, compared to an untreated Au film. Deposition of a second Au film on top of the pretreated Au film is furthermore found to strongly extend the duration of adhesion. In the second section, we show that this treatment method can be used to fabricate various well-adhering Au micro/nanostuctures at various thicknesses on SiO2 substrates, without any additional adhesion layers. In the third section, we propose the mechanism causing this adhesion enhancement, which is an increased strength of Au–Siδ bonds at the Au–SiO2 interface due to the formation of a charge-polarized gold oxide layer on the Au surface upon UV-ozone treatment.

RESULTS AND DISCUSSION

Strength of the Adhesion. Au microdot arrays were patterned directly on the surface of oxidized Si wafers using a shadow mask (Figure 1a and Figures S1–S3). Their adhesion was measured with a modified tape test using a second Au layer sputtered on the microdot array (Figure 1b,c). The adhesion strength was quantified by comparing the remaining Au area after the tape test to the initial area of the patterned Au microdots. Different experimental sequences (“cases”) were conducted for investigating the Au adhesion to the SiO2 substrate, as given in Table 1.

Figure 2 shows the fraction of remaining Au area as a function of the diameter of fabricated Au microdots after the tape test for the cases 1–4 of Table 1. Without the UV-ozone treatment (case 1), the Au microdots of all diameters were completely removed (Figure S4), thus indicating the inherently poor adhesion of Au to SiO2.9 With the 5 min UV-ozone treatment (case 2), now between 83% and 96% of Au area remained attached, depending on the Au microdot diameter (Figures S5–S7). The dependence on the microdot area is attributed to partial removal at the microdot edges (important for the small microdots) and a large contact area with the continuous second Au layer (important for the larger microdots). Immersion in DI water for 10 min (case 3, Figures S8–S10) did not noticeably affect the adhesion.

Increasing the thickness of the Au microdots to approximately 24 nm results in a decrease in the adhesion strength (case 4, Figures S11–S13), thus indicating the dependence of the adhesion effect on the Au thickness. We found in this case that the center part of almost all Au microdots was removed, leaving only their circumference on the SiO2 surface, especially for large Au microdots.

Importantly, deposition of a second Au layer on top of the pretreated Au layer of ~13 nm thick caused the adhesion to remain stable in the environmental air for more than 5 months (Figures S14 and S15). This observation, which is considered...
in more detail in the mechanism section, allowed stable patterning of well-adhering thick gold layers without additional adhesion layers, which we used for micro/nanopatterning of various Au structures. 

**Patterning Gold Micro/Nanostructures on Oxidized Silicon Substrates.** Au micro/nanostructures with a stable and strong adhesion to the surface of oxidized Si wafers could be manufactured by a combination of lithography with a two-step sputtering process of stacked Au layers and an intermediate UV-ozone treatment (Figure 3).

Figure 4a,b show the top-view optical images of Au microdots and lines of ∼37 nm thickness, patterned directly on the surface of oxidized Si wafers. The patterns were well-defined over large areas of 5 × 5 mm², with high uniformity and good adhesion. It is noteworthy that there were no defects observed in the patterned structures, indicating that the Au adhesion to the oxidized Si substrate remained stable during all processing steps. Without applying the UV-ozone treatment, removal of multiple Au microdots was observed (Figure S16). Also, a ∼90 nm thick Au layer sputtered on a UV-ozone treated ∼13 nm thick Au layer showed stable adhesion, which could be patterned using wet etching (Figure S17).

Moreover, using the UV-ozone treatment also enables the large-area fabrication of various SiO₂-supported Au nanostructures, without the use of additional adhesion layers. The top-view high-resolution scanning electron microscope (HR-SEM) images (Figure 4c,d) show well-defined patterns of Au nanodots and lines of ∼37 nm thickness, which are well-adhered to the surface of oxidized Si wafers. In addition, the postdeposition UV-ozone treatment provides a direct way of patterning Au structures on oxidized Si substrates from a thin Au layer less than 13 nm thick by using patterned UV-ozone exposure and thereby controlling the formation areas of gold oxide (Figure S18 and Video S1).

Interestingly, we also observed an enhancement in the adhesion of Pt to SiO₂ after UV-ozone treatment. Although no further characterization has been performed, we used this treatment to pattern Pt nanodots and lines supported directly on the surface of oxidized Si wafers (Figure S19).22

**Patterning Gold Nanostructures on Other Substrates.** We also applied the UV-ozone treatment to pattern Au nanodots and lines directly on the surface of other substrates, i.e., silicon nitride (SiN, ∼50 nm thick)-coated Si substrates, MEMpax glass substrates, sapphire glass substrates, and indium tin oxide (ITO, ∼100 nm thick)-coated MEMpax glass substrates (Figure 5). This successful nanopatterning indicates that the postdeposition UV-ozone treatment might also provide good adhesion of the Au to these substrate materials, although no measurements of the increase in the adhesion strength of Au to these substrates have been performed. It has to be noted that the relatively rough surface of these used substrates probably also contributed to the Au adhesion enhancement, especially in the case of the SiN-coated Si substrates, the sapphire glass substrates, and the ITO-coated

![](image)
MEMpax glass substrates. Therefore, further investigation of the influence of the surface roughness on the adhesion of Au to these substrates is necessary.

**Mechanism of the Adhesion Enhancement.** As the mechanism for the adhesion enhancement, we propose a polarization-induced increased interaction strength at the Au−SiO2 interface when gold oxide is formed at the air−Au interface during UV-ozone treatment (Figure 6). The reaction of oxygen with Au surfaces has been reported to induce the transfer of electrons from the Au bulk into the adsorbed oxygen layer.23 This electron transfer has also been described by Sun et al.,24 where details of the interaction of adsorbed atomic oxygen with Au surface atoms were studied intensively using the Hüückel theory and density functional theory (DFT) calculations.

We hypothesize that this electron transfer causes an increased Au−Si bonding strength at the Au−SiO2 interface. This hypothesis is schematically depicted in Figure 6 and is based on the work of Bauer et al.25 and Sun et al.26 These authors investigated the interaction between Au and SiO2, the former authors by soft-X-ray photoemission spectroscopy and the latter by DFT. Both reported evidence for the formation of Au−Si bonds with a polarization Auδ−Siδ+. As this polarization implies partial electron transfer to the Au layer, we expect that these Au−Si bonds will be strengthened when gold surface oxidation causes partial electron transfer from the Au to the bound oxygen.

The formation and removal of gold oxide was confirmed by different methods. Ellipsometer data obtained after 5 min UV-ozone treatment were in accordance with the growth of a gold oxide layer of approximately 2.0 ± 0.2 Å, consistent with the approximate thickness (2 Å) of a monolayer of Au−O bonds.27 The change in the peak intensity of the reflectance spectrum measured on the Au surface after the UV-ozone treatment (Figures S20 and S21) without a significant change in the Au surface roughness is consistent with the formation/reduction of a gold oxide layer.27−29 Measurements of the contact angle (CA) of a DI water drop on a Au surface after the UV-ozone treatment were also in accordance with the formation of a gold oxide layer (Figure S22).27

It is known that gold oxide is reduced in ethanol.27,30 We therefore immersed the UV-ozone-treated Au microdots in ethanol for 10 min and found that the enhanced adhesion had vanished (case 5, Figure 7 and Figure S23). Re-treating the sample with UV-ozone restored the adhesion, though with a considerable drop in the adhesion strength, especially for small Au microdots (case 6, Figure 7 and Figures S24−S26). Our measured CA of a DI water drop on a Au film re-treated with UV-ozone also indicates the renewed formation of a gold oxide layer (Figure S22).

Decomposition of gold oxide over time in the environment is reported in the literature.31 Therefore, an oxidized Si wafer with UV-ozone-treated Au microdots was stored in environmental air for 2 weeks before the tape test (case 7, Figure 7). Figure 7 shows that all fabricated Au microdots were removed after the tape test (Figure S27), indicating the loss of the adhesion strength over time in environmental air, consistent with a gold oxide origin of the effect.

Deposition of a second Au layer on top of the pretreated Au layer of ∼13 nm thickness resulted in a major extension in the duration of its adhesion to the SiO2 substrate. The adhesion of stacked Au layers remained stable in environmental air (cleanroom relative humidity: 45 ± 10%) for more than 5 months (Figures S14 and S15). Arrays of Au microdots fabricated using this stacked Au layer configuration were found to pass the tape test after sonication at room temperature in ethanol for 2 h (case 8, Figure 7 and Figure S28). This is consistent with an embedded gold oxide layer that is insensitive to reduction during the sonication. A stable and strong adhesion of these Au microdots to the SiO2 surface was
obtained (Figures S29−S31). It is worth noticing that the embedded gold oxide layer could not be seen in an image recorded with transmission electron microscopy (Figure S32), probably due to its extremely low thickness of 2.0 ± 0.2 Å measured by ellipsometry.

A further experiment supported our hypothesis of a charge-based mechanism for the adhesion. We applied an electrical potential in water (Figure S33) to stacked Au films (a ∼24 nm Au layer sputtered on a UV-ozone-treated ∼13 nm Au layer), supported on amorphous fused-silica substrates. Applying a

Figure 5. (a) Top-view HR-SEM images (scale bar: 1 μm) of periodic Au nanodots and lines supported directly on the surface of different substrates. (b) AFM images (1 × 1 μm²) of the surface of these substrates with their corresponding surface roughness (Ra).

Figure 6. Schematic diagrams of the mechanism for the adhesion enhancement of (a) ∼13 nm thick Au microdots and (b) ∼24 nm thick Au microdots with the oxidized Si substrate, using the UV-ozone treatment.
negative potential to the stacked Au films resulted in their immediate detachment from the SiO₂ support, whereas they remained attached upon applying a positive potential. We attribute this detachment to the destabilization of the Au/Si₆⁺ bonds at the Au–SiO₂ interface by the additional negative charges. Reaction of Au with Si at the Au–SiO₂ interface was eliminated, as no increase in the surface roughness of the SiO₂ substrate after removing the UV-ozone-treated Au film occurred (Figure S34).

Using UV-ozone treatment for 5 min, we found that the center part of almost all ~24 nm thick Au microdots was removed, leaving only their circumference on the SiO₂ surface, especially for large Au microdots (Figures S11–S13). We can explain this observation by the hypothesis that the charge polarization at the Au–SiO₂ interface caused by the formation of the gold oxide on the Au surface becomes insignificant at this thickness. Only the adhesion effect at the perimeter of the Au microdots, where the gold oxide is located closer to the substrate, for a certain distance remained in this case, as conceptually shown in Figure 6b.

However, treating with O₂ plasma conducted at 500 W for 10 min using a plasma system (TePla 300, PAV TePla AG, Germany) could increase the adhesion of thicker Au films of approximately 24 nm thickness. An explanation can be that the thicker oxide layer formed (~14.4 ± 0.09 Å measured by ellipsometry) in this case still leads to a significant charge polarization at the Au–SiO₂ interface despite the thicker Au film.

Finally, we believe that the enhanced adhesion observed for Pt can also be explained by the proposed mechanism. Charge polarization at the interface of Pt–oxide support has been reported elsewhere. ⁴, ³³

CONCLUSION

In summary, we report an enabling technique to significantly enhance the direct adhesion of gold to oxidized silicon, solely by a UV-ozone treatment of the deposited Au films or structures. The observed enhancement of the adhesion can be explained as polarization-induced increased Au–SiO₂ interaction at their interface due to the formation of gold oxide on the Au/air interface upon UV-ozone treatment. By embedding the gold oxide layer in between two sputtered Au layers, the adhesion increase becomes durable and independent of the influence of the surrounding environment, i.e., gases or solutions. This enables the fabrication of SiO₂-supported Au micro/nanostructures, which strongly adhered to the substrate after storing for more than 5 months in environmental air or sonication in ethanol for 2 h. With its simple operation, our fabrication technique provides opportunities for patterning of various Au micro/nanostructures at different thicknesses supported directly on SiO₂ substrates, without the need of additional adhesion layers. The absence of such adhesion layers is highly favored for biosensing and nanophotonic applications. By using the UV-ozone treatment, we could fabricate high-quality tunable Au nanogap arrays for SERS application, without the need of metallic adhesion layers. ³⁴ In addition, we believe that our proposed adhesion mechanism could play a role in the adhesion of plasmonic nanoparticles fabricated by means of rapid focused ion beam milling reported by Chen et al. ³⁵ Finally, the successful patterning of Au nanostructures on SiN-coated Si wafers, sapphire glass substrates, MEMPax glass substrates, and ITO-coated MEMPax glass substrates indicates that the postdeposition UV-ozone treatment might also provide good adhesion of the Au to these substrate materials. However, further characterization of the adhesion strength and the influence of the surface roughness on the adhesion of Au to these substrates is necessary.
to the surface of the sputtered second Au layer containing the Au microdots and subsequently peeled off perpendicularly to the surface. All images of the Au microdots before and after the tape test were captured by using a bright field microscope and converted into grayscale images—Au microdot areas are converted into black pixels—in order to be analyzed by using ImageJ software. The strength of the adhesion was quantified by comparing the remaining black pixels after the test to the number before.

**Patterning Gold Micro/Nanostructures on Oxidized Silicon Substrates.** Periodic microlines/holes made of a positive photoresist (OIR 907-17i, Fujifilm, Japan) were patterned on SiO$_2$ substrates by using a conventional lithography process with a mask alignment system (EVG620, EV Group, Austria). However, for patterning periodic PR nanolines/holes, UV-based displacement Talbot lithography (DTL, PhableR 100C, Eulitha, Switzerland) was utilized. Details of the fabrication process are shown in Figure 3. A photoresist layer of 200 ± 1.5 nm (PF188 photoresist diluted 1:1 with propylene glycol methyl ether acetate, Sumitomo Chemical Co., Ltd., Japan) was patterned using the DTL technique with a photomask purchased from Eulitha. The patterned PR nanstructures were subsequently transferred at a 1:1 ratio into a bottom antireflection layer coating (BARC) layer of 187 ± 2 nm (AZ BARLi II 200) by using nitrogen (N$_2$) plasma etching. The plasma etching of BARC was conducted in a reactive ion etch system (home-built TEIske system, MESA+, NanoLab Cleanroom, The Netherlands) at wafer-level, 13 mTorr, and 25 W for 8 min.

These PR micro/nanostructures were then used as templates for patterning Au micro/nanostructures using a lift-off process. To improve the duration of the adhesion strength of the patterned Au micro/nanostructures, a combination of a two-step sputtering process of Au with an intermediate UV-ozone treatment was used. A Au layer of approximately 13 nm was sputtered over the PR structures, treated with UV-ozone for 5 min. Subsequently a second Au layer (~24 nm thick) was sputtered on top of the UV-ozone-treated Au layer, followed by lift-off in a 99% HNO$_3$ solution.

**Characterization.** The thickness of the deposited Au layers and formed gold oxide films was measured by ellipsometry (M-2000UI, J.A. Woollam Co., United States) at an angle of 75°. The surface roughness of the deposited Au layers was measured by atomic-force microscopy (AFM, Dimension Icon, Bruker Corp., USA) with a contact mode in air. HR-SEM images were captured by using an interfacial microscopy (AFM, Dimension Icon, Bruker Corp., USA) with a roughness of the deposited Au layers was measured by atomic-force microscopy (AFM, Dimension Icon, Bruker Corp., USA). Contact angle measurements, and contact angle measurements, and contact angle measurements, and chrononanopreometry, respectively.

**REFERENCES**


