Controlling surface effects in extremely high aspect ratio gold plasmonic electrodes

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ABSTRACT

Nanofabrication is key to many technological advances, especially the challenge of merging nanophotonics with electronics. Here, we investigate the fabrication process of plasmonic interdigitated gold electrodes having a very high aspect ratio (i.e. long and thin geometries) and a large surface area. Stringent stability issues that arise when these structures are fabricated using inorganic adhesion layers, such as titanium or chromium, on silica substrates are highlighted. We ascribe these problems to thermodynamical non-equilibrium states of freshly deposited gold and, in particular, discuss the role of surface energy in determining the structural properties of high aspect ratio gold nanostructures. We then show that the use of organic silane self-assembled monolayers improves the long term stability of these structures and, finally, characterize the fabricated electrodes. This technology can unleash the potential of hybrid optoelectronic circuits where current and light are manipulated with the same component.

1. Introduction

The continuous evolution of nanofabrication techniques in the past decades has enabled the controlled fabrication of devices with sub-100 nm features, allowing the investigation and control of physical phenomena at the quantum level and the nanoscale [1]. Arguably, the field that has benefited most from this miniaturization trend is electronics, where the number of electronic components on a single chip has steadily increased over the years [2], as anticipated by Moore. Consequently, longer and narrower interconnections are now required to join different active components located on the same substrate [3–5], and to interface these devices with the macroscopic world. Combining long and narrow intrinsically goes along with increasing the surface to volume ratio of the nanoscale structures [6,7] and makes properties such as interfacial adhesion, surface energy and diffusion of key importance. Parallel to this, there is an ongoing trend to integrate electronic and photonic capabilities into a single component that would outperform conventional semiconductor devices [8–10]. In particular, plasmonic electrodes are set to become a key component of future optoelectronic circuits thanks to their ability to both carry electronic signals and manipulate optical radiation [11]. The mutual coupling between the constituents of these complex systems gives rise to unexpected optical properties [12,13], offering compelling platforms for signal processing [10,14–16], biosensing [17,18] and hot-electron chemistry [19,20], to name a few examples. In this context, reliable fabrication strategies of high aspect ratio metallic nanowires are in strong demand. Among other metals, gold (Au) has found wide reaching applications in both electronics and plasmonics thanks to its high electrical conductivity and chemical stability, together with the ability to generate a plasmonic response in the visible and near infrared range [21–24]. Unfortunately, the fabrication of elongated gold nanostructures having extremely high surface to volume aspect ratios is a challenging task. On gold, surface self-diffusion occurs even at room temperature and, as a consequence, a gold nanostucture tends to spontaneously change its shape towards configurations with lower free energy and, hence, with a smaller surface [25–27]. In particular, freshly deposited gold thin films are especially unstable since they are in a partially amorphous phase [28,29]. This state, combined with a large surface and, hence, a high surface energy, is thermodynamically unfavorable, which further enhances surface diffusion. In addition, when working with gold films deposited on silica substrates, one has to also consider the adhesion between these two materials [30], which is neither mediated by strong chemical binding – since gold oxide is very unstable – nor by diffusion – as bulk diffusion is relatively low at room temperature [31]. Formally, good adhesion implies

\[ \gamma_{\text{Au}} + \gamma_{\text{SiO}_2} < \gamma_{\text{Si}} \]  

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and the silica, leading to a thermodynamically downhill reaction with introducing a layer of titanium (Ti) or chromium (Cr) between the gold substrate by the gold. Traditionally, good adhesion can be achieved by using inorganic adhesion layers and subsequently demonstrate the long term stability. First, we unveil the thermodynamic instability of different inorganic and organic adhesion layers on their experimentally and through the development of an empirical model, the semi-quantitative model that readily explains our experimental results in terms of change in the surface energies of our system.

2. Materials and methods

Let us describe the fabrication process of plasmonic circular gold dimers with long interconnections arranged into an interdigitated electrode array, as shown in Fig. 1. Each finger has an average aspect ratio (length/width) exceeding 220, while the whole structure possesses a surface to volume ratio greater than 40 μm⁻¹, as can be readily calculated by considering the dimensions of the large contact gold stripes. The electrodes are fabricated following the electron-beam lithography process outlined in Fig. 2. Briefly, 4-in. fused silica wafers (Schott AG, 525 μm thick) are first dried under a constant nitrogen flow for more than one week before being further dehydrated through a thermal treatment on a hotplate at 180 °C for 5 min, in order to promote resist adhesion [57]. Subsequently, 120 nm of MMA ELG (Micro-resist Technology GmbH) are spin-coated (ATMscale OPTispin SB20 manual coater, 6000 rpm) on the wafer, followed by 60 nm of PMMA 495K A2 (Micro-resist Technology GmbH, spin-coated at 1500 rpm). This way, the substrate is covered with a double layer of electron beam resist, which helps promoting the lift-off thanks to the formation of an undercut at the edges of the exposed areas after the development [58]. To avoid charging issues during the electron-beam exposure, a 20 nm conducting sacrificial layer of Cr is further evaporated on the resist (Alliance-Concept EVA760) and removed in a (NH₄)₂Ce(NO₃)₆ + HClO₄ solution (TechniEtch Cr01 from MicroChemicals) after the exposure. This is carried out with a Raith EBPG5000+ system at a 100 kV acceleration voltage, with varying beam doses between 500 and 1000 μC/cm² and beam currents ranging from 200 pA to 100 nA. After the Cr removal, the resist is developed in a MiBK:IPA 1:3 developer solution during 1 min under continuous circular agitation, rinsed for 1 min with isopropyl alcohol (IPA) and dried with a nitrogen gun. To fabricate the electrodes using inorganic adhesion layers, an 8 s. oxygen plasma treatment is applied to remove the residuals of undeveloped resist (Oxford PRS900, 300 sccm, 2 Torr, 500 W RF power) and to activate the surface for an improved adhesion. The same machine (Leybold Optics LAB600H) is then used to evaporate both the Ti or Cr adhesion layer and the gold film (thickness: 40 nm, deposition rate: 0.5 Å/s), without breaking the vacuum between the consecutive evaporations. For an organic adhesion layer, after developing the resist the substrate is first exposed to an oxygen plasma (Oxford PRS900, 300 sccm, 2 Torr, 500 W RF power) for 40 s. This longer plasma treatment, compared to the one used for inorganic adhesion layers, ensures both the removal of undeveloped resist and the creation of hydroxyl groups, needed for a proper silanisation, on the silica areas of interest. The sample is then readily placed for 10 h into a vacuum desiccator together with a vial containing (3-Mercaptopropyl)

Fig. 1. Sketch of the design under study. On the left, the full interdigitated geometry is shown, where the fingers of the gold electrodes are seen extending from larger contact gold stripes (1 μm × 1.2 cm) that allow for external electrical connection. The distance between adjacent fingers is 5 μm. The central panel shows a magnified view of one electrode pair and shows how each finger is composed of two connected successive sections (first 150 nm wide × 20 μm long followed by 70 nm wide × 5 μm long). At their extremity, these are joined to a 140 nm diameter disk, as displayed in the rightmost panel. The gap between two adjacent disks is 30 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
trimethoxysilane (MPTMS, 95%, from Merck, used as received). The released MPTMS molecules, shown in Fig. 3(a), adsorb on the sample, where the silane groups of the molecules establish weak hydrogen bonds with the hydroxyl groups present on the available glass surface. To stabilize the silane-glass bond, the sample is subsequently baked for 20 h at 80 °C, allowing the MPTMS to form siloxane bridges with the substrate and cross-link with adjacent molecules. The temperature is kept at 80 °C in order to prevent the destruction of the nanostructures shaped in MMA/PMMA, which has a glass temperature of about 110 °C [59, 60]. Afterwards, 40 nm of gold are evaporated on the sample (Leybold Optics LAB600H, deposition rate: 0.5 Å/s), where the metal atoms covalently bind to the available thiol groups of the SAM as shown in Fig. 3(b). After the gold film deposition, an extra stabilizing baking step is performed at 80 °C for 24 h. Finally, regardless of the type of adhesion layer used, the resist is stripped by immersing the sample into an acetone bath for 24 h. Prior to the SEM characterization (ZEISS Merlin), 1.5 nm of Cr are sputtered (Alliance-Concept DP650) onto the sample to avoid charging during imaging.

The optical characterization of the plasmonic electrodes is carried out on an Olympus IX73 inverted microscope setup. Briefly, with the help of a custom-made dark-field condenser, the white light from a halogen lamp is focused on the sample and a 60×/0.7 Olympus LUC-PlanFLN objective is used to collect the forward scattered light. This is normalized with respect to the spectrum of the lamp and analyzed with the help of an Andor Kymera 328i-A spectrograph equipped with a Newton 920 CCD detector purchased from Andor. The electrical characterization is carried out on a commercial probe station from Cascade Microtech, while the data is analyzed with a Keithley 4200A-SCS parameter analyzer. These measurements were taken in air atmosphere at room temperature. To ease the characterization of the electrodes, after the lift-off a 2.5 μm protective layer of photoresist (AZ 1512 HS) is spincoated (1000 rpm, followed by a 2 min baking at 107 °C) on the wafers before these are diced into chips using a Disco DAD321 automatic dicing saw machine (25,000 rpm, cutting speed of 1 mm/s). The resist is then stripped with acetone and IPA right before the measurements are performed.

3. Results and discussion

Let us now delve with more detail into the fabrication process of plasmonic gold electrodes on silica substrates employing inorganic and organic adhesion layers, before describing a semi quantitative model that fully explains our experimental observations.

3.1. Inorganic adhesion layers and surface effects

At first we discuss the configuration with a 3 nm Ti adhesion layer. Fig. 4(a) displays the SEM images of the fabricated structures recorded within 30 min after the lift-off step and demonstrate a successful
fabrication of both the plasmonic disks and the long connecting rods, albeit with a significant roughness for the latter. Interestingly however, after the sample is stored for more than three hours under cleanroom conditions, one can see from Fig. 4(b) that most of the fabricated structures are destroyed. In particular, the gold diffuses over the silica surface and reorganizes into spherical aggregates. To this regard, the diffusion of gold on a glass substrate is not surprising, as the small enthalpy of formation of gold oxide hampers the creation of a stable metal-oxide interface and prevents proper wetting of the silica by the metal [34]. As a consequence, surface diffusion sets in and the gold accumulates in spherical particles, since such a shape provides the lowest surface energy for a given volume [25,34,61]. However, the ability of gold to diffuse despite the underlying Ti adhesion layer is surprising since, as we show in the Supporting Information with the help of contact angle measurements, Ti locally increases the substrate surface energy promoting wetting of gold and counteracting surface diffusion. The gold is further anchored to the substrate likely thanks to the establishment of Ti–Au bonds [62,63]. In this configuration, the gold is usually tightly anchored to the glass substrate and can even be exposed to a variety of different gaseous and liquid environments without altering its shape [64–66]. Obviously, this thermodynamic stability breaks down for configurations having adversely high surface energies and high aspect ratios such as the one reported here. Similar behaviours have been observed for heated low aspect ratio gold nanorods, which change shape and transition to a sphere in a surface-driven reorganization process [29,67–71]. However, we can safely exclude the presence of any thermal effect in our system, as all the samples are stored at room temperature. On the other hand, comparing with two other commonly used plasmonic metals such as silver and aluminum, we see that they both require specific fabrication processes when deposited onto silica [33,57]. We hypothesize that standard thin inorganic adhesion layers provide enough surface energy to properly stabilize gold nanostructures having low aspect ratios. On the other hand, structures with larger aspect ratios possess extensive surface areas, resulting in higher surface energies. These configurations, such as the one reported here, can become thermodynamically unstable up to the point where surface effects begin to dominate their stability [72] and surface diffusion sets in. When this happens, the system evolves towards a more favourable thermodynamic state with a smaller surface area, as can be noticed when comparing Fig. 4(a) with Fig. 4(b). In this case, similarly to what happens with low aspect ratio silver structures [33], improved adhesion layers can prevent the detrimental surface diffusion of gold, revealing how the controlled modification of the metal-oxide interface is a key criterion to stabilize high aspect ratio gold structures. As an additional evidence, we show in the Supporting Information that such high aspect ratio plasmonic structures can be readily fabricated using aluminum, which easily forms a stable metal-oxide interface with the glass substrate that leads to a much higher adhesion energy [34].

We therefore tested different treatments to modify the metal-oxide interface, with the objective of preserving the shape of the structures. In particular, we fabricated large area interdigitated electrodes using Ti and Cr adhesion layers of various thicknesses – namely 3 and 10 nm – as shown in Fig. 5. The structures fabricated using 3 nm adhesion layers were completely destroyed within one day after their fabrication. The better results achieved with 3 nm Cr layers, compared to 3 nm Ti layers, can be attributed to the more favourable enthalpy of formation of chromium oxide compared to that of titanium oxide, which results into a better chromium bonding to the substrate and into a higher diffusion of Cr into gold [63]. On the other hand, as we also discuss in the Supporting Information, the use of 10 nm adhesion layers greatly increases the substrate’s surface energy thanks to a better coverage, resulting in a better bonding between the silica and the gold structures and in an improved long term stability. However, we show in the Supporting Information that such high aspect ratio plasmonic structures can be readily fabricated using aluminum, which easily forms a stable metal-oxide interface with the glass substrate that leads to a much higher adhesion energy [34].

Fig. 4. SEM images of the interdigitated electrodes, with an underlying 3 nm Ti layer, recorded (a) 30 min after the lift-off and (b) more than three hours later.
Information that further processing of the wafers, notably dicing them into chips for optoelectronic measurements, can easily damage the electrodes, making them not suitable for practical applications. Moreover, as mentioned in the Introduction section and confirmed in the Supporting Information with the help of numerical simulations, 10 nm thick metallic adhesion layers significantly alter the plasmonic properties of the electrodes [44], notably by increasing their losses [73, 74], and are therefore not suitable for the fabrication of plasmonic structures. To this end, different strategies have been proposed to minimize these harmful effects, but they all require the use of special geometries [75] or dedicated tools, such as for example cryogenic equipment [76], which are not commonly found in standard micro/nanofabrication facilities.

With the idea of developing a simple and accessible fabrication process, we thus explored the use of molecular monolayers to covalently attach the gold electrodes to the silica substrate while, at the same time, keeping their optical properties unaffected.

3.2. Organosilane adhesion layer

The self-terminating deposition of molecules on a substrate, resulting in the formation of a SAM, has been a subject of study for decades now [77, 78] and different techniques have been developed to produce ordered molecular layers for a variety of applications [79–82]. In particular, MPTMS has been shown to be an appropriate molecular linker between gold and silica [44, 45] thanks to its thiol head group that covalently binds to gold [83, 84], while the opposite methoxy groups are known to hydrolyse in the presence of water and bind to hydroxyl groups on an activated glass surface [85]. In particular, we stress the fact that the fabrication process that we propose in the Methods section allows the creation of hydroxyl groups on the exposed areas of a silica surface covered with electron-beam resist, without severely damaging the resist layer. This is a more gentle treatment when compared to standard surface activation protocols employing a Piranha solution [45, 46], which can easily dissolve the PMMA layer. Once a thin layer of gold is subsequently deposited on top of a MPTMS SAM grafted onto a glass substrate, it stably binds to the available thiol groups and attaches to the underlying silica surface through a series of covalent bonds, as described in the Methods section. In the latter, we also highlighted that a post-baking step, carried out after the metal evaporation, improves the quality and stability of the nanostructures. This additional thermal treatment was found to be a crucial step in the fabrication process since freshly deposited gold is in an unstable, partially amorphous [28], state and this additional baking step stabilizes the gold structures by promoting a transition from the as-deposited unstable gold phase to a thermodynamically more stable polycrystalline morphology. To this end we note that similar structures, albeit of lower aspect ratio, have been successfully fabricated in monocrystalline gold [16, 86, 87], hinting at the importance of the structural properties of the metal for its stability.

The chosen temperature of 80 °C is sufficient to stimulate a reorganization of the deposited gold, while preventing the destruction of the MMA/PMMA structures and the thermal desorption of the S atoms on gold, which occurs above 100 °C [83]. With an eye on optical applications, this sets a constraint on the maximum optical power that the conjugated thiol–gold system can absorb, and power densities above 1.6 mW/μm² in an air environment, or 11 mW/μm² in water, are therefore to be avoided [88]. On the other hand, the siloxane bond is stable up until about 1000 °C [49, 89, 90], making the thermal desorption of the silane head group from the silica substrate unlikely. However, at temperatures above 500 °C the hydrocarbon chains begin to decompose into gaseous carbon oxides, leading to the destruction of the SAM [49, 89–91]. In light of all this, optical characterization of the electrodes with continuous wave light sources having power densities in the μW/μm² range.
μm² regime carries no damage to the SAM.

Fig. 6(a) shows the nanoelectrodes fabricated with organic adhesion layers. One can notice that the fabricated structures have an excellent shape, close to the reference geometry, with remarkably smooth boundaries compared to those manufactured with inorganic adhesion layers shown in Fig. 4(a). We note that the SEM images provided here were recorded more than a week after the lift-off process, which confirms how organic MPTMS adhesion layers dramatically reduce surface diffusion and improve the long term stability of the plasmonic electrodes. Further SEM and optical characterization has also shown that the structures remain stable up to 6 months after fabrication and can survive the dicing process, allowing their experimental characterization. To this end we provide, in Fig. 6(b), the measured optical and electronic responses of the plasmonic electrodes. In particular, the left panel of Fig. 6(b) shows the measured dark-field scattering spectrum of a single disk dimer in a water environment (n = 1.33). This clearly reveals a plasmonic dipole resonance at a wavelength around 1000 nm, which is in good agreement with the simulated response calculated with COMSOL Multiphysics 5.6. In the right panel, the current-voltage (IV) characteristics of the electrodes is provided, which shows a typical resistance-like behaviour. The linear fit of these data demonstrates an excellent electrical insulation between the disks, with an open-circuit resistance of 567 GΩ that allows the creation of electric fields with strengths up to 1.66 · 10⁸ V/m. These results perspicuously demonstrate the possibility to fabricate plasmonic nanostructures, connected to interdigitated electrodes, with very good optoelectronic properties, paving the way for the experimental study of more exotic nanophotonic and nanoelectronic processes [13]. However, we found it challenging to fabricate smaller plasmonic structures with resonances in the visible range, even when employing very small (< 500 µC/cm²) electron beam doses. This limitation presumably stems from the relatively long oxygen plasma treatment used to activate the silica substrate before grafting the SAM, which is likely to slightly etch the MMA/PMMA bilayer and enlarge the apertures in the resist mask. All in all, the procedure described here results in a reliable fabrication process having a yield exceeding 90%, enabling routine production and long term stability of the written structures. However, the additional baking induced some difficulties in completely lifting off the large areas between the electrodes, decreasing the electrical insulation between them. This is likely due to the removal of residual solvents during the additional baking steps, altering the resist layers towards a more compact configuration. To this end, the creation of additional sacrificial apertures in the mask was found to significantly improve the detachment of the resist.

3.3. Empirical model

After showing the beneficial effects of thiolated organic layers to stabilize high aspect ratio gold nanostructures, we describe here an
empirical model that shines light into the role that surface energies play in these structures, and explains how different adhesion layers can affect the thermodynamic equilibrium of the system. Let us refer to Fig. 7, where a schematic of the mechanism leading to the destruction of the plasmonic electrodes is proposed. In particular, we can see that this process can be ideally split into two different steps. The first is shown on top and describes the reorganization of the gold film towards a more favourable configuration with reduced surface area, all while keeping the surface between the substrate and the vacuum $\Lambda_{sv}$ unchanged. The second mechanism, shown at the bottom of the figure, is a dewetting of the substrate by the gold film that occurs while maintaining the contact area between the gold and the vacuum $\Lambda_{sv}$ constant. We stress the fact that the system concurrently explores both these pathways as it relaxes from the initial configuration, where the gold is arranged in high surface area structures, to the final one, where the metal forms spherical aggregates on the substrate. A spontaneous evolution from the former to the latter case, i.e. a spontaneous destruction of the electrodes, occurs if the energy of the final configuration is lower than that of the initial one, that is

$$dE = \frac{dE}{dA_{sv}}|_{A_{sv}=\text{const}} - dA_{sv} + \frac{dE}{dA_{sv}}|_{A_{sv}=\text{const}} - dA_{sv} = \gamma_{sv} dA_{sv} + \left(\gamma_{sv} + \gamma_{sv} - \gamma_{sv}\right) dA_{sv} < 0,$$

where $dE$ has been rewritten using the surface energies introduced in Eq. (1), shining light into the way these quantities govern the stability of our system. Let us start by analyzing the first term of this equation, which is evidently negative since $dA_{sv} < 0$ when the system moves from a configuration having high surface area to one possessing a lower surface. This represents the main mechanism behind the reorganization of the gold film, which is clearly driven by a preference for smaller surface areas and, hence, smaller surface energies. To this end, we can write

$$dA_{sv} = 0.5 \cdot V^{2/3} dk,$$

where $k \geq 1$ is a shape factor that characterizes the degree to which the area of a gold structure of volume $V$ parts from its minimum value $0.5 \cdot V^{2/3}$ that is achieved when the gold takes the form of a semi sphere on the substrate. Higher $k$ implies higher surface and thus $dk < 0$ in our system, as shown in Fig. 7, with its magnitude increasing for initial configurations of the structure having a higher surface area. This explains the higher instability of high aspect ratio systems when compared to low aspect ratio structures. If we now consider the second term, we see that this is composed of three contributions: the first takes into account the energy to build an area $dA_{sv}$ at the substrate / vacuum surface, the second is the energy required to create a similar area at the metal / vacuum surface, while the third represents the energy required to split the initial substrate / gold interface. We see that $dA_{sv} > 0$ and therefore this term generally counteracts the effect of the latter. This can be explained by rewriting $dA_{sv} = -L_c dr$, where $L_c$ is the length of the contact line between the gold and the substrate and $r > 0$ is its distance from the center of the structure. Clearly, when the electrodes evolve towards a spherical shape the contact line shrinks, as shown in Fig. 7, making $dr < 0$ and consequently $dA_{sv} > 0$. As for the surface energy associated to this term, it can be easily appreciated now how the increase in $\gamma_{sv}$ brought about by the

Fig. 7. Schematic of the process leading to the spontaneous destruction of the electrodes. The changes $k \rightarrow k'$ and $r \rightarrow r'$ of the parameters describing the geometry of the structure is shown for each mechanism. The bottom SEM images of Fig. 4, representing the initial and final state of the process, are also reproduced here for convenience.
deposition of a thick inorganic adhesion layer can make this term big enough to yield $dE > 0$ and completely stabilize the structures. On the other hand, we have shown in the Supporting Information that an MPTMS adhesion layer actually decreases $γ_{\text{Si}}$ and does therefore not ensure proper wetting of the silica by the gold. However, when this metal is deposited on an organic layer that exposes thiol groups at its surface, these spontaneously bind to gold releasing an energy equal to the enthalpy of adsorption $ΔH \approx 80 \text{kJ/mol}$ of this process [92,93]. This chemical contribution to the thermodynamic stability of our system is neglected in the above discussion, but needs to be fully accounted for to thoroughly describe our structures. To this end, we can express the total interfacial energy at the thiolated substrate / gold interface as the sum of a pure surface term and a chemical term:

$$ γ_{\text{S/Au}}^c = γ_{\text{S/Au}}^b + γ_{\text{S/Au}}^c, \quad (3)$$

$$ γ_{\text{S/Au}}^c = ΔHφ, \quad (4)$$

where $γ_{\text{S/Au}}^c$ is the (positively defined) surface energy originating from the energy difference between surface and bulk molecules, while $γ_{\text{S/Au}}^b$ is the energy required to form S–Au bonds at the surface, expressed through the molar surface density of thiol groups $φ$. Clearly, $γ_{\text{S/Au}}^c > 0$ and it is therefore possible, when $γ_{\text{S/Au}}^c > γ_{\text{S/Au}}^b$, for the total interfacial energy $γ_{\text{S/Au}}$ to be negative. In such a case, the magnitude of the second term in Eq. (2) becomes larger and contributes to the lowering of the overall surface energy of the system having elongated gold structures, which is now more thermodynamically stable than that with low surface area electrodes. In practice, this situation arises only if the silica surface presents a sufficient number of thiol groups that can bind to the gold, i.e. if $φ$ is high enough. Assuming a complete monolayer formation, this parameter can be estimated by referencing to Fig. 3 (b), where it is shown that for every silicon atom on the substrate there is one corresponding thiol group at the surface. From the density ($ρ = 2.196 \text{ g/cm}^3$ [94]) and molecular weight ($w = 60.08 \text{ g/mol}$) of silica, one can estimate the number of molecules of silica inside a cubic centimeter of material as $N_{\text{A}}ρ/w$ and, therefore, their surface density as $(N_{\text{A}}ρ/w)^{2/3}$. On the other hand, this is not the case for the inorganic adhesion layers studied here, where the lower enthalpy of formation of Ti–Au and Cr–Au bonds provide a less stable binding of the gold to the substrate [95,96]. Moreover, the low surface coverage and high oxidation state of these layers greatly reduce the number of Cr or Ti atoms available to bind to the gold, i.e. $φ$, and therefore make the contribution of $γ_{\text{S/Au}}^c$ negligible in these systems.

4. Conclusions

The downscaling and merging of optical and electronic technologies often requires structures with very large surface to volume ratios. For such devices, surface effects become the dominant interaction and limit their stability and robustness. In this work, we have confirmed that these effects are especially prominent for high aspect ratio gold nanostructures and are responsible for their structural degradation shortly after their fabrication. We have demonstrated how the quality and long term stability of such structures can be improved by enhancing their adhesion to the substrate and shown the benefits of employing organic silane adhesion layers to establish strong binding forces between the metal and the underlying surface, without affecting the optical properties of the device. Furthermore, we have shown how an additional baking favors the reorganization of the gold from a freshly deposited – thermodynamically unstable – morphology towards a more stable configuration. Surface diffusion can be dramatically reduced by carrying out the baking prior to the lift-off procedure since the metal remains confined within the PMMA mold. These findings enable the fabrication of plasmonic devices with extremely high aspect ratios, which are likely to play a major role in emerging signal processing and quantum technologies since they provide a bridge to connect the nano- to the macroscales, as well as the photonic to the electronic worlds.

CRediT authorship contribution statement

Marco Riccardi: Conceptualization, Investigation, Validation, Formal analysis, Visualization, Writing – original draft. Christian Santschi: Resources, Methodology, Formal analysis, Writing – review & editing, Supervision. Olivier J.P. Martin: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

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Appendix A. Supplementary data

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