Generating Multiscale Gold Nanostructures on Glass without Sidewall Deposits Using Minimal Dry Etching Steps

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ABSTRACT

The advent of recent technologies in the nanoscience arena require new and improved methods for the fabrication of multiscale features (e.g., from micro- to nanometer scales). Specifically, biological applications generally demand the use of transparent substrates to allow for the optical monitoring of processes of interest in cells and other biological materials. While wet etching methods commonly fail to produce essential nanometer scale features, plasma-based dry etching can produce features down to tens of nanometers. However, dry etching methods routinely require extreme conditions and extra steps to obtain features without residual materials such as sidewall deposits (veils). This work presents the development of a gold etching process with gases that are commonly used to etch glass. Our method can etch gold films using reactive ion etching (RIE) at room temperature and mild pressure in a trifluoromethane (CHF₃)/oxygen (O₂) environment, producing features down to 50 nm. Aspect ratios of two are obtainable in one single step and without sidewall veils by controlling the oxygen present during the RIE process. This method generates surfaces completely flat and ready for the deposition of other materials. The gold features that were produced by this method exhibited high conductivity when carbon nanotubes were deposited on top of patterned features (gold nanoelectrodes), hence demonstrating an electrically functional gold after the dry etching process. The production of gold nano features on glass substrates would serve as a biocompatible, high conductive and chemically stable materials in biological/biomedical applications.

Keywords: reactive ion etching (RIE), gold etching, nano gaps, nanopatterns, nanoelectrodes, sidewall veil

The development of suitable and relatively simple to implement processes to pattern metals that are challenging to etch such as gold, silver and copper is of major importance in a wide range of areas including electronics (*e.g.* high speed signal transmission in devices such as hybrid circuits and superconducting electronics), optoelectronics and electromagnetic sensors.^{1–5} Wet and dry etching methods present several advantages and disadvantages for the patterning of these metals. Wet etching methods (liquid solutions or chemical vapors) provide high selectivity when etching metals (e.g. copper, silver and gold).^{6–10} But, as new technologies require sub-micron features (< 1 μ m) these processes fail to produce the critical dimensions needed due to its isotropic etching nature, which contributes to loss of pattern conformity, ultimately leading to faulty or non-compliant devices.⁵ On the other hand, dry etching methods using plasma have the advantages of generating anisotropic etching profiles as well as enhanced etching rates, ^{11–16} providing the opportunity to pattern features of hundreds and in some cases even tens of nanometers.

Plasma etching requires a reaction between neutral gas-phase radicals and the solid metal to form volatile products, which ultimately are desorbed from the surface producing the etched structures.¹⁷ However, metals such as gold have specific requirements to be etched out of surfaces using traditional halogen-based plasmas. Indeed, gold and other metals fail to form volatile halogenated-metal species in conventional halogen plasmas.^{18,19} Thus, special conditions such as higher temperature and ion bombardment energy, as well as a wet etching step are commonly used to better remove the product of the etching reaction. Typically, gold is dry etched using chlorine (Cl₂) based gases which are dangerous to handle, requiring special safety equipments.¹⁸ Gold etching has also been reported under mixtures of Cl₂ gas with tetrafluoromethane (CF₄) and tetrachloromethane (CCl₄), at temperatures up to 125 °C.^{5,18} However, surface roughness and sidewall veils were observed with these methods. In addition, the selection of masks is limited by the temperature used (e.g. photoresist at low temperatures versus SiO₂ at higher temperatures). Other components in these mixtures, such as oxygen at high concentration (e.g. 20% of the

flow), have produced reductions in etching rate. Overall, these studies showed that dry etching in a halogen/oxidative environment have serious limitations for the nanometer-scale etching of gold and other metals.

Physical, more energetic etching processes have been developed to produced submicrometer metal structures. The use of hydrogen bromide/argon (HBr/Ar) and Cl₂/Ar gas mixtures using titanium (Ti) as a mask to obtain $<1 \mu$ m features was achieved.²⁰ This process utilized an inductively couple plasma (ICP) dry etching process that generates features of sub-micron size. However, the features obtained were not at the lower end of the nanometer-scale and required post-processing for the removal of the Ti mask layer. Other alternatives, as for example a process that combined CF₄ and argon to etch gold via reactive ion etching with enhanced ion sputtering was developed.²¹ This method produced an etched gold film, but not with the best sidewall and overall profile nor the best etch rate. In general, this method did not produce a better process than the ones using chlorine to etch gold. Low temperature plasma-assisted etch of gold films was achieved using purely hydrogen plasma at 10 °C. However, a SiO₂ mask was used to avoid degradation of organic photoresist masks by hydrogen plasmas. Also, they reported that the etch rates in hydrogen plasmas were not optimal for large scale fabrication processes.²² In a different study, the same group used CH₄ plasmas at low temperature (10 °C) on Si wafer to avoid some of the challenges when using hydrogen plasma (*e.g.*, organic photoresist degradation and low etch rate). CH₄ plasma selectively etched gold films using photoresist masks, but sloped sidewall profiles occurred due to redeposition of gold.²³ Therefore, the development of a method for etching nanometer scale features that could be carried out at low temperature, mild pressure, and low power as well as safer conditions will be critical in a number of applications that span from integrated circuits (ICs) to plasmonics.⁴

The work presented here uses only CHF_3 and a low oxygen concentration (at room temperature), to etch gold and produce a working device with features and gaps between 50 nm to 200 nm. Our combination of RIE gases and other parameters transformed a conventional glass etching method into a gentle gold etching process where features down to 50 nm can be generated. In addition, our method does not require other steps to remove

veils generated as a result of the etching process. The only extra step our method requires, as in virtually all other etching protocols, is a cleaning step in the same RIE chamber using oxygen plasma. This cleaning step removes photoresist that remains after the gold etching process is completed. The compatibility of this method with glass biocompatible substrates provides a system that could be used in creating nanopatterned surfaces applicable in the development of life sciences/biomedical *in vitro* devices.^{24–26}

RESULTS AND DISCUSSION

The presence of gas-phase AuF during processes such as gold etching was reported by Saenger and Sun²⁷ and later corroborated by others.^{28–30} Their work demonstrated that gold etching in the presence of oxygen will produce the diatomic gold molecule AuF. The formation of AuF was considered based on the known relative volatility of AuF₃, a molecule that in the presence of oxygen can produce AuF. The reaction to produce AuF is as follows,

$$AuF_3 + 0 \rightarrow AuF + F_2 0. \tag{1}$$

No specifics regarding the oxygen concentration used was provided by Saenger and Sun. However, others studies had reported reductions in etching rate when using Cl_2 mixed with CF₄ and CCl₄.^{5,18} Thus, we sought to develop a gold etching process that would not require a hazardous gas, will be mild (moderate to slow etching rate) and would provide a "clean" etching of gold producing only a small or negligible redeposition of gold at the edges. Based on these observations we determined that the gas to be used would be a precursor of fluorine and we would have oxygen present in our reactive ion etching chamber. Also, fluorine is not as corrosive as chlorine which requires special corrosive lines for the RIE equipment. In addition, all the gases are purged out before the RIE chamber is opened thus ensuring safety from any hazardous by-products (*e.g.* possible production of HF) during the plasma etching process. We started at the oxygen level commonly used to etch glass (5 sccm) and from there we lowered the oxygen concentration down to 0 sccm. To study and assess the etching differences at different oxygen concentrations we designed a grid consisting of lines of 100 nm, 200 nm, 300 nm, 400 nm, 500 nm, 1000 nm and 1500 nm.

Devices containing this grid were etched across a 10 μ m wide Au/Ti (50nm/10 nm) pattern (6 different samples). The oxygen flow rate was varied from 0 to 5 sccm, while the rest of the parameters were kept constant (CHF₃ flow at 45 sccm, 3.33 Pa, 25 °C, DC 300 W and 8 min etch duration time). The images obtained from atomic force microscopy (AFM) profiling in tapping mode (Fig. 1A) were used to obtain the etch profiles at different experimental conditions (Fig. 1B and 1C).



Figure 1. Comparison of etching depth when varying oxygen flow. A) AFM topography of the line grid consisting of 100 nm, 200 nm, 300 nm, 400 nm, 500 nm, 1000 nm and 1500 nm etched in gold on a glass substrate. B) 3D overlay and C) individual line profiles of the etched grid extracted from the AFM images at each oxygen flow rate (and thus concentration). Increase in oxygen flow rate from 0 sccm to 3 sccm increases the etch depth, while the veil formation is virtually non-existent at 2 sccm oxygen.

The etching depth increases as oxygen flow rate increases from 0 sccm to 2 sccm (Fig. 1B and 1C). While the etching depth is comparable at 2 sccm and 3 sccm oxygen flow rate, a decrease in etch depth and an increase in veil formation are seen when the flow rate of oxygen increases to 4 sccm. At 5 sccm the etching depth is negligible, suggesting that higher concentration of oxygen hinders the etching of gold as previously reported.^{5,18} At 0 sccm and 1 sccm, the 60 nm gold layer was not etched all the way through. These results along with the etching observed at higher oxygen flow rates show that the optimal flow rate for removal of gold is observed at 2 sccm and 3 sccm, where the root-mean-square (RMS) roughness of gold surfaces are as small as 2.05 nm to 4.7 nm (respectively), and the gold veils are none and minimal with respect to other oxygen conditions (respectively). Although the gold veils are small at 0 sccm and 1 sccm, they are still present and are 2 to 5 times higher than the roughness observed at 2 and 3 sccm (approx. 10 nm). In addition, the etching depth for 100 nm and 200 nm gaps at 0 sccm, 1 sccm, and 3 sccm are shown to be none or less than 30 nm, which indicate incomplete etching of gold and titanium films. At 4 sccm oxygen, even though the metal layer has been etched all the way through for gaps larger than 200 nm, the veils (or gold accumulations) at the edges are significantly larger (~ 40 nm) than at 0 sccm and 1 sccm oxygen.

Samples etched at the optimal oxygen concentration of 2 sccm were obtained and analyzed before and after the oxygen plasma cleaning process (Fig. 2, Fig. S2 and Fig. S3). Figure 2 shows scanning electron microscopy (SEM) images of samples before (A and C) and after (B and D) oxygen plasma cleaning. The absence of veils is evident in both images. In addition, it was observed a rougher surface in the samples that were not oxygen plasma cleaned, specifically in the areas where photoresist was left to protect the gold during the etching process. A decrease in surface roughness from 19.4 nm to 7.2 nm was observed after oxygen plasma cleaning was carried out (Fig. S2). This change in roughness suggested the presence of photoresist in the rough areas prior to oxygen plasma cleaning, and its removal after the oxygen plasma cleaning process. Further surface analyses demonstrated that the samples analyzed before oxygen plasma cleaning, specifically in the areas where the roughness was the highest, had a carbonaceous material in the area where photoresist was present. Elemental analysis using electron dispersive spectroscopy (EDS) indicated the presence of carbon at approximately 44 atomic percent in those areas with larger roughness (see Fig. S3C and Table S1). Whereas carbon was not detected in the area where photoresist was left during the gold etching (RIE) process and later oxygen plasma cleaned (Fig. S3D). No carbon was observed in the areas that were etched in the sample that was not oxygen plasma cleaned (Fig. S3E). However, a very small amount (approx. 4 atomic percent) of carbon was observed in the areas that were etched and later oxygen plasma cleaned (Fig. S3F). This could be attributed to traces of the photoresist that were not completely removed after oxygen plasma. Nevertheless, in those same areas 89 atomic percent of Si and O, combined, was observed thus demonstrating that the etching process removed the gold that was exposed during that process (only approx. 4 atomic percent gold was detected), thus exposing the glass substrate. It was also observed that oxygen plasma cleaning was the most efficient process to remove the carbonaceous material (*i.e.* photoresist) that remains after the RIE step.



Figure 2. SEM images of structures before (A) and after (B) oxygen plasma cleaning. Panels (A and C) show a visible difference in surface roughness versus the post oxygen plasma (B and D). Surface analysis demonstrated that the larger roughness in (A) is the result of photoresist that has not been removed by the oxygen plasma cleaning process. SEM imaging parameters for panels A

and B: EHT = 3.00kV. Panel C: EHT = 2.00 kV. Panel D: EHT = 1.00 kV. Scale bars: panels A and B = 600 nm; panel C = 200 nm; and panel D = 300 nm.

Features with right angles (rectangular), sharp and angular forms (triangular), and smooth rounded (circular) were etched with gaps of 50 nm, 200 nm and 500 nm. These patterns were chosen to investigate the range of shapes and feature sizes possible to etch gold on glass substrates using the following reactive ion etching (RIE) parameters: CHF_3 at 45 sccm, O_2 at 2 sccm, 3.33 Pa, 25 °C, and DC 300 W.

The top view of these patterns is illustrated in the AFM micrograph in Fig. 3. As the gap is gradually decreased from 500 nm to 50 nm the removal of gold decreases to the point where features are absent, when using the smallest gap. However, the 200 nm and 500 nm gaps had features that were resolved within the range of \pm 50 nm. A minimum gap defined by e-beam lithography of approx. 200 nm and 500 nm resulted, as shown in figure 3, in a gap of approx. 199 nm and 550 nm for a semicircular gap, approx. 200 nm and 519 nm in the triangular pattern and, approx. 199 nm and 513 nm for a rectangular gap, respectively. In addition, the etching depth of different patterns shows that for 200 nm gaps, only the triangular pattern is able to resolve the depth of ~ 60 nm.



Figure 3. AFM topography of circular, triangular, and rectangular patterns etched in gold with gaps of 500 nm, 200 nm and 50 nm. The RIE parameters used for etching were CHF₃ at 45 sccm, O₂ at 2 sccm, 3.33 Pa, 25 °C, DC 300 W. A) Top view of the etched structures. B) Profiles across the center of the etched structures.

The slow etch rate (~ 8.4 nm /min, Figure S1, supporting information) when using CHF₃ at 45 sccm, O_2 at 2 sccm, 3.33 Pa, 25 °C, DC 300 W RIE parameters, suggests that this technique is applicable for thin gold films since removal of e-beam resist PMMA occurs during the etching of gold. It is expected that longer etching times would lead to complete removal of PMMA and therefore thicker gold coatings will require a thicker layer of PMMA to allow for the removal of gold in the exposed areas.

Two kinds of patterns were etched to investigate the advantages and limits of this etching process: array of gold nanopillars (squares of 100 nm, 200 nm, 400 nm in width) and electrode arrays with nanogaps. The 3D surface of the gold nanopillar arrays were determined by AFM, the top view of these arrays is shown in Fig. 4. The densities were varied by keeping the ratio of inter pillar distance to widths of 1:1 and 1:2.



Figure 4. AFM topography of A) 400 nm, C) 200 nm and E) 100 nm rectangular pillars with pitch distance 1:2. These structures were etched at 2 sccm oxygen flow rate while the rest of the RIE parameters were being kept constant (CHF₃ at 45 sccm, 3.33 Pa, 25 °C, DC 300 W and etch time of 8 min). B), D) and F) are the etching profiles for the nanostructures in A), C) and E), respectively.

The micro- and nanopillars with gold on top are evenly dispersed but wider in size distribution and inter distance, when compared to the original mask design. The

nanopillars showed no veils (completely flat surfaces), and show broadening of the pillar at the bottom, for all sizes. To demonstrate the feasibility of fabricating a viable device using this technique nanoelectrodes were etched across parallel gold stripes to create nanogaps of 200 nm (Fig. 5A). The line profile (Fig. 5B) shows a nanogap of 200 nm and a 100 nm deep trench demonstrating that the gold was completely etched and approx. 40 nm of the underlying glass substrate was etched. To display the scalability of the developed process to wider structures (in x-y) we etched gold from an interdigitated microelectrode array design consisting of 16 parallel-10 μ m wide gold stripes with gaps of 500 μ m and connected to contact pads (2400 μ m x 4200 μ m) for electrical access (Fig. S4, supporting information).



Figure 5. (A) AFM images showing 600 nm wide electrodes patterned with triangular edges with a gap of 200 nm and 100 nm deep trench. (B) Line profile of the electrodes form after RIE shows absence of gold veils across the edges of the electrode.

Dielectrophoretic trapping of multi-walled carbon nanotubes (MWCNT) across these electrodes were conducted to demonstrate the functionality of this device after the RIE etching process. Post deposition I-V curves show an increase in current with linear curve (Fig. 6), suggesting connection between the two electrodes with a conductive entity, in this case multiple MWCNTs forming a mesh (Fig. 6, AFM inset). The measured currents are in the margins of previous reported work of dielectrophoretically deposited carbon nanotubes.^{31,32} When compared to the I-V curve of post deposition to the I-V curve prior to MWCNT deposition, in the bottom right inset, a striking contrast is observed. The predeposited MWCNT device (only gold electrodes) suggests that there is no ohmic connection between the electrodes.



Figure 6. Current as a function of voltage of MWCNT deposited via dielectrophoretic (DEP) trapping across circular edge patterned electrodes 500 nm (diameter) with minimum distance of 200 nm and a 137 nm trench running across the electrodes. Prior to deposition, current as function of voltage was measured across the electrodes as shown in the inset at the bottom right side suggesting the electrodes were not connected prior to the MWCNT DEP trapping. AFM inset (top left) shows a mesoporous mesh of trapped MWCNT across the electrodes.

CONCLUSIONS

The objective of this work was to demonstrate the etching of thin gold film on glass at a low-pressure and room temperature plasma environment using CHF₃ and O₂ to carry out the reactive ion etching process. The study describes the method to fabricate micro- and nanostructures of thin gold films on top of glass substrates. This method allows for batch fabrication of micro and nanoscale gaps (\geq 200 nm) between metallic electrodes as well as simultaneously etch the underlying glass substrate.

This method used the e-beam lithography resist PMMA, as the mask for the RIE etching process, and produced features with aspect ratios of up to 2. These features are completely

free from sidewalls deposits, providing virtually flat surfaces that could be used for the deposition of other materials on top of the generated features, as well as for ICs and electromagnetic applications. The optimal oxygen concentration required in eliminating veil formation during gold etching was shown to be 2 sccm with a 45 sccm flow of CHF₃, and there was no need for a sacrificial metal (mask) layer, elevated temperatures or relatively non-corrosive gas (fluorine based instead of chlorine).

The method developed in this study creates patterned structures such as periodical microand nanostructures and individually addressable interdigitated electrodes simultaneously on glass. Micro- and nanostructures, down to 50 nm, can be obtained after minimal RIE etching steps. We anticipate these micro- and nanostructures could be applied towards biodiagnostic devices with tunable surface properties, as for example, wettability, electrochemical bimolecular detection and cell monitoring devices.

METHODS

Device Fabrication: 10 μ m x 10 μ m squares and continuous 3 μ m wide lines each 500 μ m apart were photolithographically patterned using a bilayer photoresist method. 100 mm diameter glass wafers (Valley Design Corp.³³, MA, USA), were baked at 200 °C on a hotplate for 10 min to dehydrate the surface. LOR3A (MicroChem Corp, MA, USA) was spin coated at 2500 rpm (262 rads/s), followed by a 200 °C bake for 5 min. S1813 (MicroChem Corp, MA, USA), was spin coated on top of LOR3A at 4000 rpm (419 rads/s) followed by a 2 min post-bake at 115 °C. The samples were exposed to 405 nm UV light using a Karl SUSS MA6 mask aligner (SUSS MicroTech AG, Garching, Germany), followed by a 2 min post-bake at 115 °C. The samples were developed in TMAH (Tetramethylammonium hydroxide) based developer Microposit MF-319 (MicroChem Corp, MA, USA).

After the development process a 10 nm thick titanium adhesion layer followed by 50 nm thick gold layer were deposited by electron beam evaporation. The resist was stripped off in 1165 microposit remover (MicroChem Corp, MA, USA), followed by cleaning steps using 1165 microposit remover, isopropanol, de-ionized water, and N₂ blow drying. The device was then spin coated with poly(methyl methacrylate) (PMMA 495K A4, (MicroChem Corp, MA, USA) at 1000 rpm (105 rads/s) and baked at T =180 °C for 90 s. The process required a thick PMMA coating as gold and glass substrate were simultaneously being etched to create electrodes with nano trenches. Thicker PMMA reduces the etching of underlying glass when creating trenches (nano) of required depths between the electrodes.

The surface charge build up on insulating surfaces (glass) interferes with the exposing electron beam. To prevent this problem a thin 10 nm aluminum layer was deposited using electron beam evaporation over the PMMA layer. This provides a grounding path for the accumulated charge. Patterns with micro (0.5 μ m to 1.5 μ m) and nano (50-500 nm) features, to disrupt the continuous gold lines made photolithographically, were written via e-beam lithography. After these patterns were drawn, the aluminum layer was removed by dipping in the TMAH based developer MF-319. The exposed PMMA was developed in 1:3 dilutions of methyl isobutyl ketone (MIBK) and isopropanol. Next the micro- and nano-patterns through Ti/Au and glass were simultaneously dry etched using reactive ion

etching (RIE, Unaxis 790, RF: 13.56 MHz). The RIE tool is a parallel plasma etching system where the RF is fed at the top electrode (25.4 cm) and the wafer is clamped via vacuum seal to the bottom electrode. For RIE, the etching gas consisted of CHF₃ and O_2 with a flow rate of 45 sccm (Standard Cubic Centimeters per Minute) and 2 sccm, respectively. The samples were etched for 8 min at a chamber pressure of 3.33 Pa and 300 W etch power, at room temperature (25 °C). Temperature was controlled by a water cooling system and kept between 25 °C to 26 °C throughout the process. The temperature remained constant during the entire etching procedure. After etching the samples, a 10 min oxygen plasma (2 sccm, 26.7 Pa, 200 W) was used to remove any remaining photoresist and any organic contaminants. The etched samples were cleaned immediately with 1165 microposit remover, IPA, deionized water and blow dried with N₂. To investigate the influence of oxygen effects on etching, the oxygen flow rate was varied from 0 sccm to 5 sccm, while keeping the rest of the RIE parameters constant. To estimate the etching rate time was varied while keeping the rest of RIE parameters constant.

Pattern and Surface Characterization: Patterns were observed by atomic force microscopy (AFM) (contact or tapping mode; AFM Bruker Dimension FastScan and Dimension 5000 CA, USA). Trenches were characterized using Fastscan A probe tip, triangular shaped with a tip height between $2 \mu m$ to $8 \mu m$ and typical radius of 5 nm. While the pillars were characterized with a longer PPP-NCHR tip (Nanosensors, CA, USA), with tip height of 10 μm to 15 μm and tip radius < 7 nm.

SEM and EDS Analysis: A Zeiss FE-SEM (Zeiss Ultra 60 Field Emission Scanning Electron Microscope, Zeiss, NY, USA) outfitted with an Oxford EDS system, specifically an Oxford XEDS 80 mm² X-Max silicon drift detector for elemental composition analysis was used to image and .

Dielectrophoertic deposition: Dielectrophoretic trapping of multi-walled carbon nanotubes (MWCNT) was performed using the fabricated devices with patterned interdigitated electrodes. 15 μ L of aqueous based MWCNT solution (0.01mg/mL) was

applied on top of the electrodes, while a 5 MHz, 10 Volts (peak to peak) signal was applied for 45 secs, followed by a DI water wash.

Electrical Characterization: Electrical characterization of the devices was conducted using a Solartron 1287 Electrochemical Interface. I-V characteristics were measured across the electrodes to validate any deposition of conductive nanotubes. The voltage was cycled from -1 V to 1 V at a rate of 500 mV/s. I-V characteristics of each pair of electrodes were measured prior to MWCNT deposition to check for any electrical shorts due to metal redeposition or incomplete etching. Post MWCNT deposition, the I-V characteristics were measured to confirm MWCNT trapping.

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