Abstract—This paper explores the electrochemical patterning of thin metal films using a scanning probe tip as an electrode. In particular, a masking nickel film is etched to reveal a gold pattern to which biomolecules like liposomes and proteins can be attached after treatment with functionalized self assembled monolayers (SAMs) of gold-thiolate. The machining is performed by ultracompliant polyimide micromachined probes (with tip diameter <200 nm) as the machining tool in NaCl:HCl electrolyte. These probes provide an embedded electrical lead as well as high mechanical compliance that eliminates the need for servo control, which is typically needed to maintain the proximity between the workpiece and the tool. By applying 500 ns, 2 V pulses, 3 \( \mu \)m wide patterns were fabricated. Experiments suggest that they can be scaled down to tens of nanometers by using 5 ns pulses. Selective adsorption of undecanethiol SAMs to the patterned gold was confirmed using XPS spectroscopy.

I. INTRODUCTION

For rapid prototyping and low volume applications, electrochemical micromachining (ECM) can provide cost and speed advantages over lithography-based methods of selective deposition or removal. Maskless patterning can be achieved with ECM by locally and selectively etching metals with a scanning electrode tip. This kind of etching not only creates very precise patterns, but also reduces chemical wastes and effluents [1]. Furthermore, with the right conditions, the machining tool does not get degraded during etching. The use of ECM to fabricate microstructures dates back at least to 1955, when it was used for micromachining germanium and silicon with minimal debris [2]. More recently, the precision of ECM has been shown by machining nano patterns on bulk metals like stainless steel and copper using the nano tips of sharpened metal electrodes and applying nano second pulses of voltage signals between the workpiece and the tool separated by a servo-controlled micron-sized gap [3, 4].

In this effort, a micromachined polyimide probe with a metal coated tip of diameter <200 nm and embedded electrical leads [5, 6] is used as a scanning electrode for ECM. Using short electrical pulses, the probe patterns a thin-film Ni layer that covers a layer of Au. The low mechanical stiffness of the probe (typically ~0.1 N/m) eliminates the need for servo control to maintain proximity between the workpiece and the tool, further simplifying the fabrication process. In this approach, probes can touch the substrate without causing an ohmic contact. The low spring constant ensures that the contact pressure of the probes remains low and does not vary significantly as they are rastered over minor topological variations.

As one possible application, this method allows inexpensive non-lithographic patterning of functionalized chemicals for chemical and biosensors. After gold patterns are revealed, the surface can be treated with functionalized thiolates to form self-assembled monolayers (SAMs). Various biomolecules such as liposomes [7] and proteins [8] can be selectively attached to the SAMs and used in biosensor applications as depicted in Fig. 1. SAMs have been routinely used for micro-patterning proteins and cells for biosensors and fundamental studies in cell growth and proliferation. They have also been used in chemical sensors [9].

Past approaches to forming SAMs on gold substrates include micro-contact ‘inking’ with an elastomeric stamp, as well as conventional lithographic patterning of gold [7]. Gold is a preferred substrate for adsorbing alkanethiol SAMs because it reacts strongly with sulfur atoms, and it is resistant to atmospheric contamination. Oxidizable metals such as Ni, on the other hand, tend to resist the formation of SAMs because the metal oxides hinder the formation of a stable
chemical bond between sulfur and the metallic atom. Additionally, they tend to oxidize thiolates into sulfonates and sulfoxides which do not bind strongly to the surface. Unless it undergoes an electrochemical reduction pretreatment [10], Ni can act as a mask to block SAM formation.

II. ELECTROCHEMICAL ETCHING

In an electrolyte, the charge transport is achieved by the motion of ions whereas in the electrode it is by the electrons. Electrochemical cells use at least two electrodes separated by at least one electrolyte phase. The overall chemical reaction in the cell consists of two half-reactions, each at one electrode. In this work, a gold electrode on the surface of the probe tip was used as a machining tool, a nickel surface used as the workpiece, and NaCl/HCl solution used as the electrolyte form the electrochemical cell. A very short square voltage pulse (around 500 ns) with a small duty cycle (usually ~10%) was applied between the workpiece (anode) and the tool (cathode) while the probe, mounted on an XYZ stage, was moved with a constant feedrate, selectively etching nickel in the tip area (Fig. 1). The z-axis control of the stage was only used to initially touch the probe tip to the substrate. However, this does not cause an ohmic contact between the probe tip and the substrate because of the low contact pressure permitted by the mechanical compliance of the probe shank.

With the application of short duration voltage pulses, two kinds of processes occur at the interface between the electrode and the electrolyte: non-faradaic and faradaic processes [11]. In the non-faradaic process, a capacitative action such as charging of the double layer, takes place. Most solid surfaces, including metals, acquire a finite charge density at the interface upon contact with an aqueous solution. The charged surface attracts counter-ions and repels co-ions in the solution forming a double layer of ions, consisting of a compact immobile layer and a mobile diffuse layer in the liquid. Some of the electrons from the applied AC voltage source are used to charge and discharge this double layer. In parallel to this, faradic processes (chemical reactions) take place involving the exchange of electrons across electrode-electrolyte interface causing electrochemical etching according to the Faraday Law:

\[
\text{Rate (mols}^{-1}\text{cm}^{-2}) = \frac{i_f}{zFA} \tag{1}
\]

where Rate is the dissolution (etching) rate of the material in mole per second per square centimeter, \(i_f\) is the faradaic current flowing through the electrode with a cross-sectional area of \(A\), \(z\) is the number of electrons involved in the reaction and \(F\) is Faraday’s constant. The Faradaic process that is utilized in this work is the dissolution of nickel on the workpiece and the evolution of hydrogen gas at the gold tool piece as summarized below.

Cathode: \(2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-\)
Anode: \(\text{Ni}(s) + 2\text{Cl}^- \rightarrow \text{NiCl}_2 + 2e^-\)

An electrochemical reaction does not start unless the interface potential, \(V_{int}\), is greater than the equilibrium potential, \(V_{eq}\), of the reaction. When the interface potential exceeds this, the reaction at the electrode-electrolyte interface is proportional to the current passing through the interface and this current is exponentially dependent on the potential difference, \((V_{int} - V_{eq})\), which is referred to as overpotential. The relation between the current and the overpotential across the interface can be approximated by the following equation, which is a simplified Butler-Volmer equation [11]:

\[
i_f = i_0e^{\alpha(V_{eq}-V_{int})/zF} \tag{2}\]

where \(i_f\) is the exchange current density, \(\alpha\) is the transfer coefficient, which is usually 0.5, and \(V\) equals to 25 mV. This process can be modeled by a diode. However, even though this relationship at the interface is highly nonlinear, for simplicity, it is usually represented by a charge-transfer resistance, \(R_{ct}\), which is a linearized value for the exponential relation for a small potential difference across the interface. This process is said to operate in the charge-transfer region, meaning that the reaction is limited by the time it takes to transfer charges across the interface. The overall electrochemical cell can be represented as shown in Fig. 2, with bulk of the solution represented as an ideal resistor, \(R_b\), \(C_{par}\) represents the parasitic capacitance between the insulated metal lines on the polyimide probe shank and the bulk solution. \(R_{par}\) represents the parasitic resistance from the power source to the tip of the probe.

For larger interface potentials, the electrochemical process becomes diffusion limited and a maximum current level is reached because now all the reactants are depleted around the electrode interface and have to come from the bulk through mass transport, i.e. diffusion. Because of this, the reaction is said to be diffusion limited and the system becomes even more nonlinear [12]. In this work it is believed that the applied potential does not cause the system to go into the diffusion limited case, but stays within charge-transfer limited region.

Short voltage pulses in the nano second range charge double layers, increasing the potential across them. This increased potential causes a faradaic current flow at the interface, in turn causing an electrochemical etch. Because this current is exponential with the developing potential across the interface as shown in (2), and because the etch rate
is proportional to the current passing as shown in (1), the etching is confined to the area very close to the probe tip. As a result, the etch rate and confinement of the etch depend on the amplitude of the applied voltage, its duration, the gap between the probe and the workpiece and the conductivity of the electrolyte.

III. MICROMACHINED POLYIMIDE PROBES

In electrochemical etching, the gap between the workpiece and the machining probe tip determines the distribution of current flux, and hence the spatial confinement of the etch. It also determines the solution resistance between the tip and the sample. Because of this, the gap is kept around one micron with closed loop control [3, 4]. This requires a circuit to sense the gap and a computer interface to control it dynamically. However, in this work, the micromachined ultracompliant polyimide probe eliminates the need for servo control. The contact force between the tip and the sample is less than 300 nN for a probe shank deflection of 1 \( \mu \text{m} \), which is too low to form an ohmic contact. Consequently, the probe can be rastered across the substrate to make patterns while accommodating significant topographical variations [5].

The fabrication details and some other applications of this probe are provided in [5] and references therein. The final structure is a cantilever (typically 360 \( \mu \text{m} \) long and 120 \( \mu \text{m} \) wide) in which two layers of polyimide sandwich two 250 nm-thick Au leads. At the distal end, this layer is exposed and extended over a protruding pyramidal tip. The entire structure is attached to an insulated Si substrate on which metal pads provide electrical access to the embedded leads. A schematic and an SEM picture of the fabricated probe can be seen in Figs. 3 and 4, respectively. The probe die is attached to a PCB and wire bonded. As a final step, PCB, wires and electrode pads of the probe is painted with polyvinyl butyral (Wacker Chemicals) dissolved in IPA. After IPA evaporates, the structures are coated with a thin insulating polymer layer.

IV. EXPERIMENTAL RESULTS

Electrochemical etching of evaporated nickel (800/400/200 nm Ti/Au/Ni) on a silicon substrate was performed using the setup shown in Fig. 1. The electrolyte was composed of 1 M NaCl and 0.5 M HCl solution, corresponding to a pH of 0.3. In all experiments, the probe tip was in mechanical contact with the substrate but there was no ohmic contact because of the low contact force as describe earlier. Pulses of 500 ns width, 22.8 \( \mu \text{s} \) period, and different amplitudes were applied between the probe and the substrate. The resulting patterns for 2 and 3 V amplitudes are shown in Fig. 5. Figure 6 shows the current response to an applied voltage pulse. The current flow is typical of an RC circuit, indicating the absence of a short circuit between the tip and the sample.

The dependence of etched pattern widths on applied voltage amplitude is shown in Fig. 7. As expected from (2), the etch rate increases exponentially with the developing potential at the interface; therefore, the pattern width has an exponential dependence on the amplitude of the applied voltage pulse. Also shown in Fig. 7 is the impact of varying the pulse duration. Here, electrochemical etching with a fixed 3 V amplitude, but different pulse durations (corresponding to a change in duty cycle), was performed in a 0.2 M NaCl and 0.1 M HCl solution. Assuming that the interface potential is due to charging of an RC circuit with a specific time constant, the developing potential depends exponentially on the duration of the applied pulse. From (2), the etch rate also depends exponentially on the pulse duration in agreement with the etching results in Fig. 7.

A separate experiment was conducted to verify the formation of SAMs on the electrochemically exposed gold surfaces. Here, a 1.2 \( \mu \text{m} \) diameter tungsten microprobe tip was insulated with a thin layer of polyvinyl butyral everywhere except the tip region, which was left uncoated. Several large (>500 \( \mu \text{m} \)) gold patterns were formed by electrochemically etching the nickel mask with 2V, 500 ns pulses in a 1M NaCl and 0.5 M HCl solution. After rinsing the sample in DI water and IPA, it was immersed in a 1 mM ethanol solution of undecanethiol (Aldrich) for 6 h to form a hydrophobic alkanethiol SAM. The samples were then rinsed in ethanol to remove excess SAM molecules.
The formation of the SAM was verified by X-ray photoelectron spectroscopy (Al-Kα source, 1486.6 eV). XPS spectra in the S(2p) region were obtained on both the exposed gold and the unetched nickel regions. Figure 8 shows that the thiolates selectively adsorb to the etched gold regions but not the nickel mask. The sulfur doublet observed in the gold spectrum consists of two peaks, S(2p1/2) at 163.3 eV and S(2p3/2) at 161.8 eV. The 1:2 ratio of the respective peaks, commonly observed in gold-thiolate SAMs, represents a shift towards lower binding energies and indicates that the free thiols are bound to the metallic surface [10]. No thiolates are detected in the nickel spectrum.

V. CONCLUSIONS

In this work, selective electrochemical etching of nickel films on gold was achieved by applying nanosecond voltage pulses between the nickel film and a micromachined ultracompact polyimide probe. Application of short voltage pulses confined the etch area to the probe tip area by causing an exponential dependence between the distance and the etch rate. The mechanical compliance of the probe shank to topographical variations eliminated the need for servo control to maintain the gap between the probe tip and the substrate in the one-micron regime for precise machining. By applying 500 ns, 2 V pulses, 3 µm wide patterns were achieved in a 1 M NaCl and 0.5 M HCl solution. Experiments suggested that they could be scaled down to tens of nanometer by using 5 ns pulses. Selective adsorption of alkanethiol SAMs to the Au regions was verified using XPS, and Ni was shown to be an effective mask.

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