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In-situ transient current detection in local anodic oxidation nanolithography using conductive diamond-coated probes

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Abstract

Achieving precise control over oxidation growth has become a key bottleneck in quality control in local anodic oxidation (LAO) nanolithography due to the lack of effective process monitoring and feedback control approaches. In this context, this paper proposed and presented an *in-situ* current detection approach to monitor the status of oxidation growth in real-time in the LAO processes using highly durable conductive diamond-coated probes. Research findings indicate that the use of diamond-coated probes can induce controllable LAO with transient current at the microampere level and create nanostructures with heights exceeding 18 nm, which are notably superior to those obtained using doped silicon probes. It was also demonstrated that, within a certain range of voltage, the detected current could reflect the oxidation growth during the fabrication of nanolines, with the detected current correlating to the conductivity of the oxidised surface, indicating the extent of oxidation. It is expected that the combination with flexible pulse modulation will promise a flexible and simple approach to tuning oxidation growth, paving the way for the production of high-quality oxide lines.

Atomic force microscopy, Monitoring, Nano manufacturing, Oxidation

1. Introduction

Local anodic oxidation (LAO) nanolithography is emerging as a flexible and versatile nanofabrication technique [1,2] to advance the development of next-generation nano and quantum devices, such as nanopore-based single molecule detection devices [3], nanowire transistors [4], nanooptics [5], etc. Through applying a positive voltage to the substrate with respect to the probe in ambient or environment-controlled condition, LAO can create nanostructures on various materials with a variety of shapes [1,6,7]. Moreover, it has shown various advantages, including atomic-level resolution, direct surface patterning, high reproducibility and compatibility, and low environmental requirements and instrument costs [1]. However, as LAO is a complex electric field-assisted nano-oxidation process [8], the final quality of the processed structures is controlled by various parameters, such as voltage amplitude and duration, substrate materials, environmental humidity, tip scan parameters, etc. Due to its open-loop nature, the lack of effective process monitoring and feedback control approaches has become a key challenge in achieving precise quality control in the LAO process.

Fundamentally, LAO is an electrochemical reaction process, with the oxidation growth governed by Faradaic current. Thus, in-situ detection of Faradaic current is a dominant factor that reflects the reaction status and promises to become an ideal indirect measurement target to create an effective process monitoring and feedback-controlled process [9]. In previous studies, current detection has been performed in combination with various analyses for LAO on silicon surfaces. Avouris et al. [10,11] measured current evolution during LAO and found it aligned with Faraday current calculated from the measured volume growth according to the electrochemical reaction:

$$Si + 4h^{+} + 2OH^{-} \rightarrow SiO_2 + 2H^{+} \quad (1)$$

noting a charge efficiency of 50%. Similarly, Ruskell et al. [12] associated the current observed during LAO with the reduction of H^{+} ions on the AFM probe. Dagata et al. [13,14] determined that the majority of current in high voltage LAO does not contribute to surface oxide growth. They also investigated the roles of ionic and electrical contributions during LAO, finding that contact currents were much larger than noncontact despite similar volumes. Martin et al. [15] simultaneously measured force and current versus tip-surface distance, successfully gauging the electrical conductivity of the water meniscus. Murano et al. [16] focused on the initial moments of LAO through measuring current during tip separation from the surface, which provided insights into oxide growth kinetics, the influence of meniscus geometry on electrical conduction, and the role of space charge at small tip-sample distances. Kuramochi et al. [17–20] achieved precise current detection at sub-picoampere levels by enclosing electronic components in a sealed unit, eliminating the effects of humidity. They monitored the LAO process using Faradaic current detection, noting that current flow starts promptly once the tip-substrate bias exceeds a certain threshold and decreases over time as oxidation progresses. Kuramochi et al. [21] also used current detection in carbon nanotube probe-induced LAO, demonstrating sensitivity for detecting thin oxides and small features, and evaluated the meniscus dimension during nano-oxidation through *in-situ* Faradaic current detection and edge broadening. Current detection was also performed for LAO on other substrates. Kim et al. [22] explored the reaction kinetics of LAO on Ti substrates using transient current data, revealing insights into space charge buildup and oxide morphology, and determined the optimal exposure time. Kuang et al. [23] studied LAO in Ti thin films, finding a linear relationship between protrusive oxide line heights, applied voltages, and tunneling currents. Perez-Okada et al. [24] measured the current during the LAO of GaAs and found that the electron transport follows the Fowler-Nordeim tunnelling mechanism over a range of bias. They also studied the current flow, which revealed the relationships between Faradaic current and leakage current in LAO processs [25]. Fernandez-Cuesta et al. [26,27] disclosed two distinct AFM-induced oxidation mechanisms on thin Si_3N_4 layers on silicon by studying the kinetics via electrical current detection during LAO: the transformation of Si_3N_4 to silicon oxide, and the integration of silicon into the base of the Si_3N_4 layer. Shimada et al. [28] and their group [29] investigated the Faradaic current during the LAO of NiFe thin films and Si substrates. They discovered that LAO on silicon consistently shows a 50% current efficiency, unaffected by tip scan speed, and that larger nano-oxide structures result from increased bias voltage. In addition, they found that NiFe exhibited lower current efficiency than silicon, with excess non-oxidative current that could be minimised by insulating oxide layers, which also stabilised oxidation due to their hydrophilicity, benefiting nanostructure and nanodevice fabrication. Schneegans et al. [30] noted Faradaic currents were minimal compared to total current in the AFM probe contact-junction during the LAO of $(TMTSF)_2PF_6$. Faucett and Mativetsky [31] conducted in-situ current measurements during oxide reduction on graphene, revealing that the process is rate-limited, governed by the generation and transport of hydrogen ions. Martin et al. [32] monitored the current during the LAO of PMMA films, uncovering a local electrochemical reaction involving the transport of OH^- ions through the PMMA.

In addition to mechanism study, *in-situ* current detection promises the feedback current control of the LAO process, with potentials to achieving improvement of accuracy and controllability of LAO for rapid prototyping of nanoproducts or devices. However, this has rarely been reported in comparison with using current detection to reveal reaction mechanisms. Johannes et al. [33] developed a velocity-controlled approach for LAO nanolithography through adjusting translational speed in reaction to in-situ detected current fluctuations. This method successfully maintains a steady current flow at the tip-sample interface, proving to be effective for real-time quality control. Pellegrino et al. [34] used current as a feedback to perform voltage controlled LAO nanolithography on $SrTiO_{3-\delta}$ thin films. They demonstated that constant current control can realise lines with uniform widths down to 150 nm over a total length of hundreds of micrometers. However, these methods were focusing on structures with simple shapes, limiting their applications in developing next-generation nanoscale products and devices. Constant current power supply was also used for LAO, in order to achieve consistent oxidation. Through this method, the single-electron transistor [35] and self-aligned gate structures [36] were fabricated. However, there have been relatively few studies of LAO on silicon using diamond-coated probes. It is not clear what effect the conductive diamond coating will have on oxidation growth and current characteristics while bringing improved wear resistance and conductivity.

In this work, we studied the LAO experiments using conductive diamond probes and silicon substrates in combination with *in-situ* current monitoring, aiming to reveal more insights on the oxidation growth and current features. We expect this study can provide necessary guidance to develop feedback-controlled, reliable, and durable LAO nanofabrication process.

2. Methods

LAO experiments and monitoring were performed using a Bruker D3100 atomic force microscope (AFM) combined with a pulse generator power supply (Aim-TTi TGF4042) and D22 picoammeter. During the LAO, AFM is operated under contact mode with the vertical position of the cantilever kept constant by maintaining the same referenced setpoint. The schematic of LAO reaction is illustrated in **Figure 1**. To induce oxidation, a voltage signal was introduced onto the AFM, with the conductive probe at a negative bias to the sample substrate. The bias could induce the formation of highly nonuniform electric field between the tip and sample, further inducing a series of physical and chemical reactions, enabling the nanopatterning on the sample surface. In an atmosphere of a certain humidity, tip-sample interface is filled with water. The applied voltage induces current passing through from the substrate to the probe, which is measured using a picoammeter. As concluded in previous research [25], the transient current during contact-mode LAO includes two different types, Faradaic current and electrical current (ohmic and tunnelling), while the Faradaic current is responsible for the electrochemical reaction within the water bridge and forms the oxides in the reaction region.

The wafer used in this work has been double-side polished, resulting in a surface roughness (Ra) of less than 0.3 nm. Before performing the LAO experiment, the wafers were cleaved into small pieces using a diamond cutter. Then, these small-piece samples were cleaned by sonication in an $NH_4OH/H_2O_2/H_2O$ (1:1:5) solution for 10 mins to remove surface contaminations. Finally, they were rinsed with deionised water and blown with a dry N_2 gas jet. Conductive AFM probes (model CDT-CONTR) with a nominal tip radius between 100 and 200 nm and nanoroughness of 10 nm were used for the nanofabrication and imaging. These probes were made by silicon cantilevers with highly doped diamond coatings to increase the conductivity and wear resistance. Given the significant impact of humidity on the LAO process, the nanofabrication conducted in this work was always carried out under atmospheric conditions (20 °C) with relative humidity at 25–30%. To ensure precise humidity control, a hygrometer with an accuracy of ±1% was employed to monitor and maintain the desired humidity levels throughout the experiments. The oxide patterns were imaged right after their creation, and the AFM images were analysed using the Bruker NanoScope Analysis 1.7 software.

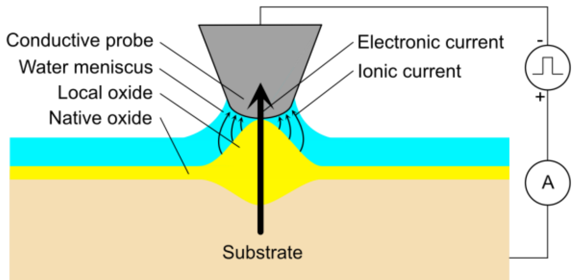

Figure 1. Schematic of local anodic oxidation with current feedback.

3. Results and discussions

This experiment encompasses the fabrication of nanodots and nanolines, with the evaluation involving current measurement and topographical mapping of the resulting nanostructures.

3.1 Dots

Nanodots were generated by applying two pulses separately with the voltages of 8 and 9 V and the same duration of 5 s to a static probe in contact with the surface. This process produced two distinct nanodots by maintaining the probe's position over targeted areas on a silicon surface. The morphology of the nanodots and their cross-sectional profiles are depicted in **Figure 2** (a) and (b). The results indicate that the oxide dots have heights of 11.8 and 13.6 nm, respectively, significantly surpassing the heights of oxide dots fabricated in prior studies using contact conductive probes [18]. The progression of the transient current during LAO is illustrated in **Figure 2** (c). It is evident that an increased pulse amplitude can promote oxidation growth and augment current flow. In addition to the enhanced oxidation resulting from this increased current, the low stiffness of the cantilever may also contribute to the process by imposing fewer constraints on oxidation development.

Contrary to the patterns observed by Dagata et al. [13] and other researchers, where current typically first reached a peak and then decreased over the pulse duration, the current in our study fluctuated between 3 and 8 μA. This current is significantly higher than the anticipated Faraday current, calculated based on experimentally measured volume growth and incorporating charge transfers for a standard silicon anodic reaction, as per Equation (1). Our measured current exceeds the calculated value by more than six orders of magnitude. The findings indicate that the majority of the measured current is electrical, with the Faradaic current responsible for oxidation growth, representing only a small portion. This could be due to the probe's low resistance and the substrate's thinness, allowing for a greater flow of electrical current during the LAO process. As shown in **Figure 1**, additional leakage pathways will also be generated, which contributes to the recorded current and extend beyond the Faraday current and direct tunnel current through the oxide layer. These observations are consistent with previous research [25].

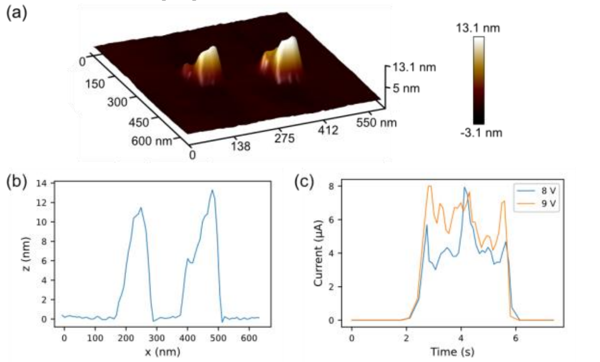

Figure 2. (a) Schematic of oxide dots created by LAO. (b) Cross-sectional profile for two nanodots. (c) Current evolution during LAO.

3.2 Nanolines

Nanolines are commonly fabricated to demonstrate their practical use in the device development of transisters and sensors [4]. In our study, we applied a sequence of pulses to conductive diamond probes at the same scanning speed of 200 nm/s to assess the production of oxide nanolines. These pulses were of uniform duration, each lasting 4 seconds.

Implementing four pulses with amplitudes ranging from 5 to 9 V resulted in the formation of four distinct line nanostructures, as depicted in **Figure 3** (a). **Figure 3** (b) and (c) demonstrate that both the height of the oxide lines and the transient current surge correlated with an increase in pulse amplitude from 5 to 9 V. Oxide lines with relatively consistent shapes were observed with pulse amplitudes between 5 to 7 V. Above 7 V, the oxidation process appeared discontinuous, exhibiting multiple peaks with heights fluctuating between 8 to 18 nm, as observed in **Figure 3** (d). The maximum oxide height appears to be around 18 nm, which is much higher than the results obtained from LAO using doped silicon probes. We posit that the intermittent formation of oxide lines stems from an unstable water meniscus, likely due to ununiform water film thickness at low humidity conditions. According to previous conclusions from experimental and simulation results [7,37], LAO at higher voltages can incur intense oxidation, leading to rapid oxide growth and simultaneous depletion of the water meniscus. This process can occur so rapidly that water diffusion fails to replenish the water meniscus sufficiently to maintain consistent oxidation. Therefore, while the tip scans, the LAO leads to intermittent oxide lines. In contrast, at lower voltages, severe oxidation is less likely to happen, allowing for a continuous oxidation process with an adequate consumption of water. As a result, this leads to the formation of oxide lines with fairly continuous shapes. However, the nanolines created do not seem to be straight but present a curved shape compared with the nanolines created by tapping-mode LAO [6]. The underlying reason could be the randomness during the lateral diffusion of oxynians during contact-mode LAO. The large-radius probe in contact with the sample increases the linewidth and at the same time, facilitates the oxidation growth at lateral direction, making the centre of oxide lines not directly underneath the tip.

The current detected during our experiments is significantly higher than the Faradaic current calculated from the oxidation growth volume by approximately a million times. Consequently, we are unable to observe the expected changes in Faradaic current, such as peak heights corresponding to maximum current. Interestingly, at certain points, an inverse relationship was observed, where insufficient oxide growth led to higher current levels, as shown in **Figure 3** (b). It is hypothesised that the current flowing through the tip depends on the height of oxide protrusions at the tip-sample contact region. Since LAO reaction can happen in a very short time scale of picoseconds, the detected current mainly reflects the electrical current passing through the reaction cell, which is mainly affected by the conductivity of a closed circuit. These results agree well with a previous study on LAO using Rh-coated probes [33], demonstrating that the current detection can serve as a process monitoring approach that reflects the difference in the oxidation status due to the variation in the oxidation conditions.

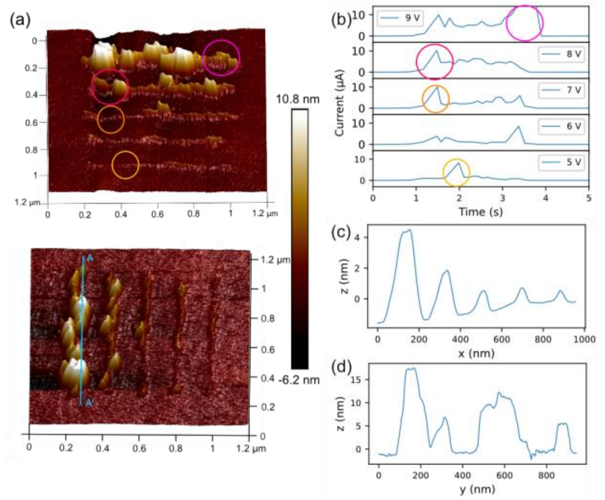

Figure 3. (a) Schematic of oxide lines created by LAO. (b) Current evolution during LAO. (c) Average height profile from 'Step' analysis. (d) Cross-sectional profile along A-A'.

4. Conclusions

This paper details the nanofabrication outcomes and current monitoring used for LAO nanolithography with conductive diamond probes. By fabricating nanoscale dots and lines and monitoring transient currents, we have deepened our understanding of the LAO process using these probes. Notably, these probes can induce LAO to create oxide dots exceeding 18 nm in height, surpassing the results achieved with doped silicon probes. Current measurements indicate that the transient current is significantly higher than expected and previously reported, reaching microampere levels. This suggests that the Faradaic current constitutes only a small fraction of the total current. However, the measured transient current can indicate the degree of oxidation, as higher currents typically occur in areas where oxidation is insufficient.

This study establishes current detection as a valuable tool for real-time monitoring in LAO nanolithography, offering insights into the reaction process as it occurs. Looking ahead, integrating this approach with a feedback-controlled system, complemented by pulse modulation, holds great potential for augmenting LAO's nanofabrication capabilities, particularly in enhancing durability, reliability, and controllability. These aspects will form the cornerstone of our future research endeavors.

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