Atomic-Scale Modification via Local Anodic Oxidation Using Peak Force Tapping in AFM

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Atomic and close-to-atomic scale manufacturing (ACSM) represents a key future trend in manufacturing technology. Atomic force microscopy (AFM), with its exceptional spatial resolution, enables atomic-level precision in material processing, with local anodic oxidation (LAO) being a notable technique applied successfully in the semiconductor industry, such as for nanowire fabrication. However, detailed exploration of LAO technology's potential for material removal at the atomic and close-to-atomic scale is still lacking. While increasing the scanning speed can significantly reduce modification time and oxide thickness, traditional LAO processes, typically performed in contact mode, face challenges such as contact instability and increased lateral forces at higher probe writing speeds. To investigate the limits of LAO capabilities, this study explores the potential of AFM LAO for single atomic layer modification. The results demonstrate that using peak force tapping (PFT) mode, single-layer depth oxidation was successfully achieved, with process efficiency enhanced by 2 to 3 orders of magnitude compared to contact mode LAO. This provides new evidence for the feasibility of atomic-scale fabrication and lays a foundation for future precision fabrication technologies.

NOMENCLATURE

D_s = deflection sensitivity of the probe
h = oxide height
k = spring constant of the probe
v_1 = writing speed
V_d = deflection of the probe
P = tapping load of the probe

1. Introduction

As the manufacturing industry continues to advance, fabrication technologies have evolved from the micron scale to the nanoscale and are now progressing towards atomic and close-to-atomic scale manufacturing (ACSM) [1,2,3]. Achieving precise control over materials and structures at these tiny scales has become a core challenge in manufacturing technology. Atomic force microscopy (AFM), with its extremely high spatial resolution, has shown significant potential in atomic scale fabrication and surface engineering. AFM not only offers sub-nanometer resolution but also allows precise control of interactions between the probe and the sample under applied forces, heat, and/or electric fields, enabling localized material modification and removal [4]. Therefore, AFM is considered a powerful tool in achieving ACSM.

Various AFM-based lithography techniques have been developed in the recent years, which can be broadly categorized into force-assisted and bias-assisted methods. Local Anodic Oxidation (LAO) is a bias-assisted AFM-based nanofabrication technique, also known as field-induced oxidation, nano-oxidation, and scanning probe oxidation [5]. By applying a voltage between the AFM probe and the sample surface, an electrochemical reaction is induced, forming an oxide layer on the sample surface. The precision of the AFM probe allows LAO to generate nanostructures with specific shapes and dimensions, demonstrating excellent spatial selectivity, and enabling targeted nanoscale, and potentially atomic-scale, modifications.

In 1990, Dagata et al. first reported the modification of a hydrogen-passivated silicon surface using scanning tunneling microscopy (STM) [6]. Despite STM's stringent environmental requirements, it remains one of the few atomic precision manufacturing techniques applied in industry, often referred to as hydrogen depassivation lithography. In the following years, AFM was applied to this field due to its key advantage operating directly in ambient air. Červenka et al. demonstrated the fabrication of nanostructures on silicon (100) and gallium arsenide (100) surfaces using AFM-based LAO, showing that the formation of silicon oxide lines adheres to the Cabrera-Mott theory [7]. Similarly, Cambel et al. emphasized the role of sample conductivity and water bridge formation in the nano-oxidation process using AFM [8].

Currently, in the semiconductor industry, LAO is recognized as a high-precision, environmentally friendly nanofabrication technique that does not require masks or produce contaminants. This technology has already been applied in the fabrication of nanowires and quantum dots [9], demonstrating its potential to atomic scale manufacturing.

Despite progress in LAO technology within nanofabrication, significant gaps remain in achieving atomic-scale controlled oxidation. Reported LAO on monocrystalline silicon typically uses contact-mode scanning, producing oxide layers about 1~10 nm in thickness [9], with no documented cases of atomic-scale controlled modification. One of the main challenges in achieving atomic-scale modification is the low scanning speed of the AFM used in current LAO processes, with writing speeds typically in the range of 1 μm/s. Studies have shown that oxidation thickness has an exponential relationship with time [10]. While increasing the scanning speed can effectively reduce the oxide layer thickness, excessively high speeds can lead to unstable contact between the probe and the sample surface, introducing significant lateral forces. These lateral forces can damage the probe and reduce processing accuracy, which is particularly critical in atomic-scale modifications. Additionally, the mechanical forces in contact mode can introduce stress and deformation on the sample surface, affecting the uniformity and controllability of the oxide layer. Furthermore, in contact-mode measurements, the probe is prone to wear and can easily accumulate surface contaminants, leading to instability. Therefore, traditional contact-mode LAO processes face significant limitations when exploring atomic-scale precision manufacturing.

The primary goal of this study is to explore the limits of LAO technology in ACSM, with a focus on achieving controlled modification at the single-atomic layer level. To address the challenges of traditional methods, this study introduces the innovative load-controlled PFT mode [11]. Utilizing this technique, the research successfully achieved single atom layer scale LAO modification, with processing efficiency improved by 2 to 3 orders of magnitude compared to traditional contact scanning modes. This accomplishment not only overcomes the limitations of conventional contact-mode LAO processes but also opens new avenues for advancing ACSM technologies.

2. Experimental setup

The LAO process was conducted using a Bruker Dimension Icon AFM in PFT mode. Experiments were carried out under ambient conditions, with a room temperature of 20°C and a humidity level of 40%. The samples used were commercially available doped silicon (100) single crystals. To remove the native oxide layer from the surface, the samples were immersed in a 5% hydrofluoric acid (HF) aqueous solution for 10 seconds to obtain a hydrogen passivated surface [9].

The AFM probes used in the experiments, as illustrated in Fig. 1, were Bruker SCM-PIT-V2 probes. These probes feature a silicon nitride base with both the front and back sides coated in a platinum-iridium alloy. The tip radius is approximately 30 nm, with a spring constant of 3 N/m and a typical deflection sensitivity of 60 nm/V.

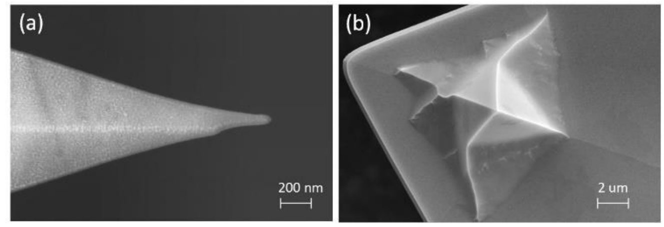

Fig. 1 Conductive AFM tip before (a) and after (b) the LAO

The PFT mode operates within a tapping frequency range of 0.125 kHz to 2 kHz. It should be noted that tapping load was calculated based on the spring constant and the deflection sensitivity of the probe. The probe's deformation during contact with the sample was monitored via the position sensitive photodetector (PSPD) feedback signal, where the voltage signal V_d represents the deflection of the probe. Consequently, the tapping load P is calculated using the following equation:

$$P = k \cdot D_s \cdot V_d \quad (1)$$

By carefully managing signal V_d, the peak tapping load was controlled within 1 nN to minimize the impact of the load on the surface structure.

3. Results and Discussion

3.1 Peak Force Tapping-Driven Local Anodic Oxidation

Peak force tapping is a widely utilized technique in various areas such as biology, material science, and nanotechnology. The principle behind PFT involves applying a controlled force between AFM probe and the sample surface, enabling the precise measurement of mechanical properties like stiffness and adhesion.

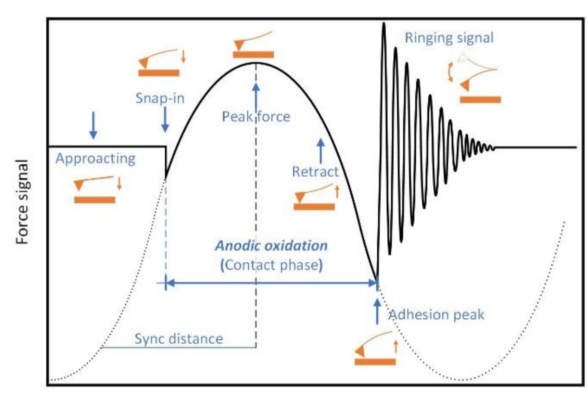

Fig. 2 Schematic illustration of PFT-based LAO

The working mechanism of PFT, as illustrated in Fig. 2, can be understood as a sequence of indentation processes. Each tapping cycle can be divided into six distinct stages: approaching, snap-in, peak force, retract, adhesion peak, and separation [11]. As the probe approaches the sample surface, van der Waals forces and other attractive interactions cause the probe to snap onto the surface, generating a characteristic negative load. Once snap-in occurs, the probe makes contact with the surface, and a meniscus forms in the gap between the probe and the surface due to the combined effects of capillary forces and the applied electric field. Oxidation occurs under the influence of the bias voltage as the probe continues to advance until reaching the setpoint, or peak force. The probe then begins to retract.

During the retract phase, adhesion forces, primarily composed of van der Waals forces, capillary forces, and electrostatic forces, play a dominant role, with capillary forces being the most significant. This dominance explains why the adhesion peak is considerably larger than the load recorded during the snap-in phase, and it reflects the size of the meniscus. As the probe retracts further, the meniscus eventually breaks, causing a sudden drop in adhesion force and resulting in probe vibration. The cycle then repeats with the next tapping event.

The principles outlined above indicate that LAO performed in PFT mode differs fundamentally from that performed in contact mode. PFT-based LAO is characterized by its intermittent and periodic nature, where each tapping cycle forms an individual oxidation point. By carefully adjusting the scanning parameters, it is possible to create oxidation patterns such as dot arrays, line arrays, and complex surface structures, as demonstrated in Fig.3 (a)-(d). The experimental results clearly highlight the unique reaction kinetics of single-atomic layer oxidation achieved through the PFT mode.

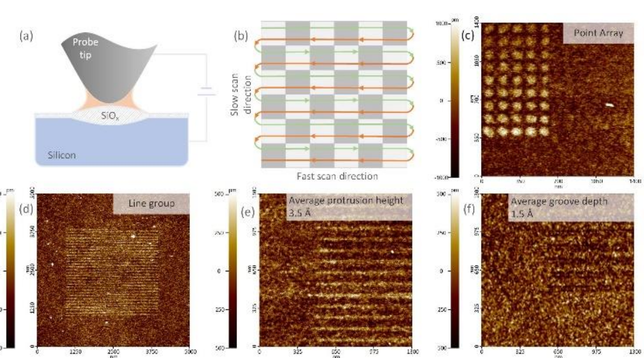

Fig. 3 PFT-based LAO. (a) Schematic illustration of LAO. (b) AFM probe scanning path. (c) Point array. (d) Line array. (e) Oxidation protrusions with a height of 3.5 Å. (f) 1.5 Å deep grooves after etching the oxidation protrusions with HF solution.

It is worth noting that the inherent characteristics of the PFT mode offer several advantages for executing LAO. Compared to contact mode scanning, PFT inherently avoids the introduction of lateral forces and operates with much lower normal loads, typically in the sub-nN range. While both PFT and conventional tapping modes involve surface tapping, PFT excels by precisely controlling the force feedback loop in every single tapping. This precise force control significantly reduces the impact of normal load-induced stress on the oxidation process, thereby preventing the force fluctuations and excessive loading that can lead to sample damage in conventional tapping mode. Consequently, PFT enables a more stable and controlled oxidation reaction.

3.2 Single-atomic layer LAO

The study of the mechanism and kinetics of local anodic oxidation (LAO) on silicon surfaces using AFM is fundamental for achieving controlled atomic layer modifications. Extensive research has been conducted to explore this process [12,13]. The reaction zone beneath the AFM probe can be conceptualized as a miniature electrochemical cell, where the anodic half-reaction of silicon is represented as:

$$Si + 4h^+ + 4(OH^-) \rightarrow SiO_2 + 2H_2O \tag{2}$$

Simultaneously, hydrogen gas is generated at the cathode (meniscus/tip interface):

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

This reaction results in the formation of SiO_2. Despite substantial progress in understanding the mechanisms, current research still lacks the detailed insights necessary for achieving precise atomic layer modifications. In particular, a comprehensive explanation of LAO kinetics at the atomic scale remains elusive.

Existing studies indicate that LAO kinetics follow the Cabrera-Mott theory [7], which was initially used to describe the kinetics and oxide growth mechanisms in LAO. The theory assumes that cation migration occurs under the influence of a potential gradient across the growing oxide film. Consequently, the height of the oxide layer is linearly influenced by the applied bias voltage [10]. Reducing the voltage weakens ion migration, thereby directly reducing the oxide height. However, due to the slow scanning speed in contact-mode AFM, even when the voltage barely reaches the threshold required for oxidation, the oxide height can still reach several nanometers [9]. Dagata et al. highlighted that space charges generated under extremely high electric field conditions ($E > 10^6$ V/cm) and rapid initial growth also significantly influence the oxide height [14]. Thus, simply lowering the voltage is insufficient for achieving atomic-scale modifications.

Apart from voltage, writing speed is another critical factor affecting oxide height h. Teuschler proposed a power-law relationship [15]:

$$h = \alpha \left(\frac{v_0}{v_1}\right)^{\gamma} \tag{4}$$

where α and γ are fitting parameters, v_1 is the writing speed, and v_0 is a constant. This relationship shows that oxidation time affects oxide height logarithmically. Thus, increasing the writing speed, which shortens the modification time, which in turn effectively reduces the oxide height.

The PFT mode, with its high oscillation frequency and intermittent contact, significantly reduces the modification time for each point. The effective writing speed can be calculated by dividing the diameter of a single point in Fig. 3(c) by the contact time shown in Fig. 2. Tab. 1 illustrates the relationship between contact time and probe oscillation frequency. According to the data in Tab. 1, the effective writing speed in PFT mode ranges from approximately 125 to 2000 μm/s, which is 2 to 3 orders of magnitude faster than the 1 μm/s writing speed in contact-mode AFM.

Table 1 The contact time corresponding to different tapping frequencies in PFT mode.

PFT frequency /kHz	0.125	0.5	1	2
Contact time /μs	800	200	100	50

At a tapping frequency of 2 kHz, the oxidation time per tap cycle is approximately 50 μs, resulting in an effective writing speed of around 2000 μm/s. Under these conditions, the experiment demonstrated that oxide protrusions as low as 3.5 Å could be achieved at the LAO threshold voltage, as shown in Fig 3(e). The oxidized samples were then immersed in HF solution to remove the modified layer, producing a groove with a depth of 1.5 Å corresponding to a single atomic layer, as shown in Fig 3(f). The volume mismatch between the pristine surface and the newly formed oxide closely aligns with previous reported experimental findings [5]. specifically, for every 1 nm of oxide formed above the silicon surface, approximately 0.4 nm of SiO_2 is formed beneath the surface. This understanding is crucial for controlling the depth and uniformity of the oxide layer, especially when aiming for precision modifications at the atomic scale.

3. Conclusions

The potential of LAO using AFM to achieve atomic-scale modifications on silicon surfaces is explored in this study. The peak force tapping mode is employed to significantly enhance the effective writing speed and precision. The experimental results demonstrated that, at a tapping frequency of 2 kHz, oxide protrusions as low as 3.5 Å can be achieved. Subsequent immersion in a 5% HF solution successfully removed the oxidized layer, resulting in grooves corresponding to a single atomic layer. This study not only overcomes the limitations of conventional LAO methods but also opens new avenues for advancing ACSM technologies.

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