PRECISION-CONTROLLED SCANNING PROBE ANODIC OXIDATION: A VERSATILE NANO-PROTOTYPING PLATFORM

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Fabrication of functional materials and devices with nanometer features is a critical proof-of-concept (POC) step in nanotechnology R&D's. Given the stringent cost, technical, environmental, and instrumental requirements, the conventional nano-fabrication techniques such as electron-beam lithography has a serious limitation as a routine tool in ordinary labs. The recent rise of interest in unconventional nano-fabrication methods like the nano-imprinting or dip pen lithography stems from the clear awareness of the need for practical techniques that can be useful in the POC phase.

The scanning probe anodic oxidation, first demonstrated by J.A. Dagata, NIST, around 1990, is one of the most attractive unconventional nano-fabrication technologies. It is applicable to virtually all materials that can be oxidized under the ambient condition with the minimal instrumental requirements other than the AFM or STM. The adsorbed or condensed water bridge filling the gap between the tip apex and the substrate serves as a medium in which electrochemical oxidations are induced by an externally applied voltage up to 10V. In the case of Silicon oxidation, the reaction scheme is simply written as

 $(A \rightarrow C)$ Si + h^+ + 2OH \rightarrow SiO₂ + 2H⁺

$$(A \rightarrow B) \qquad \begin{array}{l} H^{+} + OH^{-} \rightarrow H_{2}O \\ H - Si \equiv Si_{3} + H_{2}O + h^{+} \rightarrow^{*} Si \equiv Si_{3} + H_{2}O^{+} \\ H_{3}O^{+} + OH^{-} \rightarrow \left[H_{3}O^{+} - OH\right] \end{array}$$

$$(\mathbf{B} \rightarrow \mathbf{C})$$
 Si + $h^+ \left[\mathbf{H}_3 \mathbf{O}^+ - \mathbf{O} \mathbf{H} \right] \rightarrow \mathbf{SiO}_2 + 2\mathbf{H}^+$

but the real SPM oxidation process is known to involve additional factors such as charge trapping, electrowetting, defect generation, etc., which make the process very much complicated. Therefore, in order to establish a reliable and standardized SPM oxidation technique, it is definitely necessary to accurately control the environmental parameters (relative humidity, temperature, voltage wave form, etc.) and to monitor the process in-situ.

We developed a highly reliable SPM oxidation station, incorporating all these requirements, along with the

installation of a nanometer precision closed loop stage. Based on the environment controlled SPM, we added a humidity controlled air circulator that allows the control of humidity with 1% accuracy over a wide range. In particular, we setup an in-situ faradaic current (<1pA) detection system, which allowed us to monitor the progress of anodic oxidation in real time. With the use of a carbon nanotube probe, we have successfully fabrication oxidation lines with an width less than 10nm over several tens of micron area with the dynamic range of 10^4 . The fabricated examples in Figs. 1 and 2 are the tiny characters fabricated in the raster scan mode and the square and grid patters made in the vector scan mode, respectively.



Fig.1 Logo of the project drawn on a 2µm x 2µm area of a hydrogen terminated Si by the precision controlled SPM oxidation system. Raster scan mode.



Fig.2 15nm-wide oxidation line patterns fabricated on a hydrogen terminated Si surface by the precision controlled SPM oxidation system. Vector scan mode.

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