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Multi-step process control and characterization of scanning probe lithography

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Abstract. An atomic force microscope with a conducting tip (CT-AFM) was used to fabricate and characterize nanometer scale lines of (1) silicon oxide and (2) silicon nitride on H-terminated n-type silicon (100) wafers. In process (1), a negative bias was applied to the tip of the CT-AFM system and the resulting electric field caused electrolysis of ambient water vapor and local oxidation of the silicon surface. In addition, the accompanying current was detected by a sub-pA current amplifier. In process (2), the presence of a nitrogen atmosphere containing a small partial pressure of ammonia resulted in the local nitridation of the surface. The CT-AFM system was also used to locate and study the dielectric properties of the silicon-oxide lines as well as copper islands buried under 20 nm of silicon dioxide. A computer-controlled feedback system and raster scanning of the sample produced simultaneous topographic and Fowler–Nordheim tunneling maps of the structures under study. Detailed aspects of nanolithography and local-probe Fowler–Nordheim characterization using a CT-AFM will be discussed.

The importance of silicon oxide and nitride to the semiconductor industry is demonstrated by the continuous research in the production and patterning of these two materials. Both materials have unique, beneficial properties as dielectrics and masks that have made silicon-based semiconductors so prevalent.

Methods for production have generally focused on the patterning of a resist followed by an etching step. Dagata et al. [1], however, discovered a local growth of silicon oxide during scanning tunneling microscopy. It was demonstrated later that one could also grow patterned oxide structures using conducting tip atomic force microscopy (CT-AFM) [2]. However, it was shown that this technique is not limited to the growth of oxide, but could also be used to grow patterned silicon-nitride structures [3], one topic discussed in this paper.

The fabrication of these structures also requires the ability to characterize them with nanometer-scale resolution and preferably in situ. A commonly used technique to characterize large-scale areas on an oxide film employs the Fowler–Nordheim emission current that necessitates the fabrication of capacitors on the sample. Current vs voltage curves measured across these capacitors provide information on charge trapping, dielectric strength, and oxide degradation.

In its standard form, however, this technique lacks the required resolution. The solution to this problem is offered by a CT-AFM, where the tip–oxide–silicon acts as a nanometer-scale capacitor. As with the conventional Fowler–Nordheim technique, here too one can measure the current vs voltage to probe the oxide locally. However, the use of the CT-AFM also makes it possible to map a variety of local properties across the oxide surface, such as the dielectric strength [4], with 6 nm resolution [5]. This local probing, which is not offered by any other technique, has also been used to probe contact potential [6] and surface resistance [7].

We have used a CT-AFM system to perform local Fowler–Nordheim characterization of patterned oxide structures and copper islands buried inside the oxide, a second topic discussed in this paper.

1 Nanofabrication

The experimental setup for the fabrication of the oxide and nitride nanostructures employs a contact-mode AFM [8] operating in the constant-force mode and is shown in Fig. 1 with the switch in the up position. The dielectric tip of the AFM was replaced by a chrome-coated Si_3N_4 tip. Although the chrome wore off the apex of the tip, it could still be used to fabricate the oxide and nitride structures. The reason is that ambient water vapor involved in the oxidation process forms a meniscus between the tip and sample, creating a conduction path. Only catastrophic tip restructuring such as that due to current spikes will completely destroy the tip.

The lithographic experiments reported in this paper were performed on 100 Ω cm n-type Si(100) wafers. The wafers

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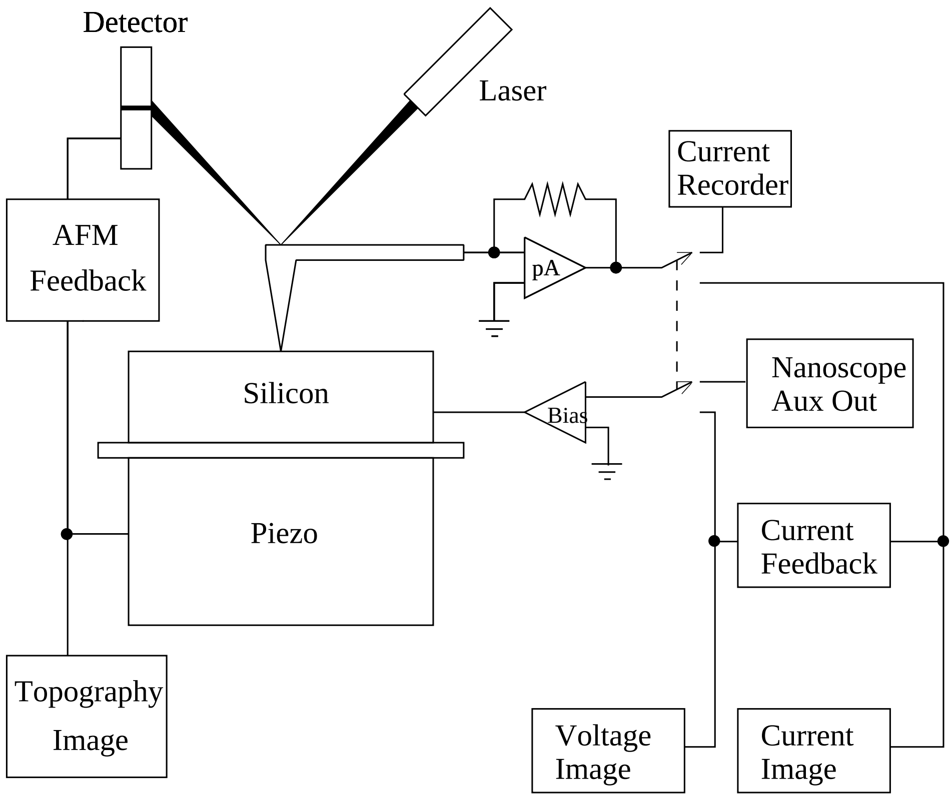

Fig. 1. Schematic diagram of the lithography and characterization system where a contact-mode AFM has been modified by replacing the standard tip with a conducting tip. Application of a bias to the tip allows the production and study of dielectric materials

were diced and etched in a 10:1 buffered HF solution for 30 s to remove the surface oxide and terminate the exposed silicon surface with hydrogen. The sample was then placed in the CT-AFM system and the tip was brought into contact with the surface. A negative tip–sample bias was applied to cause electrolysis of ambient water vapor and subsequent oxidation of the silicon surface [9]. The tip was then stepped through a set of programmed motions across the sample to produce lines. A negative bias was used as it was found that a positive bias promoted oxidation of the tip and produced uneven oxidation of the sample. Factors affecting line quality included the writing speed and the magnitude of the applied bias. A larger bias produced a thicker line, as did a slower writing speed.

It was recently discovered that a finite current, of the order of 100 fA, will accompany the electrochemical growth of the oxide [9] and nitride. To measure this ionic current and for use in the following Fowler–Nordheim study, an amplifier based on the Burr Brown OPA128LM electrometer op-amp was constructed and mounted directly on the AFM head to reduce extraneous pickup. The entire microscope was then enclosed within a bell jar having a metal guard that acted as a Faraday cage to further reduce noise.

To produce lines of silicon nitride, we replaced the ambient water vapor with ammonia in the bell jar holding the CT-AFM. The chamber was evacuated to 300 mTorr and purged with ultra-high purity (UHP) N_2 (99.999%) three times. It was then evacuated to less than 1 mTorr and NH_3 was bled in until the pressure reached 50 mTorr. The tip of the CT-AFM was then biased at -10 V with respect to the sample and the lines were again written at 60 nm/s. Following fabrication, the chamber was evacuated and purged with UHP N_2 several times to remove all traces of ammonia.

2 Fowler–Nordheim characterization

Local Fowler–Nordheim characterization of thin insulating layers, such as silicon oxide and nitride, is a recently developed technique for determining their relative thicknesses, locating defects, and studying dielectric break-down strengths quantitatively. Figure 2 shows band diagrams of a metal-oxide-semiconductor structure with a low field (left) and a high field (right) applied across it. The low-field case relates to the direct-tunneling regime where the tunneling current is significant only for oxide thicknesses less than 3 nm. The high-field case, or Fowler–Nordheim regime, occurs when the bias is large enough to lower the conduction band of the SiO_2 layer to the energy of the tunneling electrons allowing them to enter the band. This shortens the distance across which the electrons must tunnel, increasing the current. Approximating the tip–oxide–substrate as a plane-parallel MOS structure, the tunneling current is given by [10]

$$I = A_{\mathrm{eff}} \frac{e^3}{8\pi h\phi} F^2 \exp\left(\frac{-8\pi\sqrt{2m_{\mathrm{eff}}}}{3he} \frac{\phi^{3/2}}{F} \right) \qquad (1)$$

where F is the electric field across the oxide layer, ϕ the metal-oxide barrier height, A_{eff} the effective emission area, h Planck's constant, and m_{eff} the electron effective mass in the oxide. Modifications to this equation are required to take into account image charge, depletion effects, and inhomogeneity of the field associated with the geometry of the tip. A more thorough discussion of Fowler–Nordheim tunneling in metal–insulator–metal and metal–insulator–semiconductor structures, useful for a quantitative study of samples, is given in [11].

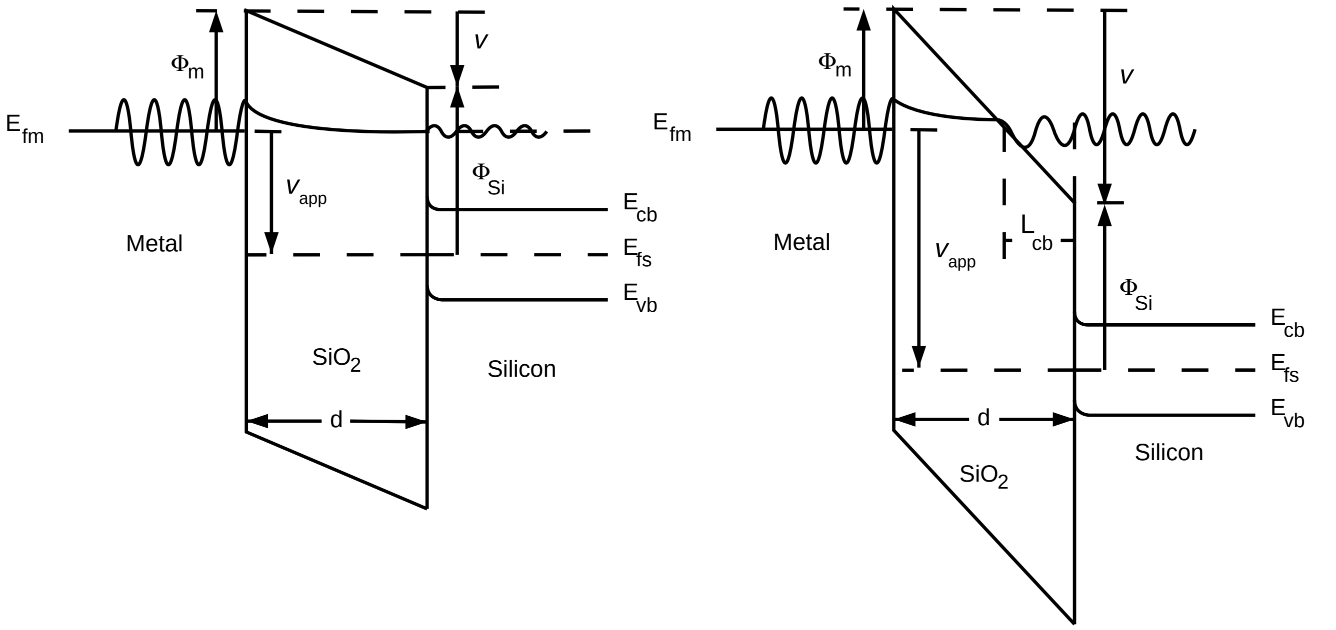

Fig. 2. Band diagrams of the metal–oxide–semiconductor structure consisting of the CT-AFM tip, silicon-oxide layer, and silicon substrate. In the field-emission regime shown on the left, the applied bias is small and the electron must tunnel through the entire oxide. In the Fowler–Nordheim regime, shown on the right, a large enough bias is applied to shorten the tunnel distance

Switching the operation of the CT-AFM system from nanolithography to Fowler–Nordheim characterization was made possible by moving the switch shown in Fig. 1 from the up to the down position. The data from the current amplifier was thus routed to a second input of the AFM system producing current maps at constant applied bias. This current was also fed to a second system to enable a feedback to the applied bias [12] and the production of voltage maps at constant current. Such a setup could also be used to produce an i–v curve by placing the tip at a fixed location and ramping the applied bias. To prevent breakdown, the bias was removed once a setpoint current was reached.

Bias polarity was chosen so as to prevent carrier depletion in the substrate which can cause an increase in the bias required for tunneling. For p-type samples, therefore, the tip was negatively biased with respect to the sample and positively biased for n-type samples. Equation (1) applies to plane-parallel capacitors where the field drops linearly with distance. Since the field in this case drops mostly close to the tip, tunneling from the tip to the sample should be easier than predicted from the plane-parallel case and the opposite holds for tunneling from the sample to the tip.

The feedback system has to be adjusted differently for thin or thick oxides to make imaging possible. To obtain voltage maps of thin oxides, a strong feedback was chosen to keep the current constant. This type of feedback is most desirable as it is capable of providing direct information on changes in the thickness of the oxide under study. For such oxides, one can also operate with a constant voltage and obtain current maps. For thick oxides, where large fields are required to maintain a constant current, a large feedback is difficult to maintain without causing breakdown. Rather, disabling the feedback was considered such that the bias would be held at a constant value obtaining a current map. Some feedback, however, is required to overcome charge trapping in the sample or oxidation of the tip or sample, as these effects tend to reduce the tunneling current below detectable levels. For this reason we used a reduced feedback where the current was continuously averaged and the bias slightly adjusted to keep the current near the setpoint value.

The tips useful in lithography, such as chrome-coated Si_3N_4 tips, were commonly found to be inadequate for Fowler–Nordheim characterization because the extreme stress placed on the tip during mapping destroyed the coating at their apex. To overcome this difficulty, we used a 100 μm × 50 μm Pt/Ir flattened wire as the cantilever. The wire was bent and electrochemically etched in a 2 mol solution of $CaCl_2$ at 30 V AC (volts alternating current) to form a tip. The lengths of the cantilevers used were approximately 3 mm to keep the force constant low and the shanks of the tips were etched as short as 50 μm to minimize tip torsion.

Another concern was the formation of oxides or other materials on either tip or sample during Fowler–Nordheim scanning. To remove the water meniscus and minimize this effect, the bell jar was evacuated to 300 mTorr and purged with UHP N_2 twice, since it has been shown that no lithography on bare silicon was observed in a dry nitrogen environment [3]. In the case of a low-feedback current map, the degree to which the bias needed to be adjusted by the feedback system was a good measure of the validity of each experimental run. On a sample with a 20 nm oxide, for example, production of oxide on the surface of the sample was clearly of little concern. However, after a short time of scanning slowly at 34 V the current image was lost due to oxidation of the tip. Increasing the scanning rate eventually brought the current back, albeit with a reduced resolution, possibly by wearing away the oxide layers. Leaving the bell jar overnight in UHP N_2, with subsequent pumping and purging the next day, removed enough water such that oxidation of the tip was no longer a problem.

Equation (1) shows that the Fowler–Nordheim current is dependent on the applied field, barrier height, effective emission area, and effective electron mass. The emission area is

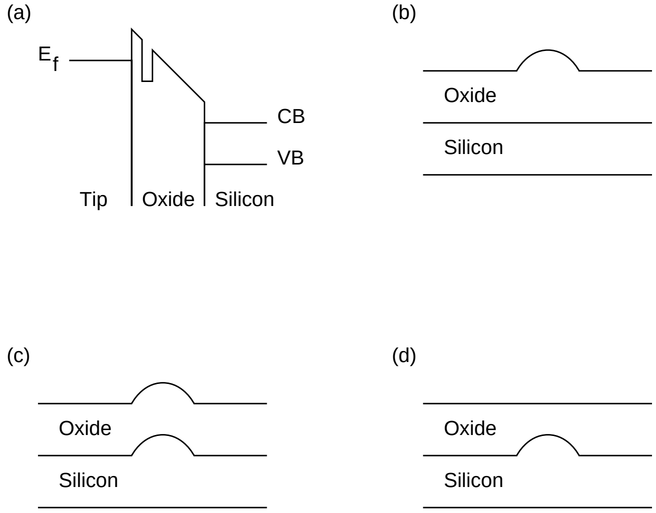

Fig. 3a–d. Local changes in the electron effective mass and energy barrier can modify the band diagram, making it easier or more difficult for an electron to tunnel. In **a** the barrier height has been locally lowered, increasing the tunneling current. In **b**, **c**, **d** other combinations of substrate and surface features that an AFM alone cannot distinguish are illustrated

a function of the tip–sample force, which is held constant by the AFM, and therefore is not considered to cause features in the image. However, local charge trapping by the oxide bulk or the Si–SiO_2 interface can modify the effective mass of the electron and produce features across the mapped surface. Figure 3 illustrates four other possible mechanisms that can give rise to a contrast in Fowler–Nordheim maps. Figure 3a depicts a local lowering of the conduction band, possibly due to an impurity, effectively decreasing the distance the electrons must travel and increasing the current. Note that this local effect will not be observed as a topographic feature. Figure 3b shows a case where the interface is flat yet the oxide has a bulge. This feature can be detected by both Fowler–Nordheim and topography maps. The feature in Fig. 3c, where a defect on the silicon surface is reproduced in the oxide above, can be detected by the AFM but not the Fowler–Nordheim system. Finally, a feature such as that shown in Fig. 3d, where a defect on the surface is buried, will be seen only by the Fowler–Nordheim system and not by the AFM. To distinguish between these four cases one needs therefore to obtain both AFM and Fowler–Nordheim maps.

Figure 4 shows AFM (left) and Fowler–Nordheim (right) maps of three lines of silicon oxide written by applying -12 V to a chrome-coated Si_3N_4 tip at a speed of 60 nm/s in an ambient environment. The Fowler–Nordheim voltage map was produced from the voltage required to keep a constant 10 pA tunneling current. A bias of -32.5 V was required at the location of the lines.

The CT-AFM system was next applied to characterize copper islands buried in a thin silicon oxide. The samples, produced at Sandia National Laboratories Development Laboratory, were used to study the effect of metal contamination during HF cleaning [13]. Sample preparation started with an n-type silicon (100) wafer that was subsequently cleaned in 5:1 Piranha, rinsed in water, dipped in copper-contaminated buffered oxide etch, and again rinsed in water. The samples were then thermally oxidized to various thicknesses before our examination.

AFM images were taken of unoxidized, contaminated surfaces as a measure of size and density of copper islands. Similarly, images of the oxidized surfaces were taken to determine the degree to which these islands were still visible, as shown in the left part of Fig. 5. It was found that a copper concentration of 1×10^{10} atoms/cm^2 was suitable to produce isolated islands.

A sample with a 20 nm thick oxide having several large islands of copper extending above the surface was placed in the bell jar which was pumped and purged three times with UHP N_2. Several i–v curves of areas of the oxide away from the copper islands were taken, using a chrome-coated Si_3N_4 tip. These curves were used both to determine the quality of the tip and the approximate voltage range required for the ex-

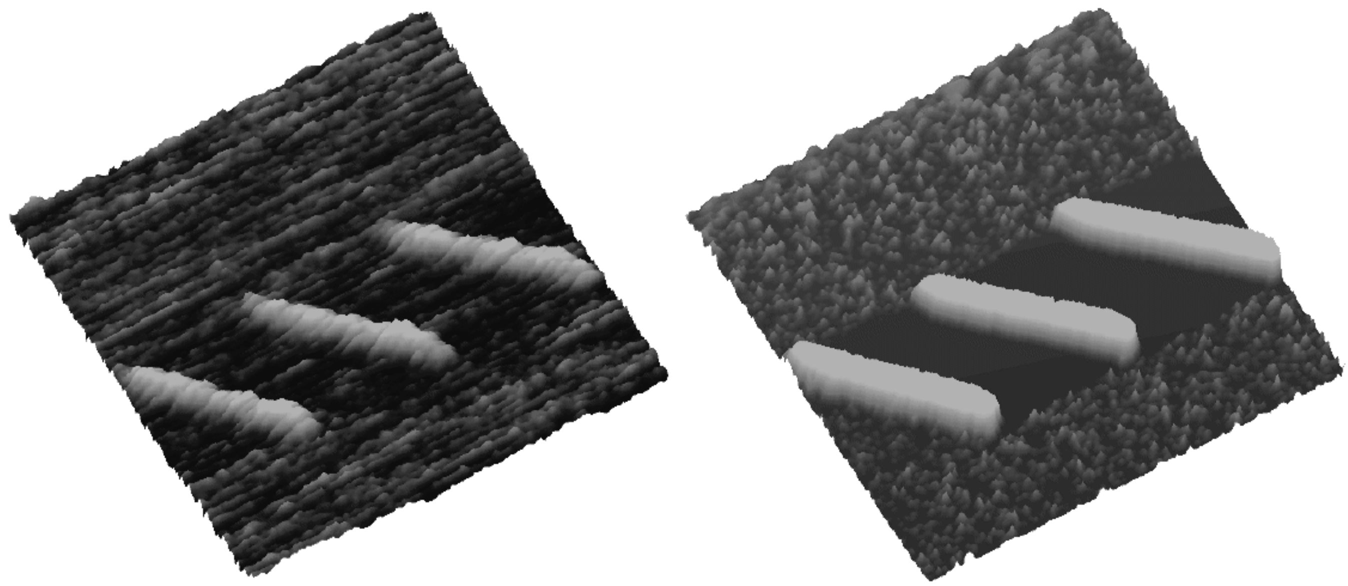

Fig. 4. Left: An AFM image of silicon-oxide lines written using a chrome-coated Si_3N_4 tip. The image size is $3 \times 3\ \mu m^2$ and the line height is approximately 2 nm. Right: a simultaneous constant-current map of the lines produced using a Pt/Ir tip by maintaining 10 pA through the sample

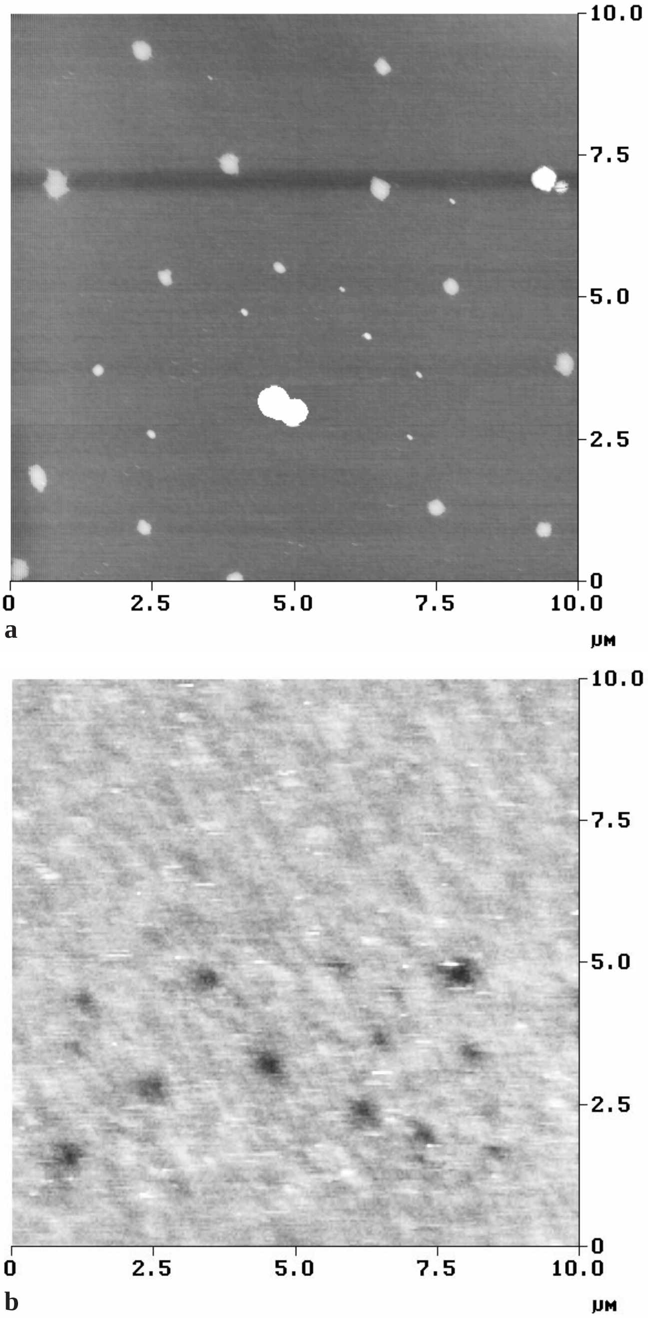

Fig. 5a,b. Copper islands deposited on a silicon wafer and buried by 20 nm of thermal silicon oxide. A conventional AFM map of the copper islands (left) shows that the tallest islands are only partially buried. A Fowler–Nordheim current map (right), produced by applying a constant -34 V to the sample, shows that the islands may have been partially oxidized as demonstrated by the drop in tunneling current through them

periment. A copper island was then located and an i–v curve taken. It was found that the voltage required to reach the setpoint value of 5 pA was higher on the island than on the oxide, suggesting that either the copper had been partially oxidized or that an enhanced silicon oxidation had occurred at the site of the copper.

Finally, the Si_3N_4 tip was replaced with a Pt/Ir tip and the system returned to the dry N_2 environment. Several constant-voltage maps were produced at varying setpoint currents and it was found that the lowest current that produced a good contrast of the desired features was 5 pA. The right part of Fig. 5 depicts the copper islands as dark features, indicating a locally reduced current and further suggesting oxidation of the copper islands. A tip bias of 34 V with respect to the sample was required to maintain an average of 5 pA, implying that little oxidation of the sample or tip occurred during scanning.

3 Conclusion

It was demonstrated that a CT-AFM can be used to fabricate not only oxide but also nitride nanostructures on silicon wafers, and that the fabrication is accompanied by a tunneling current. A Fowler–Nordheim characterization system was also built around a slightly modified CT-AFM, making it possible to locally characterize the fabricated structures in situ. It was found that a combination of AFM and Fowler–Nordheim characterization of nanometer-scale structures complement each other, enabling one to extract more information from the surface maps.

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