Nanolithography by non-contact AFM induced local oxidation: Fabrication of tunneling barriers suitable for single electron devices.

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Abstract

We study local oxidation induced by dynamic atomic force microscopy (AFM), commonly called TappingMode AFM. This minimizes the field induced forces, which cause the tip to blunt, and enables us to use very fine tips. We are able to fabricate Ti/TiO$_x$ line grids with 18 nm period and well defined isolating barriers as small as 15 nm. These junctions show a non-linear current-voltage characteristic and an exponential dependence of the conductance on the oxide width, indicating tunneling as the dominant conduction mechanism. From the conductance - barrier width dependence we derive a barrier height of $\Phi = 178$ meV.

Numerical calculations of the lateral field distribution for different tip geometries allow to design the optimum tip for the most localised electric field. The electron-beam-deposition (EBD) technique makes it possible to actually produce tips of the desired geometry.

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Proximal probe based lithography has developed over the last years into a well established tool for the fabrication of structures and electronic devices with nanometric dimensions. Especially the tip-induced oxidation - or in more general, tip induced local chemical reactions - have been very successful and appear to be one of the most promising approaches: they preserve the high lateral resolution of the scanned tip by omitting a subsequent etching step and thus avoid the problem of transferring the pattern into an underlying electron system, e.g. metallic thin films or heterostructures. Furthermore, it enables one to monitor the process in situ by measuring electronic properties, e.g. the conductance of a thin channel, defined and constricted by AFM induced oxide or the formation of a barrier across a conducting channel. To optimally use this process in nanofabrication requires (1) the understanding of the underlying electrochemical mechanism and the parameters that control it, (2) a tip, which is optimised for laterally focusing the electric field strength under the experimental conditions and (3) a scanning technique which allows one to use these tips and retain their properties.

Here, we show that operating the AFM in a dynamic, non-contact mode is suitable for inducing local oxidation. Hereby the damage to the tip is reduced significantly and allows us to address questions involving the importance of the tip radius and the overall geometry of the tip.

We start with thermally oxidised (250 nm SiO$_2$) n-type (10 Ωcm) Si (100) material, on top of which 30 Å to 50 Å Titanium are thermally evaporated at high evaporation rates ($\approx 10$ Å/s) and low background pressure ($p \leq 10^{-8}$mbar). This metallic film is then patterned using optical lithography and a HF wet etch, finally wire bonded. Local oxidation is performed using a commercial AFM (Digital Instruments) and highly doped n$^+$-Si tips (NanoSensors), which we additionally sharpen by oxidation. Tip radii are well below 100 Å, typically around 50 Å. The relative humidity is kept constant at 40% during experiments shown here. The cantilever oscillates near its resonance frequency (approx. 250 kHz) with high amplitudes (10-100 nm). The applied tip bias for local oxidation induces additional charges on the tip, which bends the cantilever towards the surface. This force adds to the normal loading force and can easily damage either the tip or the surface. Moreover, in dynamic AFM the force gradient $\partial F/\partial z$ due to the electric field changes the force constant $k$ to $k^* = k - \frac{\partial F}{\partial z}$, shifting the resonance frequency to $\omega^*_0 = \sqrt{k^*/m}$. The driving bimorph oscillates unchanged at the fixed frequency $\omega < \omega^*_0 < \omega_0$, and therefore the oscillation amplitude is increased. The change in amplitude for a given tip bias can easily be measured from amplitude versus distance curves, which then can be used to readjust the working setpoint. As the feedback is enabled all the time and the damping of the amplitude does not change if only the setpoint is readjusted, the overall loading force remains unchanged even for applying voltages up to 30 V. In Fig. 1(a) and 1(b) we show two grids of oxide lines written at a rate of 300 nm/sec at a tip bias of -6.5 V. The lines are very regular in width (18-20 nm) as well as in height, even for relatively large scan fields of 3x3 mm and above. Reducing the period from 120nm to 23nm, parallel conducting wires of 6nm linewidth are formed, which are still conductive along the channels ($\approx 100$ kΩ) but isolating in perpendicular direction ($\gg 80$MΩ, at room temperature). This demonstrates a complete oxidation process for at least the average of the oxide lines. The observed oxide height is 3nm, which agrees very well with what is expected from the change in density and molecular
weight $d_{TiO_2}/d_{Ti} = \rho_{Ti}/\rho_{TiO_2} \cdot M_{TiO_2}/M_{Ti} \approx 3nm/5nm$. It should be noted that at a tapping frequency of $f_T = 250$ kHz and the observed damping of the amplitude, the contact time $t = 1/(2f_T)$ between the tip and the sample surface per cycle is below $10^{-3}$ ms. As the oscillation amplitude is very large (10-100nm), it is unlikely that a stable water meniscus forms between tip and sample. Evidence for this is provided by force versus distance curves in contact AFM using the same cantilevers (data not shown). If the experiment is to be explained in a classical electrochemical set-up, wherein the tip acts as cathode, the water film as electrolyte and the sample as anode, the total exposure time is much shorter than in contact AFM. However, the total amount of oxidized material is very much the same as seen by contact AFM, e.g. by Avouris et al. [8] for Si, or by H. Sugimura et al. [9] for Ti. We therefore conclude to a corrosion at the Ti/TiO$_2$ interface, enhanced by the tip-sample electric field in the presence of humidity.

To define a tunneling barrier we first constrict a predefined 1 mm Ti wire by oxidising two large oxide pads, enclosing a 30 nm wide channel (Fig. 2). The barrier, perpendicular to the channel, is then oxidized at 2 Hz scanning frequency and a tip bias of -4.5 V. In order to avoid the formation of too thick barriers with too small tunneling probability by overexposure, we monitor the conductance along the channel. As soon as the conductance drops below the capacitive signal, oxidation is stopped. The quality of the AFM induced oxide is characterized on wide barriers ($\approx 100$nm). Resistivities of $\rho = 2 \cdot 10^{11}$ $\Omega$cm and max field strength $V_D = 2 \cdot 10^6$ V/cm are measured. These values are similar as for macroscopic anodic oxides [10] [11].

At room temperature the devices show an asymmetric, non-linear IV-characteristic. This may be understood in the picture of an asymmetrical, shallow barrier, which is no longer isotropic for forward and reverse bias. To determine the conduction mechanism for these devices, we investigate the dependence of the (tunneling) current on the geometrical width of the barrier as obtained from AFM images. For four different devices, with barriers varying from 15 nm to 30 nm, the current decays exponentially with barrier width, indicating tunneling as the dominant conduction mechanism (Fig.4). Hereof, we obtain a barrier height of $\Phi=178$ meV.

To determine the parameters that affect the lateral resolution of the oxidation and therefore to estimate the ultimate limit for this technique, we model the lateral field distribution for different tip geometries, namely tip radii and cone angles. In a first step we place the tip 10 nm in front of a conducting surface. The calculated electric field for a 10 nm sphere (radius in each case), 10 nm spherical tip with 50$^\circ$ pyramidal cone and 5nm spherical tip with 40$^\circ$ cone are shown in Fig. 5. As expected, the pyramids widen the lateral field compared to the free standing sphere, whereas smaller spheres increase the local field underneath the tip. At this stage we did not consider the growing oxide itself as well as the focusing effect of the water layer or meniscus because of its large $\epsilon$. However, for an optimised focusing of the lateral fields, we would like to have a needle like tip, which is still sufficient conductive. So called electron beam deposited material (EBD) is known to be suitable to define scanning tips with tip radii $\leq$5nm and very small cone angles [12]. If deposited at high electron energies and low beam current densities, they appear to be conductive. Fig. 6 shows an SEM image of an EBD tip deposited on top of an NiCr coated Si tip. This tip shows an overall resistance $R \leq 1M\Omega$, which is sufficient for applications in electrochemical AFM and local oxidation and gives - in contrast to e.g. carbon nanotubes - the unique possibility to
design the tip to exact the requested geometry.

In summary, non-contact AFM has been used for locally oxidising Titanium thin films. In this mode, the tip-sample forces remain unchanged when applying a tip-sample bias. This allows us to use oxide sharpened Si tips, with which we are able to fabricate line grids with 6nm structure sizes and 18nm pitch. In situ electrical measurements gives fine control over the lithographic process. In this way we fabricated tunneling barriers as small as 15 nm. The current-voltage caracteristic and the current on barrier-width dependence clearly indicates that tunneling is the dominant transport mechanism in these devices. Numerical calculations of the lateral distribution of the tip to sample electric field indicate an further improvement in the lithographic resolution, if only needle like tips with small radii and small cone angles are used. We show, that 5nm radius, 5° cone angle EBD tips are sufficient conductive to be used for local oxidation.

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FIGURES

FIG. 1. Two Ti/TiO\textsubscript{x} grids written by TappingMode AFM induced local oxidation at -6.5V tip bias and a scan speed of 300nm/s. At room temperature, the resistance parallel to the lines is 100 k\ohm, and perpendicular to them \( \gg 80 \text{M}\ohm \).

FIG. 2. In situ control of the barrier formation. The source-drain conductance through the device is monitored while oxidising. The tip is biased at -4V and repeatedly scanned at 2Hz across the 30nm wide Ti channel to form a 17nm wide barrier.

FIG. 3. Room temperature current-voltage characteristic of a 20nm wide barrier.

FIG. 4. Dependence of the current on the geometrical barrier width. 4 different devices are measured at 100mV bias and T=300 K. The current depends exponentially on the barrier width, indicating tunneling as the dominant conduction mechanism.

FIG. 5. Calculated electric field distribution for 3 tips with different \((r,\Phi)\) geometry, 10 nm in front of a conductive plane in vacuum: 10nm sphere, pyramidal tip with 10nm radius/50° cone angle and 5nm radius/40° cone angle, respectively.

FIG. 6. SEM image of a EBD tip, deposited onto a commercial Si tip, coated with NiCr. Taken from this image, the radius is \( \approx 5 \) nm and the cone angle 5°. The tip shows a resistance of \( R \leq 1 \text{M}\ohm \), which is sufficient for local oxidation.
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