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Submicron fabrication by local anodic oxidation of germanium thin films

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Abstract
Here we describe a lithography scheme based on the local anodic oxidation of germanium film by a scanning atomic force microscope in a humidity-controlled atmosphere. The oxidation kinetics of the Ge film were investigated by a tapping mode, in which a pulsed bias voltage was synchronized and applied with the resonance frequency of the cantilever, and by a contact mode, in which a continuous voltage was applied. In the tapping mode we clearly identified two regimes of oxidation as a function of the applied voltage: the trench width increased linearly during the vertical growth and increased exponentially during the lateral growth. Both regimes of growth were interpreted taking into consideration the Cabrera–Mott mechanism of oxidation applied to the oxide/Ge interface. We also show the feasibility of the bottom-up fabrication process presented in this work by showing a Cu nanowire fabricated on top of a silicon substrate.

1. Introduction
Since the seminal paper by Dagata et al [1] in 1990, local anodic oxidation (LAO) of surfaces by using a scanning atomic force microscope (SPM) has become an increasingly powerful technique for the development of future nanodevices. They used a scanning tunneling microscope (STM) metal tip for the nanometer-scale patterning of an H-passivated silicon surface by applying a voltage between the tip and the silicon surface. Soon after Dagata’s work, Day and Allee [2] demonstrated the feasibility of the LAO technique on a silicon surface by using an atomic force microscope (AFM), where the AFM tip was coated with a metal layer (Cr or Au). Nowadays AFM-induced LAO is an extensively used technique to fabricate a variety of metal or semiconductor nanodevices and nanostructures such as mesoscopic devices of titanium thin films [3], lateral superlattices [4], and silicon gratings [5] in the nanometer range, and to pattern two-dimensional electron gas heterostructure [6]. Over the last few years a number of articles and reviews have been published on the feasibility of nanofabrication by using SPM-based techniques [7–12]. In particular AFM-induced LAO has become a practical technique for pattern transfer on either semiconductors or metal surfaces [9]. It consists of an electrochemical reaction between the surface and the negatively biased AFM tip where the water layer due to the ambient humidity serves as the electrolyte to locally oxidize a small region of metal or semiconductor surface with feature sizes down to tenths of nanometer. By using this technique an oxide pattern is transferred to the surface and afterward it can be selectively etched, producing a mask useful for lithography. This method has many advantages over other techniques such as being simple, it can be accomplished at room conditions, it enables nanofabrication in the sub-100 nm feature sizes, and it does not need sophisticated and expensive apparatus. In order to become attractive for nanofabrication the oxide created by the LAO technique has to be easily etched. Here we demonstrate that Ge oxide, which can be easily removed by simple water dissolution, is a suitable material to fabricate metal nanostructures through a Ge/polymer bilayer and a subsequent lift-off process.
2. Experiment

In this work we present an alternative scheme for the fabrication of planar structures with feature sizes in the submicron scale. Here we use Ge as a high resolution ‘resist’ film that can be patterned by using LAO with AFM in a humidity-controlled atmosphere. In a subsequent step, the germanium oxide is easily dissolved by simple water leaving the desired pattern on the film surface, which in turn acts as a mask for plasma etching of the underlying layer. The fact that germanium oxide is easily dissolved and washed away with water with no aggression to the Ge film is a key aspect of the overall success of this technique.

Using this method we were able to fabricate metallic magnetic nanowires of nickel, iron, cobalt, and their alloys. The overall process is described as follows. The samples were prepared by cleaning a silicon substrate in an ultrasonic acetone bath and then soaking it in isopropanol, and finally blowing it dry with nitrogen gas. A layer of high molecular weight polymethylmethacrylate (PMMA) solution of 2 wt% in anisole was spin coated on the cleaned Si substrate at a speed of 2000 rpm for 40 s, and hot-plate baked at 90°C for 5 min. Using these conditions we were able to obtain a 80 nm PMMA layer. At the end of the process a thin film of germainium with a thickness of 7 nm and a root mean square (rms) roughness of 1.106 nm was RF sputtered on top of the PMMA layer. The final rms roughness is <1.1 nm, which is adequate for the AFM oxidation of the sputter-deposited Ge film cladding the PMMA layer.

Figure 1(a) illustrates the final deposited structure showing the positive electrode attached on top of the Ge film. Figure 1(b) shows a 2.5 μm × 2.5 μm topographical image of a Ge film of 7.0 nm thickness deposited on an 80 nm thick PMMA layer. The final rms roughness is <1.1 nm, which is adequate for the AFM oxidation of the sputter-deposited Ge film cladding the PMMA layer.

The LAO experiments were carried out in a commercial AFM (5500 AFM/SPM, Agilent) at room temperature equipped with environmental control and the relative humidity was kept at 75% by injecting H2O-saturated nitrogen. Two types of AFM oxidation processes were used. In contact mode we used low force constant (0.2 N m⁻¹) AFM probes (model contAl-G, Budgetsensors), and in tapping mode we used high force constant (42 N m⁻¹) AFM probes (model Arrow-NCR, Nanoworld). During the oxidation process the AFM tip was grounded and the Ge surface kept at positive voltage. As the final dimensions and state of the oxide structures depend on processing conditions we investigated the oxidation dynamics by continuous and pulsed voltage at contact and tapping modes, respectively. In the contact mode the force between tip and surface remained constant in 4.0 nN and in the tapping mode the oscillation amplitude was set to 60% of the value used during topography acquisition. The pulsed voltage synchronized with the cantilever oscillation was generated by a pulse modulator circuit in which the reference signal was taken from the AFM PZT driver. We have found reasonable oxidation results when the pulse voltage is applied at the minimum of the reference signal. Figure 1(c) shows a positive pulse of 1 μs width, 308 kHz, and 30 V of amplitude, synchronized with the negative peak of the reference sinusoidal signal.

Figures 2(a)–(d) show schematically the processes carried out after the pattern transfer to the Ge surface by the LAO technique as described above. The germanium oxide pattern (figure 2(a)) was removed by soaking the sample in deionized water for 10 min and then blowing it in nitrogen, leaving the PMMA surface exposed, as shown in figure 2(b). The underlying PMMA surface can now be easily removed by reactive ion etching (RIE) with 50 sccm O2 gas flow, where the substrate was kept at room temperature. Thus the patterned Ge film can be used as a mask to transfer the appropriate pattern to the underlying substrate surface, see figure 2(c). The plasma etching was carried out by a Batchtop VII system from Plasma-Therm, where the conditions of a typical operation cycle were: RF power of 100 W and pressure of 30 mTorr for 1 min. This operation cycle was repeated four times with intervals of 2 min between each step. The reason we used this operation cycle instead of a continuous operation for 4 min
is because in the continuous step we observed spots on the Ge surface, indicating surface damage. We then deposited the material of interest by dc sputtering. Afterward, the lift-off process was done in an acetone bath for 5 min, as shown in figure 2(d). A few words on the resolution limit reached by this technique should be given here. The minimum size of the structures fabricated by using this technique depends primarily on the AFM tip sharpness as well as on the Ge film thickness and roughness. Thinner and smoother layers of Ge can be uniformly oxidized along the vertical direction with negligible lateral growth producing oxide lines with sizes below 100 nm [8].

3. Results and discussion

In order to investigate the versatility of the technique described above we wrote oxide lines as a function of the tip scan rate for the two different AFM modes of operation: (i) contact (continuous voltage); (ii) tapping (pulsed voltage). The height and width of the oxide lines were measured and then the oxide patterns were thoroughly removed by deionized water. Afterward the trench widths and depths were carefully measured to compare with the widths and heights of the oxide lines, respectively. Figures 3(a) and (c) show the measurements of line height (open squares) and trench depth (open circles) for the pulsed voltage oxidation mode at two different AFM tip scan rates: $v_{\text{tip}} = 0.5 \mu m s^{-1}$ (top panel) and $v_{\text{tip}} = 2.0 \mu m s^{-1}$ (bottom panel). Note that the trench depth dependence on the pulsed amplitudes becomes constant for $V \geq 18$ V (at $0.5 \mu m s^{-1}$) and $V \geq 20$ V, (at $2.0 \mu m s^{-1}$). It indicates that the 7 nm thick germanium film under the AFM tip tracks was completely oxidized for pulsed voltages above 18 V with $v_{\text{tip}} = 0.5 \mu m s^{-1}$, as well as for voltages above 20 V with $v_{\text{tip}} = 2.0 \mu m s^{-1}$. Figures 4(a) and (c) show measurements of line height (open squares) and trench depth (open circles) for the continuous voltage mode, for two different write speeds: $0.5 \mu m s^{-1}$ (top panel) and $2 \mu m s^{-1}$ (bottom panel). For the range of voltages used in the continuous voltage processing ($8 V < V < 30 V$), the trench depths indicate that the entire Ge thickness under the AFM tip tracks was completely oxidized.

Much more interesting phenomena can be investigated for the condition in which the Ge film is not completely oxidized, as depicted by the voltage dependence of line (stars) and trench (triangles) widths in figures 3(b) and (d), respectively. These figures show clearly that in the pulsed voltage mode there are two different regimes of oxidation for the samples under investigation. In the first regime the oxidation process did not reach the bottom of the Ge film and the oxide grew along both the vertical and lateral directions. The second regime occurs after the saturation of the vertical oxide growth and all the oxidation occurs in the lateral direction along the plane of the Ge film. Evidence for the vertical oxide saturation is provided by the voltage dependence of the trench depth, as shown in figures 3(a) and (c). The vertical oxidation process stops as the trench depth becomes identical to the original Ge film thickness ($\sim 7.7$ nm). As expected, the saturation voltage ($V_s$) depends on the tip speed $v_{\text{tip}}$. $V_s = 18$ V for $v_{\text{tip}} = 0.5 \mu m s^{-1}$,
applied voltage.

oxidized. The trench width increases linearly as a function of the thickness indicating that the layer under the AFM tip is completely applied voltages the depth is identical to the original Ge film

Figure 4.

- Figure 4(b) and (d) show the voltage dependence of the line and trench widths for continuous voltage at the two different tip speeds.
- Figures 3(b) and (d) show the flow of anions across the oxide film to the Ge surface (positive potential) is sufficiently strong to ionize water at the meniscus that forms at the tip surface.

One of the advantages of using pulsed voltage processing is that the space charge that builds up at the oxide/Ge interface tends to vanish during the time in which the voltage is turned off. It has been proposed that this space charge buildup restricts the oxide growth and the application of pulsed voltages should minimize this effect [13–17].

Observe that the duty cycle of the pulse train used in this work is only 30%, thus the electric field is turned off for 70% of the tip oscillation cycle. In order to explain the pulsed voltage dependence of trench width and the existence of two growth regimes as a function of the pulsed voltage amplitude we have considered the field-assisted Cabrera–Mott mechanism [18], which should be valid in the absence of space charge.

A few words on the basic oxidation mechanism are in order here. The voltage applied between tip (grounded) and Ge surface (positive potential) is sufficiently strong to ionize water at the meniscus that forms at the tip surface. Here we will assume that: (i) the oxide growth is due to the transport of OH\(^-\) ions across the oxide film to the oxide/Ge interface; (ii) the anion transportation across the oxide is assisted by the intense electric field created by the external applied voltage; (iii) the anions diffuse through the oxide by hopping between adjacent sites. Letting the distance between adjacent sites be \(a\), and the activation energy for diffusion be \(U\), the probability that an anion moves from one site to the next is given by \(\nu \exp(-U/k_B T)\), where \(\nu\) is the attempt frequency, and \(k_B\) and \(T\) are the Boltzmann constant and absolute temperature, respectively.

The applied electric field \(E\) lowers the energy barrier by \(qaE/2\) in the forward direction, so the probability for hopping becomes \(\nu \exp(-U/k_B T) \exp(qaE/2k_B T)\), where \(q\) is the anion charge. Considering that the flow of ions across the oxide/Ge interface is the oxidation mechanism, we can define the volume flow rate of anions \((\Delta \phi)\) as the volume of anions \((\Delta V)\) that passes a given cross sectional area \((\Delta A)\) per unit of time, as \(\Delta \phi = \Delta V/\Delta t = \bar{u} \cdot \Delta A\), where \(\bar{u}\) is the drift velocity of the ions across the area \(\Delta A\), given by \(\bar{u} = u_0 \exp(-U/k_B T) \exp(qaE/2k_B T)\). Considering flow perpendicular to the area, the volume of oxide \((\Delta V_{ox})\) formed by the anions crossing the oxide/Ge interface is proportional to the volume \(\Delta V\), i.e., \(\Delta V_{ox} = \alpha \Delta V = \alpha \Delta t \cdot \Delta A \cdot u\). Therefore, the volume of oxide growth can be given by

\[
\Delta V_{ox} = \Delta V_{ox}^* \exp(qaE/2k_B T),
\]

where \(\alpha\) is a proportionality constant and \(\Delta V_{ox}^* = \Delta t \cdot \Delta A \cdot u_0 \exp(-U/k_B T)\). As the oxide lines can be generated with different lengths, we are interested in the oxide volume that can grow per unit length along each line. This is given by equation (1) divided by line length (L):

\[
\frac{\Delta V_{ox}}{L} = \frac{\Delta V_{ox}^*}{L} \exp(qaE/2k_B T).
\]
behavior has been observed for oxidation of Ge films with different thicknesses. Solid diamonds in figure 6(a) show the voltage dependence of the trench depth values summed to the line height values of the data shown in the bottom panel of figure 3. This sum characterizes the oxide vertical growth. In the first regime of vertical oxidation, for \( V \leq 20 \text{ V} \), the voltage dependence of the oxide growth shows a nonlinear behavior. In the second regime, for \( V > 20 \text{ V} \), the total oxide thickness (line height + trench depth) saturates at a value of around 15 nm, see the dashed line drawn to guide the eyes. Solid circles in figure 6(a) show the voltage dependence of the trench width, which characterizes the lateral oxidation process. Notice that for \( V \leq 20 \text{ V} \) the trench width exhibits a nonlinear growth regime that is different from the one shown for \( V > 20 \text{ V} \).

We also explored the dependence of the two-dimensional (2D) oxide growth as a function of the applied voltage. Figure 6(b) shows the product of the vertical oxide growth (given by the solid diamonds in figure 6(a)) times the lateral oxide growth (given by the solid circles in figure 6(a)). The results for the oxide volume per unit length of line are shown in figure 6(b) where the open squares correspond to the first regime of oxidation \( (V \leq 20 \text{ V}) \) and solid squares to the second regime of oxidation \( (V > 20 \text{ V}) \).

Figure 7. Voltage dependence of oxide volume per unit length of line that was calculated from the DC voltage oxidation process of the bottom panel of figure 3, with tip speed 2.0 \( \mu \text{m s}^{-1} \).
Figure 8. Three-dimensional images of the oxide line and trench before and after oxide removal are shown in (a) and (b), respectively. (c) and (d) show AFM images of a Cu wire fabricated by the LAO lithographic process described in this work. Clear shapes, sharp edges and smooth surfaces at the nanometer scale can be seen in the 3D (a) and 2D (b) images.

lines are best fits to the experimental data obtained by the exponential equation for the volume of oxide: $\Delta V_{\text{ox}}(V)/L = A(e^{\alpha V} - 1)$, where $A$ and $\alpha$ are fitting constants. Considering $E = V/x$ where $V$ is the potential difference between Ge and the adsorbed anion layer and $x$ is an effective distance along the line field, and using equation (2), the exponential parameter can be defined as $\alpha = qa/(2k_BT)$. From the best fittings to the data we obtained $A = 2$ and $\alpha = 0.397$ for the first regime (solid line) of oxide growth and $A = 126$ and $\alpha = 0.168$ for the second regime (dashed line). In the 2D oxide growth the mechanism of hopping can well explain the exponential dependence on the applied voltage. As $q/(2k_BT) = 19.32 \text{ V}^{-1}$, a relation between $x/a$ can be extracted from the fittings. In the first regime of oxidation, where the oxide mechanism occurs laterally and vertically, we obtained $x/a = 49$ and 115 in the second regime, where only the lateral growth exists.

Figure 7 shows the voltage dependence of oxide volume per unit length of line obtained for the DC voltage oxidation process. The data correspond to the feature size shown in the bottom panel of figure 4. Observe that the value of oxide volume per unit length of line produced by the DC voltage technique for 30 V (42 000 nm$^2$) is around twice that produced by the pulsed technique (20 000 nm$^2$) at the same voltage. Also notice that the behavior shown in figure 7 is clearly linear, contrary to the exponential voltage dependence of the pulsed voltage mode investigated in figure 6(b).

In order to test the feasibility of the proposed technique, we have fabricated different planar magnetic metallic devices [19]. Figures 8(a) and (b) show AFM images of an oxide line and the trench obtained after the oxide removal. Figures 8(c) and (d) show 3D and 2D images, respectively of a copper nanowire fabricated by using the mask shown in figure 8(b), with a width of 560 nm, thickness of 16 nm, and a length of 2.0 $\mu$m. In order to show the well-defined shapes with sharp edges and smooth surfaces in the nanometer scale the nanowire images were cropped.

In summary, we have shown the feasibility of an AFM lithography scheme based on the local anodic oxidation of Ge thin films. As the Ge oxide can be easily removed by simple water with no other damage to the surface, it is possible to use the patterned Ge film as a mask to transfer the suitable mold to the underlying substrate surface. We also investigated the oxidation kinetics by comparing the tapping mode with the contact mode in which a continuous voltage is applied between tip and substrate. In order to avoid the charge space effect we applied a pulsed voltage (duty cycle of 30%) synchronized with the oscillation of the tip at tapping mode. Two regimes of oxidation as a function of the applied voltage were clearly identified in the tapping mode. During the vertical oxide growth the trench width exhibited a linear dependence with the applied voltage until the Ge film became completely oxidized at the region underneath the AFM tip. For voltages above this saturation value, the oxidation growth occurred along the lateral direction which is characterized by an exponential dependence of the trench width on the applied voltage. The exponential growth was interpreted by taking into consideration the Cabrera–Mott mechanism of oxidation applied to the oxide/Ge interface.
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