Nanoscale patterning of Si(100) surfaces by scratching through the native oxide layer using atomic force microscope

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We demonstrate selective electrodeposition of Cu into nanocratches produced in native oxide covered p-type and n-type Si(100). Nanosize grooves were produced with a diamond-coated atomic force microscope tip at heavy forces. Onto these grooved surfaces, Cu was electrodeposited from a 0.01 M CuSO$_4$+0.05 M H$_2$SO$_4$ electrolyte under various conditions. The results clearly show that these scratches represent activated sites for metal electrodeposition—the surrounding intact oxide layer acts as a highly efficient mask. After optimization of electrochemical parameters, we were able to achieve the deposition of uniform and well-defined structures with a lateral resolution in the 100 nm range. In general, the process opens alternate perspectives for selective electrodeposition and direct patterning of Si surfaces. © 2001 American Institute of Physics. [DOI: 10.1063/1.1404195]

In recent years, copper electrodeposition has become of great interest to microelectronics and microsensor industries. Copper layers are used as electrical interconnects with a thickness ranging from several micrometers down to a few nanometers. More recently, copper deposition on insulating interlayers has been introduced as a replacement of aluminum in ultralarge-scale integration metallization for improved interconnects (see e.g., Refs. 2–4). But also, direct metal deposition onto silicon is of interest to device technology, for example, to build Schottky diodes on semiconductor surfaces.

Patterned metal deposition on semiconductor surfaces is typically carried out by different indirect ways such as photolithography combined with metal evaporation, electrodeposition, or molecular-beam epitaxy. In contrast to indirect patterning techniques which demand masking, direct patterning approaches have been far less explored. Except for ion beam (see e.g., Refs. 8 and 9) or electron beam (see e.g., Refs. 10–12) techniques, writing nanopatterning approaches are also based on scanning probe microscopies such as atomic force microscopy (AFM) or scanning tunneling microscopy. AFM based investigations have also been used to probe the mechanical properties of surfaces, or to nano-machine surfaces in the micro and nanoscale, e.g., in scratching and wear experiments. This type of study showed that it is possible to produce nanosize scratches on silicon surfaces using AFM equipment with a single crystalline diamond tip. The aim of the present study is to exploit nanocratches produced in and through the native oxide layer on silicon for selective electrochemical metal patterning.

Experiments were carried out on silicon (100) wafers (p type: 1 to 10 Ω cm; n-type: 2 to 6 Ω cm). The wafers were cleaved to samples of 0.7 cm $\times$ 0.7 cm and the pieces were degreased by subsequent sonicking in acetone, isopropanol, methanol, and rinsed with distilled water. These samples carried a native oxide layer of 1.5–2.0 nm thickness [obtained from Auger electron spectroscopy (AES) profiles]. AFM scratching and imaging performed with an Auto Probe CP from Park Scientific Instruments. AFM imaging was carried out in contact mode at a constant force of 100 nN. The images were treated using the software from the manufacturer with a 2nd order flattening routine. The surface of the Si samples was scratched using an AFM with a diamond-coated tip (Park Scientific Instruments) at a load $> 13$ μN. In order to achieve scratching, the feedback loop of the AFM was turned off and the samples were pressed against the tip by stepping the sample stage upward by an increment of 0.5–1.5 μm (the value of this displacement corresponds to different scratching forces). Grooves were made by scanning the samples in the x or y direction at 20 μm/s for 10 cycles. Scanning electron microscope (SEM) investigations of the tip showed a certain degree of degradation after extended use (> 200 scratches). Therefore, in the present investigation, tips were replaced after 50 scratches. After scratching the samples, they were again cleaned in a sonicating bath using the procedure just described and dipped in HF 1% for 5 s to H-terminate the surface within the groove. Back contact to the Si electrodes was established by smearing InGa eutectic on the back side of the samples. The samples were then pressed against an O-ring of the electrochemical cell leaving 0.113 cm$^2$ exposed to the electrolyte, which consisted, for copper deposition, of 0.01 M CuSO$_4$+0.05 M H$_2$SO$_4$. For electrodeposition, a conventional potentiostat (Jaissle 1002 N) and three electrode setup was used.

AES with a PHI 670 was used for chemical surface analysis. During the experiments, the probe beam was scanned on the sample in the perpendicular direction to the scratches and the Si signal at 922 eV, the Cu signal at 1621 eV, and the O signal at 510 eV was registered. SEM images were acquired with a Phillips XL-30 field emission gun.

Figure 1(a) shows an AFM image of a silicon surface carrying four 40 μm long AFM scratches that are 5 μm spaced. The scratches were produced with different loads (from the left- to right-hand side using: 23 μN, 20 μN, 17...
mN, 14 mN, respectively). It is apparent from Fig. 1 that the scratches are very well defined. No debris can be seen in the image because the abraded particles were swept out of the observation window during the observation scanning of the surface. This was evident from optical microscopy and SEM investigations. Such surface cleaning is possible because the created Si particles do not adhere well to the silicon surface. This is in line with literature where it has been suggested that the wear debris is lost and the material is removed layer by layer.18 In the present study, it was observed that a sonicating treatment is also able to eliminate the debris. This latter method of cleaning the surface was found to be more effective and faster than AFM scanning of the surface.

The topography of the scratches is apparent from the AFM height profile in Fig. 1(b). As expected, the scratch size increases linearly with increased load. The grooves show a uniform V-shape and the dimensions range from 8 nm for 14 mN to 25 nm for 23 mN in depth, and between 90 nm for 14 mN and 240 nm for 23 mN in width. The protrusions along the sides of the scratches correspond to surface deformation induced by the mechanical treatment and indicate the presence of stress. It should be noted that the depth to width ratio is comparably small (approximately 0.1).

Electrochemical deposition was carried out by cathodic potential steps in a CuSO₄ (0.01 M) + H₂SO₄ (0.05 M) electrolyte. Figure 2 shows three scratched samples produced as in Fig. 1 after Cu deposition at a potential −400 mV (vs Ag/AgCl) during 1 (a), 15 (b), and 30 s (c). The inset in (a) shows a higher magnification of the thinnest line.

The four grooves were produced identically with a force of 15 mN leading to a groove width of approximately 100 nm. From Fig. 2, it is clear that highly selective metal deposition is obtained. In all cases, no copper crystallites are present outside the scratched surface and the deposited Cu lines are very well defined and confined within the grooves. It is apparent that the longer the deposition time, the wider the deposit lines. Figure 2(a) shows the result for the shortest deposition at a higher magnification providing some information on the initial step of the copper growth. The image suggests that deposition is initiated on the scratch edges. In general, for short deposition times, two copper lines are apparent along the scratch edges. For longer deposition times, coalescence of the two lines into a single Cu line occurs. The crystallite morphology suggests that initiation and growth of the three-dimensional (3D) metal (Me) phase follows the Volmer–Weber or island growth mechanism.19 This is in line with the observation of generally weak Me_ads–semiconductor interactions.20 The finding of Fig. 2 may indicate that at the Si/SiO₂ interface copper nucleation is facilitated which may be attributed to a high defect concentration at the interface zone. For extended deposition times, copper overgrowth of the insulating native oxide layer...
occurs. The best defined lines were obtained for deposition a
time of 15 s [Fig. 2(b)]. In this case, copper overgrowth was
minimized and homogeneous and continuous Cu lines were
obtained.

The Cu deposits were characterized by SEM, AFM, and
AES. From AFM and SEM observations, the dimensions of
typical lines were extracted. As expected, both width and
thickness increase with the polarization duration. After an
initiation period, the width increases almost linearly with the
deposition time from 370 nm for 1 s to 960 nm for 30 s.
Thus, it is evident that even for the shortest deposition time,
the width of the Cu deposit results significantly larger than
the nominal scratch width of approximately 100 nm. This
must be attributed to the 3D growth mode and the initiation
process along the borders of the grooves. After a rapid in-
crease for polarization times shorter than 1 s the height of the
deposits also increases in a linear manner from 160 nm for
1 s to 310 nm for 30 s.

In order to characterize the copper distribution over the
surface, the intensity of the Auger Cu and Si peaks were
acquired as a function of the distance perpendicular to the
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In summary, the results clearly show that a native oxide
layer present on Si can efficiently be used for masking metal
deposition on both p- and n-type Si. Scratches produced
through this oxide layer using an AFM tip can be used to
open “activated” patterns on the Si surface. Onto these pat-
terns, metal electrodeposition can be performed selectively,
and hence can be used for semiconductor patterning and
functionalization in the submicrometer lateral resolution
range.

For copper electrodeposition, initiation sites of deposition
are the scratch edges. The morphology of the initial
deposits strongly suggests a 3D growth mode that also
would be expected due to the comparably weak
Meads–semiconductor interaction.

The process presented opens alternate perspectives for
selective electrodeposition and direct patterning using the ac-
tivating effect of mechanical oxide removal by an AFM tip
together with the masking effect of the native oxide layer.
This technique should essentially be applicable to any mate-
rial that can be electrochemically deposited and thus bears
the potential to create nanopatterns of a large palette of ma-
terials.

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