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Generation of ultrasmall nanostructures in oxide layers assisted by self-organization

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We explored the structural limits of unconventional electron-beam lithography by directly writing with an electron beam into ultrathin SiO_2 films. The obtained structures were analyzed by tunneling microscopy. The Auger excitation process (Knotek–Feibelman mechanism) necessary for electron-stimulated oxygen desorption allows generation of ultrasmall structures. The subsequent processing step combines thermal desorption of the remaining monoxide and simultaneous etching promoted by thermally activated silicon atoms, which turns out to be a strongly anisotropic process close to step edges. Applying this combination of processes to a regularly stepped Si(557) sample, linewidths close to the resolution of the electron microscope of 5 nm were obtained. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2896413]

I. INTRODUCTION

The controlled generation of ultrasmall structures below 10 nm is a prerequisite for further miniaturization of electronic devices and possible widespread use of quantum effects even at room temperature. One-dimensional structures well below this limit have already been produced by self-organization.[1–3] This bottom-up approach comprises carbon nanotubes,[4] for example, but also prestructured surfaces or vicinal surfaces of single crystals that allow continuous variation of step densities down to average separations of only 1 nm and formation of metallic chains that are only a few atoms wide.[5] It strongly relies on perfect epitaxial growth, on small lattice mismatch, and special relations of surface energies. Therefore, it is limited to only a few material combinations.

Generation of local chemical reactions by activation with an electron beam is the usual method to write structures of arbitrary shape, mostly into organic polymer material. The minimal width of such structures is limited by the size of the fractured polymer molecules, but also by the ability of the "cone" of secondary electrons to induce the same reaction as the primary electrons. Therefore the typical lower limit of structure sizes is about 20–40 nm, although the diameter of the primary electron beams is much smaller.

Writing with an electron beam directly into ultrathin oxide films has two main advantages, which should result in smaller structures: First, the size of the written structures is not limited by molecular dimensions. In addition, since many oxides are not volatile, the process is fully compatible with the requirements of ultrahigh vacuum. Second, thin layers of wide band-gap oxides like SiO_2 can be damaged significantly by only partial reduction, i.e., the oxide must be partially reduced by electron-stimulated desorption of oxygen atoms or molecules. This process requires at least local neutralization or even positive charging of the initially doubly negative charged oxygen ions, which can happen within the relevant time scales only via an Auger decay of core hole excitations produced by the primary electron beam (the Knotek–Feibelman mechanism.[6,7]) Due to the necessary high energies of excitation for core hole generation, most of the secondary electrons are ineffective, and smaller structures than in polymer films are expected.

In the experiments reported here, we directed a high-energy electron beam onto an ultrathin SiO_2 film grown on a self-organized regularly stepped Si(557) sample which consists of a periodic array of small (111)- and (112)-oriented minifacets[8] with an average periodicity of 5.7 nm normal to the steps. Steps play an important role in the chemical reactivity. Indeed, it turns out that the step structure leads to a self-limitation of the etching reaction described below. Thus, the structure size of bare Si stripes within the oxidized surface can be reduced to a single terrace.

The process of electron-beam-assisted selective thermal desorption (EBSTD) lithography used here was pioneered by Watanabe and co-workers.[9,10] In this process, the beam of an electron microscope is used to desorb part of the oxygen, thus converting SiO_2 locally into SiO. Subsequent heating of the sample to 760 °C leads to desorption of SiO, whereas the SiO_2 remains stable at these temperatures. During this development step, an additional etching process takes place in the electron-irradiated areas, as explained by Engstrom *et al.*[11,12] Thermally excited silicon monomers, which detach preferentially from step edges, also reduce SiO_2 and form SiO, which also desorbs at this temperature. Since the rate-limiting step in this process is the generation of free silicon atoms from the silicon surface, etching is strongly influenced by not only the step density[13] of the substrate, but also by the step direction. This makes the formation of structures extremely anisotropic, and they can be used to generate ultrasmall structures, as demonstrated in our experiments on vicinal Si(557).

II. EXPERIMENT

All experiments were performed in a combined scanning electron microscopy–scanning tunneling microscopy (SEM-STM) instrument (Jeol JSPM 4500SX). Electron-beam lithography and subsequent measurements with STM could be done without breaking vacuum. Both sample types [Si(111) and Si(557)] were cut out of low-doped

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($\geq$1000 Ω cm) silicon wafers, outgassed at 600 °C for at least 12 h, and finally heated to 1150 °C by direct current for a few seconds. Oxide films were obtained by heating the samples to 640 °C in 2×10^{-6} mbar of oxygen for 10 min. This led to the oxidation of only the topmost silicon double layer. The resulting oxide film was only 0.3 nm thick, and STM measurements were performed by tunneling directly through this ultrathin insulator. The confocal combination with the electron microscopy allowed direct and immediate observation of the structures written with the electron beam.

The structures were written at a primary energy of 25 kV and with an optimal beam diameter of 4 nm (full width at half maximum, FWHM). We used an angle of incidence of about 10° with respect to the surface plane. The electron doses given below neglect exposure by secondary electrons. Although this introduces some uncertainty of the absolute exposures, all relative values are well comparable.

Processing of structures was subsequently done by heating the samples with dc current to 760 °C for 45 s. Temperature was measured with an IR pyrometer. This procedure removed SiO completely and reliably but left sharp boundaries between the silicon and the remaining SiO_2 film in most cases.

III. RESULTS AND DISCUSSION

In a first experiment varying the exposure of the SiO_2 film to the electron beam in a rectangular field, we found that not all of the oxygen can be removed by electron irradiation irrespective of exposure time. As judged from the oxygen KVV Auger intensity, the signal saturates at about 40% of its initial value, in agreement with previous findings.[14] During this process this Auger peak shifts by about 1 eV to higher binding energies. These findings are compatible with the conversion of SiO_2 to SiO under the electron beam and a change of the bonding character to a less ionic bond. The more covalent bonds in SiO lift the concentration of the valence electrons at the oxygen sites existing in SiO_2. Thus, the Auger decay of core hole excitations involving valence band electrons is no longer concentrated at the oxygen ions. This electronic rearrangement obviously makes this process ineffective for oxygen desorption in SiO.

Technically, this saturation effect sets the useful upper limit for the electron dose to ~60 C/cm^2. However, much lower exposures in combination with the thermal development step described above yield much narrower structures. Higher exposures were found to only widen these structures due to the tails in the profile of the electron beam.

This is illustrated in Fig. 1, where we show an STM image of an oxidized Si(111) surface, onto which lines were written with the electron beam at doses between 30 and 60 C/cm^2. The sample was subsequently annealed at 760 °C for 60 s. Bare Si and oxidized Si can be discriminated in STM over a wide range of tunneling voltages (+1 to 4 V). Due to its wide band gap, however, SiO_2 does not appear with its true height but with an apparent layer height of 0.5 Å for the oxide monolayer. Due to the thermal treatment, etch pits are also formed in the oxide (see bottom of Fig. 1). As obvious from the smooth areas within the lines,

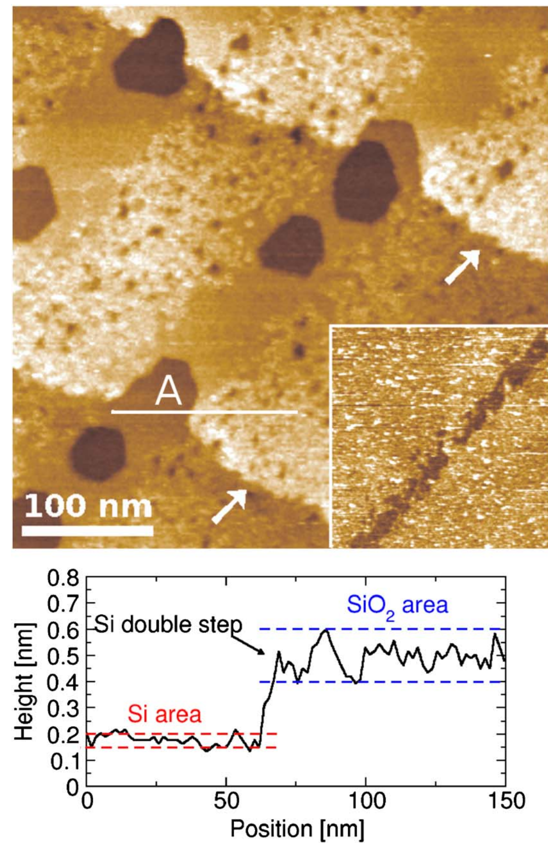

FIG. 1. (Color online) Top: STM picture (440×440 nm) on oxidized Si(111) after writing and thermal processing of lines (smooth parts) written into the oxide. Exposures: between 30 (center diagonal line) and 60 C/cm^2. Thermal treatment: 760 °C for 60 s. Preferred etching at the silicon step edges is marked by arrows. Inset (same scale): Much narrower line, but incomplete removal of oxygen within the irradiated line after exposure to 15 C/cm^2 and heating to 760 °C for 45 s on a step-free substrate. Bottom: Line scan along line A crossing a processed line with bare Si and a nonexposed area of SiO_2. Si and SiO_2 can be discriminated by a small height difference (0.5 Å) and a strongly increased roughness on SiO_2. This behavior is seen over a wide range of tunneling conditions.

and also tested by μ-Auger spectroscopy within these lines, no oxygen is left here. This is also consistent with the fact that adsorption of Ag yields perfectly smooth monolayers within the lines. The higher exposure, however, yields a wider line (70 compared to 50 nm). Both lines are crossed by steps of the substrate. Here preferential removal of Si atoms from the step edges are visible together with etch pits (only one double layer deep!) in agreement with Ref. 13. The latter are most likely produced by initial oxidation of the next layer and are widened by our thermal treatment.

Although the procedure used in Fig. 1 is far from producing optimal structures, it shows that both processes postulated above are indeed effective. Thermal removal of the oxide only happens within the irradiated areas at the chosen annealing temperature, but the structures can be widened considerably by the additional reduction process induced by Si atoms thermally detached from step edges. Since the latter process is dominant at the temperatures used here,[12] the linewidth grows exponentially with time (and inverse temperature), thereby explaining the high sensitivity to the annealing time. If both exposure and annealing time are reduced, much smaller structures result, as seen in the inset of Fig. 1. Here

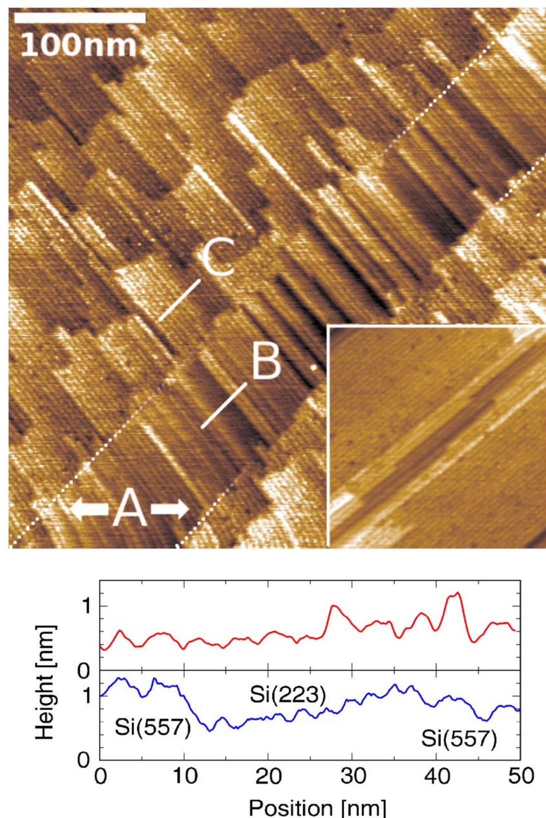

FIG. 2. (Color online) STM image (440×440 nm) after processing a line (structure A, edges are marked by dots) by EBSTD on oxidized Si(557) Same parameters as for the central line in Fig. 1 were used. The writing direction is perpendicular to the Si(557) steps. Note that as a result of the etching process, the irradiated area is almost free of "kinks," contrary to the nonirradiated parts of the surface structure, which are still covered by SiO_2. Inset: Line *along* the step direction generated with the parameter of the inset of Fig. 1. Bottom: Line scans along the lines marked B and C in the large picture. While the original Si(557) surface consists of 5.7 nm wide step structures, the irradiated part also shows Si(223) facets with 3 nm distance due to preferred etching of silicon at step edges of the Si(557).

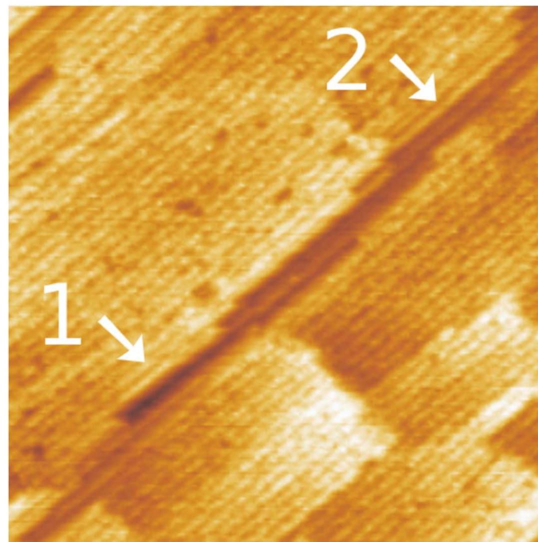

FIG. 3. (Color online) STM image (180×180 nm) of lines written along the steps on a (557) surface, but with slight azimuthal misalignment, under conditions of optimal focusing.

the line was exposed to only 15 C/cm^2, and the surface after exposure was heated to 760 °C for only 45 s. Note that there are no silicon steps either. The result of this EBSTD step is a linewidth of around 15 nm, but the transformation of SiO_2 to SiO was slowed down by missing Si atoms from step edges so that removal of oxide within the line was incomplete. This demonstrates the importance of both the electron exposure and the additional reduction process by Si atoms.

The use of vicinal surfaces with a well-defined step density and step direction in combination with the two main processes in EBSTD now allows structuring on the scale of 10 nm and below. This is demonstrated in the STM image of Fig. 2 by applying the same technique to Si(557) samples. Here the diagonal lines running from top left to bottom right correspond to the terrace structure of the Si(557) surface with a terrace width of 5.7 nm. A small azimuthal miscut of the sample introduces additional kinks, which limit the terrace length to about 100 nm. Only one line perpendicular to the Si(557) steps was written in Fig. 2 with the electron beam along the diagonal from bottom left to top right (the edges are marked by dots within area A). The same experimental parameters as for the central structure and the inset of Fig. 1 (dose 30 C/cm^2, inset 15 C/cm^2, respectively, temperature treatment at 760 °C for 60 and 45 s) were used. Figure 2 shows that the thermal etching process due to the high density of steps and kinks is much more efficient than on Si(111). At the same time, this process gets highly asymmetric: Within the exposed area all kinks are completely removed and shifted to the edges of this area. Even the local step structure has changed, as demonstrated in the line scans shown at the bottom of Fig. 2. Whereas in the oxidized parts of the surface, the (557) step structure is well-preserved, it has changed partly to a (223) facet orientation within the line exposed to the electron beam. This structure is a consequence of the fact that both the detachment of Si atoms preferentially happens at steps, and, even more, at kinks, but also diffusion is much more rapid along step edges than on flat terraces.

Thus, a "zipper" mechanism along step edges is effective here, which ends at kinks. This mechanism is now exploited for generation of ultrasmall lines *along* the step edges by reducing the dose and annealing time to 15 C/cm^2 and 45 s, respectively. The result is seen in the inset of Fig. 2. Lines were obtained that are between 2 and 4 miniterraces (10–20 nm) wide but are completely free of oxide and other visible defects. This result should be directly compared with the inset of Fig. 1, where only part of the oxide was removed after identical treatment. The comparison demonstrates that the presence of steps strongly speeds up the etching reaction, thus demonstrating the importance of the atomistic structure of the surface in the whole EBSTD process. Although not quantified in detail in our experiments, the perfect smoothness of the step edges on the atomic scale within the written structures gives evidence that the etching rates normal to the steps must be orders of magnitude slower than in parallel direction. This makes the EBSTD process in the presence of steps, to a large extent, self-limiting.

After optimization of the focus to values below 5 nm, the result of Fig. 3 demonstrates the feasibility to write lines

that are only a single terrace wide (5.7 nm in our case). This limit is reached when only this terrace is exposed to the electron beam.

Concluding, direct structuring of thin oxide films like SiO_2 by an electron beam allows the generation of very small structures, because only core hole excitations produce the necessary defects. Thus, secondary electrons become ineffective, and the corresponding broadening mechanism is strongly reduced. The use of a regularly stepped surface, on the other hand, emphasizes the importance of the atomistic morphology for the structures obtained in the oxide, which involves a thermally activated etching process. It is the extreme anisotropy of surface diffusion and detachment of Si atoms that essentially limits this process to single terraces. This combination of direct lithography in oxides with anisotropic reaction processes as those triggered by the self-organized step density here allows further structural size reduction to the true nanometer scale. Thus, exploitation of the quantized nature of ultrasmall structures far above l He temperatures becomes feasible as well as contacting of single molecules.

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