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## Electron beam-induced carbon masking for electrodeposition on semiconductor surfaces

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Carbon patterns were deposited on Si(100) by electron beam-induced contamination decomposition. The feasibility of using such patterns as a mask for a subsequent electrochemical deposition of Au is studied. We demonstrate that under optimized electrochemical conditions electrodeposition of Au can be blocked selectively by single line carbon deposits in the order of only 1 nm thickness. The lateral resolution of this negative patterning process is in the sub 100 nm range. The principle opens perspectives for high definition patterning of semiconductor surfaces by selective electrodeposition. © 2001 American Institute of Physics. [DOI: 10.1063/1.1371243]

During past decades, there has been a great deal of interest in micro- and nanometer scale pattern generation on semiconductors. The field is particularly driven by semiconductor technology and its continuous demand for shrinking dimensions in the development of established devices (such as metal oxide semiconductor field effect transistors),<sup>1</sup> as well as for the creation of devices (such as quantum effect devices).<sup>2</sup> Therefore, a range of techniques bearing the potential to achieve submicron resolution have been studied and established. Except for ultraviolet lithography, electron beam (e-beam) lithography is currently one of the most employed approaches to achieve high resolution patterning-on one hand to fabricate photolithographic masks<sup>3</sup>—on the other hand to create ultrasmall linewidths on both Si and SiO2.<sup>4-8</sup> Other lithographic techniques are based on the exposure of photoresists to x rays,<sup>3</sup> focused ion beams,<sup>3,9</sup> or employ scanning probe methods.<sup>10–12</sup> Direct writing approaches using electron or ion beams are in comparison much less reported.<sup>13–17</sup> A number of studies deal with e-beam or ion beam induced deposition reactions. The principle is that precursor vapor species (e.g., metalorganic compounds) are introduced into the vacuum chamber of the instrument where, under direct ion or electron bombardment, the precursor molecules decompose and form a deposit on the substrate surface. Such e-beam and ion-beam induced deposition has been used to create three-dimensional (3D) nanostructures<sup>13-15</sup> in the 1-100 nm range or to directly generate different single electron transistors or superconducting quantum interference devices.<sup>16</sup>

A specific and well-known case of electron beaminduced patterning is the formation of carbon rich contamination layers in scanning electron microscopes (SEMs). The e-beam activates reactions of the residual hydrocarbons (molecules from the pump oil) in diffusion pumped systems to create a highly crosslinked hydrocarbon deposit. It has been reported, for example, that such deposits can successfully be applied as a mask for subsequent ion milling leading to ultrasmall structures.<sup>18</sup> Characterization work on carbonaceous deposits in SEM chambers showed that hydrocarbons adsorbed on a substrate surface are decomposed by the e-beam and form diamond-like carbon, an amorphous structure of carbon having mechanical and electrical properties similar to diamond.19,20

The present work explores possibilities to use such "insulating" carbon masks (C masks) produced by contamination writing in a SEM to suppress selectively the electrodeposition of metals at treated surface locations and thus provide the basis for a negative patterning method in the submicron range.

To achieve electron beam-induced deposition of carbon line (C-line) patterns, hydrogen passivated samples of *n*-type silicon (100), with a resistivity of 1–10  $\Omega$  cm, were treated with the single line mode in a Philips XL-30 FEG scanning electron microscope. During the deposition the pressure of the chamber was  $3 \times 10^{-6}$  mbar, the voltage was set to 20 kV. Different electron dose exposures were achieved by varying the exposure time under a constant electron current of 40 pA.

Figure 1(a) shows an atomic force microscopy (AFM) top view of a silicon surface that was e-beam line exposed at different equidistantly spaced locations for 10, 30, 60, 120, and 180 s, respectively. Clearly, the five deposited locations can be observed as lines in the topographic image. From the cross section in Fig. 1(b) it is apparent that an increase in exposure time results primarily in an increase in height and width of the C-lines. Under the present experimental conditions the height increases almost linearly from 0.7 to 6.1 nm whereas the linewidth depends only weakly on the irradiation time; for the lowest electron dose it results as approximately 200 nm (full width at half maximum) and tends to reach a limit value at around 330 nm for higher doses. The presence of carbon and its distribution over the surface, was confirmed by recording an Auger electron spectroscopy (AES) line scan perpendicular to the deposited lines using the C Auger signal at 270 eV.

A set of C-line patterned samples as in Fig. 1 was prepared and then treated in conventional electrochemical cell

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FIG. 1. AFM image of an array of five contamination lines, e beam deposited on Si(100) at 20 kV and a gas pressure of  $3 \times 10^{-6}$  mbar. The e-beam exposure time for each line increases from the left to the right from 10, 30, 60, 120 to 180 s; (a) top view, (b) height cross section.

using a three-electrode configuration with a platinum gauze as a counter electrode and a Haber–Luggin capillary with a Ag/AgCl electrode as a reference electrode. In order to achieve electrodeposition of Au, different electrochemical polarization conditions were applied in a solution containing  $10^{-3}$  M KAu(CN)<sub>2</sub> and 1 M KCN. Figure 2 shows a SEM



FIG. 2. SEM image of a Si(100) sample carrying the same contamination line pattern as in Fig. 1 after Au electrodeposition at -1.6 V (Ag/AgCl) for 30 s from a 10 mM KAu(CN)<sub>2</sub>+1 M KCN solution.

image of a C-patterned silicon sample after electrochemical Au deposition at -1.6 V (Ag/AgCl) for 30 s. It is apparent that the surface is covered by a Au deposit except for sites that correspond to the location of the carbon lines. In the carbon free region of the sample these electrochemical conditions lead to the formation of a continuous Au film with a remarkable smoothness. The typical Au crystallite size is 10 nm. Note that even the finest C-line of a height of less than 1 nm (see AFM profile of Fig. 1) is clearly resolved and does not suffer from overgrowth.

In order to confirm the selectivity of electrodeposition, an AES line scan for C and Au (using the Auger Au peak at 70 eV) was acquired through the structure of Fig. 2. The intensities for Au and C are complementary, i.e., the intensity of C is the highest where the Au signal indicates absence of Au on the surface. Even more importantly, within the C-masked area no trace of Au was detectable with AES. This proves the high degree of selectivity that was achieved with the masking process.

For all samples investigated at different potentials [-1.3, -1.6, -1.9 V (Ag/AgCl)] and for different times (5, 30, 45, and 60 s) some degree of selectivity was observed. For deposition at -1.3 V no coherent Au coverage was obtained, rather isolated Au crystallites with an increasing size with extended polarization. When potentials cathodic to -1.6 V (Ag/AgCl) are applied, for a longer period of time, overgrowth of the C-lines occurs. Furthermore, and more importantly, significant hydrogen evolution sets in. As a result, H<sub>2</sub> bubbles that stick to the surface lead to a very inhomogeneous deposit.

For the deposition at -1.6 V, the thickness of the Au layer increases roughly from 20 to 60 nm for the sample polarized for 5 s sample to the sample polarized for 60 s. Polarization for a duration longer than 45 s results in an increasingly rougher Au film with typical feature sizes in the range of 100 nm and the lateral resolution becomes increasingly poor due to the overgrowth of the C-lines by Au crystallites.

It should be pointed out that in experiments performed with longer deposition time than 1 min at -1.6 V (Ag/AgCl), a series of undesired effects occurred. Not only did—as expected—overgrowth of the C-lines take place, but additionally the Au deposit layers showed some degree of disbonding.

To explore the lower size limit of the deposition process, a series of experiments was performed for different distances between parallel C-lines (1  $\mu$ m, 500 nm, and 200 nm). Deposition of gold was performed by applying a potential step to -1.6 V (Ag/AgCl) for 10 s. In all cases the deposited features were coherent and completely separated by the C-resist lines. Figure 3 shows an example of the best resolution attained up to now where the two parallel C-lines lead to a confined Au deposit line with a width of approximately 70 nm. It has to be pointed out that possibly even smaller structures could be achieved—the result shown in Fig. 3 corresponds to our minimum experimental e-beam displacement of 200 nm.

Some aspects of earlier results should be regarded in the light of the fact that for metal deposition on semiconductor surfaces, the interaction between metal adatoms and intact



FIG. 3. SEM image of a 70 nm wide gold line between two masking C lines. Au deposition was carried out in 10 mM  $KAu(CN)_2+1$  M KCN by a potential step to -1.6 V (Ag/AgCl) for 10 s.

semiconductor surface is typically weak and hence the deposition follows a 3D-island growth mechanism<sup>21</sup> and the growth kinetics can be described in terms of the Volmer-Weber approach.<sup>22</sup> This implies that the number of successfully triggered nucleation sites for growing a metal cluster is potential dependent. In order to grow a coherent film with a maximum local resolution it is desired to trigger as high as possible number of initiation sites. This leads to coalescence of deposit island in an early growth state (small feature size) and therefore improves the resolution of the deposition process. (If the size of the nuclei becomes large compared with the spacing between masking carbon lines, the crystallite size limits the lower resolution of the process.) According to the Volmer-Weber approach, the density of nuclei increases also with time. However, as the size distribution of clusters triggered early and late in the process becomes wide and diffusion phenomena become increasingly important with time, it is clearly preferable to achieve coalescence of islands by a high potential/short exposure time parameter combination than by a low potential/long exposure time combination.

In summary, the results clearly demonstrate that electron beam-induced C masking of a semiconductor surface can be exploited for a subsequent selective electrochemical metal deposition in the submicrometer range.

The C deposits have a sufficiently high resistivity to act as an insulator and thus to locally hinder electrochemical reduction reactions such as in our case the deposition of gold. The resolution of this negative lithographic approach depends on C-line deposition parameters as well as electrochemical parameters. It has been shown that at C levels in the pressure range of  $3 \times 10^{-6}$  mbar, C masks of a thickness of less than one nanometer can be produced. Even this low layer thickness can be sufficient to efficiently and selectively block charge transfer with the electrolyte and thus prevent a subsequent electrochemical deposition reaction.

To obtain a coherent Au deposition with a high lateral resolution and a high deposition selectivity, deposition potential and time play a crucial role. In general it was found that higher cathodic potential steps for a short period of time lead to more satisfactory results than longer exposure at less cathodic values. This is consistent with a 3D island growth mode and a Volmer–Weber approach, suggesting a higher number of activation sites being triggered with a higher overvoltage. This leads to a coalescence of islands in an earlier growth stage, and thus a finer grain size, and to a higher achievable lateral resolution.

The principle demonstrated in this work should be applicable to essentially a large palette of materials that can be electrodeposited from an aqueous environment (such as metals, semiconductors, polymers). Therefore, this technique may be employed to create patterned surfaces of a wide range of materials with a lateral resolution in the 100 nm range. Additionally, the principle bears the potential to be used on any conductive substrate and thus to be useful to locally functionalize different substrate materials.

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