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Focused ion beam high resolution grayscale lithography for silicon-based nanostructures

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Nanofabrication techniques providing a fine control over the profile of silicon structures are of great importance for nanophotonics, plasmonics, sensing, micro- and nano fluids, and biomedical applications. We report on the applicability of focused ion beam for the fine grayscale lithography, which yields surface profiles that are customized at nanoscale. The approach is based on a correlation between the ion beam irradiation dose of inorganic resist and the mask etching rate in the reactive ion etching. An exceptional property of this method is the number of gray tones that are not limited by the resist characteristics. We apply the process to fabricate unique periodic nanostructures with a slope angle varying across the structure and a period as small as 200 nm.

Fabrication methods providing arbitrarily shaped silicon nanostructures have attracted a lot of attention due to their crucial role in progress of nanoscience. Patterning with simultaneously high lateral and vertical resolution can give a colossal improvement for nanophotonics, plasmonics, micro- and nano fluids, sensing, microscopies, etc. In particular, it can address the challenging fabrication of diffractive focusing optics for extreme ultraviolet and soft X-ray radiation. The performance of widely used diffractive optical components such as photonic grating couplers can also be greatly improved with the availability of pre-designed surface profiles, analogously to the asymmetric grating concept. Moreover, accurate control over the structure height allows for mapping of effective refractive index experienced by light, and therefore facilitates the fundamental principle of gradient-index optics. Consequently, such a technology can benefit the conversion of the propagating signal mode or on-chip focusing of light by miniature aberration-free Luneburg photonic and plasmonic lenses. Unlike resonant-type structures (as, e.g., photonic crystals), where a modification of effective refractive index can be achieved by the variation of periodic features incorporated into the material, these structures remain continuous and bring no additional restrictions on the operation bandwidth. An introduction of a subsequent metal deposition can extend the use of substrates with customized profiles to non-conventional plasmonic applications such as unidirectional excitation of surface plasmon waves and rainbow trapping. For sensing applications, a required surface profile can be transferred onto a separate metal film by using the original silicon structure as a mold for 3D stripping.

In micro- and nano fluids, the implementation of three-dimensional topographies gives an opportunity to confine, isolate, and manipulate analytes within nanoscale volumes. It also enables realization of directed motion of liquid based on surface propulsion, which was found to be enhanced when a period of ratchet structures achieves sub-micrometer scale. Fluid dynamics can be complemented with nanoscale optofluidic transport, where arbitrarily shaped surfaces bring new options for nanoparticle transport and local capture of individual molecules. Ultimately, the applications of silicon nanostructures with pre-designed surface profiles merge different fields of science and are of great importance for interdisciplinary research.

Nowadays, multiple microfabrication methods for structures with a custom surface profile rely on a grayscale lithography. This type of lithography is based on the known sensitivity of a photoresist to the exposure parameters, which converts a local exposure dose into a thickness of the mask, and consequently into the height of etched structure. Typically, grayscale lithography can be performed with either an optical or an electron beam. Nevertheless, shifting the processes to nanoscale requires to use e-beam and is very challenging since the thickness of resist should be minimized to achieve both high lateral and vertical resolution. Eventually, the resolution degrades due to distortions from backscattered electrons and proximity effects that can no longer be properly tolerated by the dose correction algorithms.

An alternative way to fabricate volumetric nanostructures of a custom profile is a direct milling with a focused ion beam (FIB). Since the development of bright liquid metal ion sources in the mid 1970s, FIB has been extensively used in microfabrication and integrated circuit analysis for local removal of material with high accuracy. The performance of modern FIB systems enables the fabrication of, e.g., integrated optical components with a nm-scale vertical resolution by utilizing virtual 3D patterning maps. However, the processing time required for FIB milling is typically a few orders of magnitude longer than the exposure time in standard nanofabrication techniques. As a result, for large scale and high resolution structures, the application of FIB sputtering is not feasible. In addition, during milling, bombarding ions get implanted into the irradiated sample, damaging the surface layer, and causing the amorphization of initially crystalline material, which is unacceptable for many applications.

The modification of material by irradiated ion beam in turn gave rise to a new concept of focused ion beam...
lithography (FIBL). In FIBL, patterning is either directly applied to initial material or to an extra organic or inorganic resist layer. Originally, this type of lithography was conducted with standard resists such as PMMA. Later, it was realized with the number of compounds and multilayer coatings that have outperformed previous resists in terms of resolution and mask strength. Recently, there have been extensive studies on ion implantation directly into pure silicon and the consequent etching of formed gallium-enriched nanopatterns by either reactive ion etching (RIE) at room temperature or dry cryogenic RIE. Focused ion beam was then shown to be an effective patterning tool that returns a feature size of only few tens of nanometers. However, the effect of an alternating exposure dose has been discussed only on a general level and no dedicated grayscale FIBL process providing the control of structure height at nanoscale has been reported so far.

In this work, we demonstrate the feasible fabrication of pre-designed surface profiles by a combination of high lateral resolution and arbitrarily defined inclination angles with the accuracy that has not yet been realized with other types of lithographies. The approach employs an inorganic resist and direct patterning with exposure parameters varying across the structure. The distinctive feature of the method is that the number of definable structure levels is not limited by the resist characteristics. We apply the fabrication potential of the method to realize conceptually new periodic structures, where the angle of surface slope is gradually altered across the structure.

The proposed FIBL was realized with a Helios-600 focused ion beam system, and the process flow is schematically illustrated in Fig. 1. The figure shows two cases—when an exposure dose gradient is used (grayscale structure, left) and when a dose of exposure is fixed (binary structure, right). Prior to FIB exposure, silicon samples are first covered by a high quality 50-nm-thick Si₃N₄ inorganic resist formed by low pressure chemical vapor deposition at 770°C. The thickness of Si₃N₄ is enough for the protection of underlaying silicon from FIB irradiation. When the patterns in Si₃N₄ layer are written by FIB, they can exhibit etch-retarding behavior in RIE due to several mechanisms. The first one is a physical modification of implanted areas by impurity atoms, which changes the lattice constant, causes the associated strain effects, and eventually slows down the etching. The second is a different chemical reaction of gallium-implanted and non-implanted areas with etching chemistries. Specifically, when etching is performed by RIE containing oxygen (e.g., SF₆/O₂ plasma), the emerging in-situ formation of a thin gallium oxide layer promotes the etch retardation effect.

Another type of chemically-based masking can be acquired without oxygen through RIE with fluorine-based chemistry, which has been reported to result in a formation of a nonvolatile GaF₃ masking compound on Ga⁺-irradiated areas.

The resistance of FIB-masked areas against dry etching depends on the irradiation dose and the penetration depth of Ga⁺ ions into the bombarded material. The depth of ion penetration into Si₃N₄ is defined by the acceleration voltage and it can vary from a few nm for low acceleration voltages (5 kV) to 80 nm for higher voltages (100 kV). The dose necessary to provide the masking effect in turn depends on the acceleration voltage, and generally larger doses are required when higher acceleration voltage is used. In addition, operating with too low acceleration voltage can compromise the resolution of ion beam. Taking all this into account, we utilized acceleration voltage of 30 kV to ensure high resolution and moderate masking doses for a fast exposure. The calculated Ga⁺ ion range for this case lies within the range of 30–35 nm.

In this study, we focus on the fabrication of nanostructures with the height of up to 200 nm, which facilitates most of nanophotonic and plasmonic applications. When the thickness of Si₃N₄ overlayer and the FIBL exposure parameters are fixed, the structure profile is governed by the parameters of RIE. In order to maximize vertical graytone resolution, the mask should be almost fully consumed by the end of the etching process. Consequently, it is the selectivity of ion-implanted areas against RIE that acts as a measure of contrast and defines the height of the final structures (differences between low and high selectivity cases are schematically shown in Fig. 1(e)). The parameters of RIE define the surface quality in grayscale transition regions and the sidewall angles. For the best performance, they should simultaneously provide smooth surfaces and anisotropic etching for high lateral resolution. Since the nature of RIE process depends on the process gas, we first studied the applicability of three different fluorine-based mixtures (CHF₃, SF₆, and CF₄) for the grayscale FIBL. The etching was done by Oxford Instruments Plasmalab 80 reactive ion etcher and here we briefly report on the observed trends for different RIE regimes. The use of CHF₃ returns an unacceptably rough profile for the grayscale regions due to a strong passivation component. The application of SF₆ imposes a limitation that it should be used in a mixture with O₂ to achieve required anisotropy. The presence of O₂ in turn complicates the control of moderate etching speed and promotes the formation of Ga₂O₃ during etching, which is difficult to remove selectively. In contrast to SF₆, pure CF₄ has a significantly lower etching rate, good anisotropy of etching, and it does not require the use of O₂. It also returns a remarkably smooth profile for the graytone regions.

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![FIG. 1. Schematic representation of FIBL process sequence: patterning of grayscale structure with a dose gradient (left, (a, c, e)) and patterning of binary structure with a fixed exposure dose (right, (b, d, f)). Resulting grayscale profile (e) is different when written patterns are etched with low (h₁) or high (h₂) selectivity.](image-url)
Based on the results of our test experiments, we selected pure CF₄ as a process gas for the RIE. The performance of the corresponding grayscale scale was assessed by etching a stripe pattern written with a linearly varying dose (shown in Fig. 2(a)) with the process pressure ($P_{\text{proc}}$) of 100 mTorr and forward power ($P_{\text{forw}}$) of 100 W. The resulting structure exhibits a sidewall angle of approximately 86°, which is beneficial for high lateral resolution (scanning electron microscope (SEM) image is shown in Fig. 2(b)). All SEM images presented in this work are taken with a 52° angle with respect to surface normal for illustrative purposes. Figure 2(c) gives a sample topography characterized by atomic force microscopy (AFM), and the longitudinal structure profile measured along the dashed white line is given by the plot in Fig. 2(d). The sample height in Fig. 2(d) is plotted against the applied dose due to the linear character of dose variation in the written pattern. A clear maximum of the pattern height corresponds to the masking dose of about $1.5 \times 10^{16}$ ions/cm². Above this dose, the FIB-induced sputtering of material becomes very intensive and overweights the masking effect. Below this dose, the final structure height shows almost a linear dependence with respect to the masking dose, which is important for the control of surface profile. We therefore select the dose of $1.5 \times 10^{16}$ ions/cm² to be the maximum exposure dose ($D_{\text{max}}$) that we use for the fabrication of all consequent structures shown in this work. The maximum height of the formed feature is a parameter that can be adjusted through the shift in RIE parameters. For the structure shown in Fig. 2 it is about 125 nm.

As a next step, we apply the optimized FIBL process to fabricate a structure of a pre-defined profile that exhibits a very fine increment of gray levels. The structure shown in Fig. 3 was obtained by incorporation of linearly varying dose (shown in Fig. 4(b)), the blaze angle varies across the structure, which is unattainable by, e.g., fabrication methods employing etching of tilted sample. We present three examples of structures of different heights that were realized by the corresponding adjustment of RIE parameters to low, middle, and high selectivity, as shown in Figs. 4(a)–4(c), respectively. The blazed gratings were fabricated with the following parameters: $P_{\text{proc}} = 150$ mTorr and $P_{\text{forw}} = 150$ W for the structure shown in Fig. 4(a), $P_{\text{proc}} = 200$ mTorr and $P_{\text{forw}} = 150$ W for the structure shown in Fig. 4(b), $P_{\text{proc}} = 250$ mTorr and $P_{\text{forw}} = 250$ W for the structure shown in Fig. 4(c). CF₄ flow was always kept at 80 sccm. All these structures were patterned with the same concept—the top blaze parts received a maximum dose $D_{\text{max}}$ and the modulation of the blaze angle was performed by varying a slope of the dose gradient within each period. We did not utilize any exposure dose correction algorithms and postprocessing, the fabricated structures are shown as they were directly after the RIE stage.

In case of low selectivity process shown in Fig. 4(a), the mask is readily consumed when the height of the structure achieves 70 nm. The FIB masking acts here as a low contrast resist and such process parameters are of the particular interest for shallow etching in nanophotonics. As the etching selectivity increases (Fig. 4(b)), the mask lasts until the structure height reaches 140 nm, which is already sufficient for a strong refractive index gradient. The structure presented in Fig. 4(c) demonstrates a case when a process was tuned to significantly higher selectivity and stopped as the structure
In summary, we have demonstrated the realization of a grayscale FIBL concept that addresses the demand for volumetric silicon nanostructuring. The method provides very fine periodic patterns (200 nm pitch, up to 200 nm height) with an arbitrarily defined inclination angle across the structure. The number of gray tones in this process is not limited by the resist characteristics. If the same structures were fabricated by standard FIB milling, there would be a few orders of magnitude increase in FIB processing time (hours instead of tens of seconds). A significant advantage of the process over the competing nanofabrication methods is that it is fast and reproducible due to the minimized number of process steps. The results presented in this work were obtained with the standard FIB and RIE machines that were in common use. Consequently, the presented method can essentially promote realization of technologically challenging nanostructures with pre-designed surface profiles for cross-disciplinary research including nanophotonics, plasmonics, sensing, micro- and nano fluidics, and biomedical nanoscience.

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FIG. 4. SEM images of blazed gratings with the altered angle of slope across the structure and the following parameters: (a) period 300 nm and height 70 nm, (b) period 200 nm and height 140 nm, (c) period 200 nm and height 200 nm. The corresponding profiles of exposure dose are indicated above each structure. Scale bar is 1 μm.
22N. Koshida, Y. Ichinose, K. Ohtaka, M. Komuro, and N. Atoda, J. Vac.
23K. Arshak, M. Mihov, D. Sutton, A. Arshak, and S. B. Newcomb,
24H. X. Qian, W. Zhou, J. Miao, L. E. N. Lim, and X. R. Zeng,
25N. Chekurov, K. Grigoras, A. Peltonen, S. Franssila, and I. Tittonen,
27N. Chekurov, K. Grigoras, L. Sainiemi, A. Peltonen, I. Tittonen, and S.
(2005).
32J. F. Ziegler and J. P. Biersack, SRIM-The Stopping and Range of Ions in
Matter, 2008, also see http://www.srim.org/.
33T. W. Ang, G. T. Reed, A. Vonsovici, A. G. R. Evans, P. R. Routley, and