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Small-angle reciprocal space mapping of surface relief gratings

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Abstract

The nanopatterning of semiconductor surfaces and the subsequent preparation of bio-semiconductor hybrid devices on such surfaces will enable the application of new principles of biomolecular sensing. Nanopatterning may be achieved due to decreasing minimum feature dimensions by various techniques well established in CMOS processing. Here, the preparation and investigation of surface relief gratings (SRG) is reported that were obtained by selective n^+-doping of p-type silicon wafers via 130 nm lithography and ion implantation. B-doped Si (001) wafers with 0.01 Ω cm were used as starting material. Both, line and cross lattices of 360 and 260 nm pitch, respectively, were prepared by covering the p-doped areas and implanting with 3×10^{15} cm^{-2} 45 keV As$^+$. Wafers were subjected to annealing and cleaning procedures subsequently. The doping lattices with n^+–p periodicity were unexpectedly identified to be associated with a topographic modulation of the wafer surface, i.e. SRG peaks were observed by X-ray rocking curve scans at small scattering angles. High SRG peak intensities of up to 80% of the specular reflection were observed in the maximum case, while AFM investigations revealed the SRGs to exhibit an rms roughness of only a few 0.1 nm. It can be concluded that conventional CMOS technology allows for the preparation of SRGs with height modulations in the sub-nm range and that lateral periodicities may effectively be probed by small-angle reciprocal space mapping.

Keywords: Nanopatterning; CMOS technology; Doping lattice; Surface relief gratings; Small angle X-ray scattering; Reciprocal space mapping

1. Introduction

The minimum feature dimensions in semiconductor technology are ever closer approaching the length scales of biological molecules. The dawning convergence of the biomolecular and the semiconductor material worlds is expected to allow – among other perspectives – for new principles in biomolecular sensing and electronics. In particular, Si wafers processed by CMOS technology enable the preparation of nanotemplates that will be required for new functional material hybrids. A simple approach in the preparation of Si wafer nanotemplates is the formation of a periodic array of distinctively doped surface regions. In this paper we report about preparation and characterization of such surface-doping lattices as nanotemplates by means of X-ray scattering (XRS) and atomic force microscopy (AFM). During the characterization of the wafers by structure-sensitive techniques it turned out that next to the doping lattice also a topographic modulation was introduced by the preparation procedure. This surface relief grating exhibited a height variation on the sub-nm scale, which – next to the doping lattice – might assist the ordered immobilization of biomolecules on such nanotemplated wafers.

2. Experimental

Standard CZ Si (001) wafers of 200 mm diameter and p-type doping with a specific conductivity in the 0.01–0.02 Ω cm range were used as starting material. The goal of this work was to introduce n^+-doped surface regions by ion beam doping of selected areas with As. Line lattices and cross lattices (with the latter made from two perpendicular line lattices) were prepared by conventional CMOS photolithography processing. The width of the differently doped lines was intended to be 130 and 180 nm, respectively (pitch $p = 260$ or 360 nm). For this purpose, SiO$_2$, SiN$_x$ and photoresist layers were deposited on the Si wafers, with the nitride layer to act as anti-reflection coating.

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Lithography experiments were performed with a high-NA Nikon NSR S207D KrF (248 nm) scanner interfaced to a TEL ACT8 track for the resist technology. All experiments were done with a lens numerical aperture of NA = 0.82 and an illumination aperture of $NA_{ill} = 0.64$. The used resist system was Rohm & Haas SL4800, with a thickness of 335 nm, softbake and a post-exposure bake of 110 °C, $t = 60$ s. The development was done using NMD-W 2.38% from JSR. For the resolution and process window enhancement the bottom antireflection material of low-pressure chemical vapor deposition silicon-rich nitride of 21 nm thickness [1] was deposited on a 5 nm SiO_2 bottom layer. We optimized the antireflection requirements and the resist swing requirements for lithography [1,2]. 180 nm and 130 nm line and space pattern were used for the experiments. Fig. 1(a) shows the cross-sectional SEM image of 130 nm line and space pattern after the lithography with the grid lines of unilluminated photoresist on top. The dot structures generated by double exposure technique with 90° rotated mask for the second exposure is shown in Fig. 1(b). The double exposure technique was carried out for 180 nm line and space structures.

The patterned wafers were implanted with 45 keV As^+ ions to a dose of 3×10^{15} cm^{-2}. These parameters were chosen in accordance with simulation results in order to realize a concentration of around 10^{20} cm^{-3} at a depth of less than 50 nm. Following ion implantation, residues of the photoresist were ashed in an oxygen atmosphere. Subsequently, the wafers were processed in a rapid thermal processing (RTP) system at a temperature of 1010 °C and 15 s annealing time. Finally, nitride and oxide layers were removed by standard wet-chemical etching procedures in order to arrive at n^+–p-doping lattices in the top-most regions of Si covered only by a thin native oxide layer of 1–2 nm thickness.

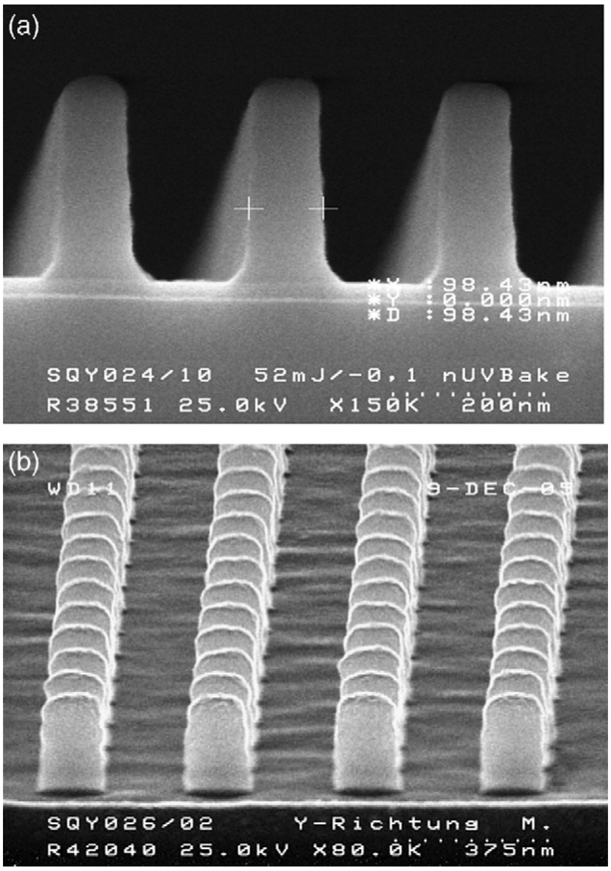

Fig. 1. (a) Cross-sectional SEM micrographs of line and space on SiN_x/SiO_2 after lithography. (b) SEM image of 180 nm line and space pattern by double exposure technique.

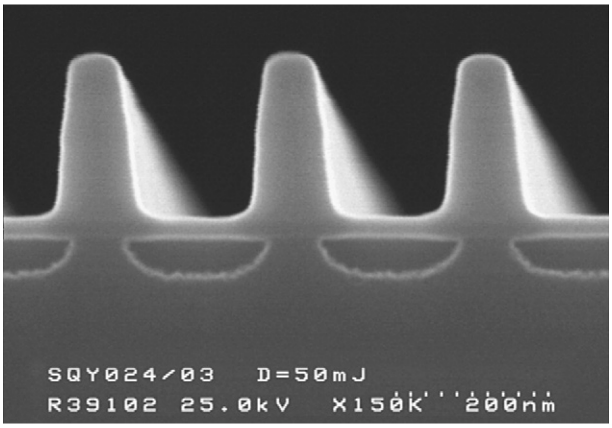

Fig. 2. Cross-sectional SEM micrographs of line and space on SiN_x/SiO_2 after implantation.

During the process flow, selected monitor wafers were abstracted from the process and fractured for SEM characterization. Fig. 2 shows the cross-sectional SEM image of such a monitor wafer that has been processed by the 130 nm line and space pattern after the ion implantation step. The fracture surface was subjected to decoration etching in order to enhance the contrast between the crystalline wafer matrix and areas amorphasized by the implantation process. In fully processed wafers, the amorphous regions were recrystallized in the subsequent annealing step yielding a plain crystalline Si surface layer with streaky n^+ doping areas. Any possible mass density between p and n^+ areas then was in the range of a few tenths of a percent.

3. Results and discussion

Si wafers with doping lattices were investigated by XRS and AFM techniques. XRS investigations were performed at the KMC-2 beamline of the Berlin synchrotron radiation facility BESSY and by usage of a laboratory-based diffractometer system equipped with a Rigaku rotating anode. Radiation of 0.154 nm wavelength was used in both experimental set-ups. Unexpectedly, the measurements at BESSY revealed the occurrence of satellite reflections in rocking curve scans in addition to the specular reflection when the scans were taken at small scattering angles 2θ. Fig. 3(a) shows a similar scan, collected with the laboratory set-up by operating the Cu anode with 50 kV and 150 mA. For a rocking curve scan the scattering angle between the incoming and reflected beam is set to a constant value, here $2\theta = 3.5°$, while the sample is rotated around the axis perpendicular to the scattering plane accounted for by the varying tilt angle ω [3]. In the case of $\omega = 0°$ the symmetrical configuration is taken and the X-ray reflection

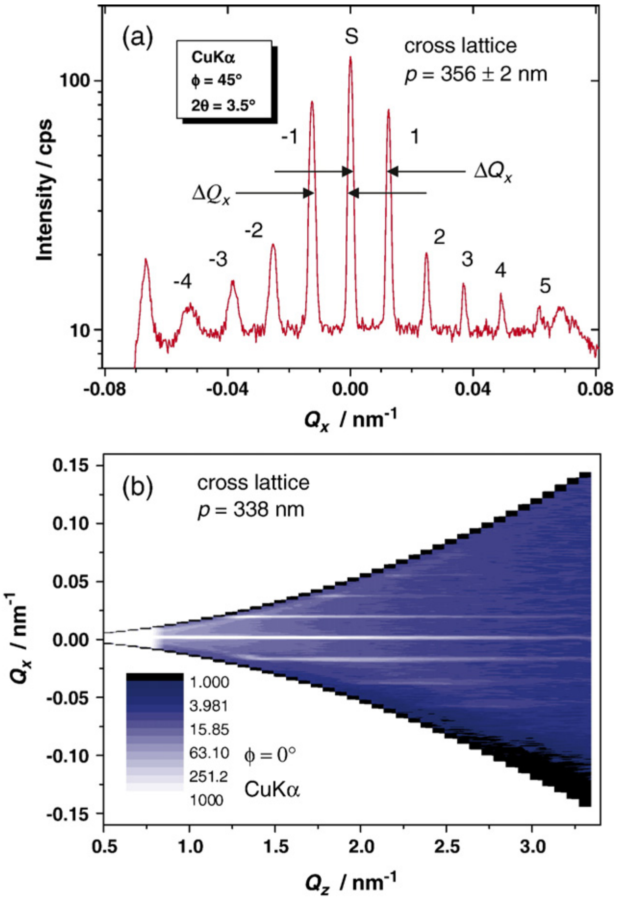

Fig. 3. (a) X-ray rocking curve and (b) reciprocal space map of p–n^+-Si doping cross lattice.

from the sample surface is denoted as specular. The scattering process may also be described by the scattering vector $\boldsymbol{Q}$, which is the difference between the wave vectors of the reflected and the incoming beam, $\boldsymbol{Q}=\boldsymbol{K}-\boldsymbol{K}_0$. For a rocking curve scan the scattering vector assumes in-plane and out-of-plane components Q_x and Q_z that are related via $Q_x=K\{\cos(\theta-\omega)-\cos(\theta+\omega)\}$ and $Q_z=K\{\sin(\theta-\omega)+\sin(\theta+\omega)\}$ with the angular setting. The rocking curve shown in Fig. 3(a) does not only display the strong specular reflection at $Q_x=0$, but, in addition, strong satellite reflections with a pronounced ΔQ_x periodicity are also observed. For the -1 satellite a relative intensity of almost 80% compared to the specular peak (S) can be realized.

At first sight these satellite peaks came unexpected and their underlying nature was unclear. In order to develop a better understanding of this phenomenon a full reciprocal space mapping (RSM) of the small scattering angle (SA) range was performed. In Fig. 3(b) the SA-RSM of a cross-lattice sample is shown; this was collected by setting the azimuth angle ϕ between the scattering plane and the doping grid lines to 45°. Also in these measurements clear satellite reflections were observed that merge in the SA-RSM to pronounced lines running parallel to the specular reflection at $Q_z=0$. The analysis of the Q_x periodicity in the SA-RSM pattern revealed that it was related with the pitch p of the prepared surface doping lattice via $p=2\pi/\Delta Q_x/\cos\phi$. Rocking curve scans of doping line lattices perpendicular to the lines exhibited the same relation, when $\phi=0°$ was inserted for this case. No satellite reflections could be observed, however, for line lattices oriented parallel to the scattering plane ($\phi=90°$). It has also been endeavored to excite such satellite peaks in combination with diffraction rather than scattering. For this purpose, the vicinity of the Si 004 reflection was scanned with a high-resolution XRD set-up. However, no diffraction satellite peaks could be observed.

It could thus be concluded that the satellite peaks visible in SA-RSM pattern indicated a topographic surface modulation of the silicon wafers that were subjected to the doping lattice formation procedures. The small difference in the measured pitch in both figures is assigned to a lateral inhomogeneity. We expect any possible contribution to the effect from mass density

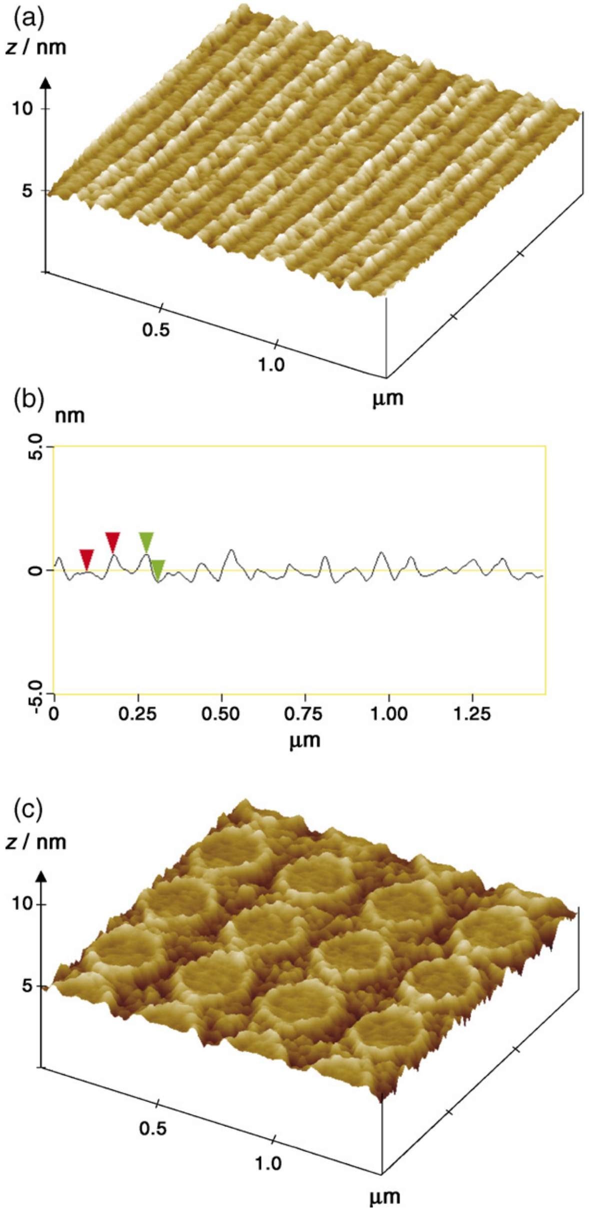

Fig. 4. AFM surface plots of line and cross lattice (a) and (c) and line profile over line lattice (b). RMS and Ra surface roughness values deduced from the latter amount to 0.42 and 0.07 nm.

differences between p and n^+ doped areas to be negligible as testified by the missing diffraction satellite peaks. Comparable investigations of surface relief gratings (SRG) have already been performed for thin polymer films, where SRG of much higher modulation amplitude might be induced by light exposure [4]. The formalism developed to account for their description under SA-RSM conditions revealed that rather high satellite amplitudes should be obtained for small modulation amplitudes [5] as observed in this work.

AFM investigations were performed with a Digital Instruments D5000/nanoscope III and a Si standard tip under tapping mode conditions. The obtained surface plots are shown in Fig. 4 (a) and (c) for the line lattices and cross lattices, respectively. A periodic modulation of the processed wafer surface can clearly be recognized. From the geometry of the cross lattice topography it can be concluded that the surface of As-doped areas is shifted slightly below the average surface of those areas that remained covered by the photoresist during implantation. The modulation amplitude of the SRG is on the order of a few 0.1 nm as can be realized from the AFM line profile displayed in Fig. 4(b).

4. Conclusions

It is finally concluded that the selective area doping procedures of Si (001) wafers applied in this work caused not only the formation of surface doping lattices, but were moreover associated with the formation of a surface relief grating. The periodicity of the SRG compares to the intended pitch of the doping lattice as was revealed by application of small-angle reciprocal space mapping. The latter technique turned out to deliver highly precise values of the average periodicity actually obtained for the SRG. The average amplitude modulations were revealed by AFM to be in the sub-nm range. At the moment we assign the occurrence of the surface relief grating to the combined effect of stress relief and preferred etching of surface areas subjected to ion damage and subsequent crystallization. This work has thus demonstrated (i) that surface doping lattices may be prepared by conventional CMOS procedures and (ii) that an additional surface relief grating with sub-nm amplitude variations can be generated concomitantly. Both surface modulations might be applied for the locally directed immobilization of biomolecules on Si wafer surfaces.

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