Microelectronic Engineering 176 (2017) 75–78

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Fabrication of diamond diffraction gratings for experiments with intense hard x-rays

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ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 17 January 2017
Accepted 2 February 2017
Available online 3 February 2017

Keywords:
Electron beam lithography
Reactive ion etching
Inductively coupled plasma etching
Nano-structure
X-ray optics
Diffraction grating

ABSTRACT

The demands on optical components to tolerate high radiation dose and manipulate hard x-ray beams that can fit the experiment requirements, are constantly increasing due to the advancements in the available x-ray sources. Here we have successfully fabricated the transmission type gratings using diamond, with structure sizes ranging from few tens of nanometres up to micrometres, and aspect ratio of up to 20. The efficiencies of the gratings were measured over a wide range of photon energies and their radiation tolerance was confirmed using the most intense x-ray source in the world. The fidelity of these grating structures was confirmed by the quality of the measured experimental results.

1. Introduction

The modern bright x-ray sources offer significant contributions to the research interest across the scientific fields, such as material physics, biomedical science and high energy density research [1–3]. More and more facilities have gone through significant progresses in order to provide brighter and more coherent x-rays, one of such advancement is called X-ray Free Electron Lasers (XFEL) which are either already in operation or about to [4–6]. XFELs offer intense, coherent femto-second pulses, resulting in characteristic peak brilliance values a billion times higher than that from conventional synchrotron facilities [4]. Such pulses result in extreme peak radiation levels on the order of several Terawatts per square centimetre for any optical component in the beam, and can reach ablation threshold of many materials. It is, therefore, of key importance to fabricate optics that are robust enough to withstand such radiation levels, and yet are capable of efficiently manipulating these x-ray beams for experimental purposes. These problems could be circumvented either by using novel materials or introducing unusual designs. Indeed several optical elements were fabricated having such concepts in mind, for example from Silicon [7], or from Tungsten [8]. However, the intrinsic properties of these materials, such as the radiation tolerance and x-ray transmission capability, limit their applicability. Among various materials available the currently ideal material for hard x-ray application is diamond, which is known for its high thermal conductivity, thermal stability and low x-ray absorption coefficient. These properties allow for robust optics to be developed using diamond structures that could be obtained combining electron-beam lithography and inductively coupled plasma (ICP) assisted reactive ion etching (RIE). We present here the development of diamond x-ray optical elements in the form of transmission-type diffraction gratings with structure widths ranging from nanometres to micrometres, and etched depths of up to 9 μm and sidewall slopes of <5°.

2. Material and methods

Polycrystalline diamond membranes (Diamond Materials, Freiburg), made by chemical vapour deposition (CVD), were used as a material for the optics fabrication. The dimensions of the membranes vary between 1 mm and 5 mm diameter, all of them are 10 μm thick and supported by a 500 μm thick Si frame.

The fabrication process started with the conditioning of the diamond membranes substrates by a cleaning procedure including a Piranha bath and rinsing with 10% Hydrofluoric acid, followed by oxygen plasma treatments. These processes steps are crucial for removing particles contaminating the surface and to promote adhesion of the mask layers in the following steps. The diamond substrates were then coated with 15 nm Cr, followed by another oxygen plasma treatment. This procedure has two purposes: (i) oxygen plasma treated Cr serves as an

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http://dx.doi.org/10.1016/j.mee.2017.02.002

adhesive layer for the used hydrogen silsesquioxane (HSQ) electron-beam resist layer, and (ii) as a conductive layer to avoid excessive charging of the electrically insulating diamond surface during electron-beam exposure. A negative-tone resist HSQ (FOx-16™, Dow Corning) was spin-coated at 6000 rpm for 60 s on the Cr-coated membranes, yielding ~450–500 nm thick resist layer. In case of structures smaller than ~40 nm, a Methyl Isobutyl Ketone (MIBK) diluted HSQ (1:1 by volume) was used, and resulted in a thickness of at the same coating parameters. The grating patterns were exposed onto the resist by electron-beam lithography at 100 keV electron energy using a Vistec EBPG 5000 + ES writer, either at 2–10 nA using a 200 μm final aperture for grating structures below 60 nm, or at 30–150 nA using 400 μm aperture for larger structures. The optimal exposure parameters were found by test exposure series. We found optimal exposure doses of between 5000 μC/cm^2 and 13,000 μC/cm^2, depending on the grating line widths and the HSQ resist shelf time, which seem to result in significantly varying sensitivity. Moreover, its adhesion generally became weaker for smaller patterns, underexposed patterns typically result in structures that are not fully developed and are prone to detach, and hence dose varying for each pattern was necessary for optimisation. For diamond membranes, which typically exhibit a curved surface, the surface height measurements for e-beam writing fields were fitted with polynomial function to compensate for its profile.

The development was performed by immersion of the exposed chips in a mixture of Sodium hydroxide (NaOH) and water (1:3 by volume), for 5–6 min, followed by rinsing in de-ionized water, and in isopropanol. For structure widths above 50 nm, the chips can be dried in a N_2 gas jet. For structures smaller than 50 nm, the chip was dried using critical point drying to avoid structure collapse due to the capillary force.

After the development, the samples were etched in a Cl_2/O_2 plasma to transfer the HSQ pattern into a Cr layer, revealing the underlying diamond. The selectivity of this etch process is relatively high, however too long treatment results in a slightly reduced HSQ mask layer. The samples are then baked at 300 °C for 40 min. This process significantly hardens the HSQ mask, therefore enhancing the etching selectivity in the subsequent pattern transfer into the diamond. The diamond is etched by oxygen ICP-RIE (OXFORD PlasmaPro100). The used recipe was optimized for anisotropy and selectivity, by tuning the ion energy and ion density in the ICP etcher. The process typically requires readjustments of these parameters after ~1–2 μm depth of etching, in order to minimise the sidewall slope.

3. Results & discussion

Fig. 1(a), (c) shows a side-view of a linear transmission grating, with a size of 2 mm by 2 mm, a pitch of 200 nm, and an etched depth of ~1.4 μm. The typical aspect ratios of the lines of these gratings are 10–20, depending on the duty cycle. Since the exposures were carried out on thin membranes consist of Carbon only, the proximity effect by back-scattered electrons was negligible.

Initial trials showed that narrow (~100 nm or below) and long (~1–2 mm) HSQ structures collapsed during the diamond etching step, presumably due to the severe heating and sputtering when going through the ICP process. To improve the structure stability during the ICP etching the grating lines were connected by support structures, where the developed HSQ pattern resembled an overlaid mesh of narrow line and wide pitch. The x-ray optical effect of these support structures turned out to be negligible, as the duty cycle of the support structures was only of the order of 0.05.

These nanoscale pitch gratings were used as a hard x-ray beam splitter to divert a small portion of the beam for quality analysis or sample probing purposes. Hence the diffraction efficiencies and the structure homogeneities of the gratings are of crucial parameters to better understand and optimise the fabrication processes. We have tested several gratings in the hard x-ray range (6–18 keV photon energy) at synchrotron facility PETRA III, Deutsches Elektronen-Synchrotron (DESY). Fig. 2(a) shows the efficiency map of a typical grating over its entire surface of 2 mm by 2 mm indicating the homogeneity of the grating structures. The variation of the efficiency across the grating lies within 30%. A faint grids shaped inhomogeneity can be observed in the image. The pitch of this grid corresponds to the stitching field size of the electron-beam exposure. This is mainly due to the curvature of the diamond membranes, resulting in small errors of the focus settings and e-beam height-mapping mismatch. This has an effect of the electron-beam size and writing fields stitching accuracy, and causes local variations of the grating line width and depth.

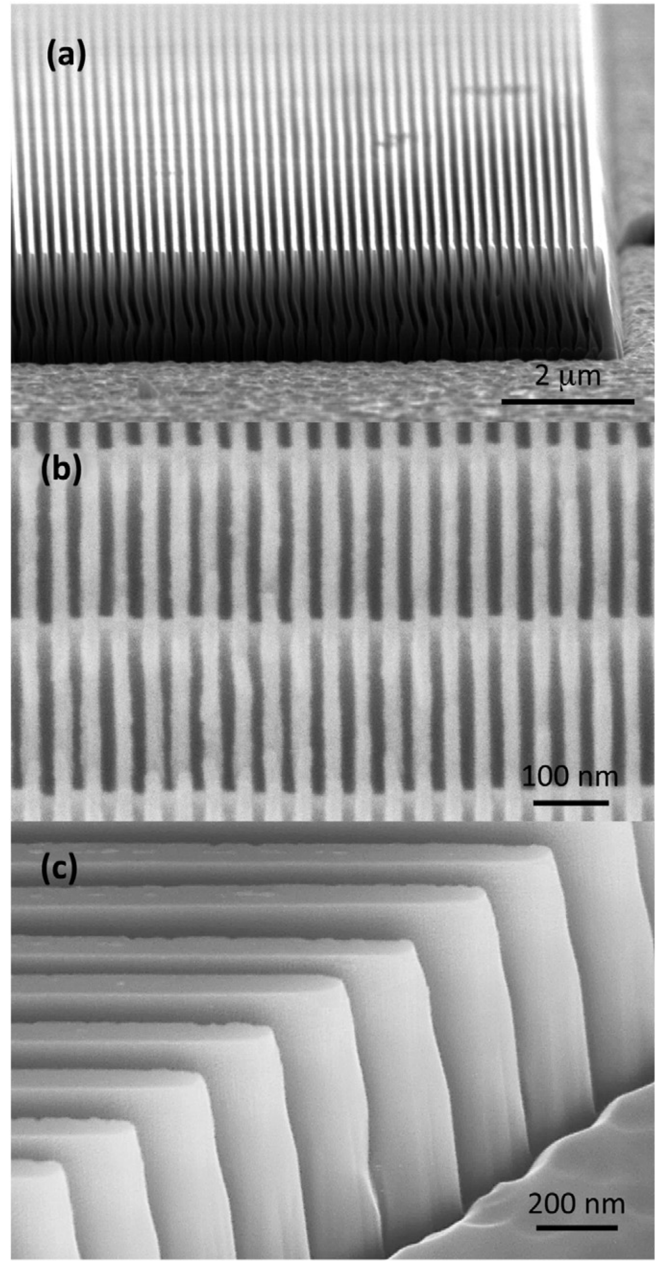

Fig. 1. (a) Side view of a linear grating with a pitch of 200 nm, and a height 1.4 μm. (b) Top view of a linear grating with a pitch of 43 nm with support structures to stabilize the grating. (c) Side-wall view of grating lines with 200 nm pitch, aspect ratio 20, after tuning the ICP etching parameters.

The diffraction efficiency dependency on the x-ray energy for two of the gratings is shown in Fig. 2(b). The measured efficiency reaches approximately 55% (sample 1) and 35% (sample 2) of the theoretically calculated values [9]. This discrepancy in efficiency values between the theory and the experimental value mainly arises from the fact that, in