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Controlling the profile of high aspect ratio gratings in diamond

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ABSTRACT

Diamond is an excellent material for infrared optics and for applications in harsh environments. Some of those desirable properties, i.e. hardness and chemical inertness, also make it a challenging material to machine and etch. In this study we have tested a wide range of etch parameters in an inductively coupled plasma etcher, in order to produce highly controlled, high aspect ratio gratings in diamond. We discuss the effects of pressure, bias power, and some gas mixture variation (pure oxygen and argon-oxygen) on the etch results and how it impacts the etch mask sputtering and redeposition. We also present a method for applying a fresh aluminum mask, in order to etch even deeper optical grating. Gratings with aspect ratios as high as 1:13.5 have been achieved with a 1.42 μm grating period.

1. Introduction

Diamond is a very challenging material to shape, due to its hardness and chemical inertness. Yet diamond has many desirable properties; for optics the broad optical transmission band, high refractive index and high thermal conductivity are of interest. Chemical vapor deposited (CVD) diamond can be used for a wide range of optical applications [1]. Some of these, such as phase masks [2], X-ray sources [3] or diffraction gratings [4], require structures with high aspect ratio and smooth sidewalls. The most successful methods use high density plasmas in inductively coupled plasma reactive ion etching (ICP-RIE) [5]–[7] and Electron-Cyclotron Resonance plasma etching (ECR) [8,9]. When using highly oxidizing chemistries (O_2 [10], O_2/Ar [9] or Ar/Cl_2 [6]) and high ion energies in these systems it is possible to physically and chemically etch the diamond to some degree. As it is a very slow process, a thick hard mask is required to stand up to the prolonged ion bombardment. When utilizing hard masks for etching, commonly used materials are aluminum (Al) [2], silicon (Si) [5] and SiO_2 [11]. To reach high aspect ratios an iterative process has been developed [12], in which a metal mask is evaporated anew to keep the sidewalls protected and to regenerate the mask.

This study focuses on etching gratings with more control of the angle of the etched sidewall and achieving a steeper wall than in our previous reported work [2]. In this study we work with polycrystalline diamond, for cost reasons. There is, however, little to no difference between etching single- and polycrystalline diamond with this kind of etching [2]. The goal is to attain higher precision and to have more degrees of freedom when producing micro-optical components. In a deep grating, such as a half wave plate grating [13] or X-ray diffracting lenses [14,15], good control of the angle becomes every bit as important as the width of the wall. A perfectly vertical sidewall has not been achieved, and is unlikely when the etching is highly dependent on the kinetic energy of impinging ions. Redeposited mask material also has an effect on the sidewall angles in gratings. In order to control this redeposition we previously showed the importance of using a thick mask with vertical edges [2]. Here we develop this masking technique further, as well as vary the pressure, substrate bias power and gas mixture during diamond etching. We also introduce a way of applying fresh mask material to an already etched grating using sputtering and a short etch step, in order to reach even greater etch depths. Our method here is similar to a previously reported one using evaporation at an oblique angle to re-mask a grating [12], but is better suited for curved gratings. In Section 2, we describe the masking process and etching, including all variations of etch parameters, followed by the etch results and discussion in Section 3.

2. Experiment

Several preparation steps are needed before the actual diamond etching. Most of these are not the intended focus of the study, but must still be described, as they are critical parts for the process. We begin with acquiring CVD diamond substrates, which undergo a cleaning process. The diamonds are then covered in metal layers, through deposition, which will later function as hard masks during the etching. For our pattern transfer process we require a soft stamp, which is copied from a predefined resist pattern [2]. The lithography steps are a bit different from the conventional standard and will thus be explained in full detail in Section 2.4. The etching is carried out in steps in order to transfer the pattern to the thicker Al layer before the

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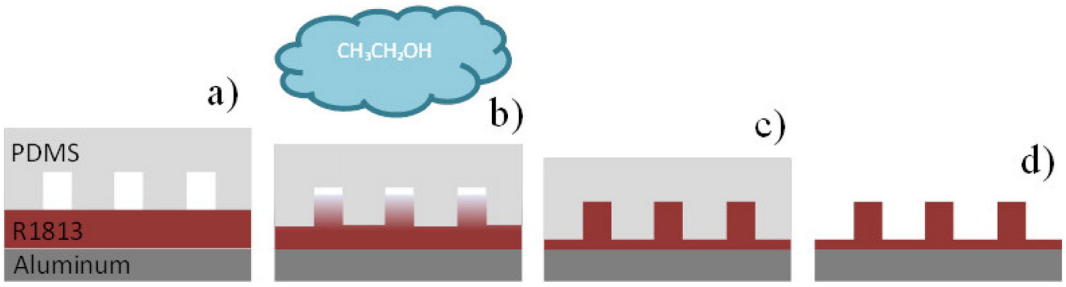

Fig. 1. Description of the SAMIM process: a) stamp positioned on resist, b) ethanol vapor dissolves the resist, c) ethanol evaporated during soft bake, d) resist hard baked.

Table 1
Deposited masking layers.

Layer	Metal	Sputtering time	Power	Thickness
Top	Al	30 s	1000 W	100 nm
Middle	Si	375 s	500 W	450 nm
Bottom	Al	265 s	1000 W	1000 nm

diamond etching can begin. After etching, the substrates are cracked and mounted in a scanning electron microscope (SEM) for characterization.

2.1. Substrates and pre-cleaning

Polycrystalline CVD diamond substrates of optical quality (Element Six Ltd. and Diamond Materials GmbH) were used in these experiments. The circular substrates were 10 mm in diameter and 300 μm in thickness. In order to evaluate more etch recipes on the same substrate, these were broken into halves or quarters before being used. The substrates were washed in acetone, iso-propanol, and water, then cleaned two different acid solutions, first in hot piranha (sulfuric acid 96% and hydrogen peroxide 31%) (H_2SO_4:H_2O_2) and then in hydrofluoric acid 50% and nitric acid 69% (HF:HNO_3). After rinsing in water and iso-propanol, the substrates were blown dry with nitrogen.

2.2. Metal deposition

Masking layers were deposited by magnetron sputtering (Von Ardenne CS 730S). Three layers were deposited on top of the cleaned diamond surface in sequence; a thick Al layer, a Si layer and a thin Al layer, see Table 1. The samples were exposed to air between the depositions of the layers. In this way a thin native oxide is formed in between the mask layers.

2.3. Stamp fabrication

In previously documented experiments [2] a grating pattern of annular grooves was used to demonstrate high-aspect ratio structures in diamond. In this study the same pattern is used to determine if higher and lower sidewall angles of the grating structures can be accomplished. The original pattern (also called "master") is a circular grating with a period of 1.42 μm and a line width of 700 nm. It was written by electron beam (e-beam) lithography in 500 nm thick ZEP resist (Zeon Chemicals) on a 2″ Si wafer. This master pattern was replicated by casting in polydimethylsiloxane (PDMS, Wacker Elastosil RT601). The base and the curing agent were mixed in a 10:1 ratio and a small amount was poured onto the patterned wafer. The wafer was carefully leveled in a laminar flow cabinet and left for 20 min, allowing the silicone to spread into a thin layer and for air bubbles to escape. Remaining air bubbles at the surface were removed by gently blowing compressed air over the surface. The wafer was then placed in an oven at 75 °C for 25 min to cure the PDMS. Finally, the PDMS stamp was peeled off from the wafer. The process does not damage the master wafer and can be repeated many times. All stamps used here were cast on the same master.

2.4. Solvent-assisted microcontact molding (SAMIM)

In order to transfer the pattern to the diamond substrates a method called solvent assisted microcontact molding (SAMIM) was used. Our method is based on that reported in [16], but differs in that we used a vapor phase solvent and a thin PDMS stamp. S1813 photoresist (Shipley) was mixed with AZ EBR 70/30 solvent (MicroChemicals) in a 1:2 volume ratio and spin coated on top of the sputtered diamond substrate at 6000 rpm for 30 s. After baking on a hot plate at 115 °C for 60 s, the resulting resist layer was 200 nm thick. The PDMS stamp was cut to a size somewhat larger than the diamond substrate and placed on top of the resist film. Ethanol (97%) was poured into a large Petri dish until it just covered the bottom of the dish. The diamond substrate, with the PDMS stamp on top, was placed in a smaller petri dish. The smaller dish was then placed open in the larger one, and the lid was put on the larger dish. This left the substrate in ethanol vapor, but without direct contact with the liquid ethanol. PDMS is permeable to ethanol, so ethanol vapor could diffuse through the stamp to reach the thin photoresist film, which is ethanol soluble. As the resist softens it fills the pattern due to capillary forces. After about 30 min the PDMS pattern was completely filled. This could be observed as a distinct lowering of the intensity of the diffraction colors from the grating. The PDMS/diamond stack was then removed from the ethanol vapor and the remaining ethanol was baked out by heating it to 60 °C for 10 min on a hot plate. The PDMS stamp was then gently removed from the diamond substrate leaving a replica of the grating pattern in the resist (see Fig. 1).

The PDMS stamp can be reused, but to avoid contamination a new one was used for each sample in this study. Finally the diamond substrate was hard baked on a hot plate at 115 °C for 5 min; the patterned resist layer was then 350 nm thick and the residual resist layer at the bottom of the grating pattern only a few nanometers thick. It should be noted that when using SAMIM, as in other micro/nanoimprint methods, it is important to match the fill factor of the micro/nano pattern with the thickness of the spin coated resist. A too thin film will not have enough resist to completely fill the pattern and a too thick

Table 2
Etch recipes for the masking layers.

Recipe	Gas [sccm]	RF power (ICP) [W]	RF power (bias) [W]	Pressure [mTorr]	Time [s]	Note
Thin Al	15 Cl_2, 50 BCl_3	600	30	6	60	Over-etched for 25 s.
Si	10 SF_6, 20 C_4F_8, 70 Ar	825	50	10	210	Does not affect Al-mask
Thick Al	15 Cl_2, 50 BCl_3/50 O_2, 20 Ar	600/400	90/10	6/10	6 cycles + 20 s Al etch step	Cycled (25 s/7 s), purge between steps

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