

Formation of high aspect ratio fused silica nanowalls by fluorine-based deep reactive ion etching

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HIGHLIGHTS

- High aspect ratio fused silica 'nano-walls' by DRIE was developed.
- The optimum conditions of DRIE for vertical sidewalls were studied.
- The etch rate was controlled with the DRIE parameters.
- Thin Al was used as a conducting layer for e-beam lithography and as a DRIE mask.

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ABSTRACT

Even though fused silica was considered as a good mold material for nanoimprint lithography due to the properties of UV-transparent and high strength, fabrication of high aspect ratio nanometer-scale mold was challenging. A fabrication process for 120 nm-wide fused silica 'nano-walls' with high aspect ratio has been developed by using fluorine-based deep reactive ion etching (DRIE). The optimum conditions of the DRIE process to result in anisotropic vertical sidewalls with high-aspect ratio and good etch rate control were demonstrated as a function of bias power, process pressure, and argon percentage of the gas mixture. One of the vast applications of this process is the fabrication of the mold for UV nanoimprint lithography (NIL). Due to the fact that the resist is cured using UV-light, it is critical that the mold is transparent. A thin aluminum layer is used as a conducting layer for e-beam lithography, then used as an etch mask for fused silica etch. In the presented study, the etch rate increases with higher bias power and lower gas pressure. The existence of Ar makes the vertical surface smoother.

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1. Introduction

Nanoimprint lithography (NIL) continues to attract considerable interest because of its great promise for future semiconductor applications since it enables mass-production of nanopatterns and nanostructures at low cost with submicrometer resolution [1,2]. Traditional NIL transfers the patterns by pressing mold onto a heated thermoplastic polymer resist [3]. Since this technology requires a precise control of high temperature and pressure, which is generally 80–200 °C and 0.1–15 MPa, respectively, silicon (Si) is normally used as a mold material [4,5]. As the pattern size reduces in nanoscale, the errors induced by the thermal and mechanical

deformation becomes significant in the thermal NIL. Alternatively, UV-based NIL is advantageous in resolution and overlay accuracy by eliminating the high temperature gradient, where the resist is imprinted by mild pressure and simultaneously cured by UV-light [6,7]. In order to expose the resist underneath the mold, however, it is required that the mold is made from a UV transparent material, such as fused silica, which also allows the alignment of overlay [8].

Among the nanopattern generation methods including interference lithography, deep UV (DUV) lithography, and electron beam lithography (EBL), EBL is an ideal fabrication tool for NIL molds due to its capability of versatile pattern generation without complex mask (or reticle) manufacturing. However, EBL on fused silica or glass materials for NIL mold fabrication requires a conductive layer to suppress the charging effect and over-exposure during electron

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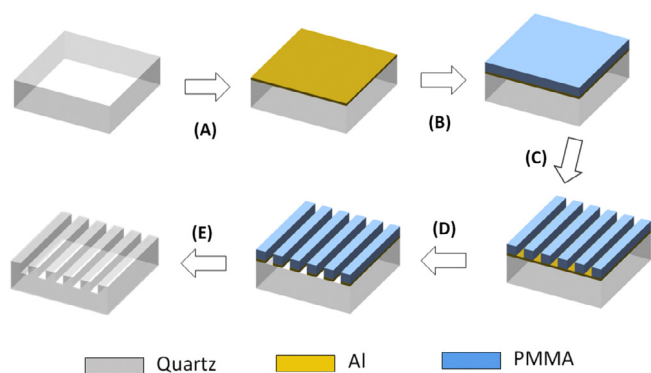


Fig. 1. UV-imprint mold fabrication schematics. Clean fused silica substrate is obtained; (a) 10 nm of Al layer is deposited as conducting layer for e-beam lithography; (b) PMMA is spin-coated as an e-beam lithography resist; (c) PMMA is patterned with e-beam lithography and developed; (d) Metal layer is etched using chlorine-based plasma dry etch; (e) Fused silica is etched using fluorine-based plasma etch then metal layer is stripped using wet etchant.

beam exposure. A widely used method is the classical chromium (Cr) and fused silica photomask fabrication, but a much thinner layer of Cr (less than 20 nm) or aluminum (Al) is used to decrease the critical dimension loss through the under etching [9]. Since imprint lithography solely relies on the resolution of the mold, a flawless fabrication of the mold is critical [10]. In particular, smooth sidewall of the NIL mold is important because the pattern transfer yield decreases significantly with rough sidewalls. Further, non-vertical NIL molds result in the errors in pattern dimensions in the subsequent anisotropic reactive ion etching (RIE) process. Unmasked substrate area is to be widened as the tapered NIL resist is simultaneously removed by RIE. Finally, high aspect ratio of NIL molds allows thicker resist coating that provides the process reliability, including easy lift-off and deep substrate etch by RIE.

2. Experiments

The fabrication of high aspect ratio nanometer-scale ‘wall’ patterns in fused silica includes the following steps as shown in Fig. 1. For the fabrication of the molds, (a) 10 nm of Al layer was deposited on 2.5 cm x 2.5 cm x 1 mm fused silica substrate using an e-beam evaporator (CHA Mark 40). Al, which provide electron conducting path, is critical to reducing the charging effect during electron beam lithography. Once conducting layer is deposited, (b) about 200-nm thick PMMA (polymethyl methacrylate) is spin-coated as an electron beam resist. Then (c) the nanopatterns are written onto the substrate by electron beam lithography (JEOL JSM5910). (d) After the exposed PMMA is removed by the development, the Al metal layer is patterned by a chlorine-based plasma etcher (Plasma-Therm SLR 770) using gas mixtures of BCl_3 and Cl_2 with the PMMA as an etch mask. Then, (e) the fused silica substrate is etched by DRIE using fluorine-based advanced oxide etching (Advanced Oxide Etching system, STS AOE Inc.) with the Al metal layer as an etch mask. Finally, Al layer and remaining PMMA layer are stripped by Al etchant and acetone, respectively.

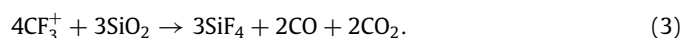
For this study, an induction-coupled plasma (ICP) enhanced DRIE process with a fluorine-based gas was demonstrated to effectively form high-aspect-ratio three-dimensional ‘wall’ patterns in fused silica. The patterns are defined in part by an etch mask in the form of PMMA and a high quality Al film. The process was developed to satisfy a need to fabricate fused silica ‘wall’ patterns for fabricating UV-NIL mold. The development of the process involved manipulation of process parameters, including the selection of gases, the mixture ratios of the gases, the process pressure, and power of the radio-frequency signal used to excite

the ICP. It was found that polymeric materials containing silicon and fluorine were formed on the side-walls during the DRIE and were subsequently etched away, resulting in anisotropic etching. It was also found that helium added to gas mixture contributes to cooling of substrates and thereby helps in forming vertical of the process. A DRIE system with an ICP plasma source was utilized to develop a fluorine-based DRIE process for fabricating nanometer-scale fused silica structures. This DRIE system can produce nearly monoenergetic, low energy (0.5–100 kV) and high flux (0.1–2 mA/cm^2) fluorine ions. Typically, the fluorine ions have an energy distribution with approximately 10 eV full-width at half maximum. Throughout these experiments the ICP power was fixed at 600 W. DRIE power is varied at 300–400 W, and sample bias was 300–500 V.

In this study, mixture ratio of CF_4 and argon (Ar) gases, process pressure, and ICP/RF power were tested to determine the optimal process conditions for best sidewall etch profiles. Good results were found for pure Ar in CF_4 and these results are presented here. During our fluorine-based DRIE processing, the following plasma enhanced chemical reactions occur to form SiF_4 , which is a volatile product at elevated temperature. A simple model of the fused silica etching mechanism is proposed as below:



It can be mediated by the presence of electrons in the plasma which generates reactive atoms, radicals, and ions as below:



In the presence of a bias between the plasma and the sample, both ion bombardment and reaction by inert ions result in the plasma as:



This reaction is believed to result in anisotropic etching due to the directional nature of the bombardment catalyzed surface chemical reactions.

3. Results and discussion

A gas mixture composed of CF_4 and Ar in the various percentage of Ar while using 30–150 W of bias power and 600 W of ICP power was found to be optimum DRIE conditions for fused silica material. The addition of Ar gas to CF_4 is found to contribute to the anisotropic etching, and results in more vertical sidewall profiles. In our experiments we obtained an etch rate of 80 nm/min with a gas mixture of 1:0.2 ratio of CF_4 to Ar, bias power of 60 W, ICP power of 600 W, and a process pressure of 3 mTorr. With these etching conditions, submicron-sized fused silica patterns with high aspect ratio sidewalls were fabricated as shown in Fig. 2. The aspect ratio here is defined to be the ratio of the height of the sidewall to the extension of the base of the sidewall from the vertical at the top of the sidewall. Fig. 2 shows an aspect ratio of 10, 1.2 μm in height and 120 nm in width.

3.1. Etching characteristics versus bias power

Fig. 3 displays increasing etch rate with the bias power while maintaining a gas mixture of 1:0.2 CF_4 to Ar, bias power 60 W, ICP power 600 W and pressure of 3 mTorr. It is typical that the etching mechanism is directly controlled by the bias power that represents the energy of ion flux brought to the substrate. It is concluded that the etching mechanism of fused silica depends mostly on the ion energy flux that impinges the surface. In other words, the etch rate would be more influenced by surface fluorination with fluorine flux than Ar percentage.

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