Cryogenic electron beam induced chemical etching

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Abstract

Cryogenic cooling is used to enable efficient, gas mediated electron beam induced etching (EBIE) in cases where the etch rate is negligible at room and elevated substrate temperatures. The process is demonstrated using nitrogen trifluoride (NF$_3$) as the etch precursor, and Si, SiO$_2$, SiC and Si$_3$N$_4$ as the materials volatilized by an electron beam. Cryogenic cooling broadens the range of precursors that can be used for EBIE, and enables high resolution, deterministic etching of materials which are volatilized spontaneously by conventional etch precursors as demonstrated here by NF$_3$ and XeF$_2$ EBIE of silicon.

KEYWORDS: electron beam induced etching, nanofabrication, silicon, nitrogen trifluoride, reaction kinetics, surface chemistry

Gas mediated electron beam induced etching (EBIE) enables maskless, beam-directed editing of materials at the nanoscale. Etching has been demonstrated using precursors such as H$_2$O, O$_2$, H$_2$, Cl$_2$, SF$_6$, XeF$_2$ and ClF$_3$.$^{1-4}$ However, the range of precursor-substrate combinations that is appropriate for EBIE has, to date, been small compared to conventional

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plasma etching\textsuperscript{5,6} because many of the precursors that yield radicals responsible for plasma etching have properties that are undesirable for EBIE. Ideally, a substrate etched by EBIE is exposed to a vapor-phase precursor that adsorbs to, but does not etch the material spontaneously. An electron beam is then used to dissociate surface-adsorbed precursor molecules, generating fragments that react with the substrate to produce species which desorb, thereby volatilizing substrate regions near the beam\textsuperscript{1} (see inset of Figure 1(a)). EBIE is typically performed at room temperature because both heating and cooling can inhibit etching by increasing and decreasing the thermal desorption rate of surface-adsorbed precursor molecules and the final reaction products, respectively.

The limited scope of room temperature EBIE is exemplified by nitrogen trifluoride (NF\textsubscript{3}), a common fluorine precursor used in laser\textsuperscript{7} and plasma\textsuperscript{8} induced etching of Si and SiC.\textsuperscript{9} NF\textsubscript{3} satisfies most key requirements for EBIE: it has a large electron dissociation cross-section;\textsuperscript{10} high vapour pressure; relatively low toxicity and broad material compatibility (in particular, NF\textsubscript{3} does not cause corrosion of components in electron microscope chambers, and does not etch most solids spontaneously, including silicon\textsuperscript{11}). Despite these favorable characteristics, NF\textsubscript{3} mediated EBIE has previously not been demonstrated, likely due to poor surface coverage at room temperature. Weak physisorption has been observed on platinum,\textsuperscript{12} gold (desorption energy = 0.219 eV)\textsuperscript{13} and ruthenium.\textsuperscript{14} Standard theory of gas mediated electron beam processing\textsuperscript{1,2,15–22} predicts that the low NF\textsubscript{3} adsorption energies (on the order of 200 meV) give rise to very low etch rates at and near room temperature (Supporting Information Section S3). Coverage can, in principle, be increased by substrate cooling since the desorption rate decreases exponentially with reciprocal temperature (Supporting Information S3). Cooling does, however, also inhibit thermal desorption of the final reaction products, and has therefore not been used to enhance EBIE.

Here we show that cryogenic substrate cooling can enable efficient EBIE in cases where the room temperature etch rate is negligible. We demonstrate efficient EBIE of materials that contain Si, C, N and O at temperatures as low as 100 K. The results show that a range
of EBIE reaction products can desorb (during electron irradiation) at cryogenic substrate temperatures, and that cryogenic substrate cooling broadens the range of precursors that can be used to realize EBIE. NF$_3$ EBIE of Si is particularly significant because silicon is most often etched using XeF$_2$ which gives rise to spontaneous etching and roughening of Si, while the electron beam merely accelerates the local etch rate.$^{23}$ The only alternatives for EBIE of Si reported to date are SF$_6$, $^{24}$ which is highly inefficient, and Cl$_2$$^{25,26}$ which is highly corrosive, toxic and flammable. Cryogenic, NF$_3$ EBIE overcomes these problems, and enables deterministic, high resolution editing of Si and associated devices.

EBIE was carried out using an FEI Nova NanoSEM variable pressure$^{27,28}$ scanning electron microscope (SEM) equipped with a magnetic immersion lens gaseous secondary electron detector$^{29}$ and a liquid nitrogen cooling stage. Substrates used for EBIE were Si, SiO$_2$, SiC and Si$_3$N$_4$. Cylindrical etch pits were fabricated under 8.4 Pa ($8.4 \times 10^{-2}$ mBar) of NF$_3$ a using a stationary, 10 keV, 3.4 nA electron beam that was under-focused to generate a top-hat flux profile (see Supporting Information Sections S1a and b for additional details). This configuration, shown schematically in the inset of Fig. 1, yields conditions that are optimal for quantitative analysis of EBIE rates.$^{3,20,22,30}$ The temperature was always above the condensation point of the precursor gas (Supporting Information Section S1c), in contrast to ice lithography and cryogenic electron beam induced deposition.$^{31–34}$

Comparisons to Cl$_2$ mediated EBIE of Si (Figure 3a) were performed using the electron exposure conditions used by Roediger et. al., $^{25,26}$ an NF$_3$ pressure of 6.5 Pa and a substrate temperature of 106 K. Delocalized etching of Si caused by XeF$_2$ precursor vapor (Sigma Aldrich, 99.99 %) was demonstrated (Figure 3b) using a gas injection capillary located $\sim 100 \mu$m from the substrate surface in high vacuum ($\sim 3.8 \times 10^{-3}$ Pa), at room temperature (Supporting Information Section S1d). A framed ‘NF3’ symbol (Figure 4) was etched into Si by a 20 keV, 9.9 nA electron beam, using an NF$_3$ pressure of 6.5 Pa and a substrate temperature of 106 K. Total processing time was 5 min with an electron beam dwell time of 13 ms per pixel.
Figures 1a and b show plots of the depth of pits made in Si (measured using an atomic force microscope (AFM), see Supporting Information Section S1f) by NF$_3$ mediated EBIE as a function of temperature ($T$). The etch rate is negligible at room temperature and increases as the substrate temperature is reduced to $\sim 98$ K. At any given temperature, the etch rate is constant with time (over the experimental time scale), as seen in Figure 2.

Figure 1b shows that the etch rate scales exponentially with $\frac{1}{T}$ at reciprocal temperatures greater than $\sim 0.0075$ K$^{-1}$. At lower values of $\frac{1}{T}$ (i.e. higher temperatures), EBIE is inhibited through a thermally-activated mechanism that we ascribe tentatively to surface diffusion of residual contaminants (such as hydrocarbons and H$_2$O)$^{35,36}$ present at the substrate surface. Residual contaminants compete for surface sites with NF$_3$ adsorbates and can therefore inhibit EBIE, particularly at elevated temperatures where the NF$_3$ coverage is low and diffusivity (of all species at the surface) is relatively high.

At reciprocal temperatures greater than $\sim 0.0075$ K$^{-1}$, the exponential increase in etch rate
rate with $\frac{1}{T}$ is attributed to a corresponding increase in the surface coverage of NF$_3$ caused by a decrease in the NF$_3$ residence time at the substrate surface (Supporting Information Section S3). We note that an exponential increase in EBIE rate with $\frac{1}{T}$ can not be explained by the temperature-dependence of the adsorbate diffusion coefficient which decreases with $\frac{1}{T}$ (Supporting Information Section S3).

In our experiments, analysis of the EBIE reaction products by mass spectrometry was not possible due to the high NF$_3$ pressure and small quantity of volatile molecules generated in EBIE. However, based on other dry chemical etch processes, and XeF$_2$ mediated EBIE of Si, the etch reaction products are most likely of the form SiF$_n$, where $n = 1$ to 4, and the thermal desorption rate increases as $n \rightarrow 4$.

The etch pit depth data shown in Figure 1b can be used to extract the thermal activation energy ($E$) of the process responsible for the observed temperature dependence. Arrhenius analyses of the curves yield an activation energy of $\sim 63 \pm 1$ meV for EBIE performed using electron fluxes of $1.7 \times 10^{17}$ cm$^{-2}$s$^{-1}$ and $4.4 \times 10^{18}$ cm$^{-2}$s$^{-1}$, respectively. This value of $E$ serves as a lower limit for the adsorption energy of NF$_3$, as discussed in the Supporting Information (Sections S4 and S5).

NF$_3$ mediated EBIE was also applied to silicon oxide, carbide and nitride to determine the etch efficiency of materials other than Si. The etch rates of all three compounds are very low at room temperature, and increase significantly at the cryogenic temperature of
Figure 3: (a) AFM image of a rectangular pit made in Si by NF$_3$ mediated EBIE, illustrating the absence of delocalized damage produced by spontaneous etching of Si. (b) SEM image of Si processed by XeF$_2$ mediated EBIE using the same electron exposure parameters as those used in (a). Red rectangles show the areas that were scanned by the electron beam and correspond to the nominal areas of etch pits made by EBIE. The image in (b) shows delocalized damage caused by spontaneous etching of Si by XeF$_2$ that occurred during EBIE.

105 K, as seen in Figure 2. The volumetric etch rates at cryogenic temperature are $9.1 \times 10^4$, $1.1 \times 10^6$, $1.6 \times 10^5$ and $1.6 \times 10^5$ nm$^3$ s$^{-1}$ for Si, SiO$_2$, Si$_3$N$_4$ and SiC, respectively. SiO$_2$ exhibited the highest volumetric etch rate, likely due to the existence of additional reaction pathways enabled by oxygen, such as the generation of SiOF$_2$ and OF species, and a lower concentration of silicon atoms in the material.

In the case of SiO$_2$ and Si$_3$N$_4$, the desorption of nitrogen and oxygen is not surprising at cryogenic temperatures. However, the carbon present in SiC needs to be volatilized by radicals produced by electron dissociation of NF$_3$ adsorbates. The volatile reaction products are most likely of the form CF$_x$ (where $x = 1$ to 4).

Next, we compare the efficacy of the cryogenic NF$_3$ etch process to room temperature alternatives reported to date in the EBIE literature. Electron exposure conditions used by Roediger et. al. for Cl$_2$ mediated EBIE of Si$^{25,26}$ were replicated using XeF$_2$ and NF$_3$. The use of XeF$_2$ results in highly delocalized damage, caused by rapid spontaneous etching of Si. For example, Figure 3b shows a substrate region that contains an etch box with a nominal area of $1.5 \times 1.5$ µm, and a region of severe damage produced by XeF$_2$ that extends $\sim 20$ µm from the rectangle scanned by the beam. Such rapid, delocalized etching by XeF$_2$ is typical when the native oxide layer is compromised (by pinhole defects, or by EBIE).
behavior is clearly unfavorable as it inhibits the ability to etch Si with high spatial resolution (Supporting Information Section S1e). In comparison, NF$_3$ mediated EBIE did not give rise to any observable spontaneous etching of the Si substrate. Instead, it yielded a well defined etch pit with a depth of $\sim 55$ nm (Figure 3a), and a volumetric etch rate that is $\sim 2.4$ times greater than that of Cl$_2$ under the same electron exposure conditions.

A complex pattern etched into Si using NF$_3$ is shown in Figure 4. It demonstrates high resolution, localized editing of Si in the absence of highly toxic, flammable and corrosive precursors that are unsuitable for use in electron microscopes (ultimate EBIE resolution is governed by the electron beam diameter, proximity effects and material roughening that occurs during etching).$^{42}$ We note that SF$_6$ has also been reported as a precursor for room temperature EBIE of Si.$^{24}$ This etch process is, however, extremely inefficient and inappropriate for high resolution EBIE, and may give rise to unintended deposition of sulphur.$^{43}$

![SEM image of a framed ‘NF3’ symbol etched into Si by NF$_3$ mediated EBIE with a line resolution of $\sim 85$ nm.](image)

In summary, cryogenic cooling was used to enable efficient gas mediated electron beam induced etching using nitrogen trifluoride as the etch precursor. The etch rate is limited by thermal desorption of weakly bound NF$_3$ adsorbates. The process was demonstrated using Si, SiO$_2$, SiC and Si$_3$N$_4$, and enables high resolution EBIE in the absence of artifacts caused by delocalized spontaneous etching of the substrates.
0.1 Acknowledgements

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0.2 Associated Content

Supporting Information

S1: Notes; S2: Modeling introduction; S3: Temperature dependence of electron beam induced etching; S4: Arrhenius analysis of single step EBIE reactions; S5: Arrhenius analysis of multi-step EBIE reactions; S6: Model input parameters. This material is available free of charge via the Internet at http://pubs.acs.org/.
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Graphical TOC Entry