# FABRICATION OF NANOFLUIDICS AND NANOPORE USING REACTIVE-ION DRY-ETCHING WITH ELECTRON-BEAM BAKED RESISTS

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## ABSTRACT

We developed a simple fabrication procedure for a fabrication of nanostructures with electron-beam (EB) lithography. We found that, an electron-beam irradiation with a density of over 50 mC/cm$^2$ have high-resistance against dry-etching, resulting preserve in a clear-pattern of fluidics and through-hole pore for the EB-lithographed image. This electron-beam "baking" procedure would be a useful for EB lithography fabrications of nanobiodevices containing various kinds of nanostructure, *e.g.*, pore, channel, pillar, and fluidics.

## KEYWORDS

nanotechnology, nano-fluidics, nanopore, and electron-beam lithography.

## INTRODUCTION

The research fields on single-cell and molecule analysis by using nanobiodevice have been recently expanding [1]-[6]. These nanodevices are generally composed of various kinds of nanostructure, *e.g.,* nanopore, channel, fluidics, gape-electrode, pillar, and so on, and have various advantages. The fabrication technique of these nanostructure significantly influence the performance of the devices. Electron-beam (EB) lithography have been widely used for a fabrication of nanodevices because of the high-resolution, high-throughput, and highly integration capability[7]-[9]. However, the EB resist itself is not high resistance for ion-reactive and/or chemical etching. Pore/fluidics devices should have a proper depth and/or deep trench so that the precise three-dimensional fabrication is key points for high-sensitive sample sensing and controlling in the nanodevices. In order to transfer clear patterned image on the silicon substrate, the metal masking and wet-etching procedures should be added in the fabrication before and after the dry-etching, respectively. In this study, we developed a simple high-resolution dry-etching method using electron-beam "baked" resist without a metal masking procedure. The resist "baking" was performed by exposing an electron-beam on a ZEP resist layer after image-development. We found that an electron-beam irradiation induced chemical reactions on the upmost resist polymer, resulting in change in the resistance for reactive-ion dry-etching. Importantly, when the electron-beam dose density was over 50 mC/cm$^2$, the dry-etching resistance was found to be drastically improved, resulting in high-fidelity pattern transfer of through-hole pore and fluidics on the substrate for the EB-lithographed image. In addition, the yield rate of the devices could be improved, compared to the nanofabrication process with the metal mask. Using this EB "baking" resist for the dry-etching, we successfully achieved a clear patterned nanodevices containing nanopore, channel, fluidics, gape-electrode (**Fig.1**). This EB lithography using electron-post-baking would be a general procedure of high-resolution dry-etching for nanofabrication..

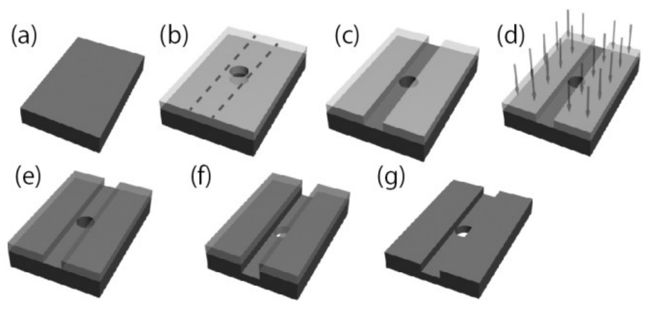


*FIG. 1. Schematics of fabrication process of a nanostructure using "EB-baking" resist. (a) silicon wafer. (b) ZEP resist spin-coated silicon wafer. The resist were a pre-thermal baked on a hot plate. (c) The first electron-beam irradiation for lithography was performed, and the lithographic images of pore and fluidics pattern were developed with developer solution. (d) ZEP resist was "baking" by the second EB irradiation with a density of over 50 mC/cm$^2$. (e) The electron-beam irradiation ("baking") (f) pattern-transfer by using ion-reactive etching (RIE).(g) The "baked"-resist were removed in DMF solution.*

## EXPERIMENT

ZEP520A (Nippon Zeon Corporation) were used for the electron-beam lithography. The resists are copolymers of α-chloromethacrylate and α-methylstyrene, and spin-coated on a silicon wafer (100) to become a membrane of about 0.2 um thickness. The resist thicknesses were obtained by varying spin-on conditions and measured by SEM and ellipsometry. The resists were prebaked at 170 °C for 5 min on a hot plate, and then the image-patterning was performed by electron-beam lithography 125 kV in a EBL system (Elionix) with the density of 0.19 mC/cm$^2$. The lithographed image was developed by immersing the sample into an organic developer solution. The developed EB resist pattern was clearly formed on the silicon wafer, which is confirmed by SEM imaging. After the electron-beam "baking" procedure, reactive ion etching (RIE) was performed with $CHF_3$/Ar (2:1) gases by 10-NR. The etched depth was estimated by profile meter.

**RESULT AND DISCUSSION**

Electron-beam (EB) lithography and the pattern transfer on silicon wafer was performed in the following. In the first step, the EB resist were spin-coated on conductive substrates, and the image-patterning was performed by electron-beam irradiation with the density of 0.05 to 0.020 mC/cm$^2$. In the second step, the electron-beam lithographed image was developed by immersing the sample into an organic developer solution. In the third step, the reactive ion etching (RIE) was performed in order to transfer the patterned image on the substrate. In this study, after the second step, the developed resist image was "baked" by electron-beam doping with the scanning electron microscope. The extent of EB doping was controlled by the scan rate.

First, we fabricated fluidics, of which the width was 100, 200, 400 nm and the etched depth was 200nm. **Figs. 2b-d** (200nm width fluidics) and **Figs. 2e-g** (100nm-width fluidics) show typical SEM images of the fluidics devices after RIE etching with EB-baking resists. When the resist have high resistance against the dry-etching, the edge of the transferred pattern were clear. From the fidelity pattern transfer, we found that the extent of the etching-resistance of EB-baked resist was mainly divided into the two phases. In the phase of high electron-beam irradiation in the range of 50 to 160 mC/ cm$^2$ (**Fig. 2b** for fluidics with 200nm width, and **Fig.2e** for fluidics with 100nm width), the EB-baked resists were found to be highly resistant against dry-etchings, compared to a no EB-baked resist. Under this condition, the dry-etching-resistance time for the EB-baked resist was about four minutes, which was longer than the time for non-baked resist. On the other hand, in the phase of low electron-beam irradiation in the range from 0.15 to 10 mC/ cm$^2$ (**Fig. 2c and f**), its etching resistance of the EB-baked resist was found to be relatively low, compared to those of non-baked resist (**Fig. 2d and g**). Importantly, the high-dosed EB resist-baking procedure significantly improved the dry-etching resistance, resulting in formations of the clear EB lithographed patterns, and the etched sidewall of the nanofluidics have smooth surface, which is expected to be low friction factor and be suitable for the smooth sorting of sample molecules in the device.

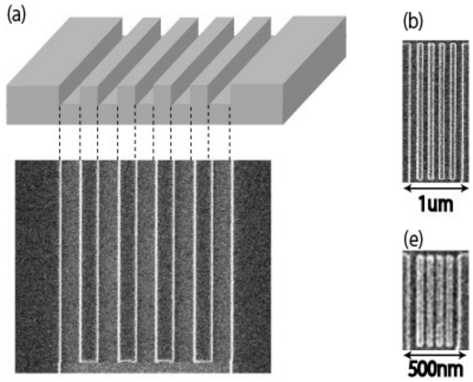


*FIG. 2. (a) Schematics (upper figure) and Scanning electron micrographs (lower figure) of nanostructure containing 400nm line-and-space structures. The SEM images of b-g show 200nm line-and-space patterned nanostructure, and the SEM images of (h-m) show 200nm line-and-space patterned ones. The patterns were produced by using ZEP-resist baking by our electron-beam irradiation procedure. The irradiated electron density, which was controlled by the irradiation time, were 160 mC/ cm$^2$,for (b) and (e), 8 mC/ cm$^2$,for (c) and (f), 0 mC/ cm$^2$ for (d) and (g), respectively. The dry-etched depth is found to be 200nm, estimated by cross-sectional SEM image of the nanostructure. The clarity of the pattern was mainly divided into the two phases. In the phase of low electron-beam irradiation in the range from 0.15 to 10 mC/ cm$^2$, the patterns of (c) and (f) were found to be unclear, and, in the phase of high electron-beam irradiation in the range of 50 to 160 mC/ cm$^2$, the pattern of (b)and (e) were found to be clear, compared to those pattern with a conventional method of (d) and (g).*

Next, by using this EB baking procedure, we fabricated a through-hole pore on silicon substrate. **Fig. 3a** show typical SEM images of through-hole pore with EB-baked resist. In the transferred image after the dry-etching, the pore image is well-transferred, and the sidewall of the no-baked through-hole pore have smooth anisotropic etched surface. On the other hand, as shown in **Fig.3b**, the through-hole pore size is smaller than the , and the sidewall of pore have some small pieces of material remaining attached to the pore. Similarly, by using this EB baking procedure, a gating nanopore composed of 1um gap-electrode 1um pore (**Fig.3c**), were fabricated. In this device, these smoothness of the etched surface for electrode and pore is important for the electrochemical sensing and estimation of the electrode surface area. **Fig.3d** shows a typical SEM image of the gating nanopore device. The image suggests that that, in the EB baked area, the resist layer existed even after the etching and the sidewall of pore and electrode also have smooth surface, while most of the no-baked resist layer was almost disappeared. This results demonstrated that this EB-baking procedure significantly improved the line-edge/surface roughness, and would be generally useful for a EB lithography fabrications of nanodevices.

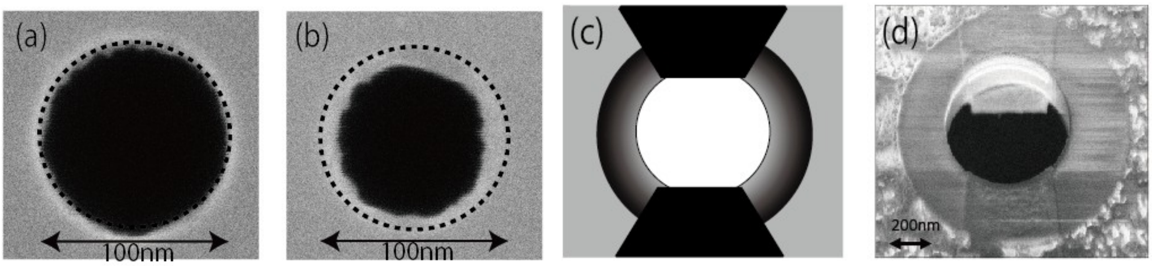


*Fig.3. Comparison of nanopore device by using electron-beam (EB) baked and no-baked resist after ion-reactive etching. Scanning electron micrographs (SEM) image of 100 nm pore by using EB baked resist (a) and by using no baked resist (b). The etched edge for the sidewall of the nanopore (a) is significantly clear, relative to that of (b). (c) Schematics of nanostructure containing 1um pore (white area) and 1um gold gap-electrode (black area). The EB-irradiation was performed around the pore. The beam density was 160mC/cm$^2$. (d) SEM imagae of the nanopore device.*

The change in the dry-etching resistance would be due to the change in the chemical structure induced by the reactions, *i.e.,* the scission or the crosslinking of resist molecules. It is well-known that the ZEP resist undergo bond breaking when ZEP is exposed to the electron-beam during the normal lithograph mode at the density of 0.05-0.25 mC/cm$^2$. Therefore, the low EB exposure at the density of 0.15 to 10 mC/ cm$^2$ on the resist in our study also induced this C-C bond cleavage of main-chain in the resist copolymer, resulting in the degradation of the etching-resistance. On the other hand, in the high EB irradiation, it was reported that cross-linking reactions of ZEP resist could be induced by high-power electron-beam, X-ray, or heavy ion beam irradiation [10]. In addition, Oyama et al., recently suggested that EB irradiation at the density of over 10 mC/cm$^2$ could induce C-Cl bond cleavage and C-C bond recovery or C=C bond formation after C-C bond cleavage of main-chain in the resist copolymer [11]-[13]. Together with these reports, in the upmost irradiated resist area, the resist polymer would be altered to the hydrocarbon/amorphous carbon layer, which improve the dry-etching resistance.

## CONCLUSION

We achieved a high-resistance electron-beam resist for fabrication of nanodevices containing-fluidics, pore and nano-electrodes for single-cell/molecule sensing. After a conventional EB image-development procedure, we added a resist-baking procedure using an EB exposure with a density of over 50 mC/cm$^2$, and then performed a reactive-ion dry-etching. We found that the EB-baked resists were highly resistant against dry-etchings, resulting in preserving a clear-pattern of the EB-lithographed image. This nano-scale dry-etching using EB-baked resist would be a general procedure for EB lithography fabrications of nano-fluidics and nanopore for single cell/molecule analysis.

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