High resolution electron beam lithography of PMGI using solvent developers

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Abstract

We report in this paper that typical solvent developers for PMMA can be used to develop PMGI (polydimethyl glutarimide) with a contrast much higher than that reported using base developers. Three developers were studied: methyl isobutyl ketone (MIBK), 2-ethoxyethanol (cellosolve), and methyl ethyl ketone (MEK). MIBK developer results in the highest contrast of 6.7 which is comparable to that of PMMA, followed by MEK (4.0) and then by cellosolve (2.6). The sensitivity is around 1000 μC/cm^2, roughly four times that of PMMA and almost independent of the developers. Higher resist baking temperature leads to higher contrast for MEK and cellosolve, whereas for MIBK the optimum baking temperature is 200 °C. Both MIBK and MEK (but not cellosolve) developers can resolve 50 nm pitch grating with slight line distortion which is similar to that achievable by PMMA. Using a single step development, a double layer of PMMA and PMGI could be employed to facilitate the liftoff process or to fabricate a T-shaped gate structure, while a multilayer stack can be used to produce 3D metal structures by electroplating.
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1. Introduction

Despite its low throughput, electron beam lithography (EBL) remains a standard tool for nanoscale fabrication of arbitrary patterns. With modern e-beam writing tools, the resolution for EBL is often limited by the resists used in the process. Positive tone resists are usually employed to fabricate by EBL and liftoff metal nanostructures such as electrical pads, while negative resists are more suitable for creating protruding structures such as nanoimprint lithography moulds by reactive ion etching using the resist as mask. Nonetheless, for deep etching (e.g. >300 nm) with vertical profile or for dense fine patterns, metal hard etching mask created by EBL using positive resist and liftoff is still preferred.

PMMA and ZEP520 [1] are two most popular positive resists. PMGI (polydimethyl glutarimide) has also shown to be sensitive to e-beam exposure [2,3] and 150 nm wide lines have been achieved by EBL using (low concentration) aqueous base developer such as TMAH. PMGI is more sensitive than PMMA but with a much lower contrast. As a matter of fact, PMGI (designed as a liftoff resist) is supposed to be dissolvable by base developers even without exposure to e-beam, though the dissolution rate drops drastically with the decrease of base concentration [2]. Therefore, PMGI (or its derivative LOR) is employed more often as a liftoff resist in a bi-layer resist system such as with PMMA [4].

While it is generally believed that PMGI will not be dissolved by solvent developers [3,5], in this paper we will show that, at higher dose (>500 μC/cm^2 for 30 kV), the common solvent developers for PMMA can actually be used to develop PMGI with a performance similar to that of PMMA. PMGI displays several advantages over PMMA: resistant to general solvents, less susceptible to

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intermix with other polymers or resists when stacked [2], slightly more resistant to acids, slower dry etch rate (by 30% in CHF_3 plasma), and higher thermal stability with a glass transition temperature of 189 °C (vs. 105 °C for PMMA).

2. Experimental

PMGI (SFG 2 S from MicroChem Corp., 60–80 kg/mol, dissolved in 80–90% cyclopentanone and 10–20% tetrahydrofurfuryl alcohol, contains surfactant) with a thickness of 60 nm was spin-coated on a silicon wafer at 2000 rpm using a CEE spinner and subsequently baked for 60 min on a hotplate at 150 °C, 200 °C and 250 °C (it begins to decompose at ~1 nm/min when baked at 300 °C). In order to obtain a film of 120 nm (twice the thickness), the first layer was baked at 150 °C for 5 min before spinning the second layer. The silicon wafers were cleaned with $NH_4OH:H_2O_2:H_2O=1:1:5$ at 80 °C for 10 min and then baked at 200 °C for 10 min to remove residual moisture.

Exposure was performed using a Hitachi S4800 cold field emission SEM equipped with a Nabity nanometer pattern generation system (NPGS), usually ~4 h after the flash for a stable beam current. The acceleration voltage was fixed at 30 kV. The beam current was 15 pA for writing high-resolution dense lines and 2000 pA for 15 μm-wide stripes that were used to obtain the exposure characteristics curves.

All development was conducted at room temperature with ultrasonic agitation. Three common PMMA developers [6] were tested: methyl isobutyl ketone (MIBK): 2-propanol (IPA)=1:3 for 60 s; cellosolve (2-ethoxyethanol): methanol=3:7 for 7 s (followed by 10 s dip in methanol); and methyl ethyl ketone (MEK): ethanol=26.5:73.5 for ~2 s. After 15 s rinse with IPA, the wafers were dried by N_2 gas. To remove possible residuals (probably from additives to PMGI, ~5 nm depending on dose and developer) after development, a 10 s plasma etching using 50 W and 10 mTorr O_2 was carried out before Cr liftoff using MF-319 developer (Rohm and Haas Electronic Materials).

3. Results and discussion

The exposure characteristics curves for the three developers are plotted in Fig. 1. The contrast γ is a measure of the ability of the developer to dissolve the resist exposed at various doses and is defined as $\gamma = [\log(D_0/D_{100})]^{-1}$ where D_0 is the extrapolated dose for complete exposure and D_{100} is the extrapolated dose for full thickness (see Fig. 1). The sensitivity of the resist is defined as $D_{0.8}$, the dose corresponding to 20% remaining thickness (here 24 nm). From Fig. 1 and Table 1 we can see that: (1) Among the three developers, MIBK gives the highest contrast comparable to that of PMMA, followed by MEK, while cellosolve gives the lowest contrast which is similar to that reported using base developer [2]; (2) the sensitivity
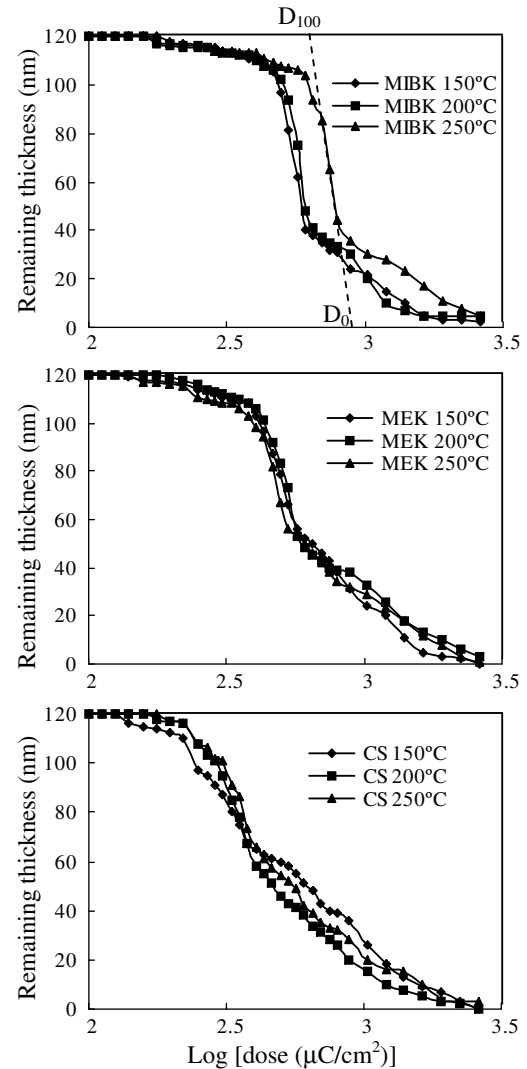

Fig. 1. Exposure characteristics curves for 120 nm PMGI prebaked at various temperatures. The thickness was measured by Dektak profilometer.

Table 1
Contrast for PMGI using the three developers

Baking temperature	150 °C	200 °C	250 °C
MIBK	5.7	6.7	6.3
MEK	3.0	3.8	4.0
Cellosolve	1.7	2.4	2.6

is less dependent on developer and baking temperature, and it mostly lies between 900 μC/cm^2 and 1100 μC/cm^2 which is about four times that of PMMA; (3) higher baking temperature leads to higher contrast for MEK and cellosolve, but for MIBK the optimum baking temperature is 200 °C and both the contrast and the sensitivity drops (by 40% for sensitivity) at 250 °C; and (4) a residual layer is usually left for MIBK, but negligible for the other two developers.

To study the resolution, grating patterns with pitch 35–100 nm were written in 60 nm PMGI baked at 200 °C for
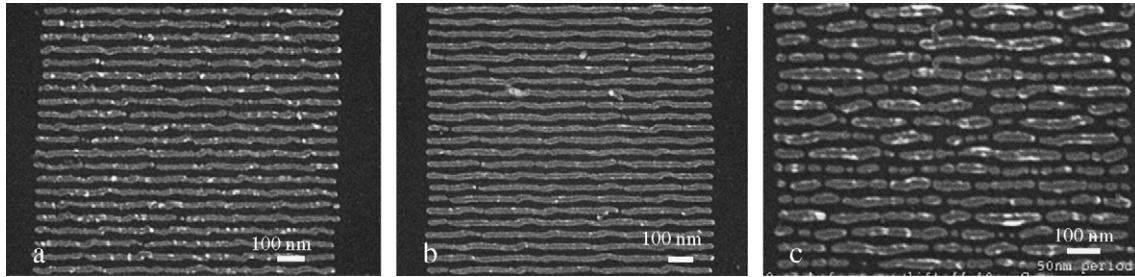
Fig. 2. Cr lines with 50 nm period fabricated by EBL and liftoff using three different developers: (a) MIBK; (b) MEK; and (c) cellosolve.
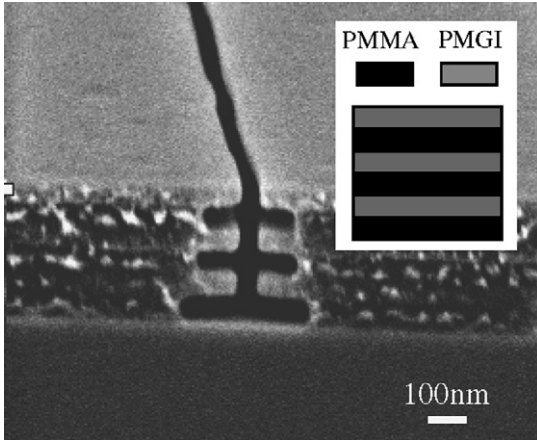

Fig. 3. Line in a stack of PMMA and PMGI created by e-beam writhing using MIBK developer. (5.7 nC/cm).

60 min. After a brief oxygen plasma etch to remove the possible residual layer, 10 nm Cr was evaporated and lifted off by MF-319 developer. Both MIBK and MEK (but not cellosolve) developers can generate acceptable 50 nm period gratings with ∼25 nm line-width (Fig. 2). Considerable line distortion and breaking occurred for 40 nm pitch grating. Again, this behavior is comparable to that of PMMA having the same film thickness and exposed at the same acceleration voltage. The resolution and minimum achievable pitch is not limited by the e-beam size (<3 nm). Instead, they are determined by resist swelling [7], proximity effect that leads to an undercut profile, and capillary force during the drying of the rinse solution, here IPA. Cellosolve developer that has a lower contrast suffers more from proximity effect, leading to more pronounced resist line distortion and collapse.

Fig. 3 shows lines written in a stack of alternative PMMA and PMGI layers (baked at 140 °C for 5 min before spinning the next layer). The lines were developed by MIBK for 3 min with ultrasonic agitation. The opening in PMMA is wider than that of PMGI due to its higher sensitivity. In addition, the opening is widest for the first PMMA layer because of forward scattering of the incident beam (back scattering is less important for isolated lines). Certainly, using a single step development, a double layer of PMMA and PMGI could be employed to facilitate the liftoff process by creating an undercut (PMGI on top), or
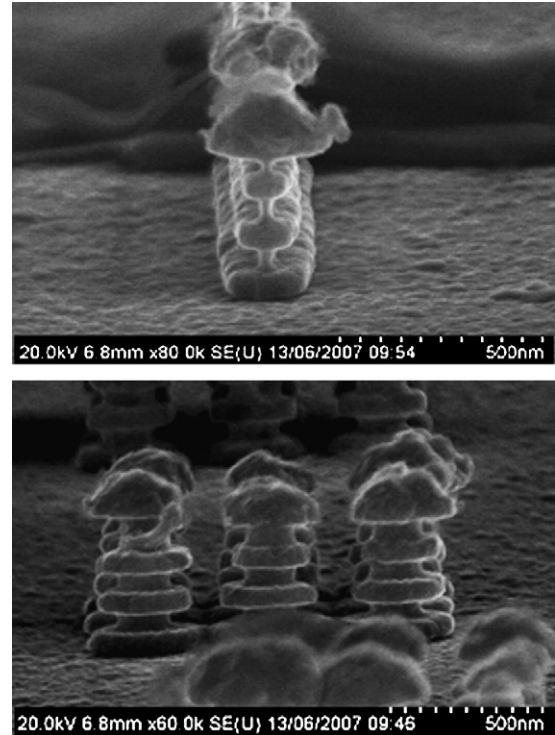

Fig. 4. 3D Ni structures fabricated by electroplating into holes created in a stack of PMMA and PMGI by EBL. Electroplating was conducted at 50 °C with 2.0 V using an electrolyte containing per liter 367 g nickel sulfamate and 30 g boric acid. A plating base layer of 20 nm Ag was evaporated on a silicon wafer before spinning the resists.

to fabricate a T-shaped gate structure (PMMA on top) [2]. Alternatively, 3D metal nanostructures with a zigzag profile can be generated by electroplating into the patterns created in the resist stack (Fig. 4).

4. Summary

Electron beam lithography of PMGI using MIBK, MEK and cellosolve developers were studied systematically. MIBK developer results in the highest contrast that is close to 7 and comparable to that of PMMA, followed by MEK and then by cellosolve. The sensitivity is around 1000 μC/cm^2, roughly four times that of PMMA. Both MIBK and MEK (but not cellosolve) developers can resolve 50 nm pitch grating with slight line distortion,

similar to that achievable by PMMA. Using a single step development, a double layer of PMMA and PMGI could be employed to facilitate the liftoff process or to fabricate a T-shaped gate structure, while a multilayer stack can be used to produce 3D metal structures by electroplating.

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