Low Temperature Development of PMMA For Sub-10-nm Electron Beam Lithography

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***Abstract*—We investigate PMMA development at lowered temperatures for its effect on the resolution, PMMA trench cleanliness and pattern quality of sub-10 nm e-beam lithography. We find that low temperature development (4~10 deg. C) results in reproducibly 4~8 nm PMMA trenches and fabrication of single-particle-width Au nano-particle lines by liftoff. We discuss development temperature and other key factors for formation of better quality PMMA trenches at the sub-10 nm scale.**

electron beam lithography; QCA; nanoparticle; liftoff; PMMA

I. Introduction

Because the ultimate resolution of electron beam lithography (EBL) can be below 10 nm, and due to its high flexibility, compatibility and availability, EBL is an important patterning method for nanofabrication processes, such as Coulomb blockade [1-3] and molecular devices [4][5], high-density magnetic storage [6], and mold making for imprint lithography [7]. Sub-10-nm EBL has been extensively studied in the last decade. The key issue now is not the quality of the electron beam system, but rather is the properties of the resist and developer combination and pattern transfer [8]. Since poly(methylmethacrylate) (PMMA) has relatively poor etch resistance, the liftoff process is most important for EBL using PMMA resist to be of practical use. The quality of narrow lines, cross-sectional shape and presence of residue at the bottom of trenches are key factors for successful sub-10-nm liftoff. There has been much effort addressing sub-10 nm fabrication using ultrasonic development techniques [9], metal deposition [9-11] and membrane substrates [8]. The goal is to make sub-10-nm EBL a feasible patterning technique for a wide range of applications in areas of nanoscience and technology.

We intend to use sub-10-nm-wide PMMA trenches for a nano-particle and molecular liftoff process [12][13] for applications in quantum-dot cellular automata (QCA) [14][5]. To this end, we are exploring an EBL process using low-temperature development, which may offer improved resolution and clean trenches for liftoff. Our experimental data indicate that using a low temperature (4-10 deg. C) development step enables us to reproducibly obtain sub-10 nm trenches. Development temperature plays an important role in the determination of the cleanliness of the surface in the trenches, final opening dimensions and properties of the pattern. Using this technique, we have also developed a liftoff process for patterning 5 nm Au nano-particles.

A study of the temperature-dependent development of PMMA is followed using atomic force microscopy (AFM) metrology [15-17] and scanning electron microscopy (SEM). Its effects on dose requirements, EBL resolution, pattern roughness, trench cleanliness, and cross-sectional shape are investigated. Our results show that decreasing the development temperature does not significantly affect contrast, but is found to decrease the sensitivity of PMMA to the developer, which proves to have positive repercussions. Also, our dose-exposure curves clearly show that low-temperature development results in a shorter "tail" past the critical dose (CD) on the developer curve. This also contributes to higher resolution.

II. Experiments And Results

A. EBL system and process

A Hitachi S-4500 cold cathode field emission (CCFE) SEM has been converted to perform beam raster writing [18] using a custom pattern generator [19]. A high-speed beam blanker has been installed in the SEM [20]. System noise has been significantly reduced by isolating noise sources and eliminating electrical ground loops.

EBL is performed at 30 kV with a spot size of 1~2 nm, as determined from high-resolution images. 30~70 nm, 950K amu PMMA is used as positive resist. Isopropyl alcohol: methyl isobutyl ketone (3:1) with 1.5 vol % methyl ethyl ketone has been used as developer because of its high contrast [21]. During development, 10 ml of developer is cooled to the desired temperature of 4 ~ 10 deg. C with a precision of 1 deg. C. The 0.5 cm^2 sample is initially at room temperature, from 22 to 26 deg. Development time varies from 7 s to 90 s depending on the PMMA film thickness, developer temperature and exposure dose. Typically, development time is longer for lower doses, lower temperatures, and thicker films.

For SEM examination, either 1-2 nm thick Cr is sputtered on the samples by an Emitech model 660 plasma sputter coater, or 1-2 nm thick AuPd is evaporated by thermal evaporation.

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B. *Intrinsic EBL resolution*

Because of the difficulty of pattern transfer of sub-10 nm EBL due to poor etch resistance of PMMA, metal grain-size limitations [22], liftoff problems with thin resist films, PMMA grain-size [16] and other unknown factors, we discuss here only the intrinsic resolution [8], i.e. the linewidth after development and before pattern transfer, to describe the resolution of our EBL process. By using a cold development process, we have reproducibly obtained PMMA trenches narrower than 10 nm, as shown in Fig. 1. Line dose is about 9×10^{-10} C/cm. These clearly resolved PMMA trenches can be used for molecular QCA patterning and Au nano-particle applications. Note that beam noise due to irregular electron emission from the cold field emission cathode is not significant. This may be due to increased averaging required of the higher dose in the cold development process.

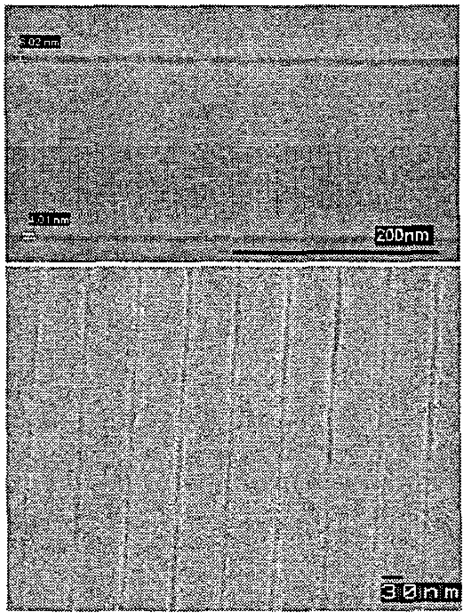

Figure 1. Intrinsic resolution of EBL on 60 nm thick PMMA by CCFE EBL system at 30 kV with development at 6 deg. C for 30 s. 4-nm-wide and 6-nm-wide lines are shown in the top figure. 6~10-nm-width grating lines are shown at the bottom. Samples are sputter-coated with 1-2 nm Cr. Linewidths are measured by our calibrated SEM measurement function and SEMICAPS [23] digital image capture system. The system is calibrated with a certified sample [24] with 0.5% accuracy.

C. *Liftoff process for Au nanoparticle*

A liftoff process of Au nano-particles was developed. Figure 2 shows the Au nano-particle attachment and liftoff process. The average diameter of the Au nano-particles is 5.7 nm as measured with scanning tunneling microscopy and AFM. Liftoff patterns after EBL and low temperature development are shown in Fig. 3. A single-particle-width liftoff line was obtained, as shown in Fig. 3c. Since the Au nano-particles do not attach to PMMA, we conclude that the trench bottom is clear after low temperature development. Au nano-particle patterns defined by EBL can potentially be used for multiple-junction single electron transistors [25].

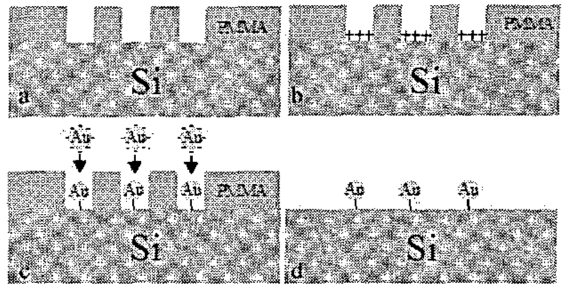

Figure 2. Schematic of Au nanoparticle attachment and liftoff process. a) formation of PMMA trenches by EBL and developed at 6 deg. C; b) sample is soaked in p-lysine for 10 min to make trench bottom positively charged; c) Au-particle attachment for 10~20 hours; d) PMMA removed by acetone or 2-dichlorobenzene [26], leaving the liftoff patterns of Au nanoparticles.

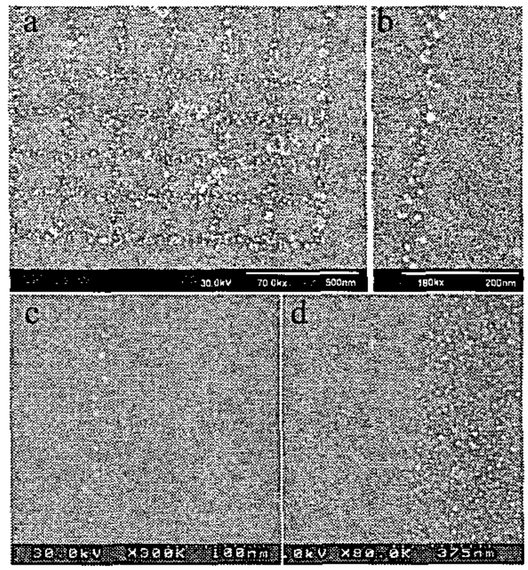

Figure 3. Liftoff patterns of Au nano-particles show the cleanliness of the developed area. a) Grid patterns; b) multiple-particle-width line; c) single-particle-width line; d) clean square edge demonstrating high quality liftoff.

D. *AFM measurement of contrast*

As described previously, by using the cold development technique, we have successfully achieved sub-10 nm PMMA trenches and liftoff of Au nano-particles. These results were not obtainable in our laboratory with the conventional room temperature process. Similar results reported in the literature [8-11] were obtained by systems with accelerating voltages of 50 to 300 kV and comparable smaller beam diameters. In order to understand our results, we performed a systematic study of cold development using AFM methodology [16][17]. We measured the contrast of PMMA resist developed at several different temperatures using the method described in [17]. However, in order to measure the square depths more precisely and therefore to minimize measurement errors, we decreased the pixel spacing in the EBL pattern generator to 1 nm and de-focused the beam slightly so that the roughness of the feature bottom is minimized. Roughness of the square bottoms is about 0.5 ~ 2 nm depending on the dose. Roughness is relatively high in squares with dose close to the CD. Figure 4 shows an AFM image of the exposed squares with graduated doses and cross-section profile. Roughness of the exposed squares is acceptable. The measured dose-exposure contrast curve is shown in Fig. 5. Variations on the tails of the curves are due to the roughness of PMMA, roughness of square bottoms, and AFM measurement errors.

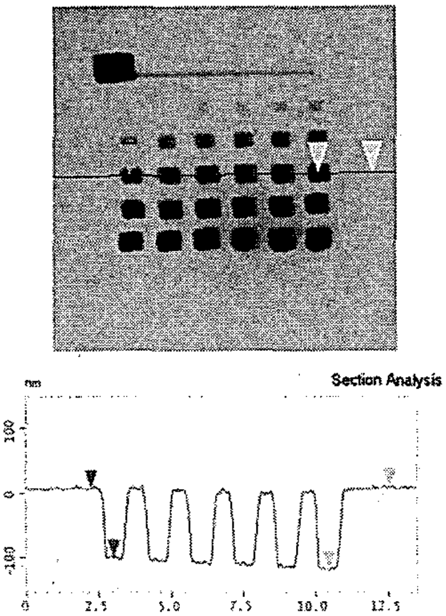

Figure 4. AFM image of exposed PMMA patterns, which are used to measure contrast curve. The cross-sectional analysis shows that the roughness of developed squares is minimized to an acceptible level.

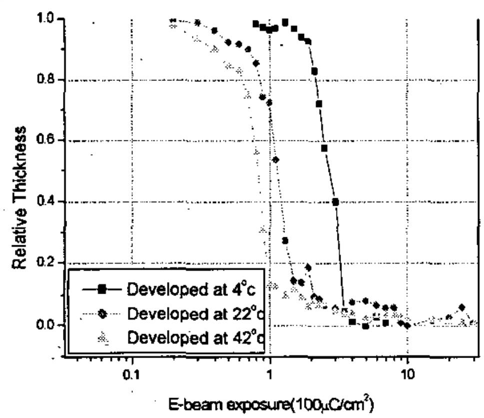

Figure 5. Development contrast at three different temperatures measured by AFM.

From the contrast lines in Fig. 5, we did not see significant change of contrast between different development temperatures. Instead, we note that temperature affects the sensitivity and therefore, for a given dose, the intrinsic linewidth. The ultimate intrinsic linewidth is determined by the combination of dose and development temperature.

III. DISCUSSION

From our experimental results, we found that low temperature development enables us to achieve sub-10 nm EBL. Another issue, though, is the quality of the pattern. The following experiment compares the quality of PMMA trenches with the same width but developed at different temperatures. Two exposures were performed with the same parameters, PMMA resist preparation and Cr thickness. The first sample was developed at 6 deg. C while the second at 26 deg. C. The exposed patterns were gratings with graded doses. The two samples were imaged side by side. Lines with different doses but with the same 8~10 nm width are compared in Fig. 7. It appears that lines on the left side, developed at 6 deg. C, resulted in better line quality, and the image is better resolved. The image contrast and brightness in both images are automatically adjusted by the SEM to achieve the same average values. The lines developed at room temperature are always poorly resolved compared with those development at colder temperatures.

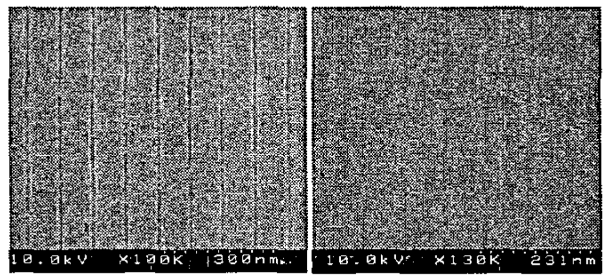

Figure 6. Comparison of 10-nm-wide intrinsic PMMA lines developed at 6 deg. C (left) and 26 deg. C. (right). The doses for the left and right lines were 8e-10 C/cm and 3e-10 C/cm, respectively.

It is useful to understand the relationship between development temperature and other key issues of high-resolution EBL, such as resolution, dose, resist thickness and bottom cleanliness. As mentioned at the end of section II, intrinsic resolution is mainly determined by the combination of dose and developer temperature. To fabricate the narrowest PMMA trenches by EBL, we can either use the lowest possible dose and develop at room temperature (normal EBL process), or use higher dose but develop at lower temperature (our cold development process). In order to compare both EBL processes, we need to specify the requirements of a successful lithography process: high spatial resolution, clean trench bottom for liftoff, high trench quality such as low line edge roughness (LER), and low unexposed resist roughness. The cleanliness of trench bottom and elimination of bridging effects between exposed pixels [8][17] are very important for the liftoff process. Chen and Ahmed [9] have reported that using ultrasonic development enabled them to achieve EBL below 10 nm, which is believed to be the ultimate limit of EBL [27]. In their case, low doses are used, and ultrasonic development helps in the removal of degraded molecules. Well-resolved intrinsic and liftoff lines were obtained [9][11] due to either the ultrasonic development that may help to clean trench bottoms or to the high-energy (80-200 kV) and small beam size (< 5 nm) of the EBL system. Instead, we use higher dose (3 times higher) to decrease further and more uniformly the molecular weight of the PMMA in the center of the line, and thereby reduce the residue. Then, using low temperature development to reduce development sensitivity, only the center part of the

PMMA trench is etched by the developer, and sub-10 nm lines are fabricated with better quality. Clean trench bottoms are insured with high-dose exposure, and proven by the nano-particle liftoff process. Our future work will investigate the combination of these two techniques.

As for the resolution, we have noted the tail shapes of the contrast curves in Fig. 5. For low-temperature development, the higher dose and lower sensitivity result in a shorter "tail" on the developer curve past the CD, D_f, so that the required dose to clear the bottom of the trench lies closer to D_f. Because of this, the minimum deposited energy to clear the trench is more narrowly confined to the center of the trench near the primary beam.

Low-temperature development requires more development time to etch through the trench [28], however the dissolution rate of PMMA is also reduced and therefore compensates the longer development time. To reduce development time, ultra-thin resist (less than 30 nm) can be used. With ultrathin resist, the height-width ratio of the trench is reduced and development will be more efficient. However, preparation of ultrathin PMMA resist can be limited by resist defects, PMMA grain size and uniformity. Reference [16] reported that with higher dose, the grating LER is improved.

As for cross-section, it has been reported that on a chemically amplified resist, cold development enhances cross-sectional shapes for liftoff [29] although no significant improvement of contrast is achieved.

Using the low-temperature development method, we can fabricate sub-10 nm clean trenches at 30 kV. Figure 7 shows the application for molecular QCA patterning.

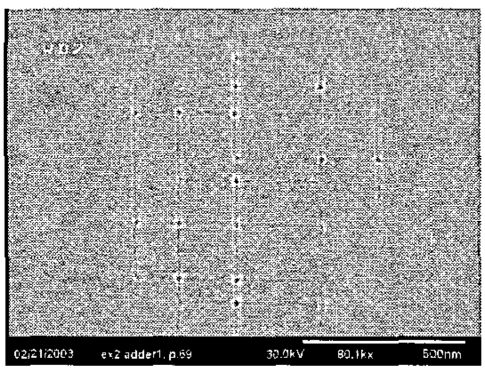

Figure 7. A SEM image of a one-bit full adder pattern defined by EBL and covered with 1 nm thick Cr using low temperature development for molecular QCA application. The linewidth is about 8 nm. PMMA thickness is about 60 nm.

IV. SUMMARY

We have reported an EBL process using low-temperature development to achieve sub-10 nm EBL and liftoff process for Au nano-particle patterning. To understand our results, we studied low-temperature development using AFM metrology. Several issues of sub-10-nm EBL were discussed and explanation for higher resolution is proposed that incorporates the slower dissolution rate and higher doses.

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