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# Nanometer-Scale Patterning of Polystyrene Resists in Low-Voltage Electron Beam Lithography

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We studied nanometer-scale patterning using a polystyrene negative resist in electron beam lithography. We found that the use of a low-molecular-weight polystyrene enables 10-nm-level patterning at low-acceleration voltage. We also found that the spot dose of such ultrasmall patterns formed at a 5 kV acceleration voltage was one-tenth of that formed at 50 kV. Low-voltage electron beam lithography is a suitable technique for organic resist nanopatterning. The Charlesby theory can still be applied to nanodot formation, and we can therefore estimate the dot sensitivity for various polystyrene molecular weights. We suppose that an exposure model is based on polymer aggregation to explain the formation of a 10-nm-level pattern with a height of 40 nm can be formed by using a small molecule, not a large one.

KEYWORDS: electron beam lithography, low-energy electron beam, nanolithography, negative resist, polystyrene

## 1. Introduction

Nanolithography is an important technique in the fabrication of ultrasmall the metal-oxide-semiconductor (MOS) transistors and quantum devices with sizes from 10 to 100 nm.[1–3] Electron beam lithography has been the most widely used and is the most useful tool in nanometer-structure fabrication. We achieved about 10 nm negative-resist patterning under 50 keV electron beam irradiation using polystyrene with a molecular weight of about 1000.[4] Polystyrene $(-CH(C_6H_5)CH_2-)_n$ is a chain of styrene monomers (Fig. 1), and various molecular weight polystyrenes with a monodispersity are available. As an electron beam is irradiated, polystyrene resist undergoes simple cross-linking without additional reactions, which enhances its sensitivity to the beam.[5] Therefore, polystyrene seems to be a suitable negative resist for investigating the resolution limit dependence on molecular weight in electron beam lithography. We previously found that the minimum feature size does not depend on the molecular structure, but on the molecular weight. We found that the use of chain-structure polystyrene with a molecular weight of 800 led to the same resolution (minimum pattern size) as that obtained using Calixarene which has a ring structure and a molecular weight of 925.[6]

It is well known that low-voltage electron beam lithography has advantages in terms of high sensitivity, and 40 nm line patterns made using a poly (methyl methacrylate) (PMMA) resist at a 2.5 kV acceleration voltage have been reported.[7] In this paper, we report on the fabrication of a 10-nm-level dot, using low-molecular-weight polystyrene as the resist under low-energy electron beam irradiation. We also report on the exposure characteristics at acceleration voltages of 3 to 50 kV and we discuss a dot formation model.

## 2. Experimental

We prepared polystyrene films by a conventional spin-coating process. The polystyrene powder (Scientific Polymer Products, Inc. and Pressure Chemical Co.) used had a dispersity of about 1. Polystyrene powders with molecular weights of 1100, 2000 and 17500 (hereafter referred to as $M_w$1100, $M_w$2000 and $M_w$17500, respectively) were dissolved at 1.5 wt% in monochlorobenzene. The resist solution was spun on Si substrates at 4000 rpm for 60 s and about 40-nm-thick resist films were obtained. After spin-coating, the excess solvent in the resist films for $M_w$17500 polystyrene was eliminated by prebaking at 120°C for 30 min. The resist films for $M_w$1100 and $M_w$2000 were dried at room temperature for 1 day in an $N_2$ gas flow chamber, because high-temperature baking would have caused the films to segregate. We used a JBX-5FE (JEOL) electron-beam writing system at acceleration voltages of 25 and 50 kV and a high-resolution scanning electron microscope (SEM), S5000 (Hitachi) with acceleration voltages from 3 to 30 kV. In forming dot patterns, the beam diameter of the JBX-5FE was measured to be about 6.5 nm ($2\sigma$) and that of the S5000 was estimated to be below 2 nm. The beam current was 100 pA at an acceleration voltage of 50 kV and 10–60 pA at an acceleration voltages from 3 to 30 kV. After exposure, the resists were developed by dipping substrates into xylene for 30 s, followed by rinsing by dipping them in isopropyl-alcohol for 30 s.

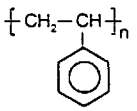

Fig. 1. Chemical structure of polystyrene.

## 3. Resist Sensitivities

Figure 2(a) shows the sensitivity characteristics of the $M_w$1100 polystyrene when a 3- to 50-keV electron beam is irradiated onto it. After development, the resist thickness of the exposed area was measured using Alpha-Step 2000 (Tencor Instruments). When the electron energy decreased, the electron dose decreased. The area dose here was defined as the dose that resulted in 50% of

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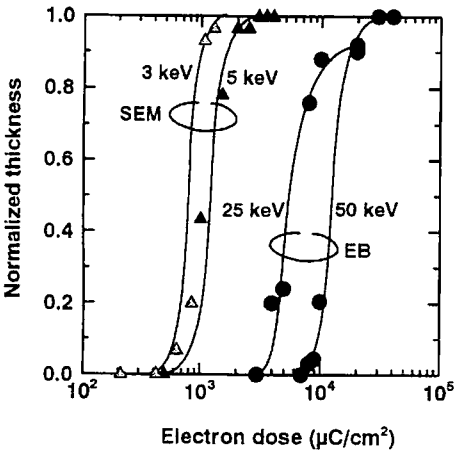
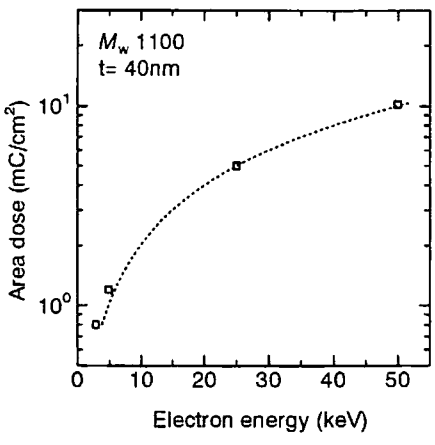
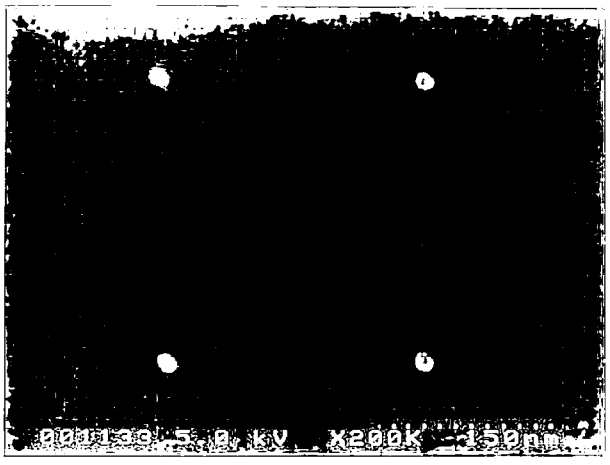



(a)

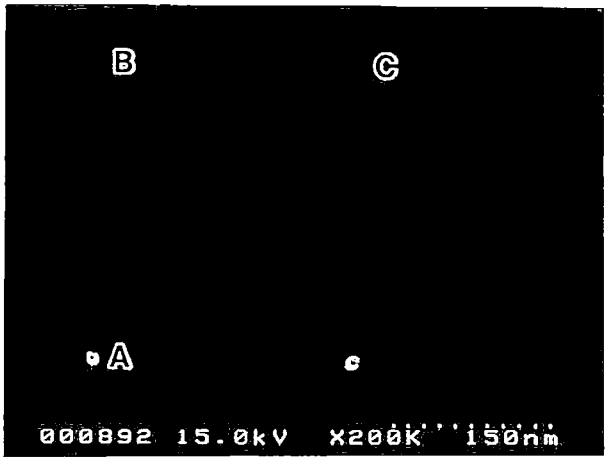



(b)

Fig. 2. Sensitivity characteristics: (a) sensitivity curves for various acceleration voltages of $M_w$1100 polystyrene, (b) sensitivity versus acceleration voltage.




(a)




(b)

Fig. 3. Typical SEM image of isolated dots for $M_w$1100 polystyrene resist; electron energy was (a) at 5 keV and (b) 15 keV. Electron dose for each pattern was 18 fC/dot at 5 keV and 23 fC/dot at 15 keV. Dot A is about 12 nm in diameter, 35 nm in height. Dots B and C fell down on the Si substrate.

the thickness remaining after development. Figure 2(b) shows the dependence of area dose on the electron energy. The sensitivity at 5 keV was 10 times higher than that at 50 keV. With decreasing electron energy, the resist attained high sensitivity, because the energy transfer ratio from the incident electrons to the resist in the unit path length became higher. This can be explained well by the Bethe equation.

$$E_{\text{loss}} \propto 1/E \cdot \log(\alpha E) \quad (\alpha = \text{constant}).$$

## 4. 10-nm-Size Polystyrene Pattern

At low electron energy, $M_w$1100 polystyrene can also be used to form 10-nm-level dots, which are the same as those at 50 keV.[4] Figure 3 shows SEM images of the isolated resist dot pattern for $M_w$1100 polystyrene formed (a) at 5 keV and (b) at 15 keV. The electron doses for each dot were designed to achieve (a) 18 fC/dot and (b) 23 fC/dot. All dots have diameters of around 10 nm. The diameter of dot A was about 12 nm and the height was about 35 nm. On the other hand, dots B and C fell down on the Si substrate because electron doses were not sufficient for the dot pillars to stand on the substrate. Also, dot C was deformed because the resist cross-link seemed to be inadequate and a part of the resist pattern may have dissolved during development. The beam current was unstable because a cold field emission gun of S5000 was used and hence the irradiated point fluctuated, resulting in fluctuations in spot dose during exposure. Therefore, fine control of the exposure dose is needed because dot formation is quite sensitive to the electron dose. In addition, this suggests that when the electron dose is below 23 fC/dot at 15 keV, dots below 10 nm in diameter cannot be formed, but deformed dots are formed. Using $M_w$1100 polystyrene resist 40 nm thick, the smallest resist pattern obtained was around 10 nm.

## 5. Polystyrene Dot Size Dependence on Spot Dose for Various Molecular Weights

Figure 4 shows the dot size dependence on the spot dose as a function of the molecular weight when the electron energy is 15 keV. For each molecular weight, dot size decreased with decreasing spot dose. The spot dose required for $M_w$1100 polystyrene to form about

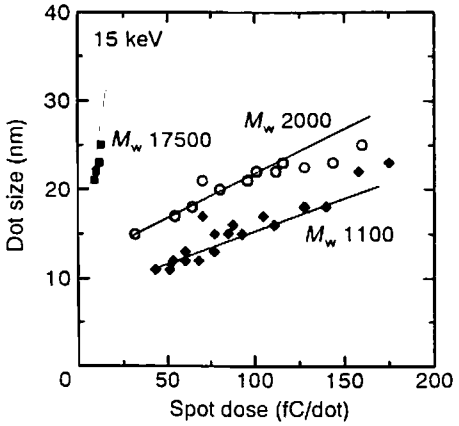



Fig. 4. Dependence of dot size on spot dose for $M_w$1100, $M_w$2000 and $M_w$17500 polystyrene at 15 keV.

a 20-nm-diameter dot was about 2 times higher than that for $M_w$2000 and about 15 times higher than that for $M_w$17500 polystyrene. The spot dose required to form the same dot size for each molecular weight was inversely proportional to the molecular weight. Moreover, the inclination became higher with increasing molecular weight: $I_{M_w1100}$:$I_{M_w2000}$:$I_{M_w17500}$=1:1.5:16.5 ($I$=inclination). Therefore, the inclination of dot-size dependence on the spot dose was almost proportional to the molecular weight. This suggests that our experiments correspond well with the Charlesby theory.[8]

$$\text{Gel point/Molecular weight} = \text{constant}.$$

At an electron energy of 5 keV, the dot size dependence on the spot dose as a function of the molecular weight had roughly the same tendency as that at 15 keV. The Charlesby theory can still be applied to such ultrasmall patterning. If we obtain the spot dose for one molecular weight, we can calculate the dot sensitivity by using the polystyrene molecular weight.

Figure 4 also shows that the minimum dot size decreased with decreasing polystyrene molecular weight. The volume of an $M_w$1100 polystyrene molecule was estimated to be about 1 cubic nanometer and that of an $M_w$17500 polystyrene molecule was about $(2.5\,\text{nm})^3$ when we assumed the polystyrene film density to be $1\,\text{g/cm}^3$. According to the experimental results, large molecules could not form 10 nm dots, but small molecules with a molecular weight of about 1000 could. In order to explain the minimum-dot-size characteristics, we suppose an exposure model from the viewpoints of molecular aggregation. The exposure model considered, based on polymer aggregation, is schematically shown in Fig. 5. One molecule of polystyrene may have an entwined structure in solution and spin-coated polystyrene film may have a structure textured by polystyrene strings. Since the length of a polystyrene string of $M_w$17500 is estimated to be roughly 50 nm. $M_w$17500 dots probably have some polystyrene strings pinned to a small exposed region, as shown in Fig. 5(a). When resist dots are developed by dipping the substrates and drying by blowing of $N_2$ gas, strings may aggregate, as shown in Fig. 5(b), and the dots will grow by the aggregation process of these

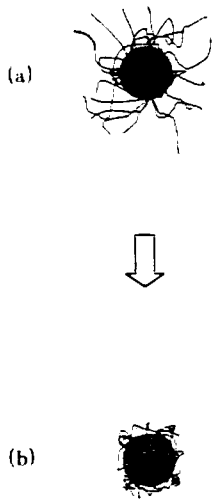



Fig. 5. Exposure models from the viewpoints of polymer aggregation. The gray circle shows an exposed area. (a) Polystyrene strings are pinned to an exposed area and (b) may aggregate.

strings. In our experiments, the resist thickness was set at about 40 nm and the aspect ratio of the dots with a 10 nm diameter was high; therefore fabrication of 10-nm-level dots was greatly influenced by the development processes. In particular, adhesion between dots and substrates seems to be important for fabricating small dots. To solve the problem discussed above, some precise experiments must be carried out on ultrathin resists.

## 6. Dot Size Dependence on Spot Dose at Various Electron Energies

The dot size dependence on the spot dose for each electron energy using $M_w$1100 polystyrene and $M_w$2000 polystyrene is shown in Fig. 6. For each molecular weight, the dot size was almost proportional to the spot dose and the inclination became larger with decreasing electron energy. The difference in inclinations was presumably due to the difference in the deposited energy distribution.

The minimum dot sizes, about 12 nm for $M_w$1100 and 15 nm for $M_w$17500, were not changed at various acceleration voltages for each polystyrene. For each molecular weight, the required spot dose decreased with decreasing acceleration voltage, and the spot dose at 5 keV was one-tenth of that at 50 keV. The minimum-dot-size dependence on the electron energy could be explained well by considering the forward electron scattering. The scattering angle of a primary electron at 5 keV is larger than that at 50 keV. Therefore, if the same electron dose was provided at both 5 keV and 50 keV, the dot diameter at 5 keV should be larger than that at 50 keV. However, the resist sensitivity at 5 keV is 10 times higher than that at 50 keV, thus a polystyrene dot can be formed at one-tenth of the dose required for 50 keV. This means that the area of effective energy deposition was estimated to be the same at both 5 keV and 50 keV.

The above results suggest that low-voltage electron beam lithography has some advantages, such as high throughput due to high sensitivity, high resolution which is the same as that in 50 keV electron beam lithogra-

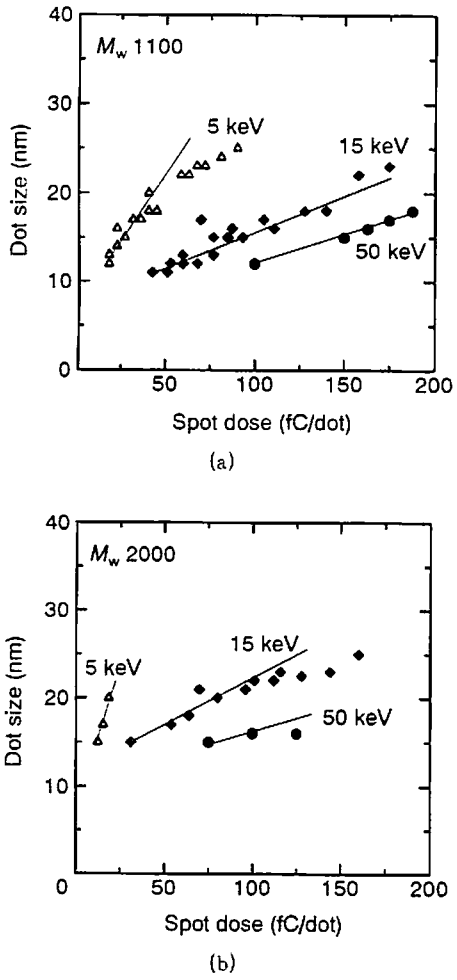



Fig. 6. Dependence of dot size on spot dose for various electron energies: (a) $M_w$1100 polystyrene. (b) $M_w$2000 polystyrene.

phy, a narrower area of secondary electron scattering, and less substrate damage.[9,10] We propose that a low-energy electron beam with a small spot size and a thin resist with a molecular weight of about 1000 is suitable for 10-nm-scale patterning.

## 7. Conclusion

We studied polystyrene nanodot formation and dot exposure characteristics using 5 to 50 kV electron beam lithography. We found that the Charlesby theory still holds in nanodot formation using polystyrene resists at 5 to 50 keV: dot sensitivity is proportional to the reciprocal of the polystyrene molecular weight. Therefore, we can estimate the dot sensitivity of a resist on the basis of its molecular weight. The minimum dot size depends on the polystyrene molecular weight and a 10-nm-level dot can be formed by using a small molecule with a molecular weight of about 1000 not a large one. We supposed a dot exposure model which is based on polymer aggregation. Low-voltage electron beam lithography at 5 keV has advantage of high sensitivity, while the minimum pattern size stayed at about 10 nm. Our results suggest that the use of a low-energy electron beam with a low-molecular-weight resist is useful for nanolithography.

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