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Dry thermal development of negative electron beam resist polystyrene

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Abstract. We report dry thermal development of negative resist polystyrene with low molecular weight. When developed on a hotplate at 350oC for 30 min, polystyrene showed reasonable high contrast and resolution (30 nm half-pitch), but low sensitivity. Resist sensitivity was greatly improved at lower development temperatures, though at the cost of reduced contrast. In addition, we observed the thickness reduction due to thermal development was higher for larger remaining film thickness, implying the thermal development process is not just a surface process and the more volatile chains below the top surface may diffuse to the surface and get evaporated.

Keywords: electron beam lithography; resist development; polystyrene; nanostructure

1. Introduction

In electron beam lithography, the exposed resist is typically developed using a solvent or aqueous developer. Potential issues with liquid developer include resist swelling, pattern detachment due to poor adhesion to the substrate, and resist pattern deformation and collapse due to capillary force during developer drying. To reduce pattern collapse due to capillary force, supercritical drying using CO_2 or fluoro-compounds (e.g., SF_6 and C_2HF_5) can be employed (Namatsu 2000 and Namatsu 2004). However, pattern collapse may still occur due to the very high pressure of ~10 MPa during the supercritical drying process (Wahlbrink *et al*. 2006). Another way to minimize pattern collapse is by using sublimation of tert-butyl alcohol whose melting temperature is slightly above room temperature (Tanaka *et al.* 1993). One drawback of sublimation drying is that contaminant may be left behind on the resist pattern upon vaporization of solvent. Therefore, dry development is still desirable for some processes. Polymer or co-polymer resists such as PMMA and ZEP-520A were previously studied for dry thermal development, but without pattern clearance that makes subsequently dry etching of the thick residual layer necessary (Zheng *et al.* 2011).

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Here it is shown that dry development can be realized using a simple electron beam resist polystyrene (PS), which has demonstrated ultra-dense patterning using low molecular weight of 2 kg/mol, or ultra-high sensitivity lithography using high molecular weight of 900 kg/mol (Ma *et al.* 2011, Con *et al.* 2012). Another advantage of this simple resist is its low cost, practically unlimited shelf life, and high drying etching resistance compared to PMMA. The dry development is possible because exposed thus cross-linked PS evaporates at a slower rate than unexposed PS; therefore the resist maintains its negative tone like regular solvent development.

2. Methods

Polystyrene powder with molecular weights of 1.2 kg/mol (broad molecular weight distribution) and 2 kg/mol (narrow distribution with polydispersity 1.10) was dissolved in chlorobenzene. Here polystyrene with relatively low molecular weight was selected because it is more volatile than high molecular weight polystyrene at elevated temperatures for thermal development. The film thickness depends on the polystyrene concentration in the solvent and spin coating speed, ranging from 30 nm for 1.2 wt/vol % to 260 nm for 10 wt/vol % concentrations. The film was baked at 60°C for half an hour on a hotplate. Though typical polymer film can be baked at temperatures much higher than its glass transition temperature (e.g., PMMA is usually baked at 180°C), the thin polystyrene film having low molecular weight was not stable at baking temperatures above 80°C, and thus we chose this very low baking temperature.

Electron beam lithography was performed at 5 keV and 20 keV using a LEO 1530 field emission SEM that is equipped with Nabity nanometer pattern generation system (NPGS) and a Raith 150^{TWO} e-beam lithography system. The pattern contains arrays of large squares with a side length of 5 μm with exponentially varying doses that were used to obtain the contrast curve, and arrays of dense periodic lines that were used to determine the achievable resolution. The lines were exposed by single-pass exposure with a step size of 12 nm. After the exposure, the samples were developed thermally on a hotplate at 200°C to 350°C for 0.5-5.5 hours. Some samples were first developed using regular solvent developers (xylene for 30-72 sec, followed by rinsing with 2-propanol), then thermally developed in order to find out the net development rate (nm/sec). After development, the contrast curves were obtained by AFM measurement, and high resolution images of the exposed pattern were acquired using LEO 1530 SEM.

3. Results and discussion

The exposed pattern consisting of micro-scale squares showed up at development temperatures as low as 200°C. However, low temperature development led to poor contrast curve, as shown in Fig. 1(a) for 1.2 kg/mol polystyrene developed at 250°C for 120 min. It is not possible to derive a meaningful resist contrast from this curve, although clearly the contrast is very low. The low contrast is not a result of the resist’s broad molecular weight distribution, as it has been shown that the polydispersity (defined as Mw/Mn, the ratio of weight averaged molecular weight and number averaged molecular weight) had an insignificant effect on polystyrene’s exposure properties (Dey and Cui 2013). The resist sensitivity, defined as dose for 50% remaining thickness, is approximately 3000 μC/cm^2, which is close to wet solvent development. The low contrast makes the resist suitable only for grayscale lithography for which low contrast offers a broad process

window and high reproducibility (Dillon *et al.* 2008, Schleunitz *et al.* 2011). Fig. 1(b) shows the contrast curve for 2 kg/mol polystyrene developed at a high temperature of 350°C for 30 min, which gives a moderately high contrast (defined as $\gamma = (\log(D_{100}/D_0))^{-1}$) of 3.2, yet low sensitivity (D_{50}, dose for 50% remaining thickness) of 16 mC/cm^2. The sensitivity can be greatly increased by using low voltage exposure such as 2 keV, because resist sensitivity (dose) is proportional to electron energy according to Bethe equation for electron energy loss (E_{loss}) in the resist: $E_{loss} \propto 1/E \cdot \log(\alpha E)$ with α being a constant (Bethe *et al.* 1938, Kanaya and Okayama 1972). It should be noted that this temperature is close to the polystyrene decomposition temperature of approximately 650K (377°C), thus some degree of degradation is expected during the thermal development. To study the high resolution capability of the thermally developed polystyrene resist, dense periodic array of lines were exposed at 20 keV. As shown in Fig. 2 and expected from the resist contrast, reasonably high resolution of 30 nm half-pitch was achieved for thermal development at 350°C for 30 min. However, the obtained resolution is still much lower than polystyrene with the same molecular weight developed using a solvent, which has demonstrated 10 nm half-pitch patterning (Ma *et al.* 2011). Due to its low sensitivity, the line dose to define the arrays was a high value of 200 nC/cm.

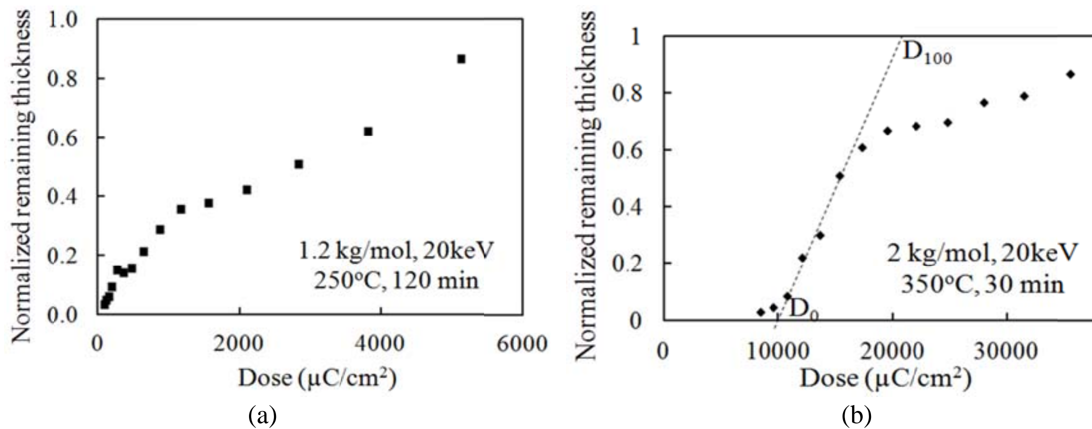

Fig. 1 Contrast curves exposed at 20 keV for (a) 1.2 kg/mol polystyrene thermally developed at 250°C for 120 min; and (b) 2 kg/mol polystyrene developed at 350°C for 30min

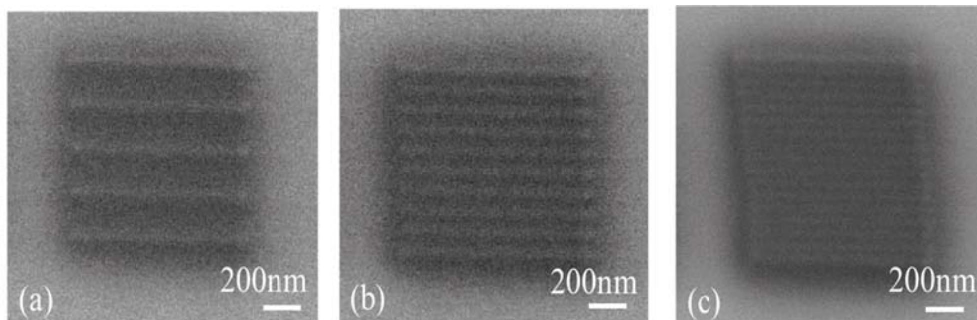

Fig. 2 SEM images of dense periodic line arrays exposed at 20 keV and 96 pA beam current in 2 kg/mol polystyrene thermally developed at 350°C for 30min.For imaging 1keV was used as it was hard to focus on pattern. (a) 200 nm pitch, 50 nm line-width; (b) 100 nm pitch; and (c) 60 nm pitch. Line dose was 200 nC/cm

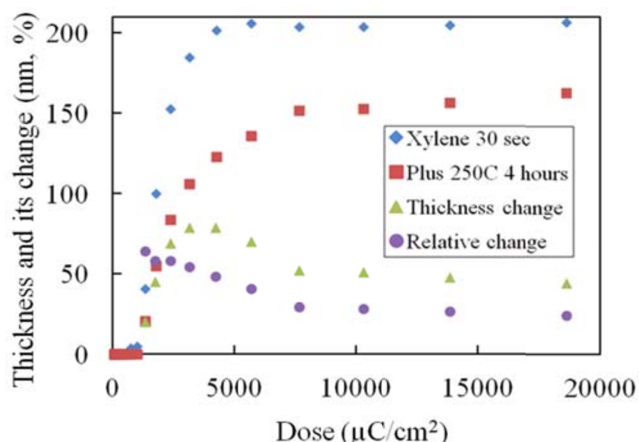

Fig. 3 Contrast curves for 1.2 kg/mol polystyrene exposed at 5 keV and developed first in xylene for 30 sec (diamond), and then thermally at 250°C for 4 hours (square). The absolute (triangle,nm) and relative (circle,%) thickness change due to thermal development are also shown for doses that led to non-zero remaining thickness after thermal development. The relative change is defined as the ratio of absolute thickness change and average thickness before and after thermal development

It is known that for regular solvent development, the development process proceeds from the resist surface towards the bottom, but not at a constant dissolution rate – for positive tone resist the kinetic diffusion-driven process predicts a reduced rate dz/dt as z increases (here t is the time of dissolution and z is depth reached at time t) (Mohammad *et al.* 2012). To investigate the thermal development process, the exposed pattern was first developed by using a solvent xylene to fully dissolve the unexposed polystyrene and partially dissolve the exposed one, thus creating an array of square pattern with different heights. Next, thermal development was used to obtain the vaporization rate. Fig. 3 shows the contrast curves for solvent development, solvent plus thermal development, as well as the absolute and relative thickness change (vaporization rate equals to thickness change divided by thermal development time). It is interesting to note that there exists a maximum thickness change, which corresponds to a large remaining thickness after wet development at moderate exposure dose. Therefore, the development process cannot be a purely surface process, for which monotonically decreasing thickness change versus exposure dose is expected since higher dose renders the resist more cross-linked and thus less volatile. This implies that the less cross-linked molecules are mobile at the high development temperature and can move to the surface and vaporize. The decreased dissolution rate for thinner resist thickness is also expected for solvent development, but due to a different mechanism (kinetic diffusion of the solvent molecules into the resist). In addition, the dependence of vaporization rate on remaining thickness for thermal development is more pronounced than solvent development. Nonetheless, the relative thickness change, defined as the ratio of absolute thickness change and average thickness before and after thermal development, decreases monotonically with exposure dose, which is expected since higher dose renders the resist less volatile at elevated temperature.

4. Conclusions

We have demonstrated dry thermal development of negative resist polystyrene. When

developed on a hotplate at 350°C for 30 min, polystyrene showed reasonable high contrast and resolution, but very low sensitivity. Resist sensitivity was greatly improved at lower development temperatures, though at the cost of reduced contrast. In addition, by developing the exposed pattern first using a solvent and then thermally, we observed the thickness reduction due to thermal development was larger for thicker patterns, implying the thermal development process is not just a surface process and the more volatile chains below the top surface may diffuse to the surface and get evaporated. However, as expected, the relative thickness change decreased monotonically with increased exposure dose.

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