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Polycarbonate electron beam resist using solvent developer

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ABSTRACT

Polycarbonate is a popular membrane material fabricated by ion track etching method and used for filtration, thus it is a sort of ion beam resist. Here we show that it can also be used as a positive electron beam resist using solvent development. Compared to the popular resist PMMA, polycarbonate is more chemically and thermally stable, and is more resistant to plasma dry etching. Various solvents, including cyclopentanone, xylene, pentyl acetate and methyl isobutyl ketone, were found to be suitable developers for polycarbonate when diluted properly with 2-propanol. The resist showed a low contrast between 0.5 and 1.0 when using those solvent developers, and thus it is not a good resist for defining high resolution dense patterns, yet is ideal for grayscale lithography to generate quasi-three dimensional structures like Fresnel zone-plate lens. Nevertheless, we achieved sub-50 nm resolution for sparse line array pattern.
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1. Introduction

Electron beam lithography (EBL) [1], focused ion beam (FIB) lithography [2], and nanoimprint lithography (NIL) [3] are currently the three most widely employed nanolithography techniques. Amongst them, EBL is undoubtedly the most popular for R&D. Sensitivity and contrast are the two most important resist properties. Higher sensitivity is always desirable since it allows fast writing. As for contrast, high contrast is usually preferable since it offers high resolution patterning. It has been proven that resists having high sensitivity tend to have low contrast, and vice versa [4]. For instance, regarding resist development temperature (keeping other experimental conditions identical), cold development of positive resists such as PMMA and ZEP enhances contrast but lowers sensitivity [4]. Regarding resist molecular weight, higher molecular weight (Mw) polystyrene (negative chain cross-linking resist) offers higher sensitivity than lower Mw polystyrene, but gives lower contrast and thus lower resolution [5,6]. Other important resist properties include chemical inertness, thermal stability, and dry etch resistance. PMMA (the most popular positive resist) is far from ideal in those aspects. The arguably second most popular positive resist, ZEP, offers much higher (roughly three times) dry etch resistance than PMMA due to the stable phenyl group in its structure. Polycarbonate (PC), which is the focus of the current study, offers significantly higher chemical and thermal stability than both PMMA and ZEP, and its dry etch resistance (to oxygen plasma RIE), though not as high as ZEP resist, is approximately twice that of PMMA.

Owing to its chemical and thermal stability, PC has been widely used for filtration and nano-wire or nano-tube synthesis applications with the through-film hole created by the ion-track etch process [7–11]. As such, PC is a sort of ion beam resist. Recently it has been demonstrated that PC can also be used as an electron beam resist with hot aqueous NaOH as developer and gold film as sublayer [12]. A serious concern is the potential attack of the substrate material by hot NaOH solution and the weak adhesion of PC to typical substrate materials such as silicon, which lead to film detachment during development. It is therefore desirable to replace the hot basic development with room temperature solvent development. In this study we show that PC can be developed using solvent, but with very low contrast. Thus, PC is a suitable resist for grayscale lithography.

Grayscale lithography is commonly used to generate 3D structures such as arbitrarily sloped sidewall, multi-level zone plate/Fresnel lens, and micro-lens with hemispherical shape [13,14]. The 3D features are achieved in a single resist layer by positive or negative tone electron beam resist. While in principle high resolution resist with high contrast such as PMMA can be used for grayscale lithography, this is not desirable because a slight variation of exposure dose (or development temperature) would result in a considerable change in resist height after development, thereby leading to a very narrow process window. In contrast, low contrast resist such as polycarbonate developed using a solvent offers a broad process window for reproducible results.

2. Experimental

To dissolve PC, we tested many different solvents including dioxane, 1, 2, 3 – trichloropropane, tetrahydrofuran,

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dichlorobenzene, and cyclopentanone. However, unlike PMMA or ZEP resist, most solvents cannot easily dissolve PC to form a homogeneous transparent solution. It was found that dissolution could be facilitated by using ultrasonic agitation for several hours. Cyclopentanone was identified as the best solvent that can dissolve PC pellets (2.5 wt/vol% that gave 95 nm film thickness by spin-coating at 2000 rpm) in ~10 h, or in ~4 h with ultrasonic agitation. For higher concentration such as 10 wt/vol% that gave 1200 nm film thickness, ultrasonic agitation was essential for the dissolution (not completely dissolving even after more than three days without ultrasonic agitation).

It is natural to first try cyclopentanone as developer. Since cyclopentanone quickly dissolves unexposed PC film, it must be diluted with a non-solvent in order to act as a reasonably good developer. We diluted cyclopentanone with 2-propanol (IPA) gradually until the mixture was found to not attack the unexposed PC film significantly within three minutes of soaking. This is obtained with cyclopentanone: IPA = 1:3. Using a similar screening procedure, we also studied other solvent developers including xylene, pentyl acetate (both are developers for ZEP), methyl isobutyl ketone (MIBK, developer for PMMA), and propylene glycol monomethyl ether acetate (PGMEA, developer for SU-8). All of those solvent developers, when properly diluted with IPA, can act as developer for PC with performance similar to diluted cyclopentanone.

We dissolved 60 kg/mol (polydispersity unknown) bisphenol A polycarbonate (Scientific Polymer Products Inc.) in cyclopentanone. We selected this molecular weight mainly due to its availability from the supplier. Unlike negative chain cross-linking resist such as polystyrene, for positive chain scission resist it is expected that molecular weight would not greatly affect the exposure properties, nor is its distribution (i.e. polydispersity). [15–16] The film was then baked on a hotplate at 140 °C for 2 min. After exposure at 20 keV using Raith 150^{TWO} electron beam lithography system, the resist was developed for 0.5–1 min at room temperature followed by IPA rinsing and nitrogen drying.

To attain the contrast curves, the pattern containing 5 × 5 array of squares each 5 × 5 μm was exposed with exponentially increasing doses. The wide range of exposure doses enabled detailed study of PC resist's performance. After development, the pattern depth was measured using atomic force microscope (AFM) to generate the contrast curves. To study PC's high resolution capability, single-pass lines at various doses were also exposed using the same condition and the lines were examined using SEM after development.

3. Results and discussion

Fig. 1 shows the contrast curve of polycarbonate exposed at 20 keV and developed using cyclopentanone: IPA = 1:3 for 1 min at room temperature. Fig. 1b is the contrast curve with dose in log-scale in order to better present the curve for low doses. The dose for clearance (D_{100}) is approximately 2000 μC/cm^2; that for 50% remaining thickness (D_{50}) is approximately 180 μC/cm^2; and D_0 is 25 μC/cm^2. This leads to a contrast (defined as $\gamma=[\log_{10}(D_{100}/D_0)]^{-1}$) of 0.53, which is a very low value. Thus, solvent-developed PC is not suitable for defining high resolution dense pattern. Fig. 1c is the contrast curve with dose in linear scale. It is not possible to derive a meaningful contrast as the D_0 value would approach 0 μC/cm^2. Fig. 1c indicates that the remaining resist thickness drops very fast with increasing doses when the dose is low (<300 μC/cm^2), but then the residual layer becomes less easy to dissolve as the dose increases.

The contrast curves for PC developed using xylene (p-, m-, o-mixed) and pentyl acetate are shown in Fig. 2 and Fig. 3, respectively. Both solvents were diluted with IPA at 1:3 volume ratio.

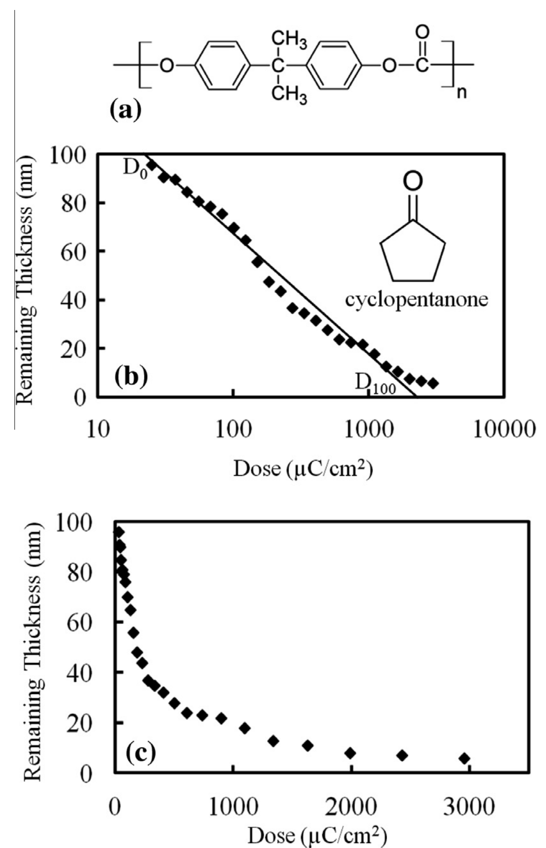

Fig. 1. (a) Chemical structure of bisphenol A polycarbonate; (b) Contrast curve for polycarbonate exposed at 20 keV and developed by cyclopentanone: IPA = 1:3 for 1 min, with the dose in log-scale; and (c) Same as (b) but with dose in linear-scale.

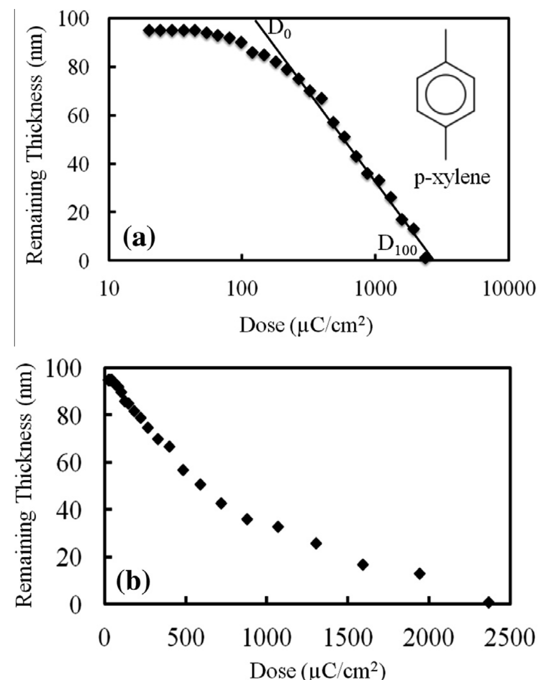

Fig. 2. Contrast curve for polycarbonate exposed at 20 keV and developed by xylene: IPA = 1:3 for 1 min, with dose in log-scale (a) and linear-scale (b). The xylene is p-, m-, o- mixed.

When using xylene as developer, the resist sensitivity (D_{100}) and contrast are 2360 μC/cm^2 and 0.84, respectively; and those for

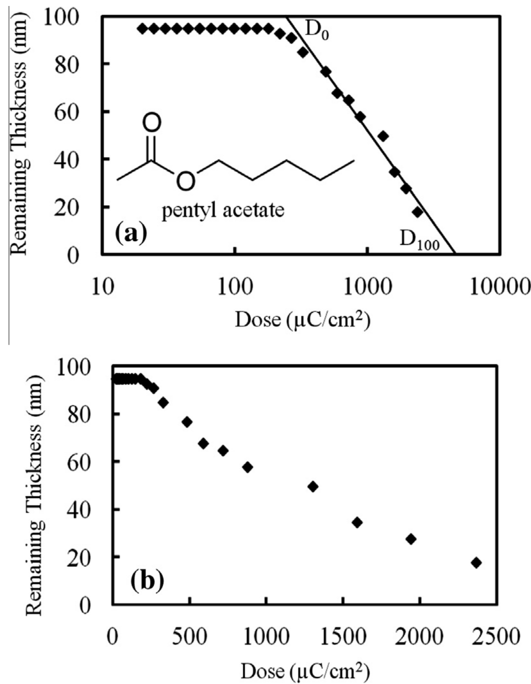

Fig. 3. Contrast curve for polycarbonate exposed at 20 keV and developed by pentyl acetate: IPA = 1:3 for 0.5 min, with dose in log-scale (a) and linear-scale (b).

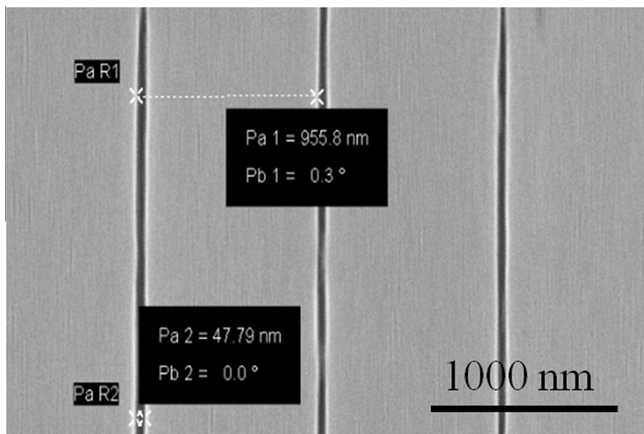

Fig. 4. SEM image of line array pattern exposed in PC at 20 keV and developed by cyclopentanone (diluted with IPA at 1:3 volume ratio). The line width is close to 50 nm and array period is 1000 nm.

pentyl acetate, 2800 μC/cm^2 and 0.91, respectively. The contrast for both solvent developers is higher than cyclopentanone, yet still much lower than typical high resolution resist. We also studied other solvent developers diluted with IPA at 1:3 ratio, such as PGMEA (developer for SU-8) and MIBK (developer for PMMA), and found that both can act as developer for PC with performance similar to the above solvent developers.

Although the low contrast suggests that PC is suitable for grayscale lithography but not for defining high resolution dense patterns, PC is able to pattern sparse high resolution features. In fact, SU-8, which is also a very low contrast resist, has demonstrated high resolution of 24 nm when exposed at 100 keV [17]. Fig. 4 shows line array pattern with 1000 nm period exposed in PC at 20 keV and developed by diluted cyclopentanone, which gives a high resolution of 48 nm. This is possible when the pattern is sparse and/or the pattern area is significantly smaller than the range of backscattered electrons, such that the proximity effect is unimportant.

4. Summary

In this study, we investigated the possibility of using solvent as developer for polycarbonate electron beam resist, which is more desirable than the usual hot aqueous solution of NaOH developer. We found that actually many solvents (including cyclopentanone, MIBK, xylene, pentyl acetate, and PGMEA), when properly diluted by a non-solvent for polycarbonate (here IPA), can be used as developers for polycarbonate. All of the solvent developers we tested give a low contrast between 0.5 and 1.0, making polycarbonate a suitable resist for grayscale electron beam lithography. Despite its low contrast, polycarbonate can also be used for high resolution lithography when the pattern is not dense and/or the pattern area is much smaller than the range of backscattered electron (thus insignificant proximity effect); and we achieved sub-50 nm line-width definition for a line array with 1000 nm periodicity.

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