Polycarbonate as an ideal grayscale electron beam resist using diluted cyclopentanone developer

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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 [1]. Though in principle high resolution resist with high contrast such as PMMA can be used for grayscale lithography, they are not desirable because a slight variation of exposure dose (or development temperature) would result in a considerable change in resist height, leading to very narrow process window. As a consequence, resist having very low contrast is preferred for grayscale lithography with a broad process window for reproducible result.

Polycarbonate (PC) is more thermally and chemically stable than most other popular polymers such as PMMA, and it is widely used for filtration and nano-wire/tube synthesis applications with the through-film hole created by the ion-track etch process [2]. As such, PC is a kind of ion beam resist. Recently it was demonstrated that PC can also be used as an electron beam resist with hot aqueous NaOH as developer [3]. One serious issue is the weak adhesion of PC to typical substrate materials such as silicon, leading to film detachment during hot NaOH development. Here we will show that, using diluted cyclopentanone as developer, PC can achieve ultra-low contrast that is ideal for grayscale electron beam lithography.

In the experiment, we dissolved 60 kg/mol bisphenol A polycarbonate in cyclopentanone to make a 2.5 wt/vol% solution that gave a 95 nm film by spin-coating at 2000 rpm on a silicon wafer. The film was then baked on a hotplate at 140^{o}C for 2 min. After exposure at 20 keV using Raith 150^{TWO} electron beam lithography system, the resist was developed in a 1:3 mixture of cyclopentanone and 2-propanol for 1 min at room temperature, followed by rinsing using 2-propanol. We started with this solvent system as (undiluted) cyclopentanone is known to be a good solvent for PC. Other solvent systems may also function as developer, and are currently under study.

Figure 1 shows the contrast curve measured by AFM, as well as the AFM images of the dose test pattern containing 5 by 5 array of squares each 5 μm × 5 μm. The range of dose is from 25 to 2955 μC/cm^2, and increases at a 1.22× step. The resist sensitivity (defined as D_{50}) is approximately 200 μC/cm^2, which is comparable to that of PMMA. We consider it difficult to derive a meaningful contrast from the contrast curve with linear dose scale, so we draw the contrast curve in log-scale, which gives a contrast (still defined as $\gamma=[\log_{10}(D_{100}/D_0)]^{-1}$) of 0.53. Such a low contrast makes PC a promising grayscale electron beam resist.

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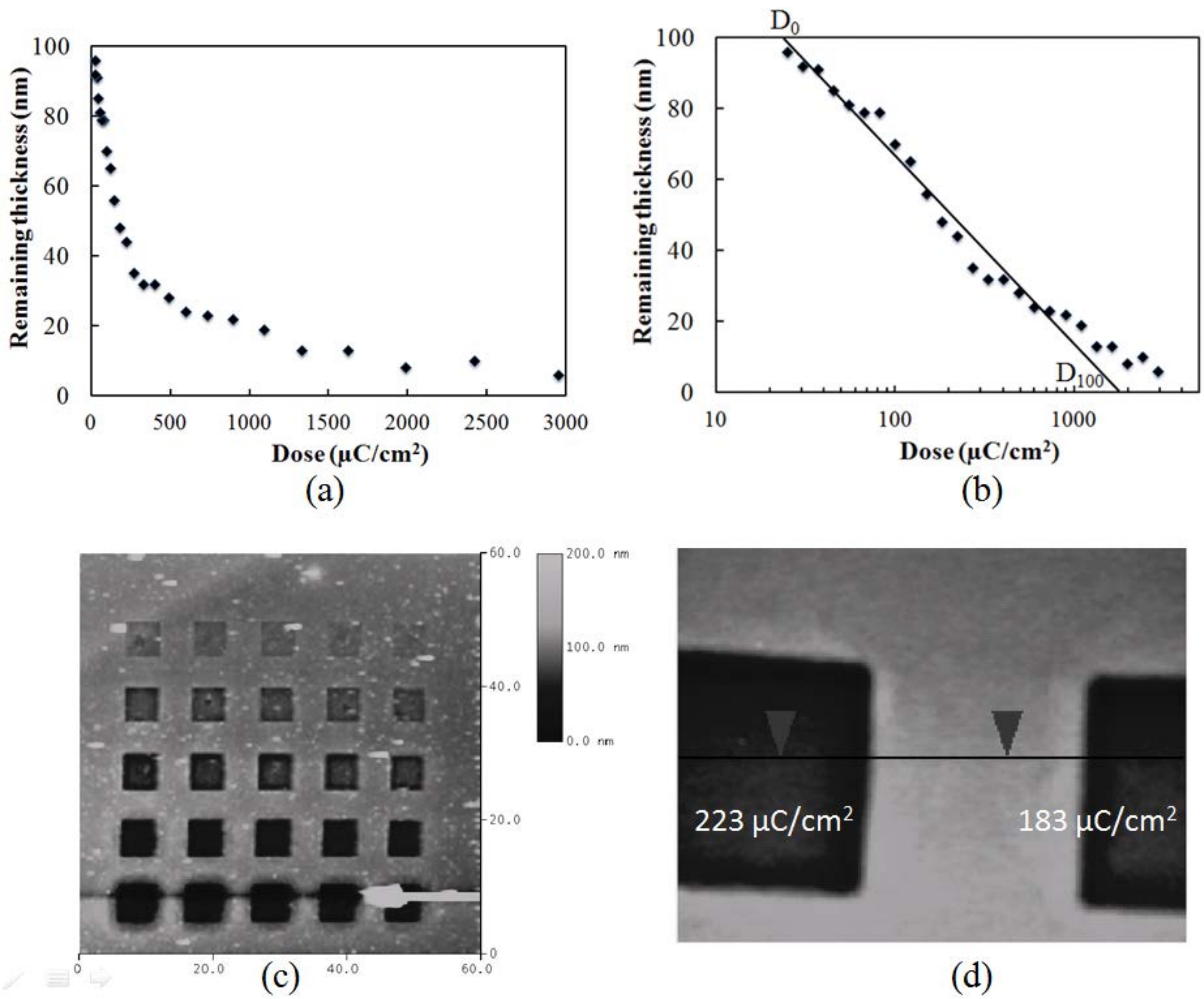

Figure 1. (a) Contrast curve for 60 kg/mol polycarbonate exposed at 20 keV and developed for 1 min in 1:3 mixture of cyclopentanone and 2-propanol; (b) Same contrast curve as (a) but with log-scale dose; (c) AFM image of the dose test pattern used to generate the contrast curve in (a-b), scan size 60 μm by 60 μm, dose increases from right to left and from top to bottom; (d) Zoom-in scan of two squares in (c) with intermediate doses, showing a smooth developed resist surface.