Visualization of NL polymer distribution in NIL guides for DSA

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One of the potent candidates for single nanometer-scale lithography is directed self-assembly (DSA). Grapho-epitaxy is one of the manners that block copolymer (BCP) is filled in the grooves formed by nanoimprint lithography (NIL). Neutralizing layer (NL) is a key material for that to orient the lamellar domains of the BCPs vertically. The NL should be coated conformally inside the grooves but its distribution is hard to be seen since it consists of only one molecular layer of the polymer. We tried to visualize the NL distribution in the NIL guiding grooves and revealed the relationship between the chemical structures and distribution of the NL polymers.

The line and space (L/S) guiding grooves were fabricated using the conventional NIL resist consisting of diacrylate monomers. The NL polymers contained polystyrene (PS) were prepared that some of them have end-terminated hydroxyl groups and the others do not have those. They were dissolved in PGMEA, spincast on the NIL resist, annealed and rinsed. Consequently, the NL was formed on the NIL resist. After that they were exposed to vapor of ruthenium tetroxide (RuO_4) aqueous solution. During this process, the Ru was adsorbed to the benzene rings of PS. As a result only the NL was stained and could be observed by a scanning electric microscope (SEM).

The SEM images after stained samples are shown in figure 1. No stained part was found in the NIL guides without the NL. On the other hand, for the sample coated with the NL, whitish Ru stained parts were observed and seemed to split to 1/2 pitch of guiding NIL L/S from the top view. In addition from the tilted SEM images, the NL was confirmed to stick to the both side of the NIL resist walls. From AFM topological images in figure 2, the L/S pitch seemed as the same as that of the NIL patterns but the phase images provided us the same aspect as the SEM images. It was concluded that the NL polymers were mainly placed at the edge sections of the grooves formed by NIL as shown in figure 3.

Using this method, we could visualize the distribution of the NL polymers according to their chemical structures as shown in figure 4. If the polymer has low affinity to the NIL resist, no NL was found on it. The polymers with high affinity to the NIL resist, the distribution of the NL depended on the end-terminated groups. The polymers without hydroxyl group were only observed at the corner edges of the grooves. On the contrary, the polymers with hydroxyl group seemed anchored at the bottom of the grooves, however, the long polymer chains reached at the both corners of the grooves and gathered there, so their distribution was not uniform.

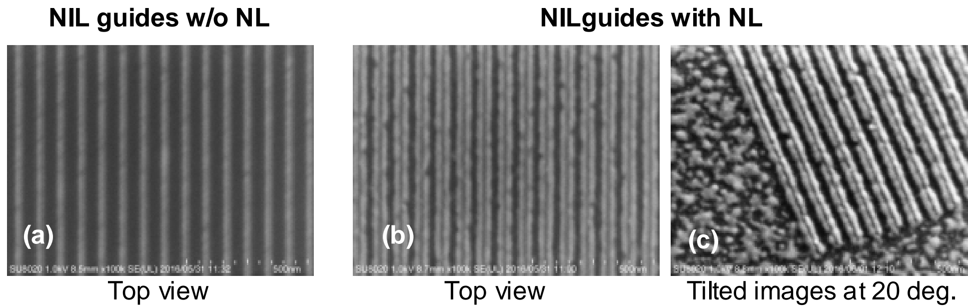

Figure 1: SEM images of samples exposed to RuO_4 without NL (a) and with NL (b, c) on NIL guides. Whitish parts in (b, c) were the NL stained by Ru since electrons are scattered by heavy metal Ru.

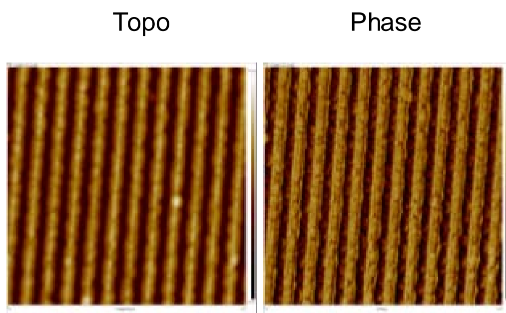

Figure 2: AFM images of samples exposed to RuO_4 with NL on NIL guides.

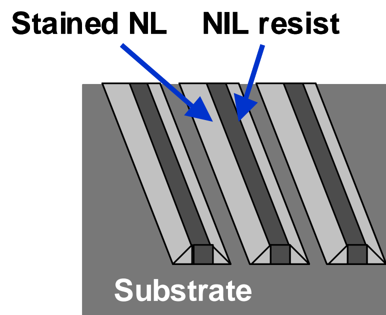

Figure 3: Models of distribution of NL polymers in NIL resist grooves.

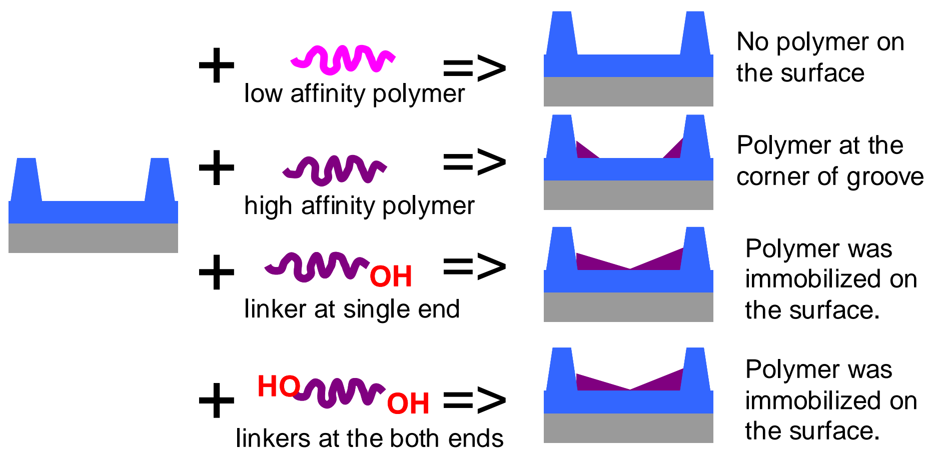

Figure 4: Effect of polymer structures of NL to their distribution in the NIL grooves. Low affinity polymer was not found on NIL guides. Polymer with high affinity to NIL resist remained at the corners of NIL guides. Polymers with hydroxyl groups were immobilized on the surface of NIL resist but still more polymers were found at the edges, however, the number of hydroxyl groups might not correlate with their distribution.