Graphoepitaxy of Diblock Copolymer on Micropatterned Substrates

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1. Introduction

Block copolymer lithography has attracted considerable attention as a promising prospect for nanopattern fabrication. In block copolymer lithography, microphase-separated nanometer-sized domains are used as lithography templates [1]. This method is superior in that nanostructures can be fabricated in large quantities with approximately consistent sizes. Further, they can be easily fabricated with low cost. Moreover, it also has great potential to exceed the resolution limit of top-down technologies such as electron-beam lithography because the domain sizes and periods involved in this case are merely determined by the chain length of a block copolymer.

Many attempts have been carried out to apply the microphase-separated domains as a dry etching mask in the process of semiconductor fabrication, which focuses on the fabrication of dot or hole structures. It is reported that these structures have been applied to magnetic patterned media [2] and FLASH memory [3]. More recently, several attempts to apply self-assembled domains in the formation of line and space (LS) patterns [4–6] have been carried out. For the LS pattern formation, it is necessary to arrange these domains parallel to each other. Sundrani *et al.* successfully demonstrated that periodic cylinder structures with a 23-nm pitch, made of asymmetric block copolymer that is composed of polystyrene (PS) and poly(ethylene-*alt*-isoprene) (PEP), could be almost perfectly aligned with the sidewall of a silicon nitride trench by the graphoepitaxy technique [5]. This demonstration creates the possibility of using block copolymer lithography as a high-resolution lithography.

In this study, we present the behavior of the self-assembly of a diblock copolymer PS-*b*-PEP on flat and micropatterned substrates covered by silicon oxide. Further, we confirm the graphoepitaxy of this block copolymer.

2. Experiments

We used an asymmetric diblock copolymer composed of polystyrene (PS) and polyisoprene (1,4 addition) (PEP) whose isoprene block is hydrogenated to a degree of over 99% (Polymer Source Inc.). The molecular weights of each PS and PEP block are 6,100 and 16,500 g/mole, respectively, with a polydispersity of 1.04. Thin block copolymer films were prepared by spin coating a 0.5 wt% toluene solution of PS_{0.27}-*b*-PEP_{0.73} onto flat and micro patterned substrates. The micropatterned substrates were prepared by standard photolithography and reactive ion etching. The spin-coated film was then annealed in an oven at 130°C under a nitrogen atmosphere for 15 h to enable sufficient microphase separation. The film thickness was measured using an ellipsometer and interferometer. The self-assembled domains were observed using an atomic force microscope (SPI3800/SPA500, SII nanotechnology) in the dynamic force mode.

3. Results and Discussion

First, we investigated the behavior of the self-assembly of the diblock copolymer PS-*b*-PEP on a flat substrate. Thermal annealing quantizes the film thickness of the block copolymer by separating it into terraces (i.e., islands and holes). It is found that the block copolymer film on the silicon oxide surface also exhibits an asymmetric wetting similar

Fig. 1(a) AFM topographic image ($600 \text{ nm} \times 600 \text{ nm} \times 20 \text{ nm}$) and (b) phase image ($600 \text{ nm} \times 600 \text{ nm}$) of self-assembled structure near the boundary between the $L/2$ and $3L/2$ terrace. (c) Topographic image and (d) phase image near the boundary $3L/2$ and $5L/2$.

to that on the silicon nitride surface. In this case, a PS block preferentially wets the oxide surface whereas a PEP block covers the free surface. The quantized thickness corresponds to odd half integer multiples of L , that is, $(2n+1)L/2$, where n is an integer and L is the thickness of a single layer of the cylinders.

Figure 1 shows the AFM images of self-assembled terrace structures on a flat substrate. The topographic image of the region near the boundary between the $L/2$ and $3L/2$ terraces is shown in Fig. 1(a). In $3L/2$ terraces, a fingerprint pattern is clearly observed. This implies that the cylinders lie parallel to the substrate. Although a PS cylinder is embedded in a PEP matrix, the cylinder structures are observed even in the topographic image because the surface immediately above the PS cylinder swells up to a height of approximately 1 nm.

The phase image corresponding to the topographic image of Fig. 1(a) is also shown in Fig. 1(b). Phase imaging is a standard technique for mapping the spatial variation in the surface elasticity. The cylinder structures can be observed due to the difference in the elasticity between the PS and PEP domains. The dark region in the phase

image corresponds to a PS cylinder domain that is harder than a PEP domain. In the topographic as well as the phase images, no specific structures due to the self-assembly are observed in the $L/2$ terrace. This is because a molecular brush layer, in which the PS block wets the substrate and the PEP block faces the polymer/air interface, is formed in the $L/2$ terrace.

The topographic image and the phase image of the region near the boundary between the $3L/2$ and $5L/2$ terraces are shown in Fig. 1(c) and Fig. 1(d), respectively. The cylinder structures can also be observed in the $5L/2$ terraces. This implies that each layer of the PS cylinders with a thickness of L embedded in a PEP matrix overlays the molecular brush layer on the oxide surface. The terrace heights corresponding to L are 22 nm between the $L/2$ and $3L/2$ terraces and 19 nm between the $3L/2$ and $5L/2$ terraces.

From these results, it was confirmed that the block copolymer film is quantized to odd half integers with a periodic spacing of $L \sim 20 \text{ nm}$. Further, it was also revealed that the structure of the PS cylinder can be formed.

Next, we investigated the graphoepitaxy of the abovementioned cylinder structures on the

Fig. 2(a) AFM phase image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of self-assembled block copolymer film near the edge region of the 26-nm deep trench. (b) Magnified view ($300\ \text{nm} \times 300\ \text{nm}$) of the boxed region in Fig. 2(a).

micropatterned substrates. Graphoepitaxy is a method that aligns the self-assembled structures with the sidewall of the patterns.

Figure 2 shows the AFM phase image of a self-assembled block copolymer film near the edge region of a trench with a depth and width of 26 nm and $1.5\ \mu\text{m}$, respectively. As shown clearly in the figure, the cylinder structure is only formed within the trench. This is due to the formation of a $3L/2$ terrace within the trench and an $L/2$ terrace on the mesa resulting from height quantization. It is noteworthy that the cylinder structure is aligned with the sidewall of the trench that has a length and width of 800 nm and 200 nm, respectively.

Figure 2(b) shows the magnified view of Fig. 2(a). It is clearly observed that the bright domain corresponding to the PS block is in contact with the sidewall of the trench. This implies that a molecular brush layer is formed on the sidewall of the trench as well as on the bottom surface of the trench. This brush layer formation is the key in inducing lateral alignment of the cylinder structures.

Moreover, it is clear that the cylinders with a 23-nm pitch are separated from each other although the cylinder is fluctuated. This indicates that block copolymer lithography is a promising prospect for the formation of extremely fine patterns.

4. Conclusion

We investigated the formation of the self-assembled patterns of a diblock copolymer. It is confirmed that the cylinder structures parallel to the substrate can be fabricated on a flat substrate covered by an oxide layer. We have also succeeded in the graphoepitaxy of a 23-nm pitch cylinder structure with a length and width of 800 nm 200 nm, respectively. The

value of this pitch is approximately equal to the resolution limit of electron beam lithography. Therefore, we were convinced that block copolymer lithography has great potential to exceed the limit of top-down lithography.

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