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Controlling of 6 nm Sized and 10 nm Pitched Dot Arrays Ordered along Narrow Guide Lines Using PS−PDMS Self-Assembly

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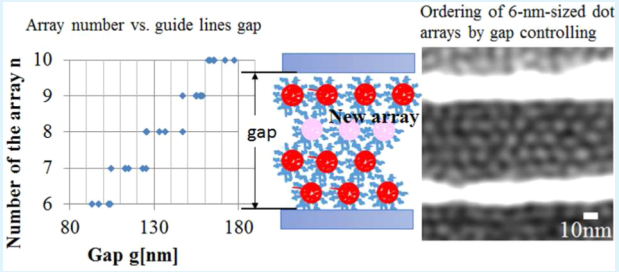
ABSTRACT: We have studied graphoepitaxy to make nanodots or nanolines ordered along electron beam (EB)-drawn resist guide using block copolymers (BCPs) of polystyrene-polydimethylsiloxane (PS−PDMS). We found out that the number n of ordered molecular dot arrays in the line gap increases stepwise with the gap between guide lines. The n self-assembled dot arrays were ordered in a gap between n and $n + 1$ times the mean PDMS pitch and self-assembled with no guide pattern. According to the ordering characteristics, 6 nm sized and 10 nm pitched PDMS dot arrays were formed using the BCP self-assembly with the guide lines.



KEYWORDS: *nanodot, self-assembly, EB drawing, graphoepitaxy, patterned media*

Graphoepitaxy[1] and chemical registration and modification[2−4] are very attractive methods in next-generation advanced lithography. A mechanism for ordering self-assembled nanodot arrays with a sub-10 nm sized dot and nanometer array pitch along ultra-narrow guide lines with a gap between the lines is of great interest in polymer science. However, self-assembly has technical issues of disordering and defects. To solve the issues and control the positions of the dots and arrays, Sakurai et al. and Bita et al. proposed graphoepitaxy of self-assembled BCPs using a one-dimensional line and two-dimensional periodic patterned templates, respectively, as guides.[5,6] In a two-dimensional periodic template such as guide post lattice, the pattern needs good arrangement and accuracy of the guide post pitch with a deviation of less than 5 nm,[5] which is highly critical in practice. It is therefore necessary to develop a practical method with a larger margin for the guide pattern position accuracy. An alternative, guide line template application, has been proposed by Sakurai et al.,[6] Black,[7] and Kitano et al.[8] They applied optical lithography to fabricate guide line templates for graphoepitaxy. They demonstrated that the technology could be applied to form nanodot arrays, particularly as patterned media with guide lines, using self-assembly. Kihara et al. demonstrated that nanodot arrays with a pitch of 10 nm × 12 nm were ordered with a wide and closed guide pattern.[9] However, this is incomplete with resist guide patterns that are several hundreds of nanometers wide, which is far from practical application. Although we have demonstrated that long-range-ordering of self-assembled PDMS nanodot arrays with a pitch of 33 nm using a guide line and post-mixing template,[10] the experiments did not demonstrate that the method is suitable for patterned media with a density of >5 Tb/in^2 using slim guide lines. Therefore, we have researched the characteristic of ordering of sub-10 nm sized nanodot arrays with a pitch of <15 nm along ultra-narrow EB-drawn guide lines using PS−PDMS self-assembly.

The fine dot size and pitch were determined by the MW of PS−PDMS based on the theoretical relationship between the product of χN (where χ is the Flory−Huggins parameter, and N is the total number of segments) and the PDMS concentration of the block copolymer.[9,11−13] There were 2 kinds MWs, 14.6 kg/mol and 8.5 kg/mol, selected for this study. Figure 1a−c show SEM image of the PDMS nanodots and distributions of average dots pitches and dot size using PS−PDMS MWs of 14.6 kg/mol that were self-assembled with no guide pattern. This study was conducted by using only guide lines. This is because we cannot form fine dot arrays with a diameter of <10 nm using EB drawing with advanced development.[14−16]

Ordering of the PDMS dots along the lines was obtained with the guide line template (Figure 1d) as shown in Figure 1e. When the line gap was about 170 nm, there are 10 PDMS nanodot arrays ordered along the guide lines in the gap. By changing the gap, we measured an ordering characteristic of the number of PDMS dot arrays along the guide lines for the gap. The number of PDMS dot arrays increased stepwise with an increase in the gap as shown in Figure 2a. The property shows that the number of ordered dot arrays n is kept constant within a range of the gap g between np and $(n + 1)p$, where the p is average dot pitch with no guide pattern. This means that it is easy to loosen the pitch of the arrays rather than packing it. This consideration is supported by the distribution of the dot pitch with no guide pattern (Figure 1c). Figure 1c shows that the probability of the pitch in a packing region being less than the peak pitch is very low, and there is a tendency for the dot arrays to exist in a loose area over a peak pitch area.

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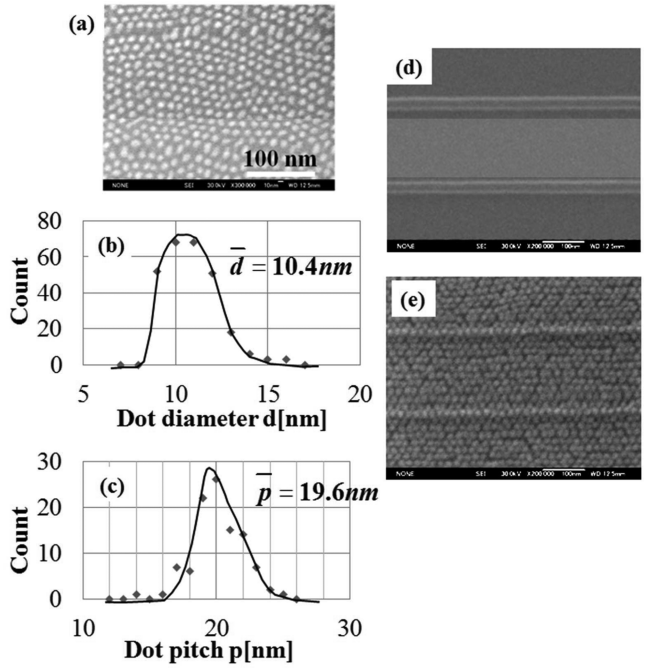

Figure 1. SEM images and dot size and pitch distribution of 14.6 kg/mol PS−PDMS self-assembly, (a) SEM images of the self-assembled PDMS dots with no guide, (b, c) distributions of dot size and pitch with no guide, (d, e) SEM images of EB-drawn guide lines on Si wafer and self-assembled PDMS dot arrays ordering along the guide lines.

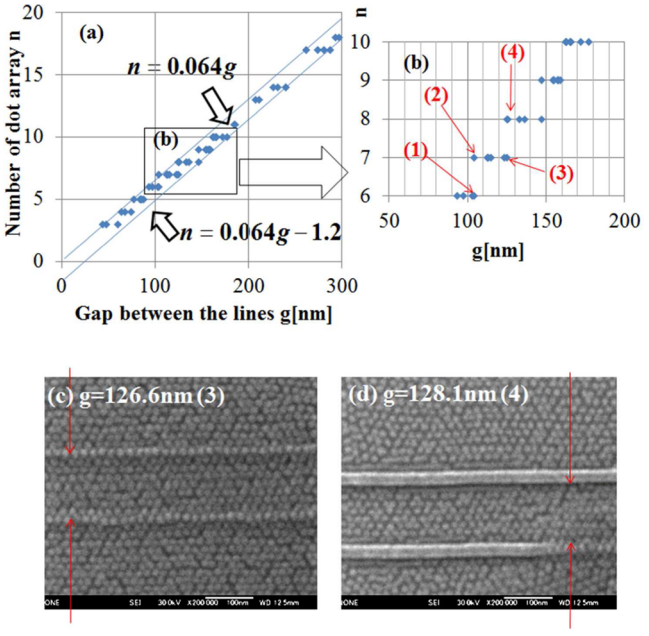

Figure 2. Relationship between the ordering array number and the guide line gap, and SEM images of the self-assembled PDMS dot arrays ordering along the guide lines, (a, b) the relationship and an enlarged section, and (c, d) SEM images of the ordering at the gaps, which correspond to points 3 and 4 in panel b, respectively.

Furthermore, the probability goes to zero in a region of >25 nm in pitch. Figure 2a shows that the array number n is in a region where the gap is from np to $(n + 1)p$. From this property (Figure 2a), we can derive upper and lower critical equations of the array number n for the gap, which can be represented by the following equations, $n = 0.064g$, and $n = 0.064g - 1.2$, respectively. These equations suggest that the number n changes stepwise with the size of the gap. The slope of 0.064 corresponds to the array pitch of 15.6 nm. This value is smaller than $p/\sin 60°$, and it corresponds to a minimum pitch of 18 nm (= 15.6/sin 60°) in Figure 1c. This stepwise property agrees well with theoretical consideration done by Tsuyoshi Koga et al.

Images c and d in Figure 2 show SEM images of the PDMS dot arrays indicated by 3 and 4 in Figure 2b, which is the enlarged property of the ordering array number of from 6 to 10 arrays. From the images, we measured the pitch between the neighboring dot arrays as shown in Figure 3a−c. The figures

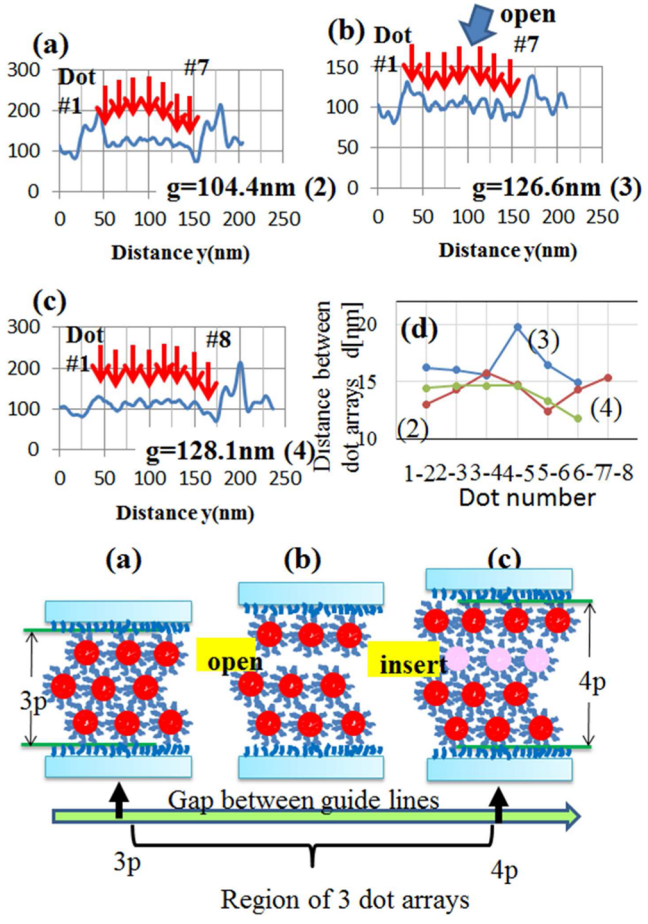

Figure 3. (a−d) Pitch distributions of PDMS dot array ordering in various gaps and (e) increment model of ordering of self-assembled PDMS nanodot arrays by increasing the number of ordering arrays from 3 to 4.

were obtained by integrating the cross-section signal along the lines. From them, Figure 3d was obtained. It shows that a distribution of the pitch changes from a nearly flat distribution to a distribution with a peak just before the gap of $p(n + 1)$.

The peak pitch is about 20 nm, and it locates in middle of the gap. The 20 nm corresponds to about 23 nm (= 20 nm/sin 60°). This value corresponds to the upper edge of the pitch distribution (Figure 1c). Consequently, when the gap expands from 126.6 nm (Figure 2e) to 128.1 nm (Figure 2f), a new PDMS nanodot array forms at the center of the arrays so that the arrays number increases from 7 to 8. In addition, because the peak pitch is at a center of the gap, the guide lines strongly attract the PDMS nanodots from both sides of the lines. Such

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an explanation predicts an ordering mechanism as shown in Figure 3e. This characteristic can be estimated by the attractive force in micro phase separation,[11] and the pitch distribution with no guide pattern.

Figure 3e shows a model of ordering the PS/PDMS dots along the PS-terminated guide lines, when the number changes from 3 to 4. The highest packing occurs at an integer multiple of the gap np ($p = 18 \times \sin 60^\circ$ [nm]) of the minimum dot pitch of 18 nm in Figure 1c. When increasing the gap, the individual pitches between the neighboring arrays are nearly unchanged. However, only the array pitch around the center of a gap becomes large. Consequently, when the increasing gap exceeds $(n + 1)p$, new dot arrays form in the large gap, and the line number increment occurs stepwise with the increasing gap. This property is due to the attractive force between the PS/PDMS dots and the PS-terminated guide line. We consider that the attractive force between the line edge and the dots was very strong because we obtained the effective range for ordering the dots along the line to be more than 20 arrays in the experiments, although the maximum array number between the lines was about 17 arrays. The change of free energy in the system of BCP chains can be reflected from the interaction between conformational entropy of BCP chains and the interfacial energy between the BCP chains. In the case of the nanodot array with the guide-line gap of np, the system reached its equilibrium condition. The free energy of the system was on its lowest, the interaction between the BCP chains was optimum. This implied the pitch of nanodot array is on its peak. When the gap of nanodot array increased near $(n + 1)p$, however, the system lost its conformational entropy and the BCP chains became uncompressed. Therefore, the PS chains were extended filling the space as shown in Figure 3f. In this condition, the pitch reached its maximum. However, the extended chains of nanodots occurred on the middle area of gap because of the influence of the brushed homopolymer on guide line. The losing of conformational entropy and the presence of the extended chains, however, tend to decrease the ordering and aligning of nanodot array on larger area. In the case that the gap exceeded the $(n + 1)p$, the system of BCP quantity satisfies to form a new nanodot array. In this case, hence, the lowest nanodot pitch was obtained due to the compressed condition.

Using PS−PDMS with a MW of 8.5 kg/mol, we measured the ordering property with SEM images of self-assembled PDMS nanodot arrays along the lines. Figure 4a shows the ordering property for the gap. The number of dot arrays increases stepwise with an increase in the gap the same as with an MW of 14.6 kg/mol. In addition, there are upper and lower critical equations in the property. The equations are obtained as $n = 0.0917g$ and $n = 0.0917g - 1$, respectively. From the equations, the dot array pitch is about 10.9 nm perpendicular to the guide lines. This corresponds to 12.6 nm pitch for self-assembled PDMS nanodots with no guide. The dot size of 5.3 nm and the pitch of 10 nm are so small that we have to pay an attention to the guide line edge roughness (LER). Considering the LER, the guide line gap should be designed to be the center of the critical equations, which is followed by an equation of $g = (n + 0.5)p$ for design.

Images b and c in Figure 4 show the guide line before annealing and the ordering the self-assembled nanodot arrays along the lines, respectively. On the basis of the above property, the guide lines with a gap of 58 nm were designed and formed by drawing with a 30-keV-EB with HSQ negative resist on Si

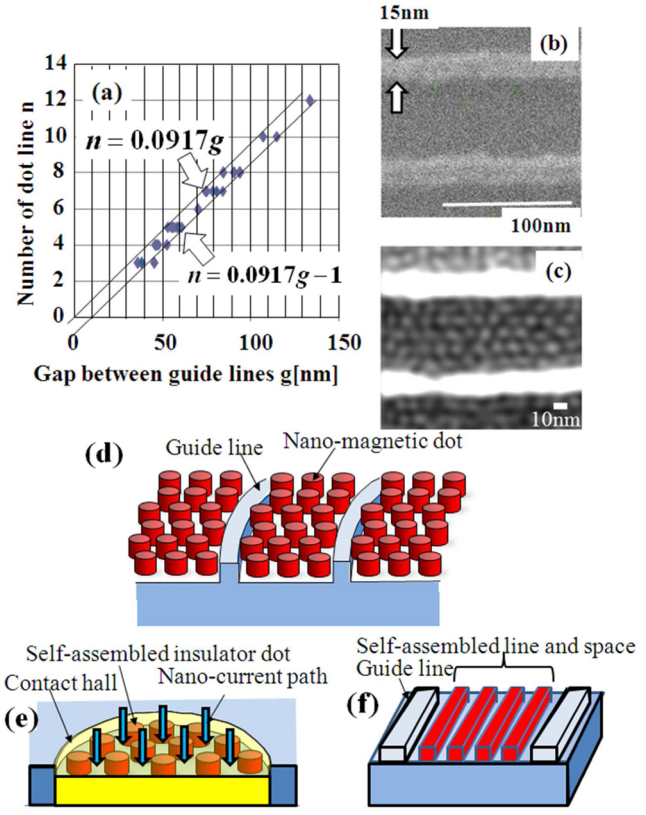

Figure 4. (a) Ordering characteristics of self-assembled PDMS nanodot arrays with MW of 8.5 kg/mol along the EB-drawn HSQ resist guide lines for the lines gap, (b) SEM images of the guide lines, (c) 5 self-assembled PDMS dot arrays with a line gap of 58 nm, and applications, (d) patterned media in ultrahigh density magnetic recording, (e) nano-contact in small consumption device, and (f) sub-10 nm wide line and space pattern.

substrate. Furthermore, we obtained 3 and 7 PDMS nanodot arrays along the designed guide lines. The dot arrays have a small dot size and array pitches of about 6 and 10 nm. This corresponds to about 5 Tb/in^2 in the application of patterned media in ultrahigh-density magnetic storage as shown in Figure 4d. In addition, we can apply it to nano-contact device in phase change memory device (Figure 4e).[17] When the dot array formation extends to form line and space pattern, we will develop a fabrication technology for 6 nm wide line and space pattern in nanodevices (Figure 4f).

In conclusion, we found out that the number n of ordered molecular dot arrays in the line gap increases stepwise with the gap between guide lines. The n self-assembled dot arrays were ordered in a gap between n and $n + 1$ times the mean PDMS pitch self-assembled with no guide pattern. According to the ordering characteristics, we formed 3−7 6 nm sized and 10 nm pitched PDMS dot arrays between the narrow guide lines using the PS−PDMS self-assembly with a MW of 8.5 kg/mol by controlling the guide line gap. The conclusion provides that it is easy to control ordering of self-assembled nanodot arrays along the guide lines and the technology makes open to advanced lithography era for patterned media in ultrahigh density magnetic storage and sub-10 nm wide line and space pattern in nanodevices, etc.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

EB, electron beam
BCP, block copolymers
PS, polystyrene
PDMS, polydimethylsiloxane
PS−PDMS, polystyrene−polydimethylsiloxane
MW, molecular weight

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