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Condensation of Nano-Size Polymer Aggregates by Spin Drying

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Abstract: Condensation control of nano-particles has become important in order to fabricate minute condensed structures. In this study, we focus our attention on condensation mechanism of polymer aggregates in a resist film. The polymer aggregate is structural component of a resist material which is used in lithography process. The condensation nature of polymer aggregates in the resist film surface is observed by using atomic force microscope (AFM). By using the AFM, the condensation of polymer aggregates can be observed clearly. The condensation of polymer aggregate strongly affects to precise fabrication of resist pattern below 100nm size. The interaction force among polymer aggregates can be analyzed based on Derjaguin approximation. We also discuss about condensation nature of polymer aggregates in the resist film surface with the help of micro sphere model.

Keywords: *AFM, polymer aggregate, nano-particles*

1. Introduction

In recent years, condensation control of nano-particles has become important in order to fabricate minute condensed structures, such as resist pattern. In this regard, the atomic force microscope (AFM) system has proven to be a versatile instrument for imaging minute structure of condensed matter[1,2]. Recently, present authors have already proposed the novel principle for direct analysis method of resist pattern adhesion[3-5]. By this method, quantitative analysis of cohesive properties of resist pattern has been conducted. In this paper, the condensation structure of polymer aggregate is characterized by using the AFM. Moreover, due to Derjaguin approximation, the condensation nature of polymer aggregate is discussed.

2. Experiment

The KrF excimer laser resist, chemically amplified type, consisting of hydroxystyrene as a base polymer was used. The resist film was coated onto a Si(100) wafer by a spinning method. The native oxide layer was removed by dipping into HF aqueous solution prior to spin coating of the resist film. The pre-baking treatment was carried out at 100°C for 1min on a proximity hot plate. The silane-coupling treatment with hexamethyldisilazane (HMDS) was performed at 80°C for 60 s. After the pattern exposure, the resist films were baked at 100°C for 1min. Then, the resist films were developed by dipping into tetramethylammoniumhydroxide (TMAH) 2.38% aqueous solution for 60 s. Subsequently, the resist films were rinsed in the deionized water for 30 s and dried by the spin method.

A commercially available AFM, integrated with a micro-tip, was used for the condensation analysis. As a tip used for the investigation, a conical tip mounted on the cantilever apex was used (Figure 1). The radius of curvature of the tip apex was approximately 8 nm. The tip was made of a Si_3N_4 film. The tips with exposure to the HMDS vapor were prepared. The calibration measurements of the spring constant correlated well with the manufacturer's given value of $k = 0.44$ N/m. With the invention of the AFM, we have been equipped in good time with the appropriate tools to understand the cohesive properties of condensed matter on a nanometer scale.

3. Results and Discussion

3.1. Condensation of Polymer Aggregate

The condensation nature of polymer aggregates in the resist surface is observed by using the AFM. Figure 2 shows an AFM image of the polymer aggregates and schematic of a condensation model. The condensation of

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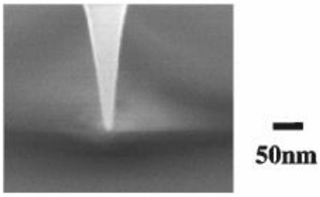


Figure 1. SEM photograph of apex of AFM tip used for the investigation.

polymer aggregates can be observed clearly. In this study, we focus our attention on condensation mechanism of polymer aggregates in the resist film. It is well known that the polymer aggregate is structural component of a resist material which is used in lithography process[2]. The size of each polymer aggregate is approximately 20 nm. In Figure 2, the large condensation composed with many aggregates can be also observed. The polymer aggregate smaller than 10 nm size could not be resolved, because the limitation is caused by tip-sample convolution. The condensation nature of polymer aggregate was also discussed by Bug[6]. Figure 3 shows a condensation model of polymer aggregates containing a solvent by spin drying. We considered that the large size polymer aggregate condensation occurs under an interaction between different size aggregates. Particularly, a small size aggregate is likely to condense around a large size one. The condensation of polymer aggregate strongly affects to precise fabrication of organic micro pattern. In this study, the condensation property of polymer aggregate is analyzed based on Derjaguin approximation in the following section.

3.2. Condensation Structure of Polymer Aggregate

In general, the size of micro condensed matter contributes strongly to surface roughness of solid material[2]. The size of polymer aggregate can be regarded as the representative value which reflects the condensation properties in the resist film surface. Figure 4 shows schematic explanation of condensation behavior of polymer aggregate based on Derjaguin approximation[7].

As shown in Figure 4, based on Derjaguin approximation, a sum F of interaction force F_n acting between a sphere R_0 and micro spheres (radius: R_1, R_2, $\cdots$, R_n) can be expressed as follows.

$$F = \sum_n F_n = \frac{A}{6} \sum_n \frac{R_0 R_n}{(R_0 + R_n)} \qquad (1)$$

where symbols A and D_n represent Hamaker constant and interaction length between two spheres. The simple simulation result of interaction force F is shown in Figure 5. It seems reasonable to suppose that the interaction force F decreases

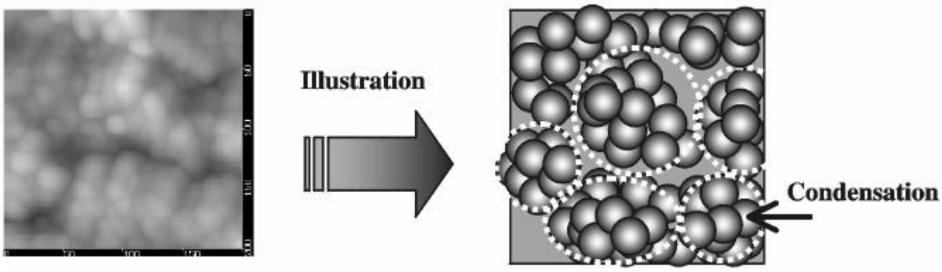
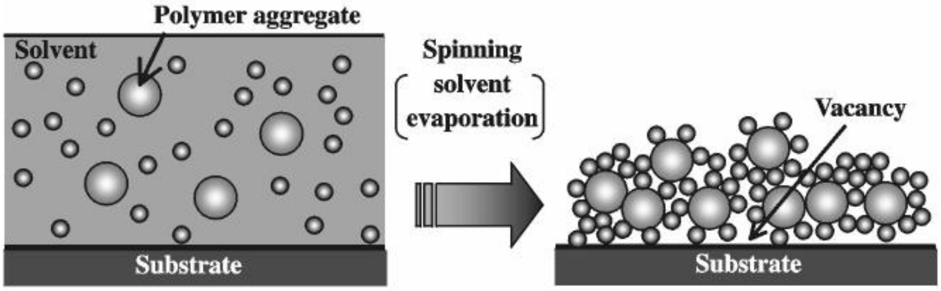


Figure 2. AFM images of polymer aggregates condensed in resist surface.



(a) Mixture of aggregate and solvent

(b) Condensation model

Figure 3. Condensation model by particles of two sizes.

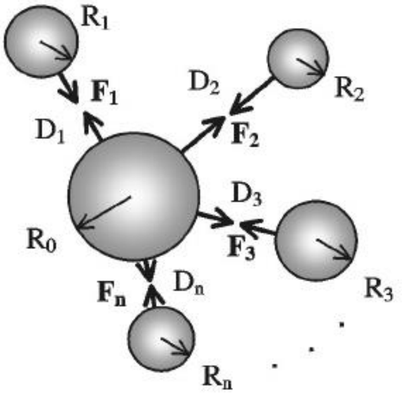


Figure 4. Interaction force model between two spheres based on Derjaguin approximation.

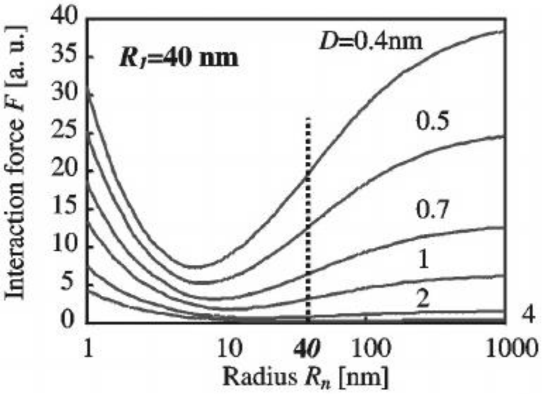
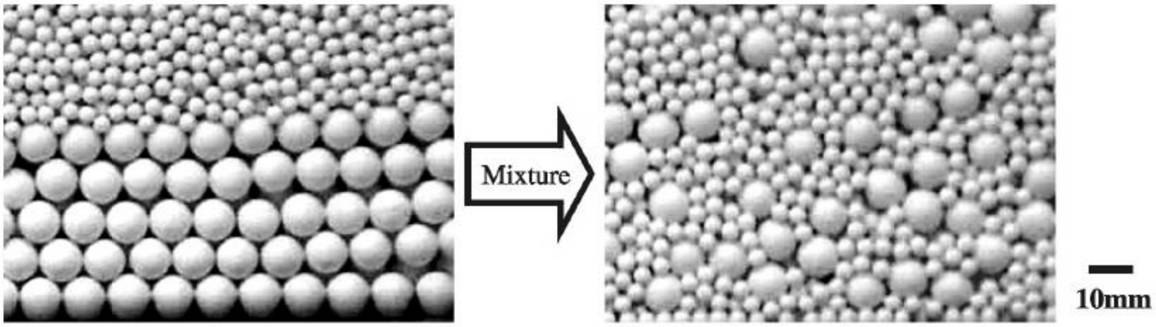


Figure 5. Dependency of interaction force on spherical radius.



(a) Two layers

(b) Homogeneous condensation

Figure 6. Condensation structure of Al_2O_3 spheres. (Cross-section view)

with decreasing size of polymer aggregates. However, when the radius R_n is less than about 10 nm, the interaction force F increases rapidly. Therefore, it can be explained that the small size aggregate is more likely to condense around the large size one. This theory provides a very simple but direct approach to understand condensation of polymer aggregate in the resist film.

3.3. Condensation Analysis by using Micro Spheres

In order to discuss the validity of the above condensation model, macro-spheres are used for the polymer aggregates. Two sizes of Al_2O_3 spheres, 5 and 10 mm, are used for the experiment. Figure 6a shows a cross-sectional view of close-packed Al_2O_3 spheres, which has a two-layer structure with the different size spheres. And then, the two sizes of Al_2O_3 spheres are mixed as shown in Figure 6b. As a result, the small size sphere is condensed around the large size one. Consequently, we considered that the condensation structure of polymer aggregates forms larger size aggregate condensation.

4. Conclusion

Condensation properties of polymer aggregate are characterized by the typical AFM techniques. The condensation model of polymer aggregate can be constructed based on Derjaguin approximation. In order to discuss the validity of the condensation model, condensation experiment of Al_2O_3 spheres is carried out. Consequently, we considered that the condensation nature of polymer aggregate in the resist film can be explained.

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