Determination of Young's Modulus of Polymer Aggregate Based on Hertz Theory

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Elastic property of polymer aggregates in a resist pattern is characterized by using atomic force microscope (AFM). In order to determine Young's modulus of polymer aggregates based on Hertz theory, a separation force between polymer aggregates is measured by using the AFM. Young's modulus of polymer aggregates composing resist pattern can be determined to be 10-25MPa. The results of our experiment clearly show that the polymer aggregates indicates relatively low cohesion property.

Keywords: resist, polymer aggregate, Young's modulus, atomic force microscope, Hertz theory, separation force

1. Introduction

Atomic force microscope (AFM) system has proven to be a versatile instrument for imaging a wide range of samples of different elastic properties.[1] In recent years, elastic property of polymer aggregate has become important in order to realize high quality resist pattern for sub-25nm lithography. By using the AFM, it is demonstrated that nano-particles can be located and moved.[2, 3] In this regard, present authors have already proposed the novel principle for direct analysis method of resist pattern adhesion, that is, direct peeling method by using AFM tip (DPAT).[4] By the DPAT method, quantitative analysis of cohesive properties of resist pattern has been conducted. In this paper, by using the AFM, the cohesion property of polymer aggregates in resist pattern is characterized. Particularly, the elastic properties (Young's modulus) of polymer aggregates composing resist pattern is determined based on the Hertz theory.

2. Experiment

2.1 Resist material and line pattern fabrication

Electron beam (EB) resist, chemically amplified type, consisting of hydroxystyrene as a base polymer was used. The resist film of 220nm in thickness 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 110°C for 90s on a proximity hot plate. The silane-coupling treatment with hexamethyldisilazane (HMDS) was performed at 80°C for 60s. The line patterns were imaged to the resist film by using an EB stepper (HITACHI-HL-750D) with the acceleration voltage of 50kV. The charge density of EB irradiation was approximately $5 \mu\text{C}/\text{cm}^2$. After the EB irradiation, the resist films were baked at 120°C for 90s. The resist films were developed by dipping into tetramethylammoniumhydroxide (TMAH) 2.38 % aqueous solution for 60s. Subsequently, the resist patterns were rinsed in the deionized water for 30s and dried by the spin method. The SEM photograph of resist pattern of 60nm width is shown in Fig. 1a. In this photograph, the line edge roughness (LER) was observed slightly.

Fig.1 SEM photographs of resist pattern and AFM tip used for the investigation.

A commercially available AFM, integrated with a micro tip was used for the investigation. As a tip used for the DPAT investigation, a conical tip mounted on the cantilever apex was used.(Fig.1b) The radius of curvature of the tip apex was approximately 8nm. 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 $k = 0.44\text{N/m}$.

2.2 Separation force measurement of polymer aggregate

Figure 2 shows a schematic explanation of an experimental flow of separation process with the AFM tip. Prior to the separation of the polymer aggregates, the resist line pattern is imaged by the AFM in the non-contact mode. (Fig.2a)

Fig.2 Separation of polymer aggregate by AFM tip.

Subsequently, the tip traverses the line pattern by moving the piezo stage under the scanning control. By directly applying a load to the top corner of the resist pattern with the AFM tip, the local part of the line pattern adhering on the substrate can be collapsed easily, as shown in Fig.2b. After the pattern collapse, the condensed polymer aggregates can be separated from the resist pattern.(Fig.2c) The condensed polymer aggregates can be separated to each polymer aggregate by the DPAT method. The separation force F is measured in order to analyze the elastic property of the polymer aggregate. Figure 2d shows a schematic diagram of separation procedure with the AFM tip. As previously mentioned, tips treated by HMDS vapor were employed in order to minimize the adhesion force between the polymer aggregate and the tip. As shown in Fig.2d, the polymer aggregate can be separated by applying a certain load with the AFM tip. In the following section, the elastic property of polymer aggregate is analyzed based on Hertz theory.

3. Theory for determination of Young's modulus

In Fig.3, the elastic micro spheres were contacted, and the two spheres approach each other by a certain distance from the point at which the two spheres just contact each other at $F = 0$. Let us consider a elastic sphere of radius R in frictionless contact with another elastic spheres. The radius of contact a is given due to Hertz theory.[5, 6]

$$a^3 = \frac{RF}{K} \quad (1)$$

where the radius of curvature of the geometry R and the effective bulk modulus K of the two adhering spheres made of same material are given by

$$\frac{1}{R} = \frac{1}{R_0} + \frac{1}{R_1} \quad (2)$$

$$K = \frac{2E}{3(1-\nu^2)} \quad (3)$$

Eqs. 2 and 3 can be substituted into Eq. 1 to find a relation between F and a .

$$F = a_1^3 \frac{2E}{3(1-\nu^2)} \frac{R_0 + R_1}{R_0 R_1} \quad (4)$$

From this equation, Eq. 4 can be derived to calculate Young's modulus of two micro spheres in this system.(Fig.3)

$$E = \frac{3F(1-\nu^2)}{2} \frac{R_0 R_1}{a_1^3 (R_0 + R_1)} \quad (5)$$

This equation can be then extended to Eq. 6 which represents Young's modulus of a micro sphere (radius R_0) contacting with another spheres (radius $R_1, R_2, \dots, R_n$).

$$E = \frac{3F(1-\nu^2)}{2} \sum_n \frac{R_0 R_n}{a_n^3 (R_0 + R_n)} \quad (6)$$

Fig.3 Adhesive Hertzian contact.

(a) Tip scanning

(b) Pattern collapse

(c) Condensation of polymer aggregates

Fig.4 Separation procedure of polymer aggregate by AFM tip.

4. Results and Discussion

4.1 Measurement of separation force between polymer aggregates

In this section, in order to calculate Young's modulus of the polymer aggregates, the separation force between the polymer aggregates was measured by the DPAT method. Figures 4a to 4c show separation of condensed polymer aggregates by the DPAT method. Prior to the separation of the polymer aggregates, the resist line pattern is easily collapsed by the DPAT method.(Fig.4a and 4b) Moreover, the condensed polymer aggregates are separated from the resist pattern by using the AFM tip.(Fig.4c)

In Fig.5a, five condensed polymer aggregates of 50nm size can be observed. The arrow illustrated indicates the scan procedure of the AFM tip.

By the scan procedure, the polymer aggregate of 30nm size can be separated. At this point, the separation force F is determined as 3nN due to the spring constant of the cantilever. The separation forces at Figs.5b and 5c are determined as 9 and 5nN respectively. Moreover, the radii ($R_0, R_1, R_2, \dots, R_n$) of the polymer aggregates and contact radii ($a_1, a_2, \dots, a_n$) are measured from the AFM images. These values are summarized in Table1. R_0 represents the radius of the separated polymer aggregate. R_1 to R_4 represent the radii of the polymer aggregate contacting with the polymer aggregate of radius R_0 . Symbols, a_1 to a_4 , represent the contact radii between the polymer aggregate of radius R_0 and another polymer aggregates from R_1 to R_4 .

Table1 Radius, contact radius and Young's modulus of condensed polymer aggregates

Separation	R_0 [nm]	R_1 [nm]	R_2 [nm]	R_3 [nm]	R_4 [nm]	a_1 [nm]	a_2 [nm]	a_3 [nm]	a_4 [nm]	F [nN]	E [MPa]
I	15.9	22.0	21.8	—	—	15.9	19.9	—	—	3	9.5
II	19.6	32.8	27.2	—	—	19.6	19.0	—	—	9	19.3
III	21.0	13.1	17.8	20.3	32.9	12.7	17.1	16.2	14.8	5	25.4

Fig.5 Separation investigation of polymer aggregates.

4.2 Determination of Young's modulus of polymer aggregate

In this section, Young's modulus E of the polymer aggregates is determined due to Eq.8. In the case of the separated polymer aggregate contacting with two polymer aggregates, Eq.8 is expressed as the following:

$$E = \frac{3F_1(1-\nu^2)}{2} \left(\frac{R_0 R_1}{a_1^3(R_0 + R_1)} + \frac{R_0 R_2}{a_2^3(R_0 + R_2)} \right) \quad (7)$$

Fig.6 Measurement of separation force between polymer aggregates.

In the calculation of Young's modulus of the polymer aggregates, Poisson's ratio 0.34 of the polystyrene is employed, which is typical polymeric material. Figure 6a shows measurement of the separation force between the polymer aggregates by the DPAT method. The separated polymer aggregate is contacted on two polymer aggregates. Then, the polymer aggregate is removed from two polymer aggregates to measure the separation force between the polymer aggregates. (Fig.6b) The separation force F between the polymer aggregates and Young's modulus E of the polymer aggregate is summarized in Table 1. The Young's modulus of polymer aggregates is determined to be 10 - 25 MPa. Consequently, the result of our experiment clearly shows that the polymer aggregates have relatively low cohesion property.

5. Conclusion

Elastic property of the polymer aggregate can be characterized by the DPAT technique. Based on Hertz theory, Young's modulus of the polymer aggregates is determined to be 10 - 25 MPa. The result of our experiment clearly shows that the polymer aggregates have low cohesion property. The low cohesion property of the polymer aggregate comes from the organization of the macromolecular strand. The elastic property of polymer aggregate can be analyzed by using AFM.

Acknowledgements

This present work was partially supported by Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science. (Scientific Research (B) 16360171) The present work was also supported by Grant-in-Aid for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology. (Exploratory research, 16656105)

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