Cohesion Property of Resist Pattern Surface Analyzed by Tip Indentation Method

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By the tip indentation technique, the condensation property of resist pattern surface can be analyzed quantitatively. The fundamental property of tip indentation depending on measurement position is investigated. The pattern edge affects strongly on indenting property of a micro tip. The indenting position should be set apart from the pattern edge at least 80nm. As the representative value of surface condensation, the indentation slope value of micro tip is employed. In the indenting curve, it is clearly indicated that a certain hardened thin layer is formed on the resist surface after pattern development. These results are enhanced by the various hardening processes such as electron beam (EB) irradiation and thermal curing. One can safely state that the surface cohesion property of resist pattern can be analyzed by the tip indentation method.

Keywords: surface hardened layer, tip indentation method, atomic force microscope, condensation, polymer aggregate

1. Introduction

In recent years, morphology improvement of resist pattern surface has become important in order to realize high quality resist patterns less than 50nm size. The surface roughening of resist pattern side-wall causes pattern width deviation from the designing rule of electronic devices. In general, it is well known that the surface morphology reflects a condensation property of the bulk material. In this regard, various surface properties of the polymer film have been analyzed in nanometer scale.[1-3] Bug et al. studied the size distribution of associating polymer aggregates due to spherical approximation of aggregate.[1] In this regard, as the important problem to be solved, nanometer scale analysis of resist surface layer has been required. In this respect, atomic force microscope (AFM) allows direct measurement of surface local properties of solid material by force spectroscopy.[4,5] Stark et al. studied the determination of elastic properties of single aerogel powder particles with the AFM.[6] In this way, the AFM has proven to be a versatile instrument for analyzing a wide range of samples which have widely different elastic properties. In

this regard, the present author has already studied the various properties of a resist micro pattern such as adhesion, condensation, deformation and manipulation.[7-10] Particularly, by using the AFM technology, a vacancy of polymer aggregate formed in the resist pattern can be found out.[10] In this paper, quantitative analysis of cohesion properties of resist pattern surface has been conducted. Particularly, by the tip indentation method, the formation of slight hardened layer in the resist pattern surface can be detected and its cohesion properties are analyzed. By combining with the finite element method (FEM), the indenting behavior of a micro tip is also analyzed quantitatively. The condensation control of the resist pattern due to various hardening treatments is also analyzed.

2. Experiment

2.1 Resist pattern fabrication and tip indentation system

A chemically amplified positive tone resist consisting of hydroxystyrene as a base polymer was used. The resist film of 160nm 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 the spin coating of the resist film. The silane-coupling treatment with hexamethyldisilazane (HMDS) was performed at 80°C for 60s. The pre-baking treatment was carried out at 110°C for 90s on a proximity hot plate. The line pattern images of 500nm width were exposed to the resist film by using the electron beam (EB) irradiation system. The acceleration voltage was 50kV and the charge density was $5 \mu\text{C}/\text{cm}^2$. After the image transfer, the resist films were baked at 120°C for 90s. Then, the resist films were developed by dipping into tetramethylammonium-hydroxide (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. Figure 1a shows the line resist pattern of 500nm width measured by the AFM.

A commercially available AFM was used for the tip indentation experiment. As a micro tip used for the indentation, a tetrahedral tip mounted on the cantilever apex was used.(Fig.1b) The micro tip was made of a Si_3N_4 film. The radius of curvature of the tip apex was approximately 8nm. The micro tips exposed to the HMDS vapor for 1h were used in order to minimize an interaction force between the micro tip and the resist pattern surface. The calibration measurements of the spring constant correlated well with the manufacturer's given value of $k = 97\text{N/m}$, which was used in all calculations.

(a) Resist line pattern
(2 μm square area)

(b) Tip apex of AFM

Fig.1 AFM image of resist pattern surface and SEM photograph of micro tip apex.

The loading force F by the micro tip can be determined by multiplying the cantilever deflection with the spring constant.

(a) Surface imaging of resist pattern

(b) Tip indentation into resist film

(c) Tip indentation at inner region

(d) Tip indentation into side-wall of resist film

Fig.2 Schematic explanation of tip indentation method into resist pattern surfaces.

2.2 Tip indentation method

Figure 2 shows a schematic explanation of experimental flow of indentation process with the micro tip of the AFM. Prior to the tip indentation, the top surface of line resist pattern is imaged by the AFM in the non-contact mode. (Fig.2a) Subsequently, the micro tip apex enters into the resist film by applying the normal load at the indenting position on the resist pattern surface. (Fig.2b) The meaningful load-distance curve can be obtained. Then, the micro tip is picked up and moved to the next position in the transverse direction to the line pattern. After that, the surface region of resist pattern can be removed using the micro tip, so that the indenting property of the inner region can be investigated. (Fig.2c) Moreover, the indentation of the micro tip can be conducted at the side-wall of the resist pattern. (Fig.2d) The micro tip movement is controlled precisely in the vector scan mode with the piezo stage. By recording the indentation curve simultaneously, the indenting behavior of the tip can be analyzed precisely. The indentation of the micro tip into the resist pattern surface offers a direct approach to determine the condensation properties of the resist pattern.

As the hardening investigation, the EB irradiation and heat treatment were performed to the resist pattern surface. In the EB irradiation, the acceleration voltage was 50kV and the charge density was $5 \mu\text{C}/\text{m}^2$. As the heat treatment, heat treatment at 150°C for 5min was conducted on the hot plate.

3 Results and Discussion

3.1 Indentation position on resist pattern

Figure 3 shows the AFM image of line resist pattern after the tip indentation. The indenting

hollows by shifting the indenting position in the transverse direction can be clearly observed. The indenting hollows are interfered with the adjoining one when the interval of the indenting positions is close each other. In this case, no interference among the indentation hollows can be confirmed because the each indenting position is apart enough to be 250nm. The indenting depth of the micro tip at each position can be determined due to the force calibration curve.

3.2 Surface indentation property across the line pattern

In this section, cohesion properties of the resist pattern surface are characterized by the indentation method. In general, a micro tip indents easily into soft samples such as polymer materials. The resulting indentation curve defined as the relation between the loading force F and the indentation depth x can be employed to determine the condensation properties of the resist sample. Figures 4a and 4b show the resulting indentation curve at the indenting points which are shown in Fig.3. Zero value of the indentation depth indicates an initial contact position of the tip apex with the top surface of the resist pattern. The maximum indentation depth of each point is ranging from 70 to 160nm. It is clearly observed that the indenting curves indicate various kinds of slope value. Particularly, at the pattern edge (1, 10), the weak load is required to indent same depth as compared with that of the center region (6). Therefore, the loading force at the center region becomes relatively large. The indentation slope is regarded as the representative value which reflects the cohesion properties of the resist pattern surface. As shown in Fig.4, the amount of indentation slope in the surface region (less than 20nm) becomes large and it

Fig.3 AFM images of indenting hollows formed on the resist pattern surface. The numbers from 1 to 10 indicate indenting positions with the micro tip.

decreases as indenting more deeper into the resist pattern. The increase of indentation slope indicates the existence of higher cohesion layer in the resist pattern surface. Therefore, it is fair certain to state that the surface hardened layer of the resist pattern can be detected by the tip indentation method. The main advantage of this approach is that the cohesion property of resist pattern can be analyzed without destruction procedure such as cross sectional observation by using scanning electron microscope (SEM). As the indentation depth is close to 160nm, the indentation slope increases gradually. The effect of the interface of resist/substrate would be reflected. Figure 5 shows the position dependency of indenting depth of the micro tip under the loading force of $5 \mu\text{N}$. As approaching the indenting position to the pattern edge ($L=0$), the micro tip is more likely to indent into the resist pattern. Therefore, in order to avoid the edge interference in the indentation

investigation, the indentation point should be apart enough from the pattern edge at least 80nm. In Fig.5, the FEM simulation results are also shown and are discussed in the following section.

Fig.5 Dependency of indenting depth on position under loading force of $5 \mu\text{N}$.

(a) Indenting positions from 1 to 6

(b) Indenting positions from 6 to 10

Fig.4 Indentation curve of micro tip at each position. The numbers from 1 to 10 correspond to those in Fig.3.

3.3 Tip indentation analysis by FEM

In this section, the indentation property of the micro tip into the resist pattern is analyzed by the three dimensional FEM (3D-FEM). Figure 6 shows the element mesh of the resist pattern and the cantilever tip used for the FEM simulation. In this case, the element model is composed with two parts, the resist pattern and cantilever tip. The model is divided into 4380 pieces of elements. Young's modulus of the resist pattern is 1.2GPa. Poisson

Fig.6 Cantilever tip and resist pattern model for 3D-FEM deformation simulation.

ratio of resist pattern is 0.34. The direction of the loading force is normal to the pattern top surface. In the simulation, the indentation curve without the surface hardened layer is employed. The indenting depth of the tip under a certain load of $5 \mu\text{N}$ can be obtained. Figure 7 shows the deformation results of the tip indentation process under the loading force of $5 \mu\text{N}$. By the FEM analysis, the indenting behavior at each indentation position can be clearly simulated. In Fig.7, in the vicinity of the pattern

(a) Simulation mesh

(b) $L = 50\text{nm}$

(c) $L = 125\text{nm}$

(d) $L = 250\text{nm}$

Fig.7 Deformation analysis of indenting micro tip into resist pattern by 3D-FEM.

edge, the resist pattern is considerably deformed by indenting the micro tip. The simulation results of indentation depth at each position are plotted in Fig.5. The same tendency between the experimental result and the simulation one can be confirmed. However, in the vicinity of pattern edge, the difference between these two results can be observed. It seems reasonable to suppose that the formation of surface hardened layer would be strongly affected to the pattern edge effect.

3.4 Indenting into inner region and side-wall of resist pattern

The formation of slight hardened layer on the resist surface is confirmed in the previous section. In this section, the cohesion property of inner region of the resist pattern is analyzed by removal process of the surface region by using the AFM, as shown in Fig.8a. Consequently, the inner region of resist pattern can be exposed to the ambient condition. The AFM image of the new surface is shown in Fig.8b. In Fig.8b, the indenting position of the micro tip is apart from the pattern edge about 100nm. Figure 9 indicates the indentation curve of the inner region of the resist pattern. In the indentation curve, no hardened layer in the new surface region can be confirmed. Therefore, it seems reasonable to suppose that the

(a) Removal of surface region by AFM

(b) Indentation position of inner region

Fig.8 Schematic of indentation method of inner area of resist pattern.

hardened layer of the resist pattern surface would be formed due to lithography processes such as solvent evaporation, chemical reaction with TMAH developer and so on.

Figure 10 shows AFM image and the indentation curve at the side-wall of the resist pattern. In the side-wall of resist pattern, a slight hardened layer can be confirmed, which is similar to that of pattern top surface.

Fig.9 Indenting curve of inner area of resist pattern.

(a) AFM image of sidewall of resist pattern

(b) Indenting curve of sidewall of resist pattern

Fig.10 Indenting curve of sidewall of resist pattern.

3.5 Cross sectional cohesion model of resist pattern

Figure 11a shows the indentation slope curve of various measurement points of the resist pattern, top surface (center), side-wall and inner region. The

surface hardened layer can be clearly observed in the pattern top surface. Slight hardened layer is also confirmed in the side-wall surface. The surface hardened layer in top surface is considerably large as compared with that in side-wall surface of the resist pattern. On the other hand, relatively soft region without hardened layer can be observed in the inner region of the resist pattern. Therefore, the cohesion model of the resist pattern is determined by the indentation investigation as illustrated in Fig.11b. It is fairly certain to discuss that the resist pattern is covered with the hardened layer.

(a) Indentation rate curve of the resist pattern

(b) Cross sectional cohesion model of resist pattern

Fig.11 Cohesion property in cross section of resist pattern.

3.6 Indentation into condensed polymer aggregate surface

In this section, the surface hardened layer of the resist surface is analyzed in nanometer scale. Figure 12 shows the AFM images of the resist surface in higher magnification. The condensation of polymer aggregate can be imaged clearly. The polymer aggregate which size is ranging from 50 to 150nm can be observed. The indenting position P is indicated in the images in Fig.12a. The center among three polymer aggregates is chosen as the indenting position. Under the loading force at $6 \mu\text{N}$, no hollows can be observed (Fig.12b). However, the loading force at $9 \mu\text{N}$, the micro tip indents into

the resist pattern and a clear hollow is confirmed. (Fig.12c) Figure 13 shows the indentation curves at the condensation surface of polymer aggregates. Figure 13a shows the indentation curve in the process of Fig.12a to 12b. Slight indentation of the tip can be confirmed. On the other hand, the indentation of the tip can be confirmed in Fig.13b

(a) Resist surface before indentation (b) After indentation at $F = 6 \mu\text{N}$

(c) Indentation at $F = 9 \mu\text{N}$

Fig.12 Indentation hollows observed in nanometer scale. (500nm square area)

(a) Indentation curve 1

(b) Indentation curve 2

Fig.13 Indentation curve at among polymer aggregates.

which indicates the process in Fig.12b to 12c. Therefore, the surface indenting property reflects strongly the binding force among the polymer aggregates which are condensed on the resist pattern surface.

3.7 Hardening process on resist pattern surface

In this section, surface cohesion properties of the resist pattern surface depending on the hardening processes are investigated. The hardening treatments, EB irradiation and thermal curing, are performed on the resist film surface. Figure 14 shows the AFM images after the tip indentation of the resist pattern surfaces under the loading force of $40 \mu\text{N}$. As the reference, the surface image of resist pattern without hardening treatment (non-treatment) is also shown. The resist film without hardening treatment indicates large hollow as shown in Fig.14a. By the EB treatment, the hardness of resist film surface is relatively high, therefore the indenting depth of the tip is shallow. (Fig.14b) By the heat treatment, the indenting hollows can be formed on the resist surface as shown in Fig.14c, but those are small as compared with those of the reference. These results reflect the hardening nature of the resist material. Figure 15 shows the indentation curve of the resist pattern surfaces. In the indentation curve, the cohesion behavior of resist surface with different hardening treatments can be observed clearly.

(a) Non-treatment

(b) EB irradiation

(c) Heat treatment

Fig.14 AFM images of indentation hollows after tip indentation under $40 \mu\text{N}$.

Fig.15 Indentation curve for various hardening process.

4. Conclusion

By the tip indentation technique with the AFM, the cohesion properties of the resist pattern surface can be analyzed quantitatively. The pattern edge effect for indentation analysis is clarified. In order to avoid the edge interference in the indentation investigation, the indentation point should be apart enough from the pattern edge at least 80nm. By the FEM analysis, the edge effect on the indentation property can be explained. The hardened layer formed on the top surface of the resist pattern can be detected. By removing the surface hardened region, the cohesion property of the inner region is analyzed. No hardened layer is observed in the inner region of resist pattern. The surface hardened layer of the resist pattern can be observed in the side-wall as well as the top surface of the resist pattern. In nanometer scale, the surface hardened layer of the resist pattern can be analyzed. The surface hardened layer would reflect the binding force among polymer aggregates condensed in the resist pattern surface. The surface cohesion properties of the resist pattern surface depending on the hardening processes are investigated. The cohesion behavior of the resist pattern surfaces with

different hardening treatments can be analyzed clearly. One can safely state that the surface cohesion properties of resist pattern are analyzed by the tip indentation method.

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