Nano-scale Deformation of Resist Film Surface by Humidifying and Drying Processes

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Nano-scale deformation of resist film surface is analyzed by using atomic force microscope (AFM) in a humidity controlled chamber. It is clarified that the condensation size of polymer aggregates of resist material are slightly changed due to humidity change. As one major factor, Laplace force acting among polymer aggregate due to surface adsorbed water is discussed. The deformation model of condensed polymer aggregates is proposed.

Keywords: resist pattern, deformation, polymer surface, water meniscus, adsorbed water, atomic force microscope

1. Introduction

Recently, the minimum design rule of resist pattern for ultra-LSI devices has been required under 25nm. In this regard, condensation control of polymer aggregates in a resist pattern surface has been paid attention in order to decrease line edge roughness. We have studied the nano-scale water meniscus formed on resist film surface observed by the tip adsorption method.[1] In this study, we focus on nano-scale deformation of the resist polymer surface during the humidification and drying processes. The deformation model of condensed polymer aggregates is proposed.

2. Experiment

A KrF resist chemically amplified positive resist consisting of polyhydroxystyrene with acid labile blocking groups and photoacid generators was coated on a Si (100) wafer by spin coating method. The blocking group was tertbutoxy carbonyl (t-BOC). The photoacid generator was trifluoromethanesulfonic acid. The heating treatment was accomplished at 100°C for 90s. The thickness of the resist film was 550nm. An atomic force microscope (AFM) system was used for observation of resist surface in nano-scale. The cantilever tip was made of Si₃N₄. The spring constant of the cantilever was 0.351N/m and the

curvature radius of the tip apex was 8nm. During the surface observation, the ambient condition of AFM chamber was humidified and dried from nearly 0%RH to 80%RH. The cross sectional profile of the resist film surface was observed.

3. Results and Discussion

The AFM image of resist surface in dry condition (5.9%RH) is shown in Fig.1. The polymer aggregates around 20nm size can be confirmed. The resist surface is undulated in 34nm topographic height. The white line shown in Fig.1 is the indication line of cross sectional profile and circles α and β are polymer aggregates for the condensation analysis, respectively.

Fig. 2 shows the cross sectional profile of the resist film surface on each humidity condition.

Fig.1 AFM image of resist polymer surface measured in dry air.(5.9%RH)

Fig.2 Cross sectional profile of resist film surface. Each contour line indicates topography in various humidity condition.

In Fig.2, the position of polymer aggregate β is defined as the height origin. It is clearly observed that the height of the polymer aggregate α is changed in both humidify and drying processes. During humidification to 40%RH, the height of polymer aggregate α increased and reached to a maximum, and then, it decreased until initial height until 80%RH. On the contrary, in the drying from 80 to 40%RH, the height of the polymer aggregate α further decreased. The height of the polymer aggregate α increased again during the drying until nearly 0%RH. However, the position of the polymer aggregate α couldn't correspond to the initial height. The surface profile change in the ambient conditions should be affected by the surface adsorbed water layer. In this regard, we already studied the nano-scale meniscus due to adsorbed water of resist film surface acts to adhere the micro tip on them.[1] The Laplace force about 20nN was measured on the resist film surface with the AFM.[1-3]

From the experimental results, the deformation model of the polymer aggregate due to the adsorbed water can be considered as shown in Fig.3. In the initial humidity condition of 0%RH, the resist surface is dried. (Fig.3 (a)) During humidification, the polymer aggregates are condensed each other due to the adsorbed water of the resist surface and are slightly deformed. (Fig.3 (b)) In the higher humidity condition, it can be considered that the nano-space among polymer aggregates would be filled with the adsorbed water. In this case, the polymer aggregates would be easy to deform. (Fig.3 (c)) During drying, the adsorbed water of the resist surface evaporates. The residual water among polymer aggregates acts to attract each other. (Fig.3 (d)) In the 0%RH condition after

Fig.3 Deformation model of polymer aggregate in resist film due to adsorbed water under humidifying and drying processes.

drying process, the resist surface is dried and the polymer aggregates condense to the initial condition. However, the topography of the resist surface is slightly different from the initial profile. (Fig.3 (e)) [2]

4. Conclusion

We discussed the nano-scale deformation of the resist surface due to ambient humidity. The polymer aggregates of resist film were deformed due to surface adsorbed water. The deformation model of resist polymer aggregates was proposed.

Acknowledgement

The present work was partially supported by Grant-In-Aid Scientific Research from Japan Society for the Promotion of Science. (Scientific Research (B) 19360157).

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