Nano-wetting of DI-water analyzed by AFM

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1. Introduction

As miniaturizing a design rule of micro electronic devices, wetting control of various solutions on micro pattern surfaces has been focused. A number of distinct experimental aspects have been employed to study contact angle of small side droplet.[1-4] Moreover, it is well known that wetting property of a liquid on a resist material strongly depends on its pattern shape.[5] In this paper, we discuss contact angle measurement of DI-water in nano-scale by using atomic force microscope (AFM). The dependence of contact angle on drop size can be explained by employing surface enhanced effect.

2. Experiment

As a flat substrate in atomic scale, a cleavage mica and a Si single crystal surface were prepared. The mica surface was prepared by cleavage in ambient condition. The Si(100) surface was cleaned with a organic solvent and etched in HF aqueous solution. Figure 1 shows a schematic of observation system of nano-scale of liquid drop. A contact mode AFM was employed for nano-drop observation and the drop shape images were obtained using a narrow and thin Si_3N_4 cantilever. For the investigation, a conical shape tip mounted on the cantilever was used. The cantilever of spring constant of 0.082 N/m was used. The curvature radius of tip apex was 8nm. The cantilever and tip surfaces were hydrophilic by treating in oxygen plasma for 3s before use. By increasing relative

humidity in the AFM chamber, some clusters of water molecular would be formed, then the growth of nano-drop can be confirmed. As the macro scale analysis, the contact angles were measured by using a goniometer. The drop size was changed from 0.2 to 8 mm in order to analyze the size dependency.

Fig.1 Schematic of liquid drop imaging by using AFM.

3. Results and Discussion

Figure 2 shows the AFM image of nano-liquid drop formed on the mica cleavage surface. The clear image of liquid drop can be obtained. The contact angle of the liquid drop can be estimated by the analysis of cross section graphical analysis. The diameter, height and contact angle of this liquid drop are 119nm, 15nm and 25 degree.

Fig.2 AFM image of nano-scale liquid drop formed on cleavage mica surface. (15°C, 73%RH)

Fig.3 Contact angle of liquid drops in various sizes.

Figure 3 summarizes the contact angle depending on liquid drop size. The contact angles on the Si substrate were observed by using the goniometer. It can be confirmed that the contact angle increases as decreasing the liquid drop size. The similar tendency can be seen in the report by Gavdos.[4] Gaydos found the increase of contact angle of organic solvent by 5 degree when the drop size was decreased from 4 to 1mm contact radius.

As the discussion, we try to estimate the contribution of surface property to wetting behavior. In the case of a sphere condensed matter. The energy ratio P of surface area / volume can be expressed as the following formula.

$$P = \frac{E_s}{E_c} = \frac{4\pi r^2 \gamma_s}{\frac{4}{3}\pi r^3 \gamma_c} = \frac{3}{r} \frac{\gamma_s}{\gamma_c} \quad (1)$$

where the symbol r denotes radius of sphere. The symbols E_s and E_c represent the energies of unit surface and unit volume. Figure 4 shows the size dependency of energy ratio P for the various shape of solids. It is clearly observed that the surface

Fig.4 Energy ratio of surface area / volume for various three dimensional shapes.

contribution is enhanced rapidly in the minute size. Therefore, it can be considered that the contribution of surface tension of liquid drop increased in the wetting phenomena. Therefore, the contact angle of liquid drop increased as shown in Fig.3. The larger contact angle indicates the lower wetting behavior. In the future lithography, a small gap less than 50nm will be employed in the device manufacture. It can be considered that some defects are more likely to generate in various wetting processes such as pattern development, plating, cleaning, wet etching and so on.

4. Conclusion

The contact angle of DI-water drop in nano-scale can be analyzed with the AFM. The surface property of liquid drop is dominant in nano-scale. This result would affect on various wet processes in micro device manufacture.

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