Atomic Force Microscopy Study on the Surface of Silver Halide Microcrystals

Katsuhiko Suzuki and Sadayasu Ishikawa
Konica Corporation
Tokyo, Japan

Abstract

The surface characteristics of silver halide microcrystals used in photographic systems were investigated in aqueous media, using the force curve method of AFM (Atomic Force Microscopy).

The short-range interaction force and the adhesive force between the surface of silver halide microcrystals and a probe tip were measured. As a result, differences in the two forces were observed between gelatin-eliminated crystal samples and gelatin-adsorbed crystal samples.

From the result, it is assumed that the two forces are attributed to presence of the gelatin layer adsorbed on the crystal surfaces. And it was found that the thickness of the gelatin layer in the aqueous media is directly estimable using this method.

Introduction

Recently, AFM has been widely applied in silver halide science. For example, it was used for observation of silver halide grain surface[1], observation of crystal surface adsorbate[2,3] and determination of crystal grain thickness[4] and so on. But the application has been limited to the region of morphological study.

On the other hand, in colloid science region, force curve method, which is one of the experimental techniques using AFM, has been used for studying the surface properties of colloidal particles[5]. This method has been used for analysis of solid surface properties by detecting forces between sample surfaces and probe tip, and is known to be useful for *in situ* investigation of surface interaction on molecular scales in various solutions.

In silver halide science, the crystal surface properties are also of great concern in relation to so many phenomena involving silver halide crystals, such as physical pressure deformation and grain aggregation.

The aim of this study is to show the usefulness of the force curve method in silver halide science.

Theory

Principles of the force curve method are as follows: Sample mounted on sample holding unit which is driven with piezoelectric scanner reciprocates vertically toward cantilever tip and backward. When the sample is in contact with the tip, the cantilever bends backward. As the sample moves away from the tip, the tip may still keep in contact with the sample surface with adhesive force while the cantilever is bending toward the sample. Thus attractive forces are measured from toward the sample component in the cantilever deflection and repulsive forces by the opposite direction component.

Figure 1 shows general force curve schematically; F represents the surface force and h represents the separation distance between the sample surface and the tip.

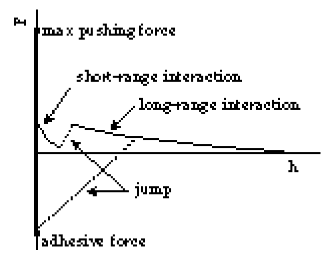

Figure 1. Scheme of the Force Curve

In this study, however, long-range interaction was not observed. Then we have directed attention to short-range interaction force and adhesive force.

Experimental

Sample Preparation

Silver bromide tabular grain emulsion was produced by conventional double jet method. The emulsion was prepared to contain 0.353mol of AgBr and 7.0g of alkali-processed gelatin in 200g of the emulsion.

Gelatin-eliminated sample was prepared as follows: 1g of the emulsion was diluted with 100ml of water (40°C), then suspension was centrifuged and solution was removed by decantation. Again, the precipitate was dispersed in 100ml of water (40°C) and washed. These processes were repeated 5 times. Finally, the precipitate dispersed in water was coated on ITO (Indium Tin Oxide) substrate with spatula and dried.

Gelatin-adsorbed sample was prepared as above without decantation and washing processes. The diluted emulsion was coated on the substrate, rinsed with water and dried.

Gelatin-re-adsorbed sample was prepared by soaking the gelatin-eliminated sample in 1% solution of the gelatin for 30min., then rinsed with water and dried.

Force Curve Method Operation

Force curve measurement was carried out in water, using NanoscopeIII (Digital Instruments) AFM system, a commercially available Si_3N_4 cantilever (spring constant 0.12N/m) and a D-scanner (maximum observation area 12.0μm x 12.0μm). The samples were stored in water following Drake et al.[6]. A transparent plate was attached with a cantilever mount, and water was held between the transparent plate and sample holder by surface tension.

Results and Discussion

Estimation of the gelatin layer thickness

Figure 2 shows short-range force curves of gelatin-eliminated sample and gelatin-re-adsorbed sample. A non-liner region of several 10nm was reproducibly observed in the short-range force curve of the gelatin-re-adsorbed samples with some deviation among each crystal grains.

Similar values for non-liner regions were obtained on the gelatin-adsorbed sample surfaces.

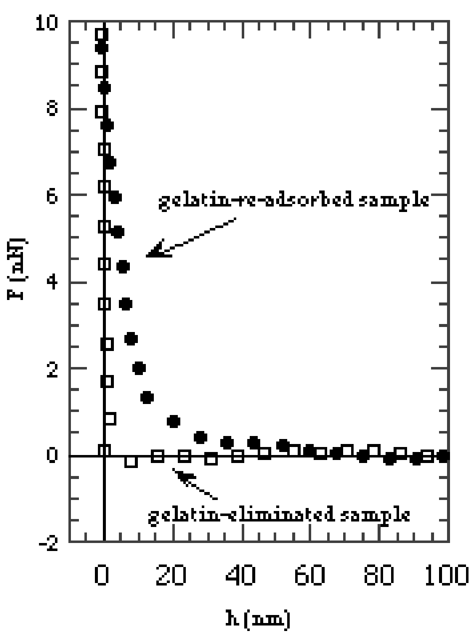

Figure 2. Short-range force curves of the gelatin-eliminated sample and gelatin-re-adsorbed sample.

Generally, such non-liner short-range force is attributed to three possibilities;

1. presence of adsorbed layer,
2. softness of sample surface itself, and
3. indistinct solid / liquid interface.

On silver halide surface, it is most possible that presence of adsorbed layer originates the non-liner region. To assure a hypothesis that the interaction force originates from the presence of gelatin layer, direct image observation of the gelatin layer was attempted. Figure 3 shows an AFM image of crystal grain in the gelatin-re-adsorbed sample. Before the image capturing, square area on the crystal grain surface was pre-scanned by probe tip with stronger pushing force (10nN or high) to sweep out the adsorbed gelatin. By profile analysis, a cavity with 15 to 20nm depth was observed. On the gelatin-eliminated sample surface, such cavity by pre-scanning was not produced. Estimated average gelatin layer thickness from the force curve for this crystal grain was 19nm. Therefore results obtained from two methods were roughly in agreement.

Compared with previously reported values[4] (4 to 6 nm), these thickness values are rather large. But as far as authors know, direct measurement of wet gelatin layer thickness would not been reported.

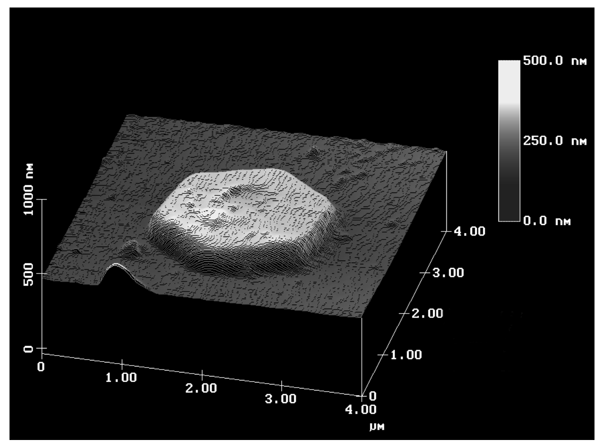

Figure 3. AFM image of the pre-scanned crystal grain

From these results, it is suggested that non-liner region of the short-range force curve shows pressing-down process of the gelatin layer by probe tip. Using this short-range force curve method, thickness of the gelatin layer adsorbed on crystal grains in the aqueous media is directly estimable.

Dependence of the adhesive force on maximum pushing force

Figure 4 shows dependence of the adhesive force on the maximum pushing force for gelatin-adsorbed and gelatin-eliminated sample surfaces. As shown in this figure, gelatin-adsorbed sample surfaces have characteristics that the adhesive force is proportional to the pushing force , while the adhesive force of gelatin-eliminated sample surface is independent of pushing force. These adhesive forces observed for gelatin-adsorbed sample surfaces are apparently stronger than van der Waals force. Similar phenomena were reported previously[5] on mica surfaces measured in water and alcohol mixture. In the report, strong adhesive forces were identified as water-bridging effect between the sample surfaces and the tip. In our case, one possibility we deduced is as follows: the stronger the maximum pushing force is made, the longer contacting time of tip and gelatin layer gets, then apex of probe tip penetrate into the gelatin layer deeper and contacting area of the tip and the gelatin layer gets wider. As the result, adhesive force becomes stronger.

For further interpretation, additional experiments are needed. Anyway, authors are interested in the result that gelatin adsorbed layer brings specific adhesive property on silver halide crystal surfaces.

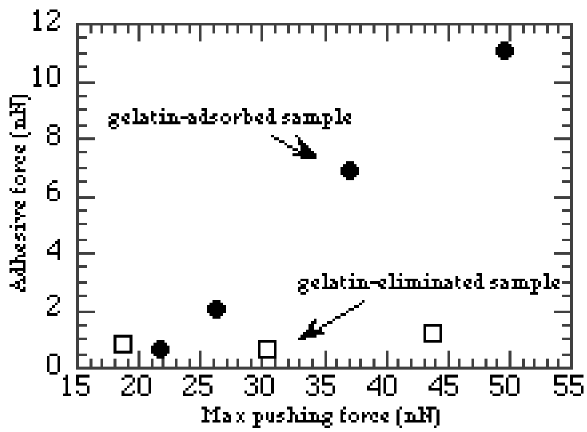

Figure 4. Dependence of the adhesive force on maximum pushing force

Conclusion

It is shown that using the force curve method, direct measurement of adsorbed gelatin layer thickness on crystal grain surfaces has been achieved. It is also indicated, using the force curve method, that gelatin adsorbed layer brings specific adhesive property on silver halide crystal surfaces.

In this report, the potential of the force curve method applied to the silver halide science was presented. There exist more possibilities and room for application of this method in this region. Authors are now preparing next study, which includes force curve measurement in gelatin aqueous solution, in various pH or pBr solutions and so on.

References

1. H. Takada and H. Nozoye, *Langmuir,* **9**, 3305 (1993).
2. K. Suzuki and H. Nozoye, *International Symposium on Silver Halide Imaging*, IS&T, Victoria, Canada, 1997, pg. 212..
3. H. Saijo and M. Shiojiri, *J. Imaging. Sci. and Technol.,* **40**, 111 (1996).
4. H. Coll and J. E. Fornalik, *J. Imaging. Sci. and Technol.,* **40**, 185 (1996).
5. Y. Kanda, S. Iwasaki, and K. Higashitani, *J. Colloid Interface Sci.* , **216**, 394 (1999).
6. B. Drake et al, *Science,* 243, 1586 (1989).

Biography

Katsuhiko Suzuki received his B.Sc. in 1987 and his M.Eng. in 1989 both in inorganic chemistry from Waseda University. He has worked at Konica Corporation since 1989, where he specializes in the research and development of AgX grain precipitation and characterization technology.