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Thesis

**Study on adhesion forces of small particles
on substrates using atomic force microscopy**

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Abstract

Small particles are actively used in various fields for industrial applications. However, small particles can cause a variety of problems. For example, external forces acting on the small particles located on various surfaces can cause them to scatter and move, for example, from the surface of the processing apparatus to specimen surfaces, resulting in product defects. It is important to understand the forces acting on small particles to control the behavior of small particles and avoid the above problems. The important forces acting on small particles on a substrate surface are the van der Waals force and capillary force, which are the main adhesion forces of small particles that are of the micrometer order or smaller.

Atomic force microscopy (AFM) is a technique able to evaluate the adhesion force of small particles quantitatively. When using an AFM probe tip with a small particle attached, or an AFM probe tip shaped to simulate a small particle, we can evaluate the adhesion force of the small particle on the substrate surface with force curve measurements using AFM. A unique feature of this method is that it enables to evaluate the adhesion force under various substrate surface conditions and surrounding environments using the same small particle. From the results of this experimental method, we may find a method of increasing the mean adhesion force or suppressing the variation in the adhesion force of multiple particles on a surface in the apparatus, which can prevent particle scattering due to external forces.

The results of two investigations on the adhesion force of small particles on a substrate surface using AFM in an experimental system that simulates systems used in industrial applications are reported in this thesis. Aluminum (Al) was used as the material of the substrate surface and silica was adopted as the material of the particles to combine materials that are applied to various products in industrial fields.

First, an investigation on the effect of surface roughness on the particle adhesion force is reported. The adhesion force of silica particles on Al substrate surfaces with different surface roughness was evaluated using AFM. From the experimental results, it was shown that not the van der Waals force but the capillary force had a profound influence on the adhesion force in the atmospheric experiments. Moreover, a new

surface roughness analysis method was proposed to predict the variation in particle adhesion force. Based on the model of contact theory, the surface roughness of the substrate was re-analyzed in the local substrate surface areas, which actually interact with small particles. As a result, a clear correlation between the surface roughness of the local area of the substrate surfaces and the variation in the adhesion force of the particles was found for the first time, which could not be found using a conventional analysis method. Furthermore, it was demonstrated that the variation in the adhesion force of small particles could be reduced when the surface roughness of the substrate was reduced to the nanometer order or less, whereas the mean value of adhesion force increased for particles of micrometer-order size and did not change for particles of sub-micrometer-order size. These findings show that reducing the surface roughness of the wall of apparatus to the nanometer order or less is effective in preventing the scattering of small particles due to external forces, which increase as the size of the small particles increases.

Next, an investigation on the effect of substrate temperature on the particle adhesion force below room temperature in high vacuum is reported. The adhesion force was evaluated on the two Al substrate surfaces with different relative surface roughness for a micrometer-sized silica particle. For the rough substrate surfaces, with surface roughness of a few nanometers, the adhesion force was almost independent of the substrate temperature as this temperature was decreased from room temperature. However, it was found that the capillary force increased the adhesion force, even in high vacuum, for substrate surfaces below room temperature when the surface roughness of the substrate was of the sub-nanometer order. The change in the adhesion force with decreasing substrate temperature was due to the surface diffusion of water molecules. The activation energy of the surface diffusion of water molecules in the range 273–213 K was estimated as 96 meV. Based on the experimental result of the adhesion force increase with increasing the contact time, the mechanism of increase in the adhesion force of small particles on a substrate surface in high vacuum was explained for the first time by the growth of the liquid bridge due to the surface diffusion of water molecules. Furthermore, it was shown that the surface roughness of the wall must be reduced to the nanometer order or less to increase the adhesion force and prevent the scattering of small particles.

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1 Introduction

1.1 Background

Small particles are actively utilized for products in various industrial fields, such as ceramics, batteries, electronic components, food, pharmaceuticals, and cosmetics. Diverse types of small particles with different sizes, materials, and surface modifications are used to meet the characteristics of such products. An example of these products is the qualitative antigen test kit used to evaluate SARS-CoV-2, which has caused significant problems in recent years. Qualitative antigen test kits contain metal or polymer particles designed to adhere specific antigens and change the color of the test line when a certain number of antigens are contained in the collected specimen.¹⁾ Techniques to inspect or measure small particles using microscopy technology have been developed for further applications of this method.²⁾

While used in various applications, small particles can cause problems in industrial fields. For example, small particles with a diameter of several hundred nanometers or less may cause health problems if taken into the human body.^{3,4)} Therefore, regulations have been established in Europe and other countries regarding the handling of nano-sized materials, including small particles.⁵⁾ Against this background, a consortium has been established in Japan to develop measurement and evaluation techniques using various microscopes for the management of fine particles.⁶⁾

Semiconductor device manufacturing is a prominent example of a field in which small particles cause problems.⁷⁾ Particle contamination in the manufacturing process is a critical issue in semiconductor device manufacturing. Particles that unintentionally adhere to the wafer surface form defects in the subsequent semiconductor manufacturing process. This problem is schematically presented in Fig. 1.1. Here, the adhered small particles form a mask during plasma etching, resulting in defects in the subsequently formed circuit. The circuit defects reduce the production yield of semiconductor devices.

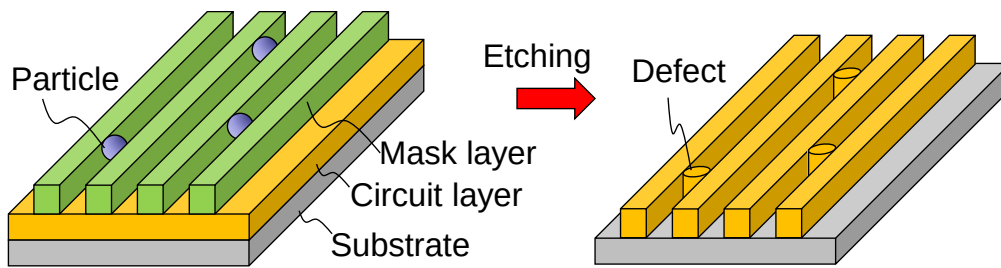


Fig. 1.1 Schematic showing a problem involving particles, which causes defects during semiconductor device manufacturing processes.

To prevent problems related to the adhesion of small particles, semiconductor devices are manufactured in clean rooms with all small particles removed. However, it is difficult to completely avoid problems related to small particles, even in such a controlled environment. First, no matter what apparatus is used, a finite number of small particles remain on the inner-wall surfaces. Furthermore, external forces, such as air flow, plasma, and electric fields, can act on the small particles on the chamber surface or chamber components of apparatus used for plasma etching, lithography, and inspection. As a result, small particles are scattered into the chamber, as shown in Fig. 1.2. If such small particles are repeatedly scattered in the apparatus, the semiconductor wafers become contaminated with small particles. Therefore, the behavior of particles must be precisely controlled during the manufacturing processes. In state-of-the-art semiconductor manufacturing processes, even small particles of a few tens of nanometers in diameter can cause crucial problems that reduce the production yield. It has been reported that the number of particles increases inversely proportional to the cube of the diameter of the particles, and consequently, there are more particles with smaller diameters in the environment. Therefore, the semiconductor field is a typical example of a field impacted by problems due to small particles.

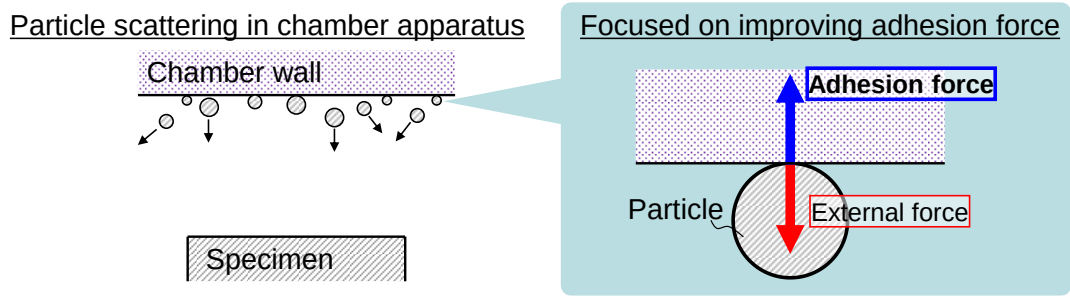


Fig. 1.2 Schematics illustrating particle scattering in chamber apparatus. The particles detach from the surface of the chamber wall when the external force applied to the particles exceeds their adhesion force.

Research has been conducted on the apparatus used to fabricate semiconductor devices, to understand the behavior of small particles and reduce their number to improve product yields.^{8,9)} In the case of a plasma etching system for semiconductor device processing, small particles may be scattered from the chamber wall surface when the semiconductor wafer is processed by plasma. An example of such small particle scattering has previously been reported.^{10–14)} Similarly, there was another reported case in which small particles were captured colliding with chamber walls and the walls of a turbo molecular pump.^{15,16)} According to these studies, it is important to proceed with research on controlling the behavior of small particles.

Adhesion forces and external forces, which determine the behavior of small particles on a substrate surface, can be considered. Adhesion forces maintain the contact state of the particles, and external forces pull the particles away from the surface. If either force is controlled, the lift-off of small particles from the substrate surface and the scattering of small particles may be prevented. This study focused on the adhesion force of particles on the surface of a substrate to obtain an approach to controlling the behavior of small particles. The reasoning is because it can be difficult to change the external force acting on small particles within apparatus in which the behavior of small particles must be controlled. Moreover, it may be possible to control the adhesion force of small particles by changing the surface roughness of the substrate via surface treatment, the materials of the substrate, the surrounding environment of the substrate, such as humidity and vacuum, or the temperature of the

substrate surface. The behavior of small particles may be controlled by first clarifying the effects of the above parameters on adhesion forces and then introducing the findings back into the systems for practical use.

Various theoretical and experimental studies have been conducted to investigate the parameters that affect the adhesion force of small particles. Using techniques such as the pendulum, centrifuge, vibrational, impact separation, electric field detachment, aerodynamic, and hydrodynamic methods.^{17,18)} However, these methods cannot be used for small particles with a radius of less than a few micrometers, and the results previously obtained were statistical data containing information on multiple particles.

Atomic force microscopy (AFM) can be used to evaluate the adhesion force of a single small particle. One AFM method involves the application of a force onto a particle adhered to a substrate from the lateral direction using the tip of an AFM probe. The adhesion force can then be evaluated by measuring the force with which the particles leave the substrate surface when a certain amount of force is applied.¹⁹⁾ However, it is difficult to repeat the adhesion force evaluation experiment for the same particles using this method. Therefore, it is not possible to evaluate fixed parameters related to small particles. In addition, because this method applies force from the lateral direction, it is impossible to directly evaluate the adhesion force acting perpendicular to the substrate surface.

In contrast, AFM force curve (force–distance curve) measurements can give direct information on the force between the AFM probe and the substrate. Here, we consider a method of evaluating the adhesion force when the surface of the substrate or the interface between small particles and the substrate surface, is different but the small particle is the same. When using an AFM probe tip with a small particle attached, or an AFM probe tip shaped to simulate a small particle, the adhesion force of the particle on the substrate surface can be directly evaluated using AFM force curve measurements. A unique feature of this method is that it enables the evaluation of the adhesion force under various specimen conditions and surrounding environments using the same small particle. This method is known as the colloidal probe technique²⁰⁾ and can be applied to investigations in not only air, but also liquid and vacuum. This feature enables the study of the adhesion forces of small particles on a

substrate surface in a simulated real system, in which small particles are in contact with the surface, by setting up an appropriate experimental system.

It is important to evaluate adhesion forces in contact conditions under various conditions; for example, substrate surfaces and small particles with different surface roughness, materials, and temperatures, in air or vacuum, and at different relative humidity. Experimental analyses and results have been reported for several of the above conditions.^{21–23)} Some present the evaluation result of the adhesion force of small particles with varying size.^{24,25)} Additionally, based on AFM measurements of the adhesion forces on several substrate surfaces with different surface roughness, models and equations have been proposed to present the surface roughness dependence of the van der Waals force and capillary force, which are the main factors behind the adhesion force of small particles.^{26–29)} Moreover, results for an AFM evaluation of adhesion forces on several substrate surfaces composed of different materials have been reported.^{30,31)} In addition, there are several reports in which the adhesion force of small particles was evaluated by AFM under various parameters that may affect the adhesion force, such as relative humidity, degree of vacuum, and the temperature of the substrate surface.^{32–35)} However, because of the variety of parameters and their wide ranges, there are limitations in evaluating all the parameters that affect the adhesion force of small particles, and the reported results may have limited industrial applicability.

Plasma etching systems for semiconductor device processing and electron microscopes used for the surface analysis of various specimens, including semiconductor devices, use a vacuum environment and may adopt a cooling method for certain components in the system. In plasma etching systems, cooling stages are used to ensure the uniform etching of semiconductor wafers.^{36,37)} In electron microscopes, hydrocarbon gas molecules, which react with the electron beam to form carbon contamination on the specimen surface, remain in the vacuum owing to the specimen or equipment.^{38,39)} To prevent the formation of such contamination, an anti-contamination trap is installed, which holds a cooled metal component near the specimen to trap residual gas, including hydrocarbon gas molecules. Wall surfaces with different surface roughness are also used in these apparatus. Further evaluation of the adhesion force of small particles in accordance with the conditions of such

apparatus would contribute to the development of industrial fields in addition to the acquisition of new knowledge.

1.2 Purpose

With the aim of applying the obtained knowledge to the industrial field, this study focused on the experimental systems and parameters that are of concern in the industrial field and evaluated the adhesion force of small particles via AFM. Using the experimental results, parameters that affect the adhesion force were investigated, and the origin of the force that causes the adhesion force was explored. In particular, the adhesion force dependence on the roughness and temperature of the substrate surface was investigated in view of practical surfaces and environments, as applied to the equipment mentioned above.

First, the reason for investigating the surface roughness dependence of the particle adhesion force is explained. Figure 1.3 shows examples of previous studies that evaluated the adhesion forces of small particles on substrate surfaces with different surface roughness, along with the scope of this study. Adhesion forces have been evaluated on mica, graphite, polished wafers, and their oxide wafers as flat substrates with surface roughness of a few nanometers or less.^{40,41)}

There are examples in which artificially fabricated substrates with surface roughness varying from a few nanometers to several tens of nanometers have been used for systematic analysis.²²⁾ These are considered ideal surfaces that are easy to systematically analyze and use to construct a model that explains the experimental results. Conversely, there have been studies on practical or near-practical surfaces including substrate surfaces where thin films have formed, or substrate surfaces with different surface roughness formed by plasma treatment.^{23,28)}

In addition, the surfaces of carbon steel and nickel alloys have been investigated as examples of equipment wall surfaces.⁴²⁾ The adhesion forces of graphite particles were evaluated in view of the wall surfaces of a high-temperature gas-cooled reactor. However, graphite particles are not practically utilized in the semiconductor process, and the researchers only measured on rough surfaces, not covering the wide range of surface roughness, including the sub-nanometer order, which can be achieved by commercially available surface treatments.

Previous studies that investigated the surface roughness dependence did not evaluate the systems of small particles in semiconductor apparatus. In this study, in

view of the practical system used in industry, a system was investigated in which small particles adhere to a wall surface material with a wide range of surface roughness.

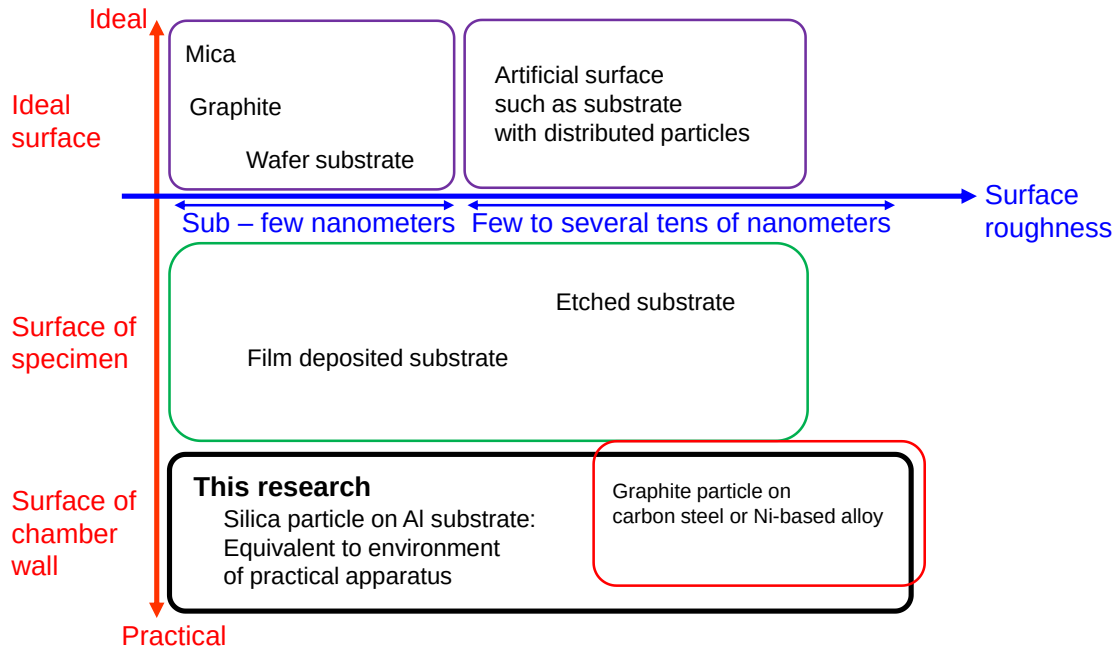


Fig. 1.3 Range of surface roughness reported in previous studies and covered by this study.^{22,23,28, 40–42)}

As mentioned earlier, when a large number of small particles exist in a system, it is important to control the behavior of individual particles. Thus, it is vital to control not only the mean value of the adhesion force, but also the variation in the adhesion force. Thus, one of the purposes of this research is to investigate the adhesion force of small particles using AFM and clarify the surface roughness dependence of the mean values and variation of the adhesion force in view of a practical industrial system.

Next, the reason behind investigating the adhesion force of small particles when substrate surfaces are cooled to below room temperature in high vacuum is explained. Figure 1.4 shows examples of previous studies that evaluated the adhesion forces of small particles on substrate surfaces in different environments, humidity, and vacuum and at different substrate temperatures. Some reported measurements in systems with

different relative humidity (RH) under atmospheric pressure.^{29,43)} They showed that the capillary force increased as the RH increased. However, the magnitude of the adhesion forces was the same in both 14%RH and 0%RH in an N₂ environment and high vacuum, even though the system had fewer water molecules than the environments mentioned above. The author noted that the capillary force due to water molecules caused the adhesion force.³⁴⁾

Furthermore, it was reported that the adhesion force was smaller in an ultra high vacuum environment, constructed by evacuating the system for several days, than in an environment with 45%RH.⁴⁴⁾ The effect of the capillary force on the adhesion force in different environments was studied, revealing that the capillary force cannot be ignored as a factor of the adhesion force. The capillary force could be removed if the temperature of the substrate surface was increased, regardless of an air, high vacuum, or ultra-high vacuum environment.^{35,45,46)}

There are examples of studies on adhesion forces in various environments in elevated temperatures ranging from room temperature to several hundred degrees Kelvin. However, there has been no systematic study on the adhesion force of small particles when the substrate surface is below room temperature. If an AFM system is utilized as the temperature of the substrate surface is lowered in air, condensation of water would occur on the components of the AFM system. To utilize AFM in low temperature environments, the system must be evacuated.

Furthermore, it is important to evaluate the adhesion force of small particles in high vacuum and at low temperatures because these are the conditions that have been used practically in modern semiconductor industry, such as in plasma etching systems and electron microscopes. Thus, another purpose of this research is to study the effect of substrate temperature, below room temperature and in high vacuum, on the adhesion force in view of a practical system.

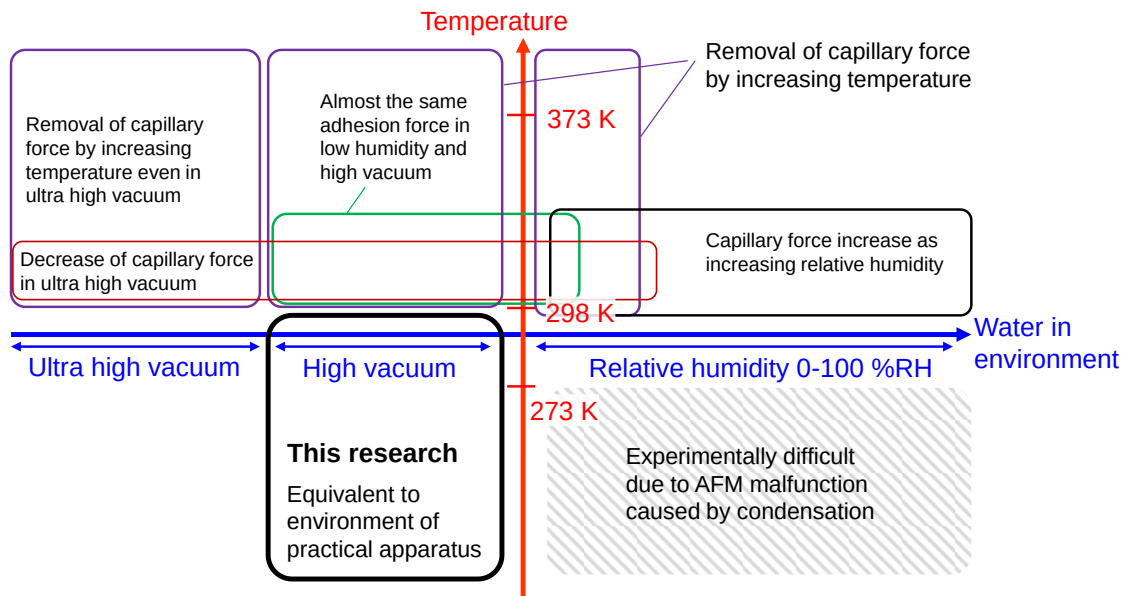


Fig. 1.4 Range of parameters of the substrate temperature and environment reported in previous studies and covered in this study.^{29,34,35,43–46)}

In this study, Aluminum (Al) substrates, which are used for the inner walls and stage components of various equipment in the manufacture of semiconductor devices and other products, were used as the substrate surface. In addition, silica was selected as the material of the small particles because Silicon (Si) wafers are used in the manufacture of semiconductor devices, and Si-based materials are used in various fields and are actively utilized in products.

1.3 Structure of thesis

The structure of this thesis is described below.

In Chapter 2, the methods and principles necessary to understand the experimental results are presented. First, technical details related to AFM, which are essential to evaluate the adhesion force of small particles, are described. The van der Waals force and capillary force are also described, which are the two main components of the adhesion force of small particles. Then, contact theory, which describes the contact interface state between small particles and the substrate surface, is explained.

In Chapter 3, the evaluation results of the surface roughness dependence of the small particle adhesion force are reported.⁴⁷⁾ Substrate surfaces with different surface roughness (obtained via surface treatments used in industrial applications) were used to evaluate the adhesion force of small particles. In view of the importance of controlling the behavior of particles in industrial apparatus, we focus on the variation in the adhesion force of small particles rather than the mean value and discuss the experimental results.

Chapter 4 reports the results of an investigation on the substrate surface temperature dependence of the adhesion force of small particles below room temperature in high vacuum.⁴⁸⁾ Based on the findings in Chapter 3, adhesion forces between small particles and the two different substrate surfaces with different surface roughness were evaluated. In this study, the capillary force was focused on, which contributes more to the adhesion force than the van der Waals force and is affected by temperature change. The experimental results are discussed based on the behavior of water molecules, which affect the capillary force.

Chapter 5 contains the conclusions of this study and future research.

2 Methods and Principles

2.1 Atomic Force Microscopy (AFM)

2.1.1 Outline of AFM

AFM is a technique that enables the analysis of mechanical properties such as surface topography and viscoelasticity, and electrical properties, such as resistance and surface potential by detecting the interaction force between the cantilever tip of the AFM probe and the substrate surface, which is fed back to a control circuit. In AFM, the optical lever method is often used to detect small displacements in the AFM probe. Figure 2.1 shows a schematic of AFM based on the optical lever method.

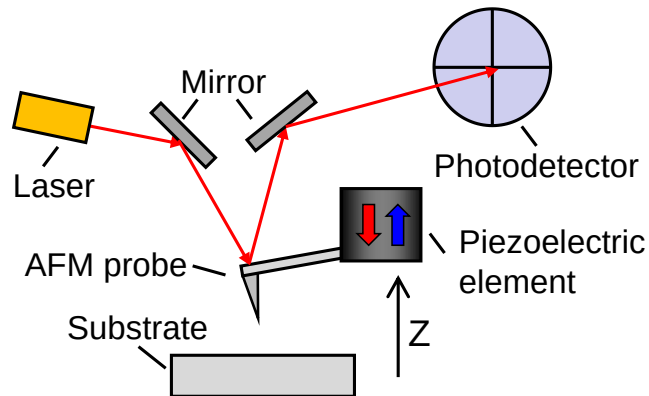


Fig. 2.1 Schematic of AFM using the optical lever method

In the optical lever method, a laser is irradiated onto the back side of the AFM probe tip using optical mirrors, and the reflected light is guided to a photodetector. The photodetector has a light receiving area that is divided into four sections and detects changes in the vertical and horizontal directions of the reflected laser from the AFM probe, converting it into a voltage signal and amplifying it. A slight displacement of the AFM probe can be detected from the change in the voltage signal corresponding to this displacement. The information on the AFM probe displacement detected in this manner is fed back into piezoelectric elements, which control the

relative position of the AFM probe and substrate in the XYZ directions. The piezoelectric elements are installed either on the substrate or the AFM probe side or both. There are various configurations depending on the apparatus. To quantitatively evaluate the force acting on the AFM probe in the above configuration, it is necessary to calculate the minute displacement of the AFM probe detected as a voltage signal by the photodetector in addition to calibrating the spring constant of the AFM probe as described below. The voltage change of the photodetector with respect to the displacement of the AFM probe can be determined by evaluating the relationship between the displacement of the piezoelectric elements and the voltage change of the photodetector.

Figure 2.2 shows the distance dependence of the force between the AFM probe and the specimen. As the AFM probe approaches the specimen, an attractive force acts between them, and at a certain distance, the attractive force reaches its maximum. The repulsion force increases sharply as the AFM probe is moved closer. The distance dependence of the potential is expressed as a Lennard–Jones type potential (Eq. (2.1)).

$$U(l) = 4\varepsilon \left[\left(\frac{\sigma}{l} \right)^{12} - \left(\frac{\sigma}{l} \right)^6 \right], \quad (2.1)$$

where ε and σ are coefficients that vary with the type of atom or molecule, σ is an index of atomic or molecular size, and ε is an index of energy intensity.⁴⁹⁾ Information on the specimen surface can be obtained by scanning the AFM probe so that the interaction between the AFM probe and the sample surface is under certain conditions, such as by feeding back a constant attractive or repulsive force onto the AFM probe.

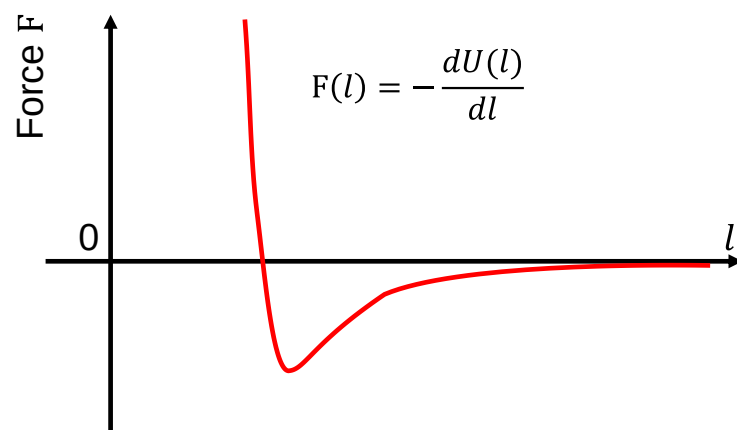


Fig. 2.2 Force between the AFM probe and the substrate surface.

2.1.2 Adhesion force evaluation

The force acting on the AFM probe can be evaluated using force curve measurements in AFM. A force curve is a plot of the force acting on the AFM probe against the amount of movement of the AFM probe by the piezoelectric element in the Z direction. An example of a force curve is schematically shown in Fig. 2.3. In the graph, the vertical axis is the force acting on the AFM probe, and the origin on the vertical axis is the point at which the force acting on the AFM probe is zero. A negative force value on the graph indicates that an attractive force is acting on the AFM probe, whereas a positive value indicates that a repulsive force is acting on the AFM probe. The horizontal axis presents the distance traveled by the Z-piezoelectric element operating the AFM probe. The horizontal axis is sometimes presented as the distance between the AFM probe and the surface of the specimen in force curve measurement plots. As the AFM probe is moved closer to the specimen, the probe is subjected to an attractive interaction just before it contacts the specimen. After contact, a repulsive interaction occurs with the AFM probe as it is pushed further toward the specimen. When the repulsive interaction reaches a certain predetermined value, the AFM probe is moved away from the specimen by the feed back system. At that moment, a pull-off force acts on the AFM probe; however, it does not immediately detach from the specimen owing to the adhesion force between them. The AFM probe detaches from the specimen when the pull-off force acting on the probe becomes larger than this adhesion force. An example force curve reflecting this sequence of behavior is shown in Fig. 2.3. The force acting on the AFM probe just before it separates from the specimen, that is, when the pull-off force exceeds the adhesion force, is determined as the adhesion force between a small particle and the specimen.

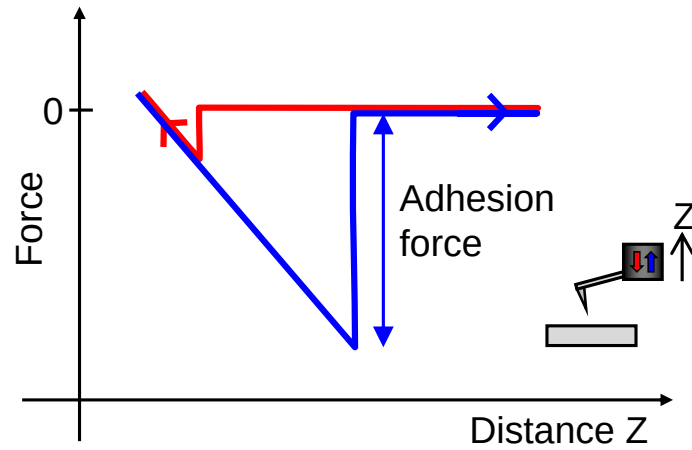


Fig. 2.3 Force curve

A method of detecting the force acting on the AFM probe via the displacement of the probe is explained above. Alternatively, another method is to control the height of the AFM probe by detecting changes in the amplitude or frequency of the probe, which is mechanically vibrated by a piezoelectric element, and feeding this back into a control circuit to quantitatively evaluate the interaction force on the probe. However, because the AFM probe is mechanically vibrated in this alternative method, the force acting in the state of contact between the probe and the specimen cannot be directly evaluated. Therefore, in this study, the adhesion force between small particles and the substrate surface is evaluated by analyzing the force curve obtained using the aforementioned method.

2.1.3 Fabrication of AFM probe

The technique used to analyze the forces acting on small particles fixed to the AFM probe is known as the colloidal probe technique.²⁰⁾ The AFM probe is also sometimes called a colloidal probe. Small particles are immobilized with glue attached to the tip of the AFM probe to fabricate a colloidal probe.

There are several ways to fix small particles in this manner. For example, the AFM probe can be placed in contact with thermoplastic resin placed beforehand on a temperature-controlled heater and fixed by contacting the fine particles on the heater. Another method is to apply a room-temperature curing-type glue to the AFM probe with a manipulator, and then place a single collected small particle on top of it with another manipulator to fix it in place. An example of the apparatus configuration for the latter method and an image of small particles glued to the AFM cantilever are shown in Fig. 2.4.

The above method, which is performed under optical microscope observation, requires the use of an optical microscope with a long focal length. This limits the spatial resolution while fixing the small particle on the AFM cantilever. Therefore, only small particles of a few micrometers in diameter can be attached to the AFM probe. If one wishes to evaluate the adhesion force of small particles of sub-micrometer diameters, the AFM probe fabricated by the above method cannot be used.

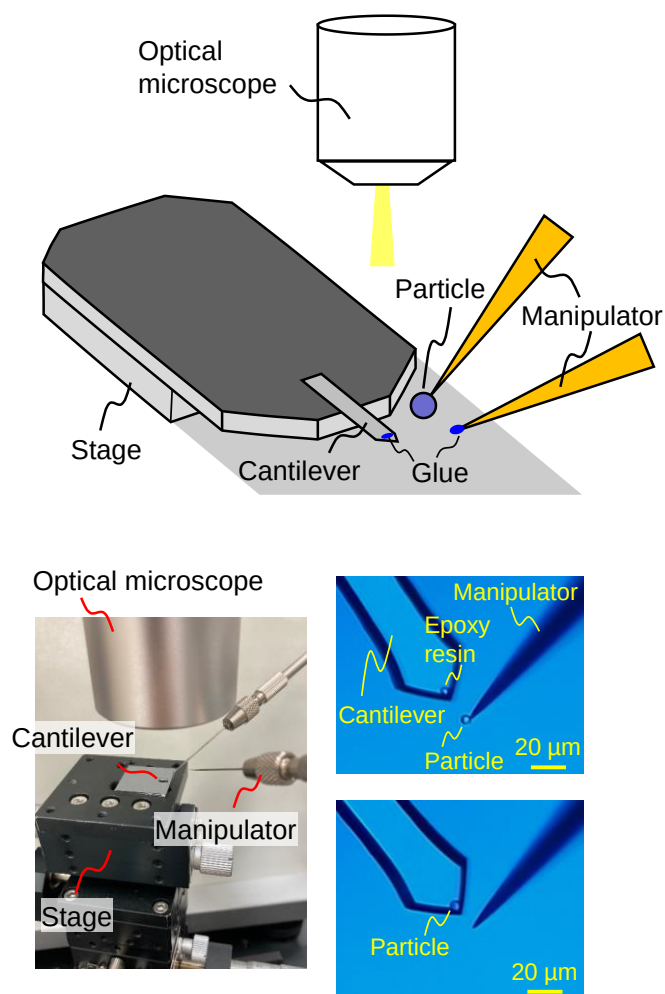


Fig. 2.4 Schematics and photograph of equipment used to fabricate an AFM probe. A particle was glued to the AFM cantilever with epoxy resin using manipulators under an optical microscope.

A method of fabricating the tip shape of an AFM probe using a focused ion beam system is one of the solutions to simulate sub-micrometer small particles. Figure 2.5 shows how the tip of an AFM probe is processed using the focused ion beam system. The tip of the small particle is sputtered by focused ion beam irradiation. It is possible to fabricate AFM probes with different tip radii of curvature by controlling focused ion beam irradiation.

In this study, a focused ion beam was irradiated to sputter the colloidal probe, and an AFM probe with a sharp tip shape, which can be used for surface topography imaging of specimens, was used for sputtering. When colloidal probes are used for

focused ion beam processing, AFM probes with different tip curvature radii can be fabricated from the same material as the colloidal probes. Therefore, colloidal probes were used for sputtering.

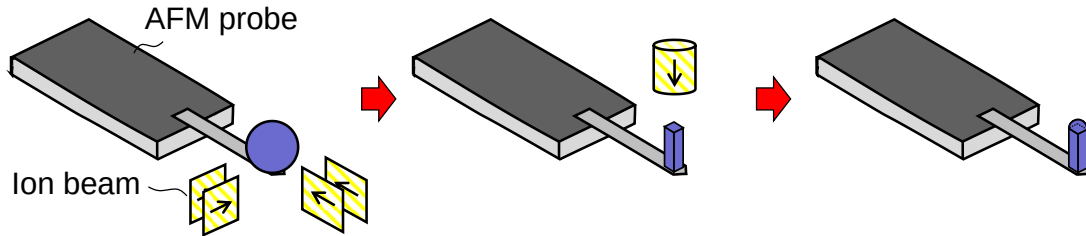


Fig. 2.5 Schematic of the fabrication of AFM probe tip shape using a focused ion beam. The focused ion beam is irradiated onto a particle attached to the AFM probe to form a rounded tip, which simulates a small particle.

It is necessary to evaluate whether the tip shape of the fabricated AFM corresponds to a small particle of any size. There is a method that uses a grating specimen with a known surface structure to evaluate the tip shape of an AFM probe.⁵⁰⁾ Figure 2.6 shows the method of assessing the tip radius of curvature of the AFM probe, which corresponds to the radius of a small particle. First, the AFM probe is used to scan the surface of the grating specimen with an array of sharp tips to obtain surface topography images. The typical tip radius of curvature of a sharp tip is less than 10 nm. The tip radius of curvature of the AFM probe can be analyzed by fitting a curve with a circle containing the portion of the height profile extracted from the surface topography image, which reflects the tip shape of the AFM probe. The radius of curvature of this circle is then determined. In this study, the radii of curvature of the circles in the height profiles along two directions were determined from the AFM images of grating specimens, which were obtained via scanning in directions that differed by 90°. The geometric mean of the radii of curvature of the circles in the two height profiles was regarded as the radius of curvature of the AFM probe tip in further evaluations.

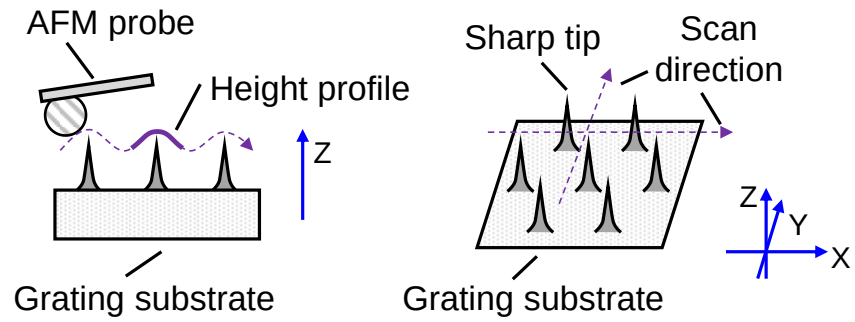


Fig. 2.6 Schematics of the evaluation process of the tip radius of curvature of the AFM probe. AFM images are obtained using the AFM probe with a grating substrate, which has an array of sharp tips. The tip radius of curvature of the AFM probe is analyzed using height profiles in the AFM images, which present the tip shape of the AFM probe.

2.1.4 Correction of spring constant of AFM probe

AFM cantilevers are fabricated by controlling the shape using anisotropic etching in the semiconductor process. The spring constant of AFM cantilevers is determined by their material and shape. AFM cantilevers are often rectangular or triangular with a thickness of the order of several micrometers. The shape of AFM cantilevers may vary despite being fabricated using semiconductor processes with high processing accuracy. Moreover, the spring constant of an AFM cantilever may vary between production lots, even for the same product. Therefore, it is necessary to calibrate the spring constant of an AFM cantilever to quantitatively evaluate the force acting on the AFM probe.

The shape method and thermal method can be used to evaluate the spring constant of AFM probes.⁵¹⁾ The shape method evaluates the spring constant based on the tip shape and Young's modulus of the material of the AFM probe. The geometry of a trapezoidal cantilever is shown in Fig. 2.7.

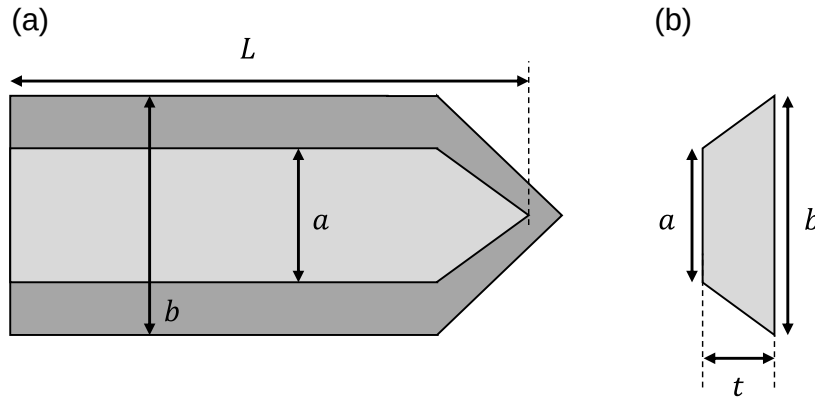


Fig. 2.7 (a) Top view from the tip side and (b) cross-sectional view of the trapezoidal cantilever.

The spring constant k of a trapezoidal cantilever is calculated using the following equation:⁵²⁾

$$k = \frac{3EI}{L^3}, \quad (2.2)$$

with

$$I = \frac{t^3(a^2 + 4ab + b^2)}{36(a + b)}, \quad (2.3)$$

where E is Young's modulus, L is the length of the cantilever, t is the thickness of the cantilever, a is the width of the tip side of the cantilever, and b is the width of the opposite side to the tip side of the cantilever. The spring constant of the cantilever can be determined from the shape of the cantilever, which is analyzed using an optical or electron microscope.

In the thermal method, the spring constant is assessed via frequency analysis of the thermal fluctuation of the cantilever tip. When we consider the AFM cantilever as a simple spring, its spring constant is k , and using the displacement x from the equilibrium position, the potential energy of the cantilever is $1/2 \times k\overline{x^2}$. According to the law of equal energy distribution, $1/2 \times k_B T$ of kinetic energy can be assigned to one degree of freedom, where k_B is the Boltzmann constant, and T is the absolute temperature. That is, a thermally vibrating spring has an energy of $1/2 \times k_B T$, which is also equal to the time-averaged maximum displacement. Therefore, the following relationship holds:

$$\frac{1}{2} k \overline{x^2} = \frac{1}{2} k_B T. \quad (2.4)$$

Using the above relationship, the spring constant can be obtained from the following equation:

$$k = \frac{k_B T}{\overline{x^2}}. \quad (2.5)$$

As shown, the spring constant can be obtained by integrating the power spectrum, which is the mean of the squared magnitude of the thermal fluctuation of the cantilever.

The displacement of the cantilever relative to the amount of movement of the piezoelectric element in the Z direction during measurement depends on the position at which the laser beam is irradiated onto the cantilever. Therefore, the sensitivity of the cantilever displacement to the amount of movement of the piezoelectric element is calibrated before the force curve measurement. It is also desirable to calibrate the spring constant at the time of measurement in the same manner. This is because the effective spring constant changes depending on the irradiation position of the laser beam.⁵³⁾ In the thermal method, the frequency analysis of thermal fluctuation can be performed at the position at which the laser beam is irradiated, which means that the spring constant is calibrated at each measurement. Conversely, in the calibration of the spring constant using the shape method, it is necessary to determine the distance between the laser beam irradiation position and the base of the cantilever; however, it is difficult to accurately determine such lengths of the order of micrometers using an optical microscope. Therefore, it is desirable to use the thermal method, which enables calibration of the spring constant according to the experimental setup in which the position of the laser beam varies. However, thermal methods are not available for all atomic force microscopes owing to the limitations of AFM systems. In this study, the thermal method was used when the frequency analysis of thermal fluctuation was available, and the shape method was used to analyze the spring constants when this analysis was not available.

2.2 Adhesion force

There are various adhesion forces that act on small particles, and these forces depend on the particle size. The particle radius dependence of adhesion forces is shown in Fig. 2.8. The parameters used in the calculation of forces are presented in later sections, assuming a silica particle on an Al substrate surface. The particle radius dependence of the gravitational force, which does not act as an adhesion force, is also shown here for comparison. The forces acting on small particles depend on the particle diameter as shown in the graph.

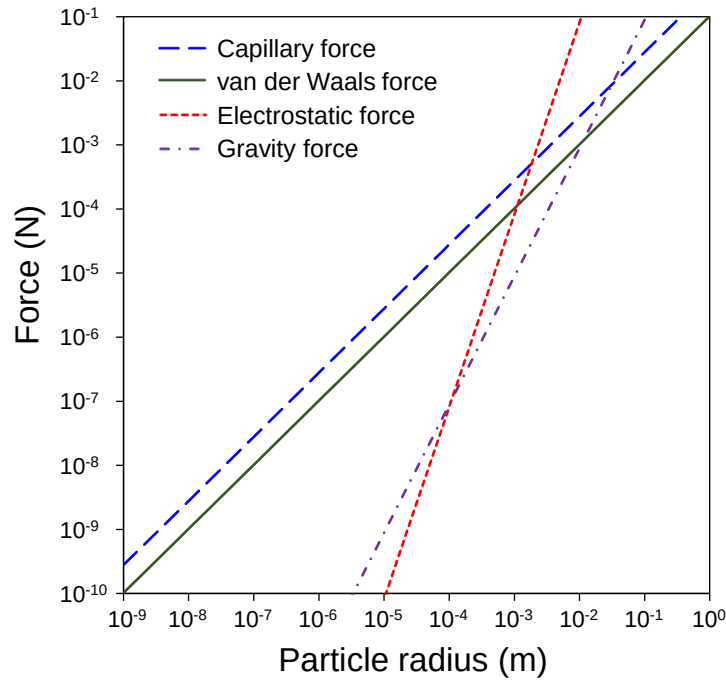


Fig. 2.8 Particle radius dependence of forces acting on a small particle.

The main adhesion forces for small particles of the micrometer order are the van der Waals force and capillary force. These forces are proportional to the first power of the particle radius. They are also relatively large compared with the gravitational force, which is proportional to the third power of the particle radius, and the electrostatic force, which is proportional to the second power of the particle radius, as the particle size decreases. The electrostatic force, which may contribute to particle

adhesion, is determined from Coulomb law, and a value of $10 \mu\text{C}/\text{m}^2$ is used for the electrostatic charge density in calculations. If the electrostatic force, which is a long-range force, is incorporated into the AFM adhesion force evaluation, it will deform the AFM probe before it contacts the substrate surface or after it is pulled from the substrate surface. However, the effect of the electrostatic force was not observed in the experiment data of the force curve and was negligible in this study. Therefore, we will not consider electrostatic forces in the following sections. instead, the van der Waals force and the capillary force are explained, and their magnitudes were calculated.

2.2.1 Van der Waals force

The van der Waals force is an attractive interaction force between atoms (or molecules) in close proximity and is caused by the dipole–dipole interaction, where the dipole of one atom induces the dipole of the other atom. The potential due to the dipole–dipole term is proportional to the negative sixth power of the distance between their centers. By integrating the potentials between atoms in a system with the geometry of interest, we can obtain potentials related to van der Waals forces. In this section, the method of obtaining an expression for van der Waals forces between a sphere and a plane is explained.

An illustration for determining the potential of the van der Waals force is shown in Fig. 2.9.⁴⁹⁾ Figure 2.9(a) shows the geometric relationship used to calculate the pair potential between an atom at the origin and the entire substrate surface at a distance d away. Figure 2.9(b) shows the geometric relationship used to integrate the potential between an atom at a distance D and the substrate surface over the entire sphere.

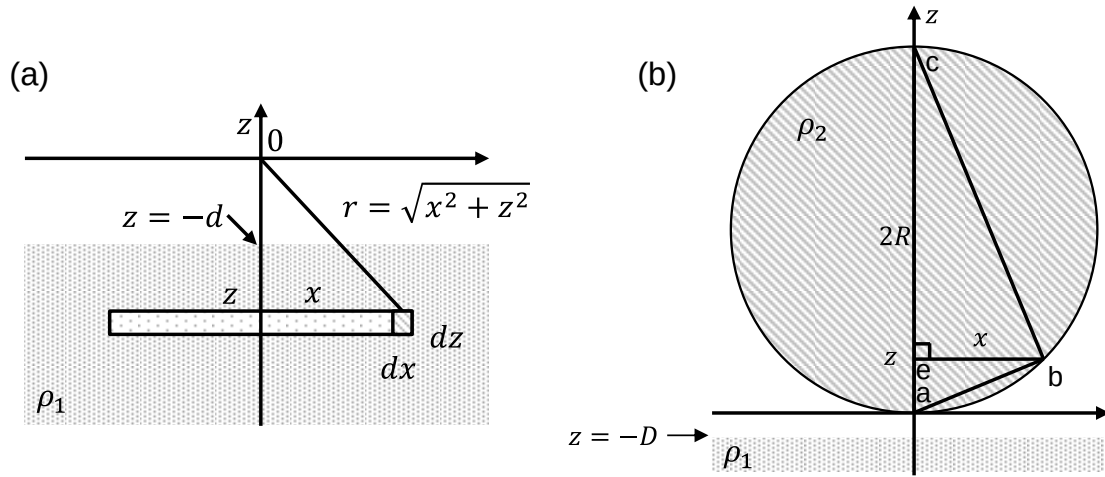


Fig. 2.9 Schematic showing the geometric relationship used to calculate the potential between (a) an atom and a substrate, and (b) a sphere and a substrate.

First, the pair potential $w(r)$ between atoms at positions separated by a distance r can be expressed by the following equation:

$$w(r) = -\frac{C}{r^n}, \quad (2.6)$$

where C is a constant. The potential is assumed to be a generalized form proportional to the $-n$ th power of r . By setting $n = 6$, we can deal with van der Waals forces. Following the illustration in Fig. 2.9(a), the formula for the pair potential $W_0(d)$ between the atom at the origin and the entire substrate surface at a distance d is expressed as

$$\begin{aligned} W_0(d) &= \int_V w(r) dV \\ &= \int_{z=-\infty}^{z=-d} dz \int_{x=0}^{x=\infty} 2\pi x w(r) dx \\ &= \int_{z=-\infty}^{z=-d} dz \int_{x=0}^{x=\infty} \frac{-2\pi C \rho x}{(x^2 + z^2)^{n/2}} dx \\ &= \int_{z=-\infty}^{z=-d} dz \int_{x=0}^{x=\infty} \frac{-2\pi C \rho x}{(x^2 + z^2)^{n/2}} dx \\ &= \int_{z=-\infty}^{z=-d} \frac{-2\pi C \rho}{z^{n-2}} dz \\ &= \frac{-2\pi C \rho}{(n-2)(n-3)d^{n-3}}, \end{aligned} \quad (2.7)$$

where ρ_1 is the number density of atoms in the substrate. Using the above equation, the interaction potential $W(D)$ between the sphere and the substrate can be obtained from the following equation if the substrate whose surface is at the origin on the z -axis is separated from the sphere by a distance D :

$$\begin{aligned}
W(D) &= \int_V W_0(d = D + z) dV \\
&= \frac{-2\pi C \rho_1}{(n-2)(n-3)D^{n-3}} \int_{z=0}^{z=2R} \frac{\rho_2 \pi x^2}{(D+z)^{n-3}} dz \\
&= \frac{-2\pi C \rho_1}{(n-2)(n-3)D^{n-3}} \int_{z=0}^{z=2R} \frac{\rho_2 \pi z(2R-z)}{(D+z)^{n-3}} dz \\
&\cong \frac{-2\pi C \rho_1}{(n-2)(n-3)D^{n-3}} \int_{z=0}^{z=\infty} \frac{\rho_2 \pi 2Rz}{(D+z)^{n-3}} dz \\
&= \frac{-4\pi^2 C \rho_1 \rho_2 R}{(n-2)(n-3)(n-4)(n-5)D^{n-5}}, \tag{2.8}
\end{aligned}$$

where ρ_1 is the number density of atoms in the sphere. The relationship $x^2 = z(2R - z)$ obtained from the geometric relationship $ac^2 = ab^2 + bc^2 = ae^2 + be^2 + ce^2 + be^2$ in Fig. 2.9 is used in the transformation of the second to third lines of Eq. (2.8), and the geometric relationship $D \ll R$ is used in the third to fourth lines of Eq. (2.8). From the van der Waals force potential corresponding to $n = 6$ in the above equation, the van der Waals force F_{vdW} can be obtained as follows:⁴⁹⁾

$$\begin{aligned}
F_{vdW} &= -\frac{d}{dD} W(D) \\
&= -\frac{C\pi^2 \rho_1 \rho_2}{6D^2} R, \tag{2.9}
\end{aligned}$$

where $C\pi^2 \rho_1 \rho_2$ is the Hamaker constant A , which is determined based on the material of the two objects. As a result, the van der Waals force between the sphere and the plane is proportional to the particle radius R . While the interaction between the plane and the sphere at a distance D is calculated, the van der Waals force becomes sufficiently large to be considered when the distance D is at its closest approach. This distance cannot be zero owing to repulsive interactions and is a finite value. This closest distance between a particle and a substrate surface is called the cut-off distance. In the following, the cut-off distance is denoted as z .

Summarizing the above, a schematic diagram showing the parameters around the region of contact between a particle and a surface used to calculate the van der Waals force is shown in Fig. 2.10. The van der Waals force is expressed in Eq. (2.10).

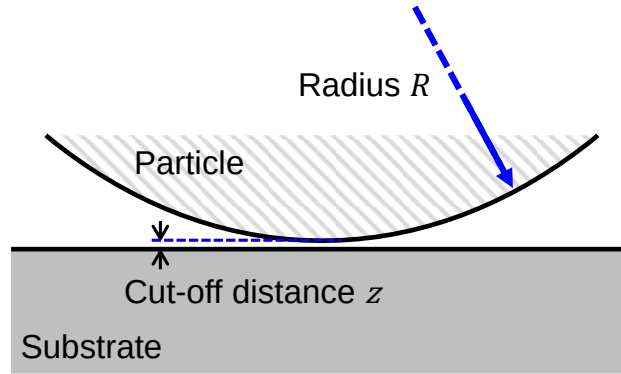


Fig. 2.10 Schematic showing the parameters used to calculate the van der Waals force between a particle and a substrate.

$$F_{vdW} = -\frac{AR}{6z^2}. \quad (2.10)$$

The cut-off distance never reaches zero, and values between 0.1 nm and 1.0 nm are generally used.⁵⁴⁾ Equation (2.10) does not include the dependence on the surface roughness of the particle and substrate surface.

The van der Waals force varies with the surface roughness of the particle and substrate surface. Several models have been proposed to show the dependence of the van der Waals force on the surface roughness of the substrate, and based on one of these models, a schematic of a geometric model used to calculate this dependence is shown in Fig. 2.11. Here, we consider a particle with radius R and a plane in which the particle has a protrusion with radius r . Figures 2.11(a) and (b) show that the base of the hemispherical protrusion is on and under the substrate surface, respectively.²⁸⁾ A case in which the sphere is most densely packed on the plane is considered.

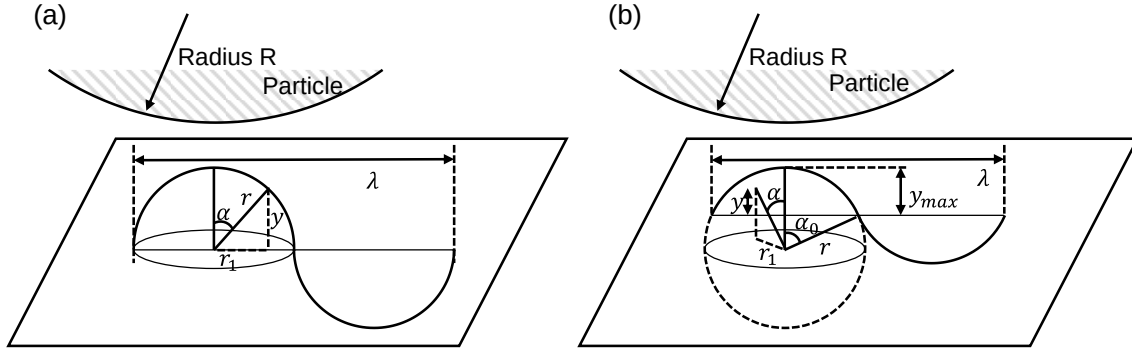


Fig. 2.11 Schematic showing a geometric model used to calculate the dependence of the van der Waals force on surface roughness. The base of the hemispherical protrusion is (a) on the substrate surface and (b) under the substrate surface.

Combining the forces of the interaction between the particle and the protrusion and those of the interaction between the particle and the plane, the van der Waals force of the particle and the surface with the protrusion is expressed by⁵⁵⁾

$$F_{vdW} = -\frac{AR}{6z^2} \left[\frac{r}{R+r} + \frac{1}{(1+r/z)^2} \right]. \quad (2.11)$$

If the base of the hemispherical protrusion is on the substrate surface, as shown in Fig. 2.11(a), we obtain the following geometric relationship:

$$r_1 = r \sin \alpha, \quad y = r \cos \alpha. \quad (2.12)$$

The root-mean-square of the surface roughness R_q can be calculated from the following:

$$R_q = \sqrt{\frac{\int_S y^2 dS}{S}} k_p = \sqrt{\frac{\int_0^r 2\pi y^2 r_1 dr_1}{\pi r^2}} k_p = 0.673r, \quad (2.13)$$

where k_p is the density of close-packing of equal spheres in an unit area, which has a value of 0.907. The content of the root in the above equation is the sum of the squares

of the heights in a circle divided by the area of the circle and multiplied by k_p , which is the ratio of the area of the spheres in the plane because the plane is not filled with hemispheres. Using the relation $r = 1.485R_q$ obtained from Eq. (2.13), the dependence of the van der Waals force on surface roughness is expressed as follows:²⁸⁾

$$F_{vdW} = -\frac{AR}{6z^2} \left[\frac{1}{1 + (R/1.485R_q)} + \frac{1}{(1 + 1.485R_q/z)^2} \right]. \quad (2.14)$$

Here, if the value of the surface roughness R_q is analyzed, we can easily apply Eq. (2.14) to estimate the dependence of adhesion force on surface roughness.

If the base of the hemispherical protrusion is under the substrate surface as shown in Fig. 2.11(b) and assuming the angles $\alpha, \alpha_0 \ll 1$, we obtain the following geometric relationships:

$$y = r(\cos\alpha - \cos\alpha_0) = \frac{r}{2}(\alpha_0^2 - \alpha^2), \quad (2.15)$$

$$y_{max} = r(1 - \cos\alpha_0) = \frac{r\alpha_0^2}{2} = \frac{\lambda^2}{32r} = k_1R_q. \quad (2.16)$$

Here, a relationship of $y_{max} = k_1R_q$ is introduced, And the relationship $r = \lambda^2/32k_1R_q$ is obtained. The root-mean-square of the surface roughness R_q can be expressed based on the following definition:

$$R_q = \sqrt{\frac{\int_0^{\lambda/4} 2\pi y^2 r_1 dr_1}{\pi r^2}} k_p = \sqrt{\frac{32 \int_0^{\lambda/4} y^2 r_1 dr_1}{\lambda^2}} k_p = 0.0172\lambda^2/r. \quad (2.17)$$

From the above equations, the coefficient k_1 value of 1.817 was obtained. Therefore, the dependence of the van der Waals force on surface roughness is expressed as follows:²⁸⁾

$$F_{vdW} = -\frac{AR}{6z^2} \left[\frac{r}{1 + (58.14RR_q/\lambda^2)} + \frac{1}{(1 + 1.817R_q/z)^2} \right]. \quad (2.18)$$

Here, λ must be analyzed to apply Eq. (2.18). In this study, we used Eq. (2.14) because of its simplicity, and it was difficult to analyze λ owing to complex substrate surface morphology used in the experiments.

Summarizing the above, a schematic diagram showing the parameters around the region of contact between the particle and the surface used to calculate van der Waals forces is shown in Fig. 2.12, and the van der Waals force versus the surface roughness of the substrate is expressed again in Eq. (2.14).

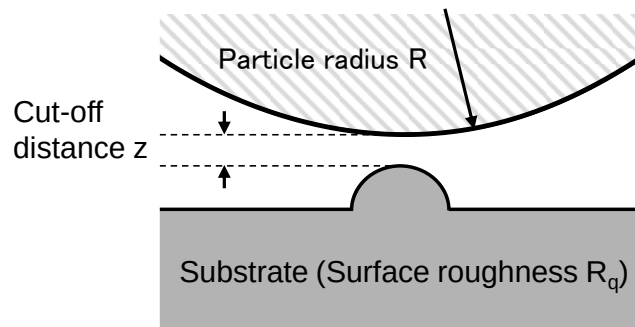


Fig. 2.12 Schematic showing the van der Waals force between particle and substrate surface with surface roughness R_q .

$$F_{vdW} = -\frac{AR}{6z^2} \left[\frac{1}{1 + (R/1.485R_q)} + \frac{1}{(1 + 1.485R_q/z)^2} \right], \quad (2.14)$$

where A is the Hamaker constant, R is the particle radius, z is the cut-off distance, and R_q is the root-mean-square roughness of the surface roughness. In Eq. (2.14), the section in square brackets is modified from Eq. (2.10) owing to the effect of surface roughness. Equation (2.14) shows the sum of the forces due to the interaction between the particles and the protrusion on the substrate surface, indicated by the first term in the brackets, and the forces due to the interaction between the particles and the flat surface of the substrate, indicated by the second term in the brackets. Equation (2.14) is based on geometrical considerations and eliminates the application limitation of the proposed surface roughness dependency equation, which assumes that the small particle is directly above the protrusion.⁵⁵⁾ Although it has been pointed out that there

is also a limitation in the range of applicability, the dependence of the van der Waals force on surface roughness is discussed below based on Eq. (2.14).

Equation (2.14) shows that the van der Waals force increases or decreases with surface roughness R_q and has a minimum value for R_q . The van der Waals force decreases monotonically with respect to the cut-off distance. The maximum value of the square brackets in Eq. (2.14) is realized at a cut-off distance of 0. When the cut-off distance is sufficiently small and the radius R of the small particle is sufficiently larger than the surface roughness R_q , the maximum value of the square brackets in Eq. (2.14) is 1. Therefore, the van der Waals force is smaller than that in the case of negligible surface roughness.

The relationship between the van der Waals force and surface roughness calculated from Eq. (2.14) is shown in Fig. 2.13. The particle radius R used in calculation is shown in the figure. The van der Waals force was calculated assuming a silica particle as the small particles and an Al substrate as the substrate surface material, using the physical properties shown in Table 3.3. As mentioned above, the van der Waals force has a minimum value for surface roughness.

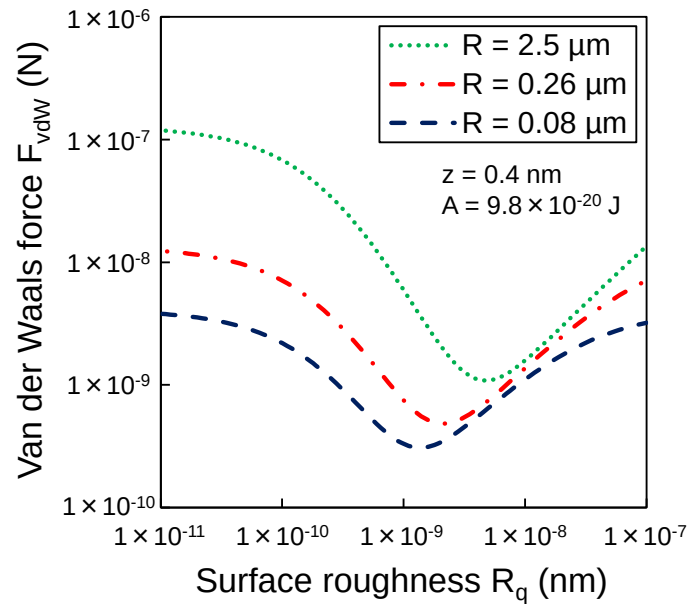


Fig. 2.13 Dependence of the van der Waals force on the surface roughness R_q .

However, the surface roughness dependence of the van der Waals force shown here is limited in its application to cases in which the surface morphology is uniformly uneven and is not applicable to cases in which the surface has uniform unevenness or irregular periodic structure undulations that occur with long periods. Equation (2.14) and a model have been proposed to show the dependence of the van der Waals force on surface roughness so that both short-period and long-period irregularities have an effect.²⁸⁾ While these methods may be able to estimate the mean value of the van der Waals force between small particles and the substrate surface, it is difficult to estimate the variation in the van der Waals force.

2.2.2 Capillary force

The capillary force is an attractive interaction force caused by the retention of liquid between two objects. An illustration for determining the capillary force is shown in Fig. 2.14.²⁹⁾

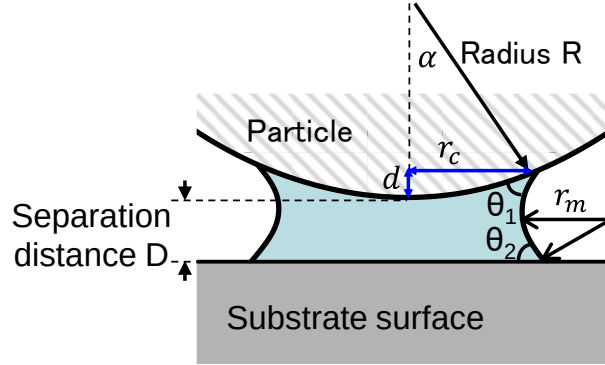


Fig. 2.14 Schematic showing the geometric relationship of the capillary between the particle and the substrate with separation distance D .

The Laplace pressure acting between two surfaces is expressed by the following equation:

$$P = \gamma_L \left(\frac{1}{r_m} - \frac{1}{r_c} \right), \quad (2.19)$$

where γ_L , r_m , and r_c are the surface tension of water, the meniscus of water, and the liquid bridge radius, respectively. The capillary force is the Laplace pressure multiplied by the capillary area πr_c^2 . From this geometric relationship, the following equations are obtained using the shape parameters shown in Fig. 2.14 with $R \gg r_c$ and $\alpha \ll 1$:

$$d = R + D - R \cos \alpha = r_m \cos(\theta_1 + \alpha) + r_m \cos \theta_2, \quad (2.20)$$

$$1 - \cos \alpha \cong 1 - \alpha^2/2. \quad (2.21)$$

Using above equations, the angle α is expressed by the following equation:

$$\alpha = -\frac{r_m \sin \theta_1}{R} + \sqrt{\frac{r_m^2 \sin^2 \theta_1}{R^2} - \frac{2D - 2r_m(\cos \theta_1 + \cos \theta_2)}{R}}. \quad (2.22)$$

Because the particle radius is larger than the separation and meniscus radii ($R \gg D, r_m$), the square of the angle α is expressed as

$$\alpha^2 = \frac{2r_m(\cos \theta_1 + \cos \theta_2) - 2D}{R}. \quad (2.23)$$

Owing to the geometric relationships $r_c \gg r_m$ and $r_c \approx R\alpha$, the capillary force is expressed as follows:²⁹⁾

$$\begin{aligned} F &= P \times \pi r_c^2 \\ &\cong \pi r_c^2 \frac{\gamma_L}{r_m} \\ &\cong \pi R^2 \alpha^2 \frac{\gamma_L}{r_m} \\ &= 2\pi \gamma_L R \left[(\cos \theta_1 + \cos \theta_2) - \frac{2D}{r_m} \right]. \end{aligned} \quad (2.24)$$

When the separation distance D is set to 0, the capillary force of particles on the substrate surface can be obtained.

Summarizing the above, a schematic diagram showing the parameters around the region of contact between the particle and the surface without surface roughness used to calculate the capillary force is shown in Fig. 2.15. The capillary force is expressed in Eq. (2.25).

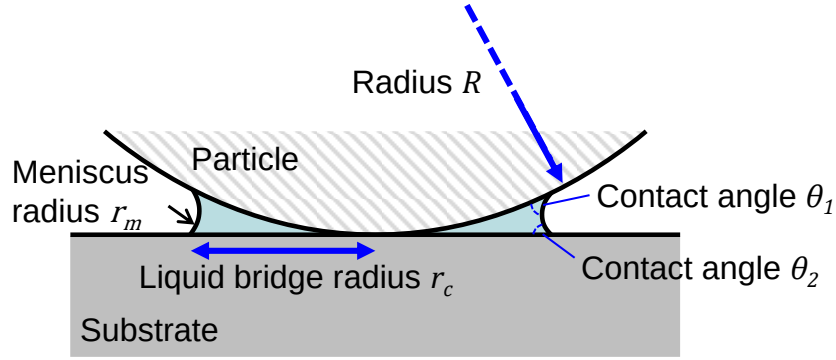


Fig. 2.15 Schematic showing the capillary between the particle and the substrate. The capillary force is calculated using the parameters labeled in the figure.

$$F_c = 2\pi R\gamma_L(\cos\theta_1 + \cos\theta_2). \quad (2.25)$$

Using the meniscus radius (Kelvin radius) r_m given by the Kelvin equation (Eq. (2.26)), the liquid bridge radius r_c can be expressed by Eq. (2.27):

$$r_m = -\gamma_L V / RT \log(p/p_s), \quad (2.26)$$

$$r_c^2 = 2Rr_m(\cos\theta_1 + \cos\theta_2), \quad (2.27)$$

where V is the molar volume of water, T is the absolute temperature, p is the vapor pressure, and p_s is the saturated vapor pressure. As shown in Eq. (2.25), the capillary force is caused by the RH-dependent liquid bridge and meniscus, defined as the ratio of vapor pressure to saturated vapor pressure. The experimental results from a previous report showed that the capillary force is negligible under low RH.²⁹⁾ In contrast, it was also reported that the capillary forces due to water molecules are formed even at 0%RH or in high vacuum.³⁴⁾ Because these results indicate that the conditions under which the above equations can be applied are limited, such as the liquid bridge radius in air being of the order of a few nanometers, these equations were used to estimate the capillary forces in this study.

Equation (2.25) does not include the dependence of the substrate surface on surface roughness. An equation that shows the dependence of the capillary force on surface roughness has been proposed and is expressed by Eq. (2.28).²⁹⁾

$$F_c = 2\pi R\gamma_L(\cos\theta_1 + \cos\theta_2) \left[1 - \frac{2 \times 1.817R_q}{r_m(\cos\theta_1 + \cos\theta_2)} \right]. \quad (2.28)$$

The above equation is calculated using Eq. (2.24) by applying $D = y_{max} = k_1 R_q = 1.817R_q$, which was calculated as shown in the previous section. Schematics showing the distance between small particles and the substrate surface when Eq. (2.28) holds are shown in Fig. 2.16.

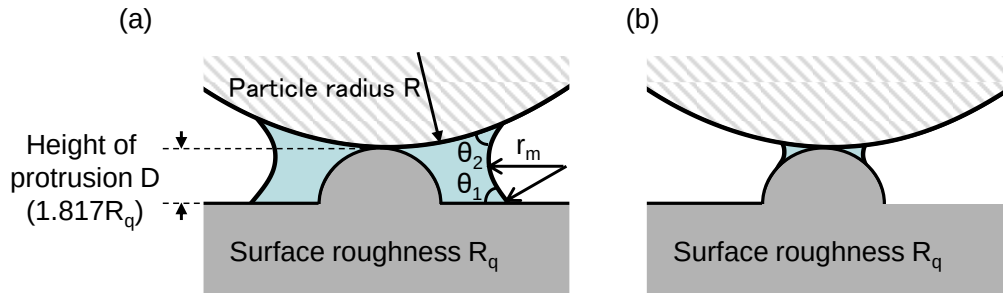


Fig. 2.16 Schematic showing the capillary force between a particle and a protrusion of the substrate surface. The relative humidity is (a) high and (b) low.

Figs. 2.16(a) and (b) show a case in which the RH is high and a liquid bridge of sufficient size is formed between the substrate surface and the small particles, and a case in which the RH is low and liquid bridges are formed only between the small particles and the protrusion on the substrate surface, respectively. In the latter case (Fig. 2.16(b)), the effective radius R_{eff} shown below is used instead of R . R_{asp} is the radius of the protrusions on the substrate surface. In both cases, Eq. (2.28) can be used to calculate the capillary force.

$$R_{eff} = \frac{RR_{asp}}{R + R_{asp}}. \quad (2.29)$$

Figs. 2.17(a) and (b) show the dependence on the capillary force on the surface roughness of the substrate and RH, respectively, according to Eq. (2.28). Here, the particle radius R was $2.5\ \mu\text{m}$, and the contact angles θ_1 and θ_2 were 52° and 90° , respectively. Using Eq. (2.28), the calculated value of the capillary force was zero below a certain relative humidity, as shown in Fig. 2.17(a). As shown in Fig. 2.17(b), the capillary force immediately decreased as the surface roughness increased, and the calculated value of the capillary force was zero when the surface roughness was above a certain level.

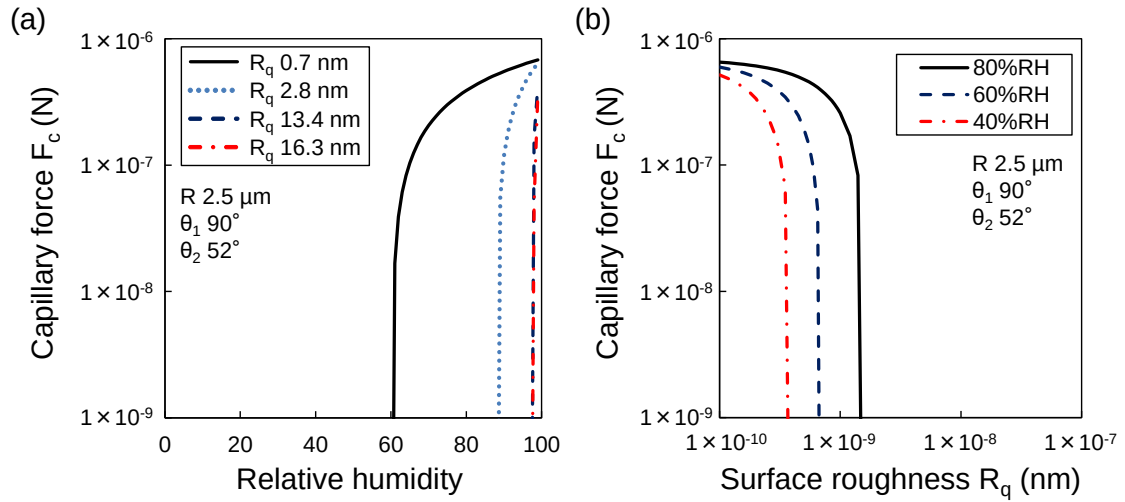


Fig. 2.17 Dependence of the capillary force on (a) relative humidity and (b) the surface roughness R_q of the substrate.

2.3 Contact model

To discuss the results of the adhesion force evaluation, the contact radius and deformation between the small particle and the substrate surface were calculated based on contact theory.

Hertz theory is one example of a contact theory and can explain elastic deformation when a contact load is applied.¹⁷⁾ However, Hertz theory does not consider the adhesion force acting between two contacting objects, and the contact area is zero without a contact load. Two contact theories that account for adhesion forces are the Johnson–Kendall–Roberts (JKR) theory and the Derjaguin-Muller-Toporov (DMT) theory.^{56,57)} JKR theory is often applied to contact between soft specimens and is said to be highly applicable in practice, whereas DMT theory is often applied to contact between hard specimens. To select and use an appropriate theory among several contact theories, a method of determining the value of a dimensionless parameter calculated from the physical property values of the contacting objects has been reported.⁵⁸⁾ In that report, an adhesion map, which maps contact theories based on the value of the dimensionless parameter, is presented.

In this study, silica was applied as the material of the small particle, and Al was chosen as the material of the substrate surface in experiments. The Al specimens were either cut from bulk material and surface-machined or taken from Al sputtered onto the surface of a 100 nm thermally oxidized film on a Si substrate. Because they were all stored in the atmosphere, their top surfaces were oxidized to alumina. When the dimensionless parameters were calculated using the properties of these materials and the diameter of the small particle, the experiment was a system for which DMT theory was more suitable than JKR theory. Therefore, DMT theory was used to estimate the contact radii and deformations between the small particle and the substrate surface.

A schematic showing the parameters around the region of contact between the small particle and the substrate surface used to calculate the deformation and contact radius based on DMT theory is shown in Fig. 2.18.

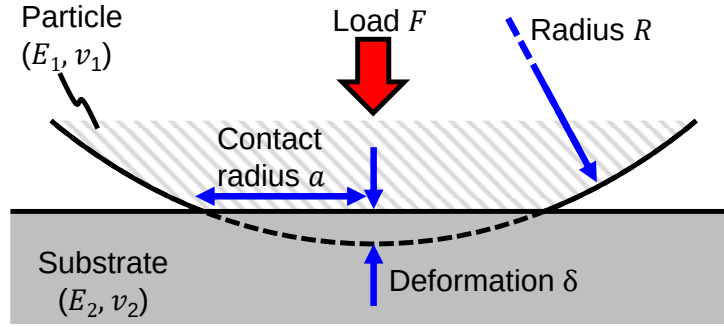


Fig. 2.18 Contact model between the particle and the substrate surface.

According to DMT theory, when a particle, which can be regarded as an ideal sphere, is loaded with an external force F onto a flat substrate surface, the deformation of the particle δ and the radius of the contact surface (radius of the contact circle) a are expressed by Eqs. (2.30) and (2.31), respectively.^{57,59)}

$$\delta = a^2/R, \quad (2.30)$$

$$a = \sqrt[3]{\frac{3}{4} \left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right) (F + 4\pi\gamma R)}, \quad (2.31)$$

where R is the radius of the probe, and γ is the surface energy between the small particle and the substrate surface. The surface energy of the interface between two objects is the geometric mean of the surface energies of each object. Note that DMT theory does not consider the effect of surface roughness, and Eqs. (2.30) and (2.31) do not include the effect of surface roughness. The surface energy is calculated from the following equation using the Hamaker constant A and the cut-off distance z :

$$\gamma = \frac{A}{24\pi z^2}, \quad (2.32)$$

The physical properties of silica and Al used to calculate the deformation of the particle δ and the contact radius a are summarized in Table 2.1.^{60–62)} The surface energy was calculated from the Hamaker constant and cut-off distance, which was set

as 0.1–1.0 nm.⁵⁴⁾ In this study, the Hamaker constant of alumina was used instead of Al which is a pure metal surface with a higher surface energy by an order of magnitude, because the top surface of the Al substrate was considered alumina, as mentioned above.

Table 2.1 Physical properties of silica, Al, and the silica–Al interface.

Properties	Silica	Al	Silica-Al
Young's modulus (GPa)	73.1	70.3	N/A
Poisson ratio	0.17	0.345	N/A
Hamaker constant (10^{-20} J)	6.6	14.5	9.8

2.4 Adsorption and diffusion of molecules on substrate surface

The adsorption and surface diffusion of molecules on a substrate surface are explained in this section. Molecules that reach the substrate surface from the gas phase (vacuum) and adsorb on the surface diffuse over a certain residence time before desorbing from the surface with a certain probability. The adsorption time and surface diffusion coefficient of molecules on a substrate surface are known to depend on the temperature of the substrate surface. The temperature dependence of the adsorption time is shown in Eq. (2.33).⁶³⁾

$$\tau = \tau_0 \exp(E_A/k_B T), \quad (2.33)$$

where τ_0 is a constant, E_A is the activation energy of adsorption, k_B is the Boltzmann constant, and T is the absolute temperature. The surface diffusion coefficient of molecules on the substrate surface is given by Eq. (2.34).⁶⁴⁾

$$D = D_0 \exp(-E_D/k_B T), \quad (2.34)$$

where D_0 is a constant, and E_D is the activation energy of surface diffusion.

Using the above surface diffusion coefficient, the root-mean-square of the displacements of a random-walking molecule in time t can be expressed by Eq. (2.35).

$$\langle \Delta r^2 \rangle = v l^2 t, \quad (2.35)$$

where v is the hopping probability and l is the hopping length. Using this equation, the surface diffusion coefficient can be expressed by Eq. (2.36).

$$D = \frac{\langle r^2 \rangle}{N_D t} = \frac{v l^2}{N_D}, \quad (2.36)$$

where N_D is the number of nearest adsorption sites that can be displaced at the next time point, which is $2n$ if n -dimensional space is considered. Considering a case in which the particles random walk on a substrate surface, the surface diffusion length L of a random-walking molecule, which is the root-mean-square of the displacements, is then expressed by Eq. (2.37).⁶⁵⁾

$$L = \sqrt{2nDt}, \quad (2.37)$$

where n is the dimension of surface diffusion, D is the surface diffusion coefficient, and t is the time. From these equations, the movement of molecules on the substrate surface can be studied.

The adsorption time and surface diffusion coefficient have an exponential dependence on substrate temperature as shown in Eqs. (2.33) and (2.34). As the substrate temperature decreases, the adsorption time of water molecules on the substrate surface increases exponentially, whereas the surface diffusion coefficient decreases exponentially. In general, surface diffusion may occur when the substrate temperature is lower than the desorption temperature because the activation energy of surface diffusion is 5–20% of the energy associated with adsorption.⁶⁵⁾

In this study, the effect of residual gases in a chamber under high vacuum of the order of 10^{-5} to 10^{-4} Pa was considered. Under these experimental conditions, the main component of residual gas in the high vacuum is water molecules.^{63,66)} Other residual gases, such as oxygen and nitrogen, do not contribute directly to adhesion, and this study did not conduct experimental evaluation in the high temperature region, where decomposition of residual gases or reactions between decomposed gases occur. Instead, an experimental evaluation and discussion was performed when the substrate temperature was reduced from room temperature to liquid nitrogen temperature. Therefore, the decomposition of residual gases and their reactions are not addressed here, but the case in which the water molecules affecting adhesion are above the substrate surface is considered.

The behavior of water molecules involved in adsorption and surface diffusion at different substrate temperatures is shown in Fig. 2.19. The surface roughness is neglected for simplicity. As shown in Fig. 2.19(a), the initial state was considered the

case in which a film of water molecules was formed on the surface, even under high vacuum. As the temperature of the substrate surface was lowered, the amount of water molecules adsorbed on the substrate increased, and the film thickness of water molecules increased, as shown in Fig. 2.19(b). At this time, the adsorbed water molecules diffused to a certain degree on the substrate surface. Figure 2.19(c) shows that the diffusion length of the water molecules decreased as the temperature of the substrate surface decreased.

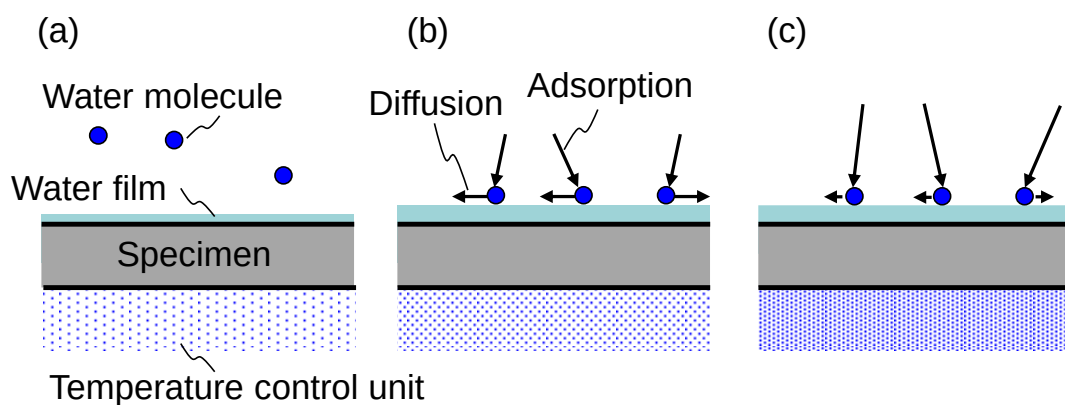


Fig. 2.19 Schematic showing water molecules on the substrate surface at different substrate temperatures. (a) Substrate temperature under initial conditions. (b) Substrate temperature is reduced from the initial conditions. (c) Substrate temperature is further decreased.

3 Effect of surface roughness on adhesion force of small particles

3.1 Preface

One approach to controlling the behavior of small particles is to change the adhesion forces of small particles in contact with the substrate surface as described in Chapter 1. However, the adhesion forces of small particles estimated based on the theoretical formulas presented in the previous chapter often do not match the actual adhesion forces of small particles on the substrate surface. One reason for this is that the size of the area where the small particles interact with the substrate surface varies because of unevenness on the substrate surface. Thus, the surface roughness of the substrate has a significant effect on the adhesion force.

Several models have been proposed and formulated to explain the surface roughness dependence of the adhesion forces of small particles based on experimental results using AFM.^{26–29)} The dispersion of the adhesion force has also been analyzed; however, the mean adhesion force has been the main subject of discussion in previous reports. In this study, the experimental evaluation and analysis were conducted with adhesion force dispersion as the main subject of discussion. This is because there are cases in the industrial field in which the behavior of multiple small particles must be controlled in the same manner. In particular, considering the case of multiple small particles on the surface of a substrate, it is important that the magnitude of the adhesion force be uniform. If there is a variation in the adhesion force and some small particles weakly adhere to the substrate surface, external forces may cause those particles to scatter from the substrate surface. Although the variation in adhesion force due to surface roughness is important, it is far from fully understood. Therefore, the adhesion force of the AFM probe corresponding to small particles on a substrate surface with different surface roughness was evaluated and the effect of surface roughness on the dispersion of small particles are discussed in this chapter based on the experimental results.

The apparatus in which the specimen chamber is under a vacuum environment was shown as an example of an industrial application in the previous chapter. However, there are also apparatus in which the specimen chamber is under atmospheric pressure with a certain degree of RH. Examples of apparatus related to the semiconductor device manufacturing process include optical inspection equipment used to check the pattern shape after lithography, and optical equipment used to inspect the number and size of foreign particles adhering to the semiconductor wafer. Thus, the dependence of adhesion force on surface roughness will be evaluated and discussed for these conditions under atmospheric pressure.

3.2 Experimental methods

An AFM system (Oxford Instruments MFP-3D) was used in the experiments described in this chapter. This AFM system can calibrate the spring constant of the AFM probe using the thermal method. As shown in the previous chapter, the adhesion force between the AFM probe and substrate surface was evaluated using force curve measurements after calibrating the acquired data in advance with the sensitivity of the voltage change of the photo-detector to the displacement of the piezoelectric element and the spring constant calculated using the thermal method.

The room where the AFM system was installed was set up in an air-conditioned environment with atmospheric pressure, room temperature (approximately 298 K), and an RH of 20–40%. To evaluate the variation in the adhesion force of small particles, force curves were obtained at least 500 times at different positions per combination of AFM probes and substrate surfaces. The AFM probe extraction and retraction speed toward the substrate surface was set to 1 $\mu\text{m/s}$, and the contact time between the AFM probe and the substrate surface ranged from tens to hundreds of milliseconds.

Five AFM probes with different tip radii of curvature, corresponding to the radii of small particles, were used for the evaluation of adhesion force. In the following, the procedure for fabricating the AFM probes according to the method described in Section 2.1.3 is presented. First, room-temperature curing epoxy resin (Ciba-Geigy Araldite) was collected with a manipulator and applied to an AFM tipless cantilever (Innovative Solutions Bulgaria All-In-One-Al-tipless) with a typical spring constant of 2.7 N/m. Next, silica particles (Micromod Sicastar) with a mean diameter of 5 μm , collected with another manipulator, were placed on top of the epoxy resin. The AFM probes were then transferred to a focused ion beam system (Hitachi High-Tech FB2100), where some parts of the silica particles were sputtered to reduce the tip radius of curvature. The AFM probes were dry cleaned in a plasma cleaning system (XEI Scientific Evactron 45) before evaluating adhesion force. This was done to remove hydrocarbon-based electron beam-induced contamination that might be formed during focused ion beam processing and scanning electron microscopy (SEM) observation for the AFM probes.

The tip radius of curvature and surface roughness of the fabricated AFM probes were analyzed using the method described in Section 2.1.4. A grating substrate (NT-MDT Spectrum Instruments TGT-1) was used in the analysis. The SEM images and the height profiles using the grating substrate for fabricated AFM probes were shown in Fig. 3.1. The tip radius of curvature and root-mean-square roughness R_q of the AFM probes are shown in Table 3.1. As shown, the AFM probes used in the experiments had tip radii of curvature of 0.08, 0.10, 0.26, 1.8, and 2.5 μm . AFM probes with a tip radius of curvature of 1 μm or less were fabricated with a focused ion beam system.

Table 3.1 Tip radii and surface roughness R_q of the AFM probes.

Tip radius (μm)	Surface roughness
	R_q (nm)
0.08	1.8
0.10	0.6
0.26	0.8
1.8	3.9
2.5	1.9

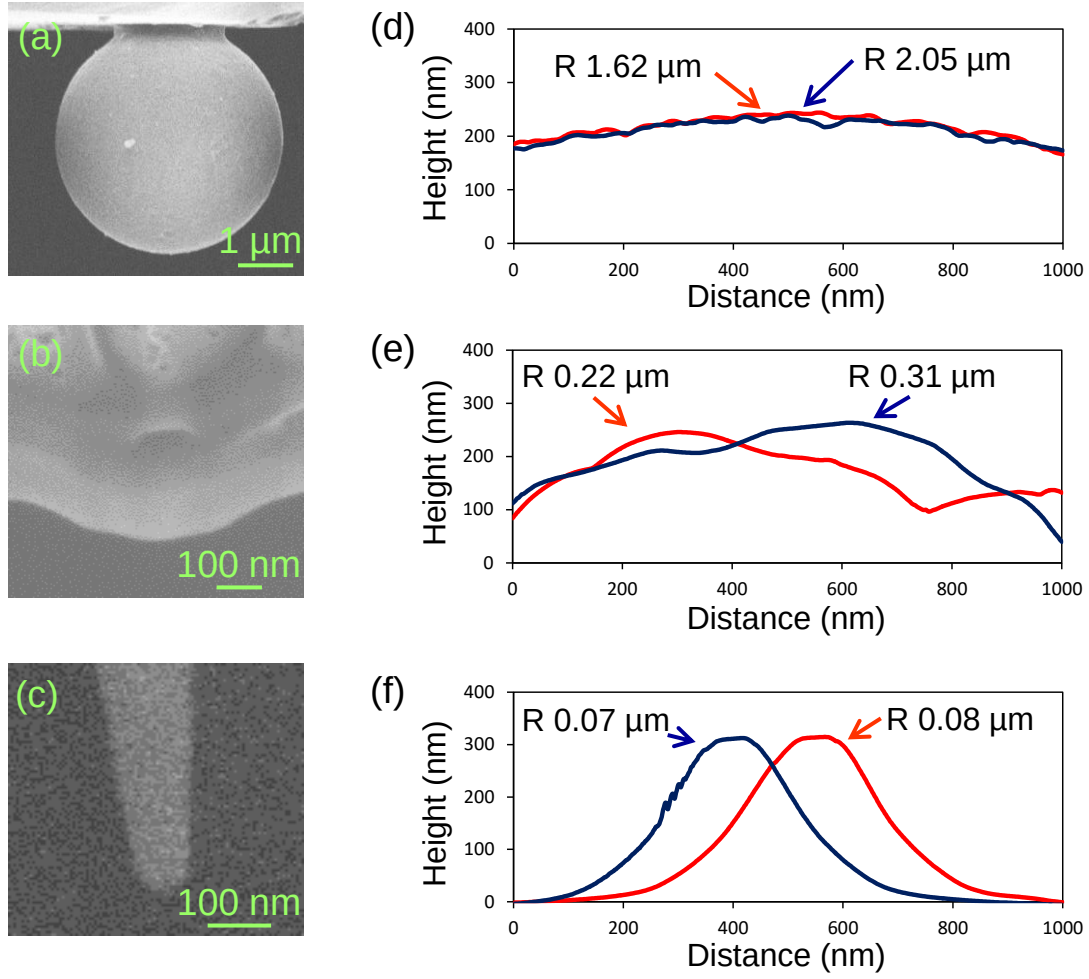


Fig. 3.1 SEM images of the fabricated AFM probes with tip radii of curvature of (a) 1.8, (b) 0.25, and (c) 0.08 μm . Height profiles of the fabricated AFM probes with tip radii of curvature of (d) 1.8, (e) 0.25, and (f) 0.08 μm . Here, profiles in two perpendicular directions (X and Y directions) are shown.

The surface roughness R_q of the four Al substrates used in this study are shown in Table 3.2. Table 3.2 also shows the types of surface treatments applied to the Al substrates to achieve surface morphologies with different surface roughness R_q . The surface treatments are lapping, chemical polishing, cutting, and sandblasting. All are commercially used as surface treatments for Al. AFM topographic images of a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ area were acquired at ten different locations on the Al substrate surfaces, and the root-mean-square roughness within each area was calculated. The mean of the root-mean-square roughness of the ten areas was used as the surface roughness R_q .

Table 3.2 Surface treatment and surface roughness R_q of the Al substrates.

No	Surface roughness R_q (nm)	Surface treatment
1	0.7	Lapping
2	13.4	Chemical polishing
3	16.3	Cutting
4	38.0	Sandblasting

Examples of the AFM topographic images of Al substrate surfaces treated by lapping, chemical polishing, cutting, and sandblasting are shown in Figs 3.2(a), (b), (c), and (d), respectively. The Al substrate with lapping surface treatment had a flat surface while the chemically polished and machined Al substrates exhibited not only periodic protrusions and height steps of several tens of nanometers on the surfaces, but also undulations. In the case of the sandblasted Al substrate, there were protrusions of the order of several hundred nanometers in height on the surface. Structures of different heights and periodicities were formed on the Al substrate surfaces, resulting in different values of surface roughness R_q in different analysis areas.

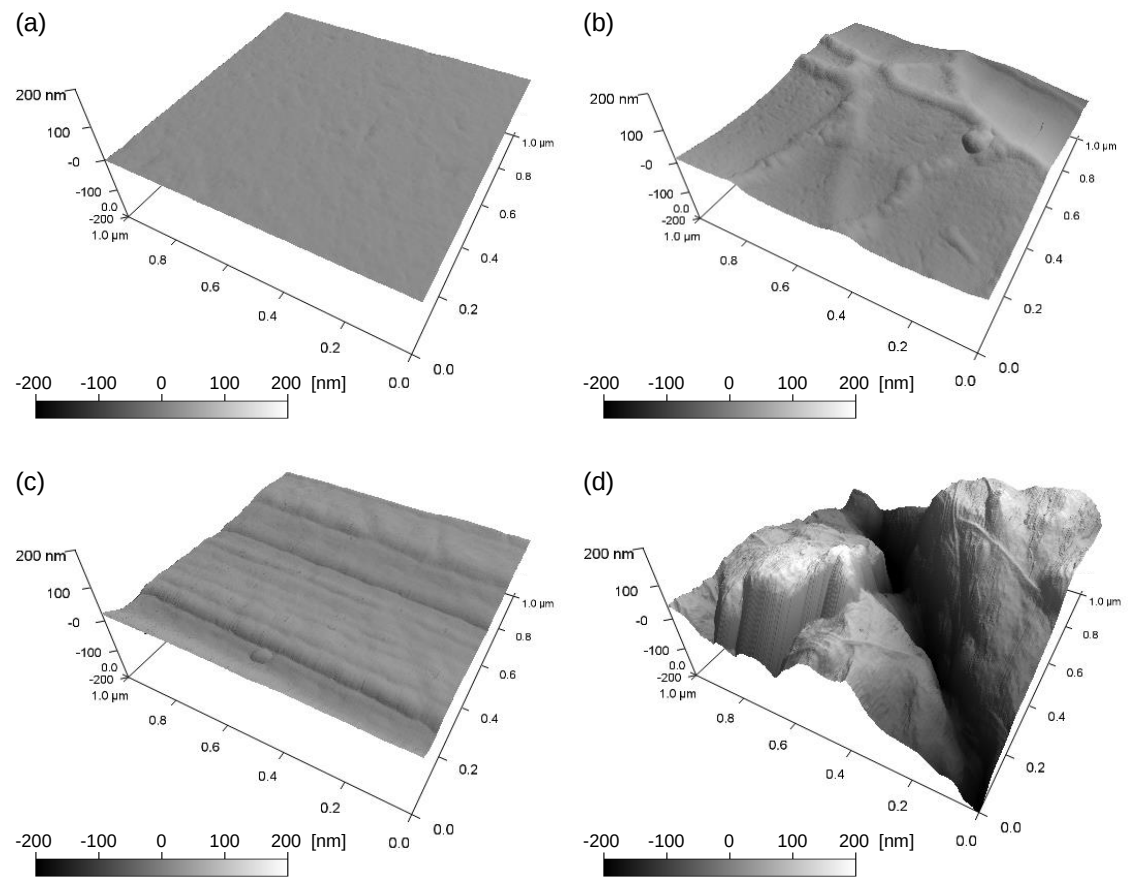


Fig. 3.2 AFM topographic images of substrate surfaces treated by (a) lapping, (b) chemical polishing, (c) cutting, and (d) sandblasting.

3.3 Results and discussion

3.3.1 Histograms of adhesion force

Histogram of the measured adhesion forces between the AFM probes and the substrates surface are presented and the results are discussed in this section. Figure 3.3 shows histograms of adhesion forces from a total of approximately 1600 measurements using AFM probes with tip radii of curvature of 0.08, 0.26, and 1.8 μm and Al substrate surfaces with surface roughness R_q of 0.7, 13.4, and 16.3 nm. Figure 3.4 shows histograms of adhesion forces from a total of 500 measurements using AFM probes with tip radii of curvature of 0.10 and 2.5 μm and Al substrate surfaces with surface roughness R_q of 0.7 and 38.0 nm. Figures 3.3 and 3.4 show that four different types of adhesion force histograms were obtained depending on the combination of the tip radius of curvature of the AFM probes and the surface roughness of the Al substrates. First, two types of adhesion force histograms were obtained for tip radii of curvature larger than 0.26 μm . The histograms shown in Figs. 3.3(a), (b), (d), and (e) and Figs. 3.4(a) and (b) exhibited a peak at a few nanonewtons and distributions with adhesion force of several hundred nanonewtons. Next, the histograms shown in Figs. 3.3(c) and (f) and Fig. 3.4(c) had distributions with adhesion forces peaking at several hundred nano-newtons, while the frequency of the adhesion forces ranged from several nanonewtons to several tens of nanonewtons. Furthermore, another two types of adhesion force histograms were obtained when AFM probes with tip radii of curvature less than 0.10 μm were used. The peak of the adhesion force in these two types of histograms was almost coincident and independent of the surface roughness. In contrast, the dispersion of the adhesion force could be divided into two cases, one large and the other small, depending on the surface roughness. The dispersion of the adhesion force was large for the histograms in Figs. 3.3(g) and (h) and Figs. 3.4(d) and (e), whereas it was small for those in Fig. 3.3(i) and Fig. 3.4(f).

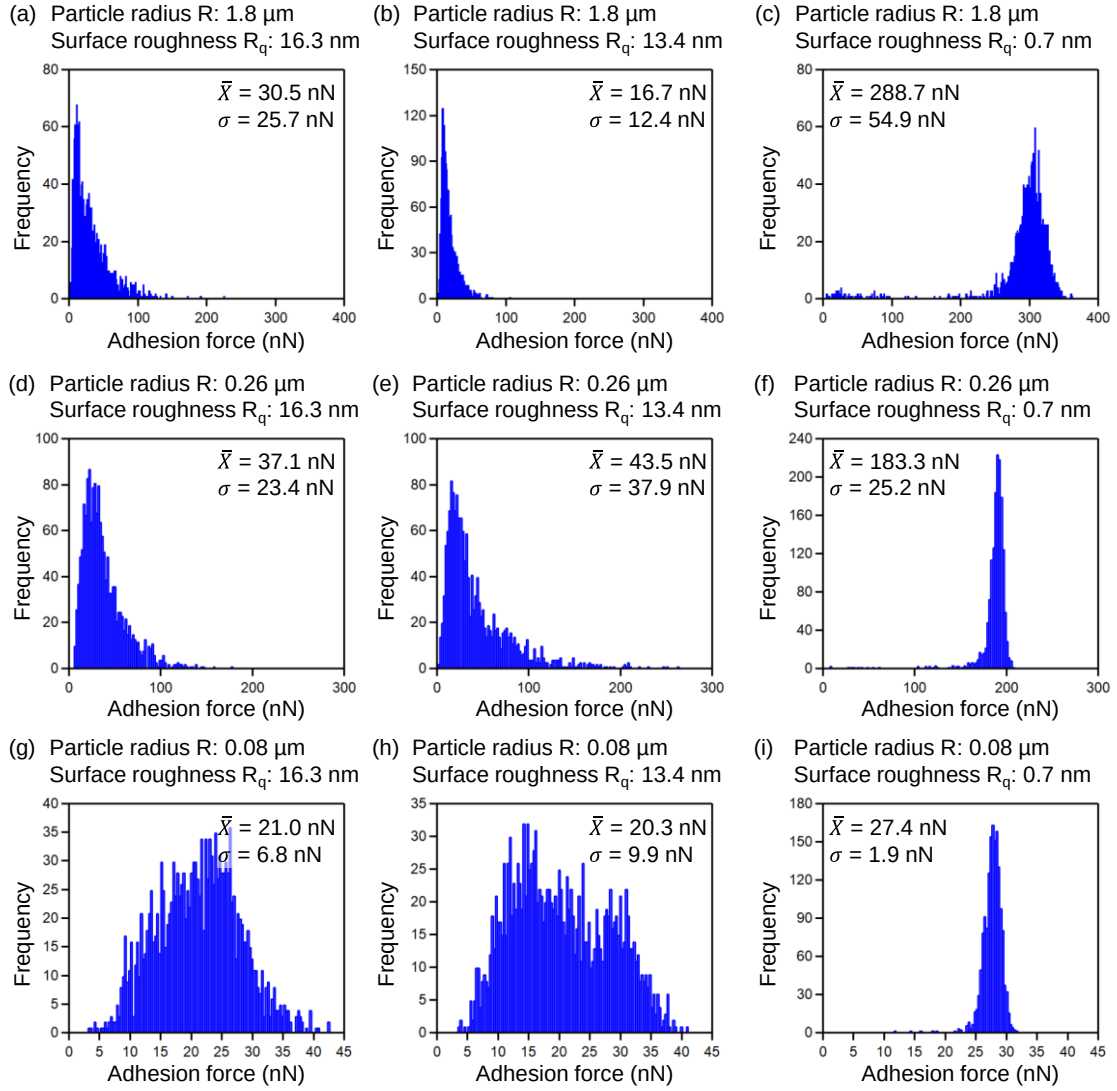


Fig. 3.3 Histograms of the adhesion force between Al substrate surfaces and AFM probes. The tip radii of curvature corresponding to the particle radius R are $1.8 \mu\text{m}$ in (a), (b), and (c), $0.26 \mu\text{m}$ in (d), (e), and (f), and $0.08 \mu\text{m}$ in (g), (h), and (i). The surface roughness of the substrate R_q , the mean adhesion force $\bar{X}$ and the standard deviation of the adhesion force σ are presented in the graphs.

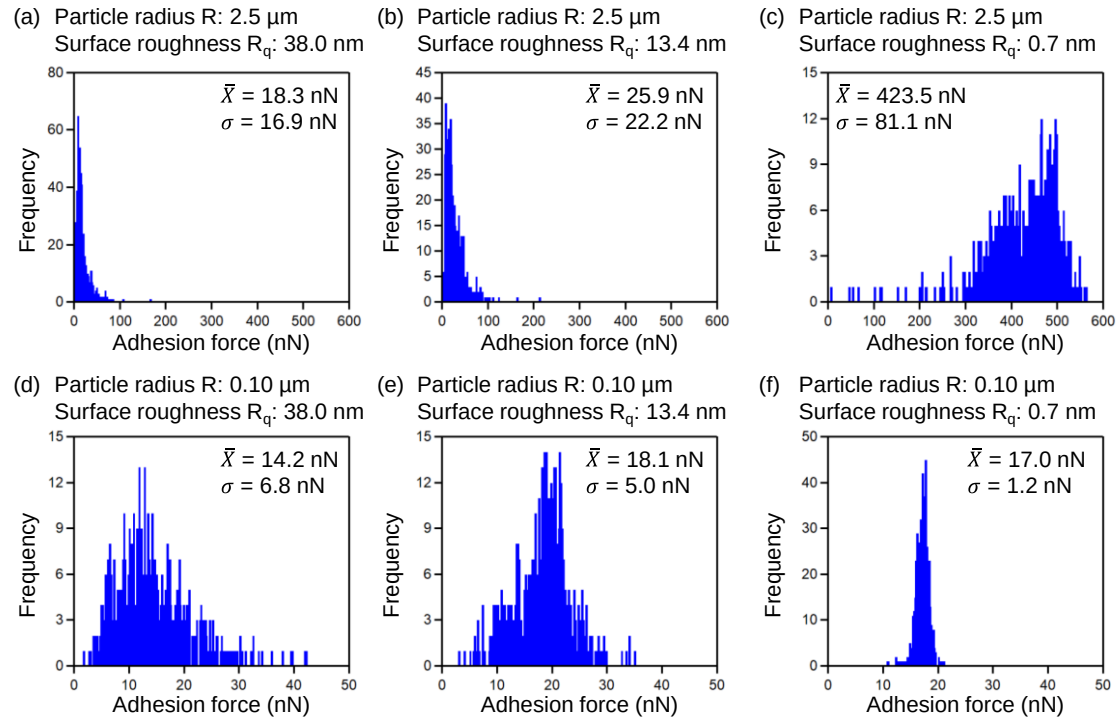


Fig. 3.4 Histograms of the adhesion force between Al substrate surfaces and AFM probes. The tip radii of curvature corresponding to the particle radius R are $2.5 \mu\text{m}$ in (a), (b), and (c), and $0.10 \mu\text{m}$ in (d), (e), and (f). The surface roughness of the substrate R_q , the mean adhesion force $\bar{X}$ and the standard deviation of adhesion force σ are presented in the graphs.

The results of the adhesion force evaluation shown in the histograms above can be explained by the geometric relationship between the substrate surface and the AFM probe, as shown in Fig. 3.5. Here, four different histograms of adhesion force are shown, as in Figs 3.3 and 3.4, corresponding to a combination of the surface roughness of the substrate and the size of the tip radius of curvature of the AFM probe.

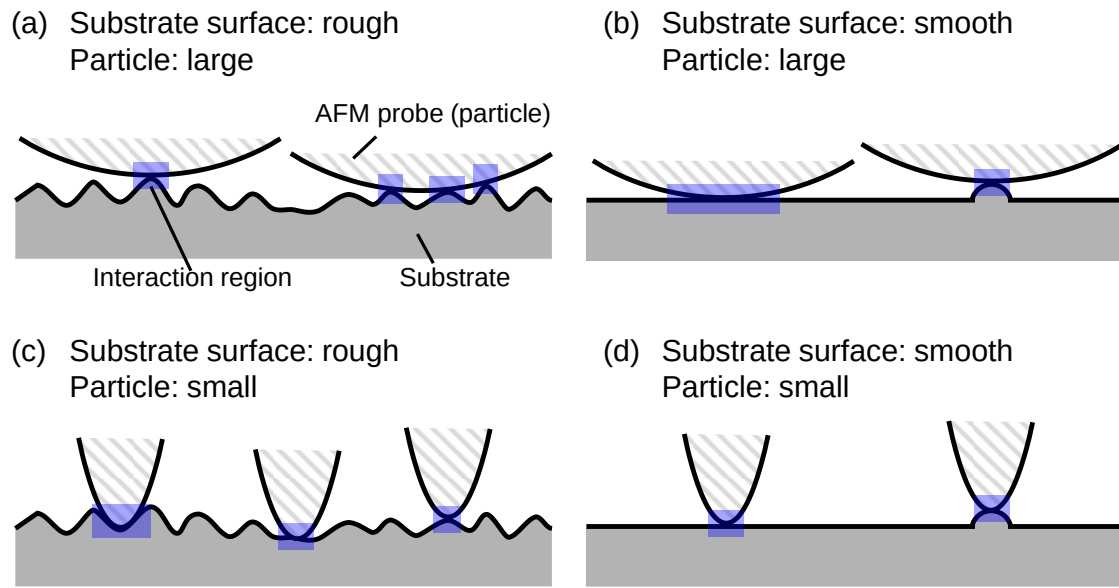


Fig. 3.5 Schematic of the interface between the substrate surface and the AFM probes, which correspond to small particles. An AFM probe with a large tip radius is interacting with (a) a rough surface, and (b) a smooth surface. An AFM probe with a small tip radius is interacting with (c) a rough surface, and (d) a smooth surface. The size of the interaction area between the substrate and the AFM probe differs.

The first two cases to be described are the cases in which the tip radius of curvature was large and the surface roughness was high and low, as shown in Figs. 3.5(a) and (b), respectively. The AFM probe interacted with only some of the protrusions on the substrate surface when the tip radius of curvature of the AFM probe was large and the surface roughness of the substrate was high, as shown in Fig. 3.5(a). However, there may be cases in which the probe interacts with flat areas or multiple protrusions. Therefore, the variation due to a large adhesion force was large, whereas the mean value of adhesion force was small. For the case in which the tip radius of curvature of the AFM probe was large but the surface roughness of the substrate was low as shown in Fig. 3.5(b), the AFM probe was in contact with a flat surface at almost all locations. Because the contact area could be regarded as that of ideal contact between a sphere and a flat surface, the mean value of adhesion force was large, and its variation was small. However, because protrusions still existed, even on the flat substrate surface, there may be cases in which the adhesion force becomes small owing to interactions

with the protrusions. This is also shown in the adhesion force histograms of Figs. 3.3 and 3.4.

The other two cases to be described are those in which the tip radius of curvature of the AFM probe is small. The AFM probe contacted with not only protrusions on the substrate surface but also concave areas because the tip radius of curvature of the AFM probe was small for the case of high surface roughness, as shown in Fig. 3.5(c). Therefore, the adhesion force was centered on the magnitude of the adhesion force in contact with the flat part, and the distribution included the magnitudes before and after that. Figure 3.5(d), which shows the case of low surface roughness, indicates that the contact conditions were similar at all locations, resulting in a smaller variation in the adhesion force.

3.3.2 Particle radius dependence of adhesion force

The dependence of the experimental adhesion force results on the tip radius of curvature of the AFM probes, corresponding to the radius of small particles, is presented and discussed in this section, including the origin of the adhesion force.

Figure 3.6 shows the adhesion force for different AFM probe tip radii of curvature R and substrate surface roughness R_q . The plots and error bars in the figure represent the mean and standard deviation of adhesion force, respectively. When the surface roughness R_q of the substrate surface was 0.7 nm, the adhesion force increased as the tip radius of curvature R increased. Although the data on the adhesion force at a tip radius of curvature of 0.26 μm deviated from the trend, the adhesion force was almost proportional to the tip radius of curvature R . Assuming a proportional relationship between the tip radius of curvature and the adhesion force, the proportionality constant was 0.17 N/m which was calculated using the least-squares method. However, the mean adhesion force was several nano-newtons to several tens of nanonewtons when the surface roughness R_q of the substrate surface was 10 nm or larger, regardless of the size of the tip radius of curvature.

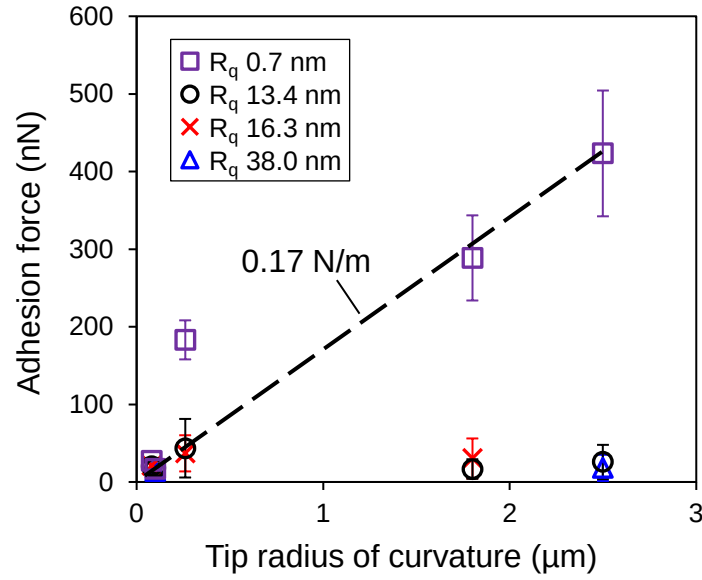


Fig. 3.6 Plot of the adhesion force as a function of the tip radius of curvature of the AFM probes.

The extent to which the van der Waals force or capillary force affected the adhesion force measurements is discussed based on the result that the adhesion force was proportional to the tip radius of curvature of the AFM probe when the surface roughness R_q of the substrate was 0.7 nm. Without considering the effect of surface roughness, the van der Waals force can be estimated using Eq. (2.10). Equation (2.10) can be viewed as an expression of the multiplication of the particle size by the proportionality constant, which is independent of particle size. Therefore, using the Hamaker constants between silica and Al shown in Table 2.1, the proportionality constants of the van der Waals force with respect to the particle radius of small particles for cut-off distances z of 0.165, 0.40, and 1.0 nm were 0.60, 0.10, and 0.016 N/m, respectively. From Eq. (2.10), the proportionality constant of the van der Waals force to the particle radius was largest when the cut-off distance was smallest. However, even with a cut-off distance z of 0.40 nm, the proportionality constant of the van der Waals force to the particle radius was 0.10 N/m, which is smaller than the proportionality constant of the adhesion force to the particle radius (0.17 N/m). Moreover, the effective cut-off distance was considered greater than 0.40 nm. This is because the surface roughness R_q of the substrate was 0.7 nm, and the surface

roughness R_q of the AFM probe tip was approximately 1 nm, which was not negligible, and the effective cut-off distance could be considered larger than 0.40 nm. The van der Waals force can be estimated using Eq. (2.14) when the effect of surface roughness is considered. However, it was found that the van der Waals force obtained with this effect was smaller than that without, and similarly, the proportionality constant of the van der Waals force to the particle radius was also smaller than 0.17 N/m. These results indicate that the experimental adhesion forces were larger than the calculated van der Waals force for all particle radii, and the origin of adhesion force in the experiments could not be explained by the van der Waals force alone.

Next, the effect of the capillary force is discussed. Without considering the effect of surface roughness, the capillary force was calculated using Eq. (2.25). The proportionality constant for the capillary force was 0.28 N/m using contact angles of 52° for silica and 90° for Al.^{67,68)} This value was larger than the 0.17 N/m constant of proportionality of the adhesion force to the particle radius obtained from the measurement of adhesion force on a substrate surface with a surface roughness R_q of 0.7 nm. If the tip radius of curvature of the AFM probe, which corresponds to the radius of small particles, is large, the contact between the small particles and the substrate surface cannot be considered ideal contact between a sphere and a flat substrate, as shown in Fig. 2.15. In this case, the effective capillary force was considered smaller than in Eq. (2.25). The reasons for this are explained in detail below.

The magnitude of the capillary force is expressed in Eq. (2.25) when the area of the interaction between the AFM probe and the substrate surface is large and water molecules fill the uneven surface across the contact interface. This corresponds to a case in which the contact radius is larger than the surface roughness of the AFM probe and substrate surface. When the contact radius is smaller than the surface roughness of the AFM probe and substrate, the area where liquid bridges are formed is narrower, and the formation of capillary forces is considered unaffected by surface roughness. Using Eq. (2.31), which is based on contact theory, the contact radius on the flat substrate surface was estimated to be several tens of nanometers for tip radii of 1.8 and 2.5 μm ; these contact radii were larger than their corresponding surface roughness R_q values of 3.9 and 1.9 nm. The meniscus radius calculated using Eq. (2.26) was 1.3

nm in a maximum RH of 40% under the present experimental conditions, which was smaller than the surface roughness R_q of the AFM probes. Therefore, it is considered that the size of the liquid bridges was small; hence, the uneven surface roughness area could not be filled with water molecules. Thus, the effective capillary force was smaller than that of Eq. (2.25).

The above investigation assumed that the contact time between the AFM probe and the substrate surface was sufficiently long and their contact interface was in equilibrium. In the adhesion force measurement experiments, the contact time between the AFM probes and the substrate surfaces was tens to hundreds of milliseconds. A previous report showed that a certain degree of adhesion force was formed within a few milliseconds, while the adhesion force between the AFM probe and the substrate surfaces increased as the contact time was increased to 1 s or longer.⁴³⁾ Another report showed that the adhesion force of the AFM probe and substrate surfaces decreased with increasing contact time.³⁴⁾ Although the experimental conditions were different, the interface between the AFM probe and the substrate surface may not have been in equilibrium, as in experiments in previous reports. The adhesion force when the contact state is maintained over a long duration, such as more than 1 s, has not been verified under the conditions of this experiment. However, the adhesion force remained almost the same, even when the contact time was reduced to 1/2 or 1/3, in experiments conducted prior to this study. Therefore, it can be concluded that a certain degree of capillary force was applied to the AFM probes by the liquid bridge, even if the contact areas were not in an equilibrium state.

As shown above, the adhesion forces obtained in this experiment cannot be explained solely by the van der Waals force. It was also found that the adhesion force was affected by the capillary force above a certain degree, even at low RH, such as 20–40% (experimental conditions).

3.3.3 Surface roughness dependence of adhesion force

The dependence of the measured adhesion forces on surface roughness is presented in this section, and the results of the investigation are discussed. Figure 3.7 shows graphs of the measured adhesion force between the AFM probe and the substrate surface as a function of the substrate surface roughness R_q . Here, Figs. 3.7(a) and (b) show the adhesion force and the coefficient of variation, which is the standard deviation of the adhesion force divided by the mean value, on the vertical axes, respectively. Because the standard deviation of the adhesion force is divided by the mean value of the adhesion force varying with the particle radius R , the coefficient of variation of the adhesion force is regarded as the value considering the shape factor, particle radius R , which influence the variation in adhesion force. Figure 3.7(a) also shows the mean and standard deviation of the adhesion force as plots and error bars, respectively. Focusing on the magnitude of the adhesion force, the maximum of the mean adhesion force for AFM probes with tip radii of curvature larger than $0.26\ \mu\text{m}$ was on the substrate surface with a surface roughness R_q of $0.7\ \text{nm}$. Conversely, for AFM probes with tip radii of curvature of $0.10\ \mu\text{m}$ or less, the mean adhesion force was approximately $20\ \text{nN}$ and was independent of the surface roughness R_q . Furthermore, the coefficient of variation of the adhesion force was smallest when the surface roughness R_q of the substrate was $0.7\ \text{nm}$, and its value increased as the tip radius of curvature of the AFM probe increased. When the surface roughness R_q of the substrate was greater than $13.4\ \text{nm}$, the coefficient of variation of the adhesion force had little or no correlation with the surface roughness R_q of the substrates or the tip radius of curvature R of the AFM probes.

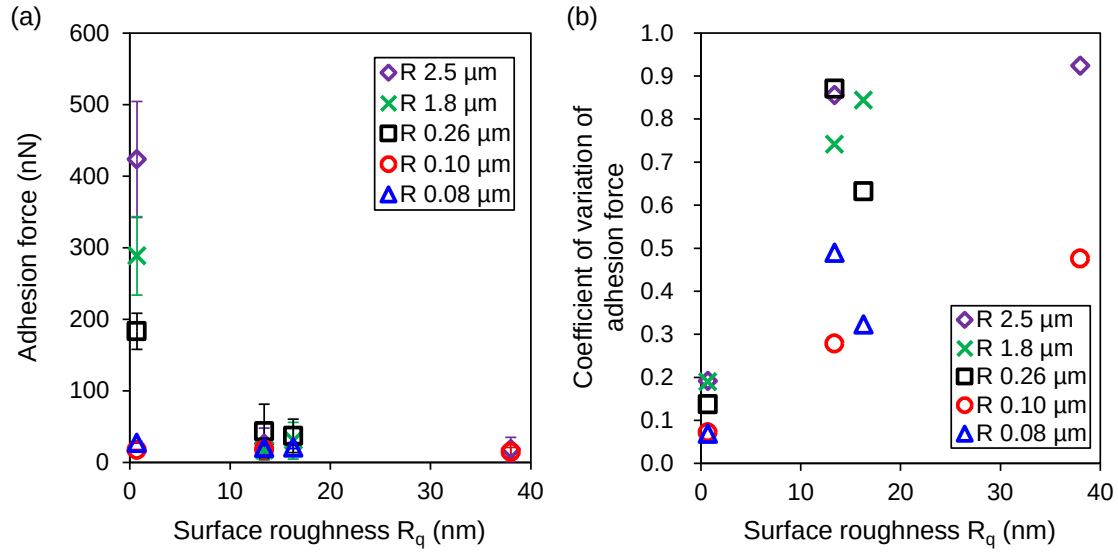


Fig. 3.7 Dependence of the (a) adhesion force and (b) its coefficient of variation on the tip radius of curvature R of AFM probes and the surface roughness R_q of Al substrates.

In the adhesion force measurement results shown in Fig. 3.7, the interaction and behavior of small particles on substrate surfaces were considered when the surface roughness R_q of the substrate was as small as sub-nanometer. The relatively large mean and the small variation in the adhesion force indicate that most of the small particles in contact with the substrate surface remained in a stable state of adhesion. However, when the radii of the AFM probes were relatively large and of the order of several micrometers, the adhesion forces could be one order of magnitude smaller, as shown in the adhesion force histograms of Figs. 3.3 and 3.4. This was due to the adhesion force between the protrusions on the substrate surface and the AFM probe, as discussed in Section 3.3.1. Subsequently, a case was considered in which the surface roughness R_q was 13.4 nm or greater. In this case, the mean of the adhesion force between the AFM probe and the substrate surface was small, and its variation was large. This indicates that when a large number of small particles are in contact with a substrate surface, many of them interact weakly and are easily separated from the substrate surface.

The reason the variation in adhesion force was almost independent of surface roughness is discussed here. From the perspective of small particles, the area in which

they interact with the substrate surface to the extent that this affects the adhesion forces is smaller than a $1\ \mu\text{m} \times 1\ \mu\text{m}$ region. Therefore, it is necessary to analyze surface roughness in the local region of interaction between the AFM probes and the substrate surfaces rather than in the $1\ \mu\text{m} \times 1\ \mu\text{m}$ region when discussing the relationship between adhesion force and surface roughness.

The contact model in DMT theory can estimate the amount of small particle deformation at the interface when they are in contact with the substrate surface, as well as at the contact region. Although DMT theory does not include a term to correct for the effect of surface roughness, the size of the contact area between the substrate surface and small particles is considered an approximation of the size of the area of interaction between the substrate surface and small particles when they are in contact in a system with surface roughness. Therefore, based on DMT theory, the contact area with the tip radius of curvature of the AFM probe corresponding to the radius of small particles was determined, and the surface roughness of the substrate within the area was analyzed.

In conventional analysis methods, surface roughness can be analyzed using the following equation:

$$R_q = \sqrt{\frac{1}{n_{x,y}} \sum_{x,y} (Z(x,y) - Z_{ave})^2}, \quad (3.1)$$

where $Z(x,y)$ is the height at the position to be analyzed, Z_{ave} is the mean height within the analysis range, and $n_{x,y}$ is the number of data points to be analyzed. Thus, the surface roughness is analyzed based on the mean height across the entire analysis range in conventional methods.

From Eq. (2.31), derived using DMT theory, the contact radius was obtained for the AFM probes, assuming that the contact load was zero. The dependence of the contact radius on the tip radius of curvature of the AFM probe is shown in Fig. 3.8, where the results are plotted for cut-off distances of 0.165, 0.4, and 1.0 nm. As shown, the contact radius increased as the tip radius of curvature of the AFM probe increased.

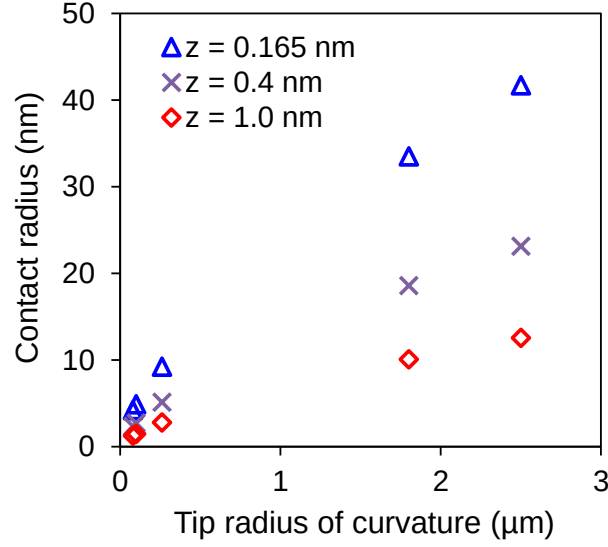


Fig. 3.8 Dependence of the contact radius between AFM probes and the flat substrate surface on the tip radius of curvature of the AFM probes. The cut-off distances z used in the calculations are presented in the graph.

Subsequently, an AFM topographic image of a $1 \mu\text{m} \times 1 \mu\text{m}$ area was divided into areas the size of a circle with a contact radius, and the surface roughness R_q was analyzed for each area. Furthermore, the mean value of the surface roughness R_q of each area was denoted as R_q' . These relationships are expressed in Eqs. (3.2) and (3.3):

$$R_{i-q} = \sqrt{\frac{1}{n_{x,y}} \sum_{x,y} (Z_i(x,y)' - Z_{i_{ave}}')^2}, \quad (3.2)$$

$$R_q' = \frac{1}{n} \sum_i^n R_{i-q}, \quad (3.3)$$

where $Z(x,y)'$ is the height at the position to be analyzed within the contact area, $Z_{i_{ave}}'$ is the mean height within the contact area, $n_{x,y}$ is the number of data points to be analyzed within the contact area, and n indicates the number of regions of the contact area extracted from the entire analysis area. Thus, the entire analysis area was divided by the contact area, and the results of each surface roughness analysis were used as the proposed method.

In this study, R_q' , which was calculated using Eqs. (3.2) and (3.3), was the local surface roughness. The local surface roughness R_q' is the result of analyzing the surface roughness in terms of the contact area corresponding to the particle radius R . Therefore, it is regarded as the value considering the shape factor of the particle radius R in surface roughness analysis. The local surface roughness R_q' obtained in this manner may have a certain correlation with the magnitude of the adhesion force of small particles and its variation.

The local surface roughness R_q' was plotted as a function of the contact radius as shown in Fig. 3.9. The results are plotted for cut-off distances z of 0.165, 0.4, and 1.0 nm in Figs. 3.9(a), (b), and (c), respectively. As shown in Fig. 3.9, R_q' increased as the contact radius increased. R_q' of the substrate surfaces was smaller than the surface roughness R_q of the substrate surfaces shown in Table 3.2. The difference in the value increased when R_q of the substrate surface was larger. Although the scale of the contact radius, which is the abscissa, was different, the spacing of the plots in Figs. 3.9(a), (b), and (c) remained the same, despite the cut-off distance z being different.

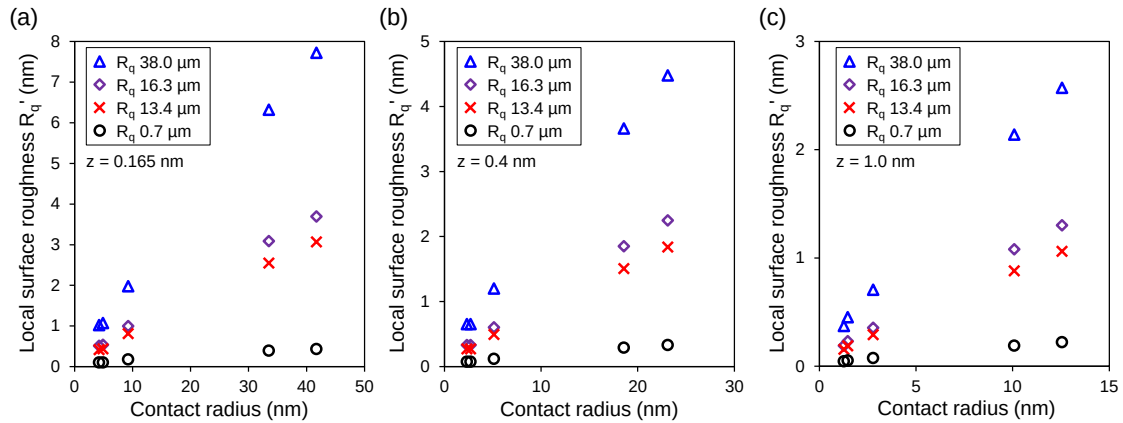


Fig. 3.9 Local surface roughness analyzed based on the size of the contact radius between the probes and the substrate surfaces when the cut-off distance z is (a) 0.165 nm, (b) 0.4 nm, and (c) 1.0 nm.

The dependence of the local surface roughness R_q' on the surface roughness R_q is shown in Fig. 3.10. The plots and error bars present the local surface roughness R_q' and standard deviation of $R_{i,q}$ in Eq. (3.3), respectively. The results are plotted for

cut-off distances z of 0.165, 0.4, and 1.0 nm in Figs. 3.10(a), (b), and (c), respectively. As shown in Fig. 3.10, the local surface roughness R_q' was proportional to the surface roughness R_q . Moreover, the standard deviation of $R_{i,q}$ increased with increasing R_q . Thus, the effect of the variation in the height of the surface morphology was included in R_q' .

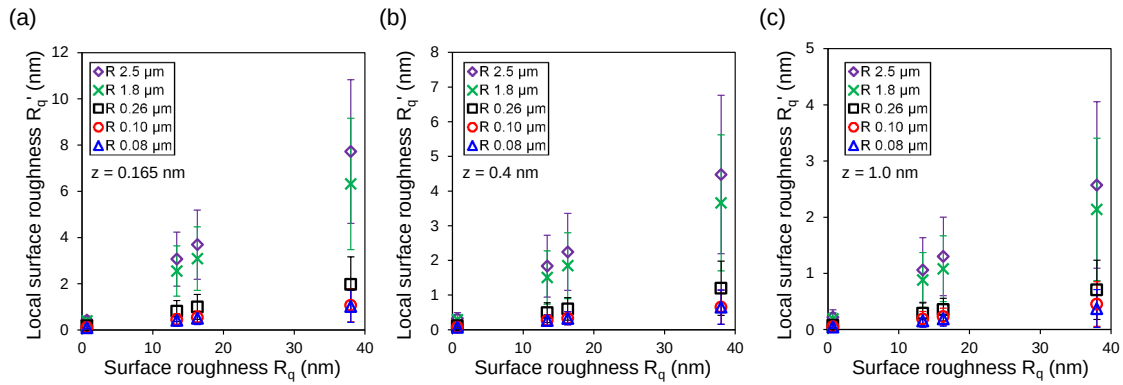


Fig. 3.10 Local surface roughness analyzed based on the size of the contact radius between the AFM probes and the substrate surfaces when the cut-off distance z is (a) 0.165 nm, (b) 0.4 nm, and (c) 1.0 nm.

The mean and coefficient of variation of the adhesion between the AFM probe and the substrate surface based on the local surface roughness of the Al substrate are shown in Fig. 3.11. Figures 3.11(a), (b), and (c) show the mean adhesion force at cut-off distances of 0.165, 0.4, and 1.0 nm, respectively, where the error bars represent the standard deviations of the adhesion forces. Figures 3.11(d), (e), and (f) show the coefficient of variation of the adhesion force for cut-off distances of 0.165, 0.4, and 1.0 nm, respectively. The mean adhesion force was large only when the local surface roughness R_q' was small, which is the same as the behavior shown in the graph of the dependence of the mean adhesion force on the surface roughness R_q in Fig. 3.7(a). Conversely, the coefficient of variation of the adhesion force tended to increase as the local surface roughness R_q' increased, as shown in Figs. 3.11(d), (e), and (f).

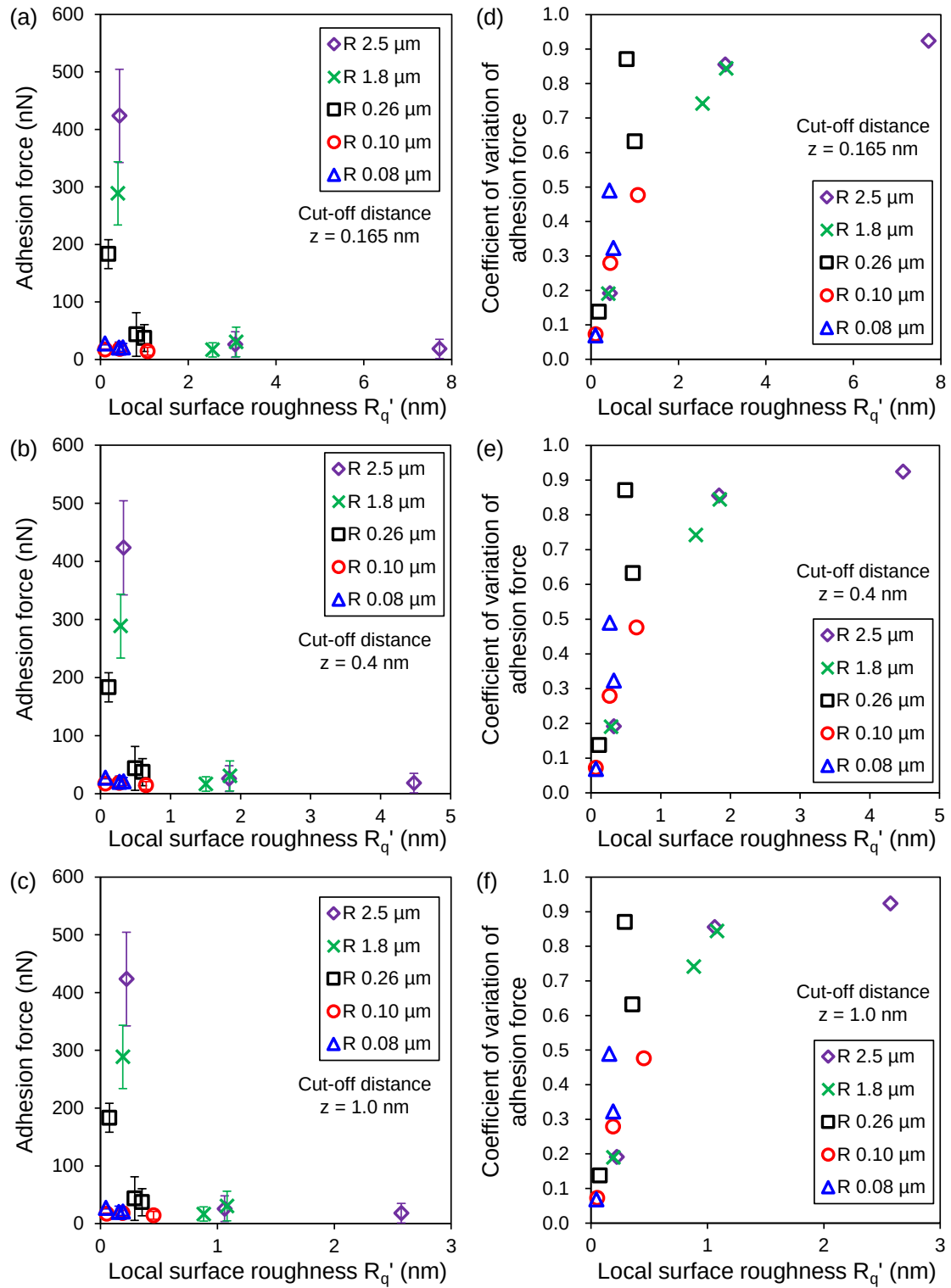


Fig. 3.11 Dependence of the (a)–(c) mean value and (d)–(f) coefficient of variation of the adhesion force on the local surface roughness of Al substrate surfaces and the tip radii of curvature R of AFM probes. The cut-off distances used in the analysis are presented in the graphs.

The cut-off distance of each graphs in Fig. 3.11 was fixed. However, the cut-off distance, which is affected by the unevenness of the substrate surface (a factor in surface roughness), may need to be set to a larger value as the surface roughness increases. An example of increasing the cut-off distance with increasing surface roughness is shown in Figs 3.12 and 3.13. Figures 3.12(a) and (b) show the local surface roughness R_q' versus the contact radius and surface roughness R_q , respectively. Figures 3.13(a) and (b) show the mean adhesion force and the coefficient of variation of the adhesion force versus the local surface roughness R_q' , respectively. These graphs were constructed for a cut-off distance of 1.0 nm when the surface roughness R_q was 13.4 nm or greater, and for a cut-off distance of 0.4 nm when R_q was 0.7 nm.

Although the scale of the local surface roughness on the horizontal axes in Figs. 3.13(a) and (b) is different from that in Fig. 3.11, the spacing of the plots in the graphs remains almost the same when comparing graphs showing the mean adhesion force and the coefficient of variation for fixed cut-off distances. Hence, even when it is necessary to increase the cut-off distance with increasing surface roughness as shown in Fig. 3.13, the relative position of the mean adhesion force and coefficient of variation plotted to the direction of the local surface roughness remains the same. Therefore, that magnitude of the cut-off distance has no effect on this discussion.

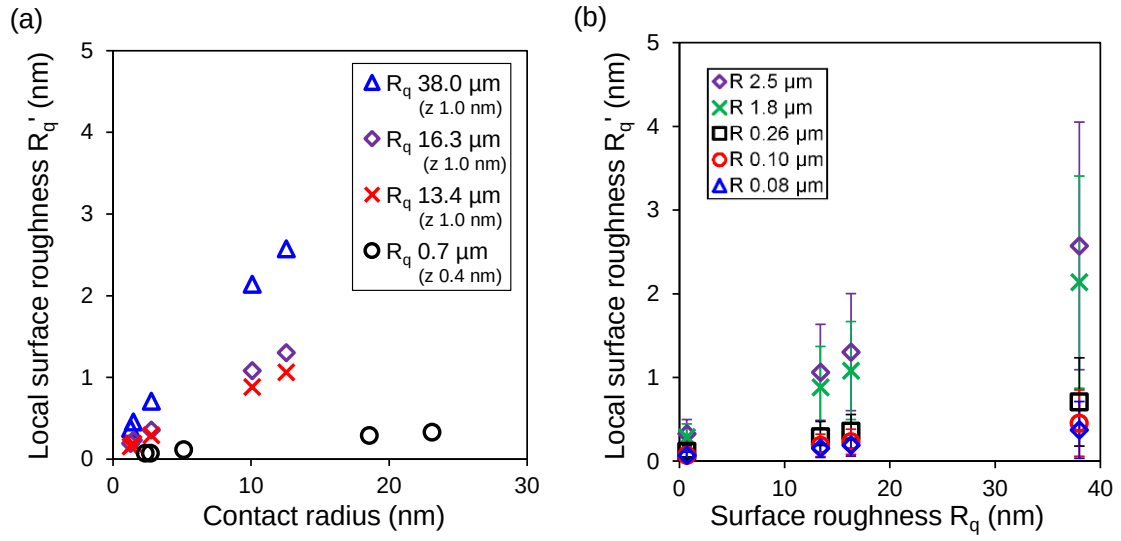


Fig. 3.12 Dependence of the local surface roughness R'_q on the (a) contact radius and (b) surface roughness R_q . R'_q is analyzed based on the size of the contact radius between probes and substrates. The cut-off distance z is set to 0.4 nm at a surface roughness R_q of 0.7 nm and 1.0 nm at surface roughness $R_q > 10$ nm.

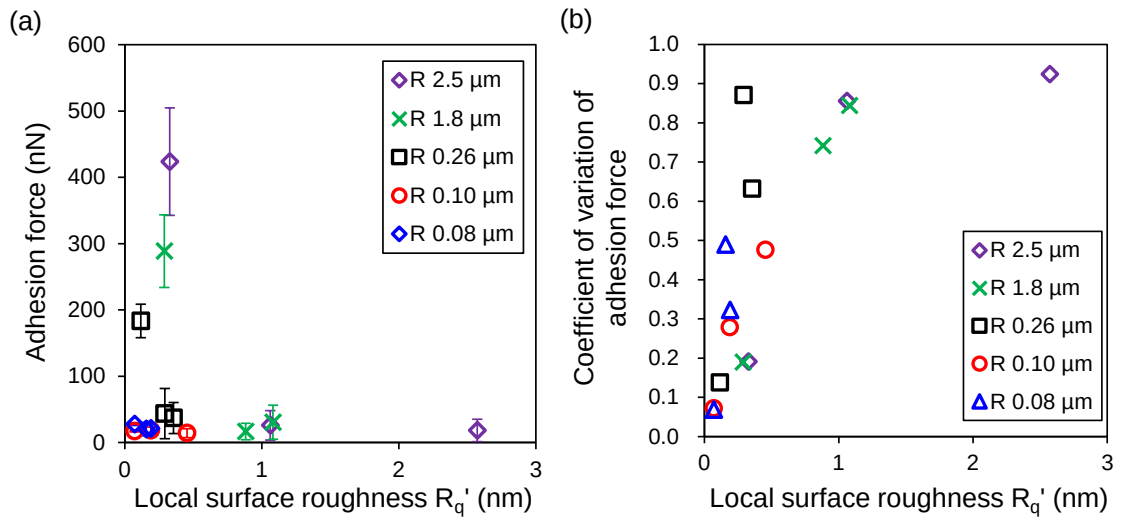


Fig. 3.13 Dependence of the (a) mean value and (b) coefficient of variation of the adhesion force on the local surface roughness R'_q of Al substrate surfaces and the tip radii of curvature R of surface probes. The cut-off distance z is set to 0.4 nm at a surface roughness R_q of 0.7 nm and 1.0 nm at surface roughness $R_q > 10$ nm.

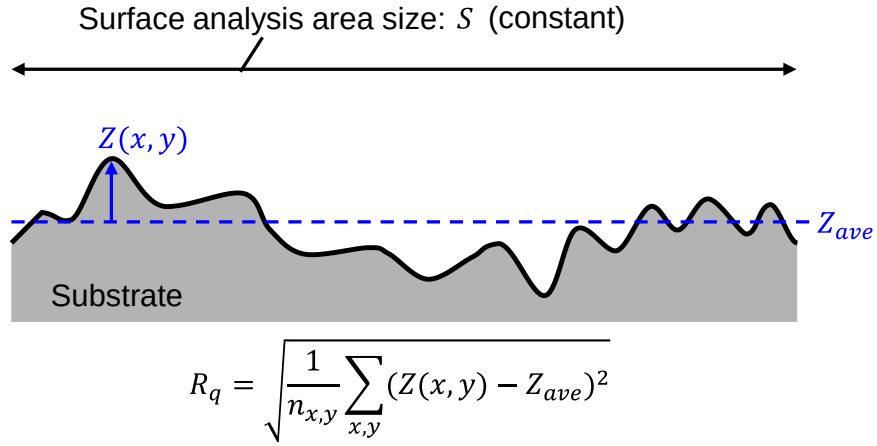
As shown in Figs. 3.9 and 3.12(a), the local surface roughness R_q' increased as the contact radius increased. This is because the substrate surfaces not only had small local protrusions and holes, but also a wide distribution of steps, undulations, convexities, and concavities, which were formed during the surface treatment process, as shown in the AFM topographic images of Fig. 3.2. As the analytical range of surface roughness increased with increasing contact radius, the structure of widely distributed unevenness was included in the analytical range. A schematic presenting the region of the surface roughness analysis is shown in Fig. 3.14. Figures 3.14(a) and (b) show that the surface roughness R_q was analyzed within a large constant area, which is the conventional method, and the local surface roughness R_q' was analyzed by narrowing the analysis area corresponding to the contact areas, respectively. The two-way arrows in the figures indicate the area in which the surface roughness was analyzed.

As shown in Fig. 3.14(a), the analysis area for surface roughness included various uneven shapes. However, the analysis area for surface roughness indicated by the circle with a contact radius did not include features such as long step size and an undulation period, as shown in Fig. 3.14(b). As shown in the AFM topographic images of Figs. 3.2(b) and (c), there was a long-period wavy structure with a period of several hundred nanometers. However, considering the analysis range when the contact radius was set from several nanometers to several tens of nanometers, it was also found that the influence of long-period structures was eliminated from the analysis range of surface roughness. The local surface roughness R_q' , which is limited to the size of the area in which small particles interact with the substrate surface, will allow us to estimate the dependence of the adhesion force of small particles and its variation on the surface roughness. This can be seen from the graphs of the coefficient of variation of the adhesion force versus the local surface roughness R_q' shown in Figs. 3.11(d), (e), and (f). The coefficient of variation of the adhesion force increased as the local surface roughness R_q' increased, which indicates that there was a correlation between these parameters. Because the local surface roughness R_q' and coefficient of variation of adhesion force are both values that considering the shape factor of particle radius R , a correlation was found between the coefficient of variation and the local surface roughness, and this method is considered to have a wide range of applicability.

Thus, one of the outcomes of this study is the proposal of a method of analyzing surface roughness in the region that matches the contact area between small particles and the substrate surface based on contact theory. The proposed method can be used to predict the variation in the adhesion force between small particles and the substrate, which has not been achieved by conventional analysis methods for surface roughness. Because surface treatment to control such adhesion force variations can be expensive, it is important to predict and select an appropriate surface treatment. Therefore, the proposed method, which enables us to estimate the variation in the adhesion force of particles on a surface in advance, will contribute to this industrial field.

Moreover, it was found that the variation in the adhesion force of small particles could be reduced when the surface roughness of the substrate was reduced to the nanometer order or less, whereas the mean value of adhesion force decreased for particles of micrometer-order size and did not change for particles of sub-micrometer-order size or smaller. This result indicates that reducing the surface roughness of apparatus wall surfaces to the nanometer order or less is effective in preventing the scattering of small particles due to external forces, which increase as the size of the small particles increases.

(a) Conventional method



(b) Proposed method

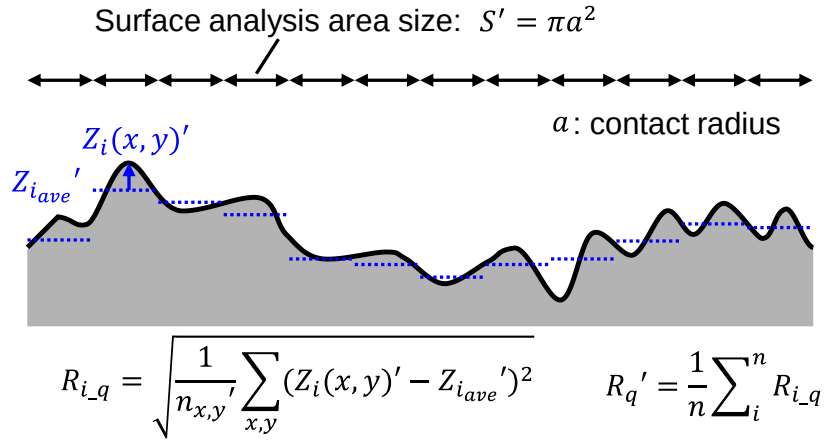


Fig. 3.14 Schematics of regions under observation for the surface roughness analysis method. (a) Surface roughness is analyzed using a constant area size. (b) Surface roughness is analyzed using a limited area, which depends on the size of the contact area between the particle and the substrate surface.

3.4 Summary

In this chapter, an evaluation of the adhesion force between the silica AFM probes with different tip radii of curvature and the Al substrates that had undergone different surface treatments is shown to study the dependence of the adhesion force of small particles on surface roughness. The findings obtained from this investigation are as follows:

- The adhesion force between the silica particles, which were sub-micrometer to several micrometers in size, and the Al substrate surface could not be explained by the van der Waals force alone. It was found that the capillary force also affected the adhesion force even under a low-humidity environment of 20–40%RH (experimental conditions).

- When the surface roughness was analyzed over a certain constant area, as in conventional methods, a correlation between the surface roughness and the coefficient of variation of the adhesion force of small particles was not found. Therefore, a method of analyzing surface roughness considering the interaction area between the particles and the substrate surface was considered to predict the variation in the adhesion force of the particles. As a result, a local surface roughness analysis method based on the contact theory was proposed, in which the analysis range of surface roughness was limited to the area in which small particles interact with the substrate surface. It was shown that the coefficient of variation of the adhesion force can be predicted for the first time using the local surface roughness calculated with the proposed method. Because the local surface roughness and coefficient of variation of adhesion force are both values that considering the shape factor of particle radius, a correlation was found between the coefficient of variation and local surface roughness, and this method is considered to have a wide range of applicability.

- It was found that the variation in the adhesion force of the small particles could be reduced when the surface roughness of the substrate surface was reduced to the nanometer order or less, whereas the mean value of adhesion force decreased for

particles of micrometer-order size and did not change for particles of sub-micrometer-order size or smaller. This result shows that it is effective to reduce the surface roughness of apparatus wall surfaces to the nanometer order or less via surface treatment in advance. This changes the surface roughness to prevent the scattering of small particles due to external forces, which increase as the size of the small particles increases.

4 Adhesion force on low temperature surface under high vacuum

4.1 Preface

In addition to controlling the surface roughness, as described in the previous section, the adhesion force of small particles can be controlled by changing the RH, degree of vacuum, or substrate surface temperature at or near the interface between the particles and the substrate surface. This is because the behavior of water molecules that contribute to the capillary force, which is affected by the above parameters, changes at or near the contact interface when the capillary force contributes to the adhesion force.

The effects of RH, degree of vacuum, and substrate surface temperature on the capillary force have been reported based on AFM evaluations. Experimental results have been reported on the parameters that affect this force when applied to AFM probes which can be regarded as small particles. For example, one report evaluated the change in the adhesion force of an AFM probe, when the RH was varied under atmospheric pressure. Another report showed that even if the thickness of the water film on the substrate is reduced by vacuum evacuation, a certain amount of water molecules adsorbed on the surface remains, which affects the adhesion force. In contrast, the temperature dependence of particle adhesion at low temperatures is not fully understood, especially in the temperature range of liquid nitrogen under high vacuum, which is used in industrial applications. Knowledge obtained by evaluating the change in the adhesion force of small particles under such experimental conditions and examining the results and fluctuation factors may be utilized as feedback for the industrial field. In Chapter 1, it was shown that there are components in the specimen chamber under a vacuum environment whose surface temperatures change. In addition, there are other equipment configurations in which the temperature inside the equipment varies. For example, in a focused ion beam apparatus, a substrate cooling system using liquid nitrogen is used to reduce thermal damage during focused ion beam irradiation.

Therefore, the temperature dependence of the adhesion force was evaluated by decreasing the temperature of the substrate surface from room temperature to liquid nitrogen temperature, and the results are discussed in this chapter. Based on the findings in the previous chapter, substrates with different surface roughness were used to ensure different adhesion states of small particles on the substrate surface.

4.2 Experimental methods

An AFM system (Hitachi High-Tech Science AFM5300E) was used to evaluate the temperature dependence of the adhesion force on the substrate surface. AFM5300E can evaluate the interaction between the AFM probe and the substrate surface under a high vacuum condition using a turbo molecular pump backed with a rotary pump to evacuate the specimen chamber. The system is also equipped with a substrate temperature control unit, which enables heating of substrates by a graphite heater built into the substrate holder and cooling of substrates by inserting liquid nitrogen into the cooling dewar connected to the substrate holder by the heat-conducting component. This configuration allows the temperature of the substrate surface to be controlled from 153 to 673 K under a high vacuum. The temperature of the substrate surface was decreased from room temperature and was controlled in the range of 298–153 K using the substrate temperature control unit.

The procedure for fabricating the AFM probes was the same as that described in Chapter 2, attaching a particle onto the AFM cantilever. Room-temperature curing epoxy resin (Ciba-Geigy Araldite) was collected with a manipulator and applied to an AFM tipless cantilever (Innovative Solutions Bulgaria All-In-One-Al-tipless) with a typical spring constant of 2.7 N/m. Then, silica particles (Micromod Sicastar) with a mean diameter of 5 μm , collected with another manipulator, were placed on top of the epoxy resin. The same method as that used for the trapezoidal cantilever was used to calibrate the spring constant of the fabricated AFM probe.⁵²⁾ The geometry of another tipless AFM cantilever with the same geometry was analyzed via SEM. The spring constant of the cantilever was 1.8 N/m, which was calculated using Eqs. (2.2) and (2.3) shown in Chapter 2.

The procedure for analyzing the tip radius of curvature of the AFM probe was the same as the method described in Chapter 2. This tip radius of curvature was analyzed using a grating substrate (NT-MDT Spectrum Instruments TGT-1). Topographic AFM images of the grating substrate with scanning directions that differ by 90° using the AFM probe and their height profiles are shown in Fig. 4.1.

The radii of curvature along the X- and Y-axes were evaluated from the height profiles in Figs 4.1(c) and (d) by fitting each to circles using the least-squares method.

The particle diameter was evaluated as $3.5\ \mu\text{m}$, which is the geometric mean of the obtained radii of curvature. The surface roughness of the particle attached to the AFM probe was $6.6\ \text{nm}$, which was calculated using the geometric mean of the surface roughness R_q for each height profile.

AFM probes prepared using the method described above were used to evaluate the adhesion force on the substrate surface as the temperature of the substrate surface was decreased from room temperature. In the evaluation of the contact time dependence of adhesion force discussed in Section 4.3, the adhesion force was examined using another AFM probe that was fabricated in the same manner as above, but the tip shape was not analyzed. Because the AFM probe was fabricated using the same protocol, the surface morphologies, that is, the particle size and the surface roughness of the tip particle, were considered similar.

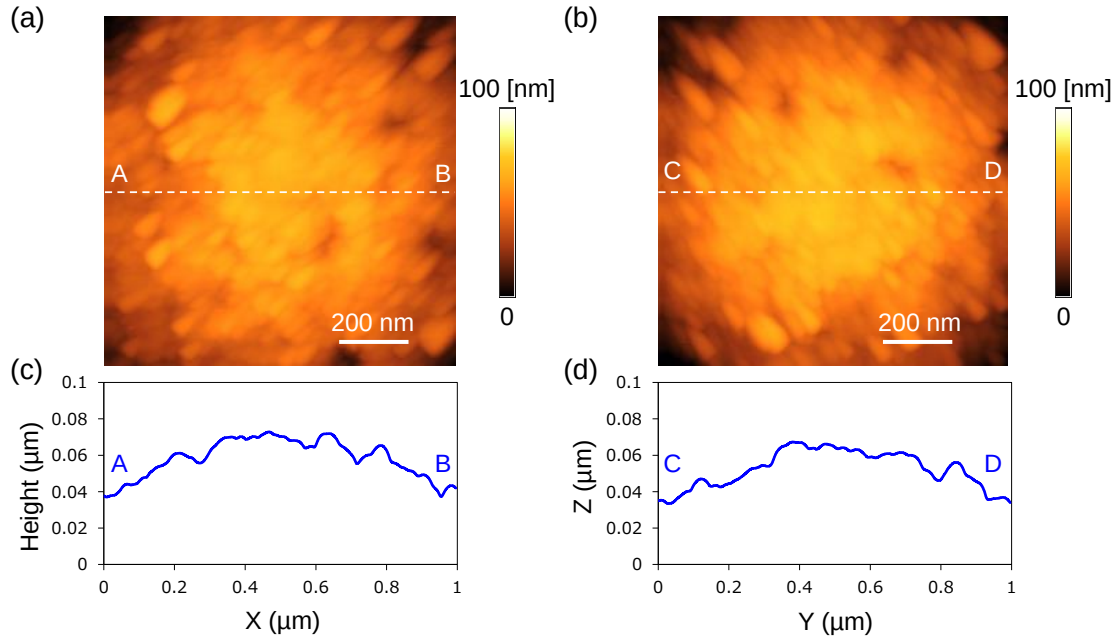


Fig. 4.1 (a) and (b): AFM images of a grating substrate using an AFM probe with a silica particle attached in two perpendicular directions (X and Y directions). (c) and (d): height profiles along the dashed lines in (a) and (b), respectively.

The material of the substrate surface was Al, which is same as in the experiment described in the previous chapter. In addition, substrate surfaces with a thin film of Al

formed via sputtering on an Si substrate with a thermal oxide film of 100 nm were installed in the substrate temperature control unit. The thickness of the Al thin film formed via sputtering was approximately 10 and 30 nm to ensure different surface roughness on the substrates. The Al substrate surfaces were each ultrasonically cleaned with ethanol and acetone for 4.5 min to measure the adhesion force. The surface roughness R_q , which was obtained using the AFM topographic image of a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area was 0.8 and 2.8 nm for the 10 and 30 nm-thick Al film substrate surfaces, respectively. A commercially available AFM probe with a sharp tip for surface morphology evaluation was used for the surface roughness analysis of the substrate surfaces. The contact angles of the substrate surfaces of the 10 and 30 nm-thick Al films were 90° and 88° , respectively. In this study, 90° was used for the contact angle of Al in the calculation of the capillary force. This value is consistent with a previous report.⁶⁸⁾ The contact angle of silica to water was 52° ,⁶⁷⁾ and 0.072 N/m was used as the surface tension of water.⁴⁹⁾

The local surface roughness R_q' proposed in the previous chapter was analyzed for these particles and substrates. For the substrate surface with the 10 nm-thick Al film, the local surface roughness R_q' for cut-off distances of 0.165, 0.40, and 1.0 nm were 0.73, 0.66, and 0.49 nm, respectively. For the substrate surface with the 30 nm-thick Al film, the local surface roughness R_q' for cut-off distances of 0.165, 0.40, and 1.0 nm were 2.5, 2.0, and 1.3 nm, respectively. Referring to Fig. 3.11, the relationship between R_q' and the coefficient of variation of the adhesion force can be regarded as a curve in which the coefficient of variation of the adhesion force approaches 1 as the local surface roughness R_q' increases. In this relationship, the substrate surface with the 10 nm-thick Al film can be regarded as a substrate with little adhesion variation before the coefficient of variation of the adhesion force approaches 1, whereas the substrate surface with the 30 nm-thick Al film can be regarded as a substrate with a sufficiently large coefficient of variation of the adhesion force, which causes adhesion force variation.

Force curves were obtained and the temperature dependence of the substrate surface on small particles was evaluated using AFM, the AFM probe with small particles attached, and the substrate surface shown above. The parameters that could be controlled during force curve acquisition for this system were the operating

distance of the probe, the time required to acquire one force curve, and the maximum contact load when switching the AFM probe from the direction of pushing to pulling away from the substrate surface via feedback control. The contact time between the probe and the substrate was controlled by varying each parameter. The maximum contact load was 337 nN for the AFM probe on the substrate surface in the experiments described in this chapter.

Here, the effect of the contact load of the AFM probe on the substrate surface at their contact interface is shown. The physical properties of the silica particles and Al substrate surface used in this study are shown in Table 2.1. An estimation of 0.8–0.9 nm of deformation was obtained for the small particles when a particle with a radius of 3.5 μm was in contact with the substrate surface with a contact load of 0–400 nN using these physical properties and analyzing the results with Eq. (2.30). Thus, the amount of deformation of the small particles was small and almost the same, and the deformation of the particles due to the contact load had a negligible effect on the evaluation of adhesion force. Therefore, it is considered that the change in contact load only changed the contact time in the results shown in Section 4.3.

4.3 Results and discussion

4.3.1 Experimental results involving water molecule behavior

The experimental results are described in this chapter to illustrate the behavior of water molecules on the substrate surface. First, the results of the evaluation of the surface morphology on the substrate surface at temperatures lower than room temperature under high vacuum are presented. Subsequently, the dependence of the adhesion force between the AFM probe with small particles attached and the Al substrate surface on the contact frequency and contact time is shown. As discussed below, these results indicate that water molecules were supplied from the vacuum to the substrate surface and diffused on the substrate surface.

4.3.1.1 Surface morphology of substrate at low temperatures in high vacuum

First, we discuss the evaluation results of the surface morphology of the Al substrate surface with a surface roughness R_q of 0.8 nm attached to the substrate temperature control unit as the temperature of the substrate surface was lowered from room temperature (298 K) at vacuum pressure of the order of 10^{-4} Pa. Figures 4.2(a) and (b) show AFM topographic images of the substrate surface at substrate temperatures of 253 and 213 K, respectively. Figures 4.2(c) and (d) show height profiles, which were extracted along the dashed lines AA' and BB' drawn across the characteristic structures in Figs. 4.2(a) and (b), respectively. Comparing the height profiles of the dashed line AA' in Figs. 4.2(c) and (d), it is clear that the width and height of protrusions, which are characteristic structures, increased as the Al substrate temperature decreased from 253 to 213 K. This contrasts with the other area showing the Al surface morphology which did not change with a decrease in substrate temperature. New protrusions were formed as the Al substrate temperature decreased, which were revealed by comparing the height profiles of the dashed line BB' in Figs. 4.2(c) and (d). The growth and appearance of these protrusions with decreasing Al

substrate temperature indicates that there was a source of gas molecules that changed the shape of the protrusions. In previous reports, the main residual gas in the chamber under high vacuum, as in the present experimental conditions, was water molecules.^{63,66)} Moreover, a gas molecule was not introduced to the vacuum chamber intentionally in the experiment. Therefore, water molecules were the only possible gas molecules that could form solid aggregates on the surface at the Al substrate temperature under the experimental condition. In other words, this experiment showed that water molecules were supplied to the substrate surface from the vacuum. It was also shown that the surface height did not change uniformly, but the formation of aggregates and their sizes changed. This indicates that the supplied water molecules diffused on the surface.

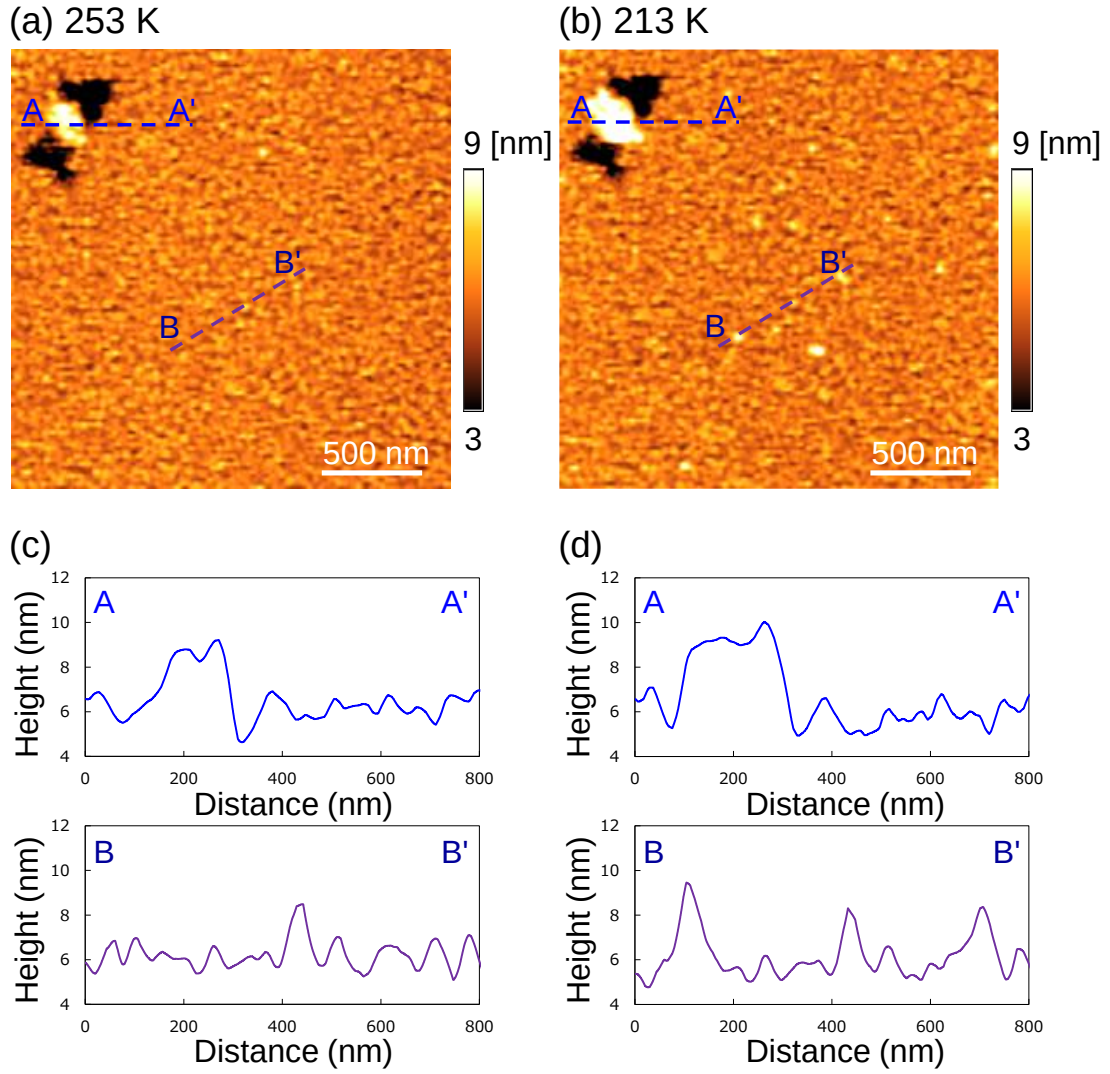


Fig. 4.2 AFM topographic images of the Al substrate surface with a roughness R_q of 0.8 nm at substrate temperatures of (a) 253 K and (b) 213 K. (c) Height profiles measured along the dashed lines AA' and BB' in (a). (d) Height profiles measured along the dashed lines AA' and BB' in (b).

4.3.1.2 Contact time dependence of adhesion force

The results of evaluating the change in the adhesion force for different contact times between the small particle at the tip of the AFM probe and the substrate surface are presented in this section. In this experiment, the controlled parameters were the operating distance of the probe, the time required to acquire one force curve, and the maximum contact load in force curve measurements. As explained in the previous discussion, the effect of the contact load was negligible, and the above parameters were considered to affect only the contact time between the small particles and the substrate surface. The substrate temperature was set as 233 K on the Al substrate surface with a surface roughness R_q of 0.8 nm attached to the substrate temperature control unit under a vacuum of 1×10^{-4} to 3×10^{-4} Pa. The location of contact between the small particle and the substrate surface was changed for each measurement.

The contact time dependence of the adhesion force obtained under the above conditions is shown in Fig. 4.3. As shown in the figure, the adhesion force increased with increasing contact time between the small particle and the substrate surface in the contact time range from 74 μ s to 22 s, with a maximum adhesion force of 531 nN at a contact time of 22 s. As in the preceding discussion, these results indicate that water molecules, which are one of the main residual gas molecules in high vacuum, were supplied to the contact interface between the small particles and the substrate surface, forming a capillary that increased the adhesion force with contact time. However, within the contact time range of this experiment, the interface between the small particle and the substrate surface was not supplied with enough water molecules, indicating that the contact interface where liquid bridges are formed, was not in equilibrium.

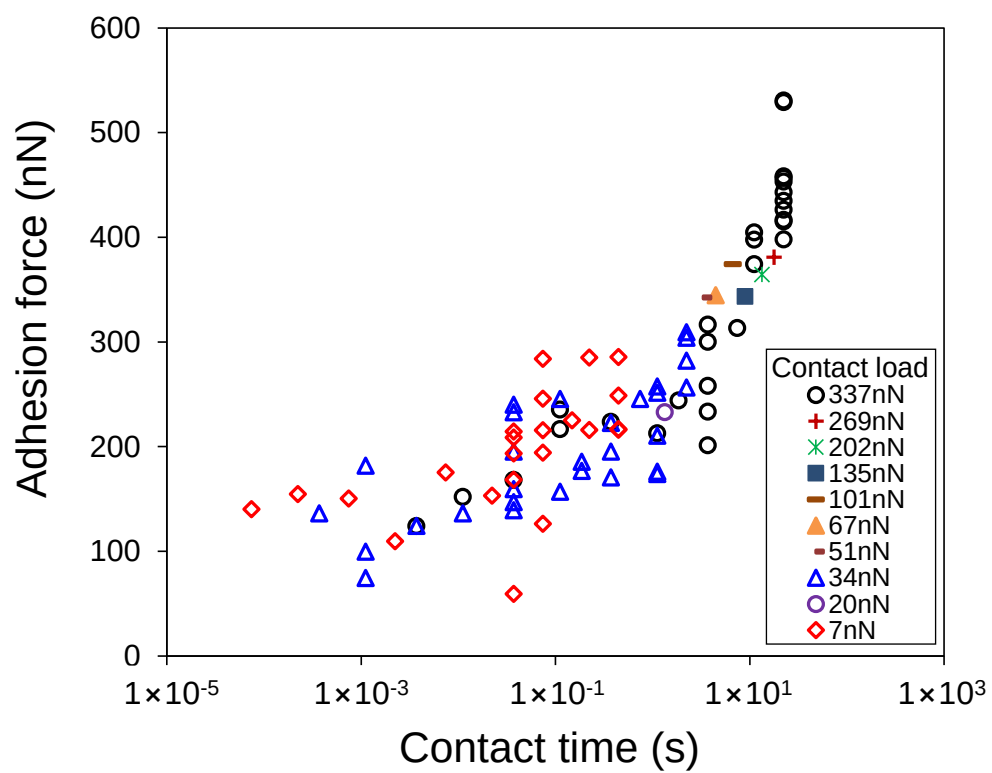


Fig. 4.3 Contact time dependence of the adhesion force between the AFM probe and the substrate with a surface roughness R_q of 0.8 nm.

4.3.1.3 Contact frequency dependence of adhesion force

The dependence of the adhesion force on the contact frequency is shown in Fig. 4.4. The vacuum pressure was 2×10^{-5} to 3×10^{-5} Pa during measurement. The temperature of the Al substrate with a surface roughness R_q of 0.8 nm was decreased from 298 to 153 K, and force curves were obtained ten times at the same position at each temperature. The contact time was 0.37 s. At a substrate temperature of 298 K, the adhesion force remained almost the same as the contact frequency increased. At substrate temperatures of 273 and 263 K, the adhesion force reached its maximum value of approximately 375 nN when the contact frequency was approximately three to six before, decreasing with an increase in the contact frequency. At substrate temperatures below 253 K, the adhesion force increased with increasing contact frequency.

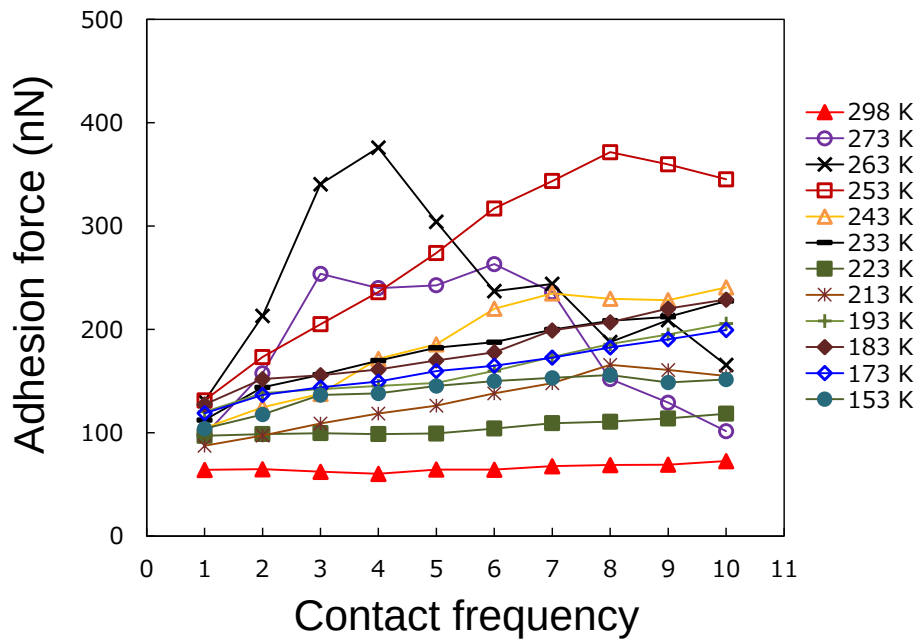


Fig. 4.4 Dependence of the adhesion force on the substrate temperature and the contact frequency between the AFM probe and the substrate.

The result revealing that the adhesion force increased as the contact frequency increased can also be explained by the behavior of water molecules between the small

particle and the substrate surface. Figure 4.5 illustrates the change in adhesion force owing to the behavior of water molecules. As shown in Fig. 4.5(a), the adhesion force increased with the contact frequency at substrate temperatures below 253 K. This can be explained by the fact that water molecules were trapped at the interface between the small particle and the substrate surface at each contact and remained there until the next contact, resulting in a thicker effective film of localized water molecules and an increase in adhesion force at the next contact. As shown in Fig. 4.5(b), the amount of water molecules supplied to the interface between the small particle and the substrate surface was larger when the substrate temperature was between 273 K and 263 K than at lower temperatures, suggesting that the aggregates of trapped water molecules grew faster on the substrate surface at these higher temperatures. It was considered that the adhesion force began to exhibit a decreasing trend with an increase in the contact frequency owing to the interaction between the small particle and the tip of the water molecule agglomerates that became protrusions via growth at the next contact.

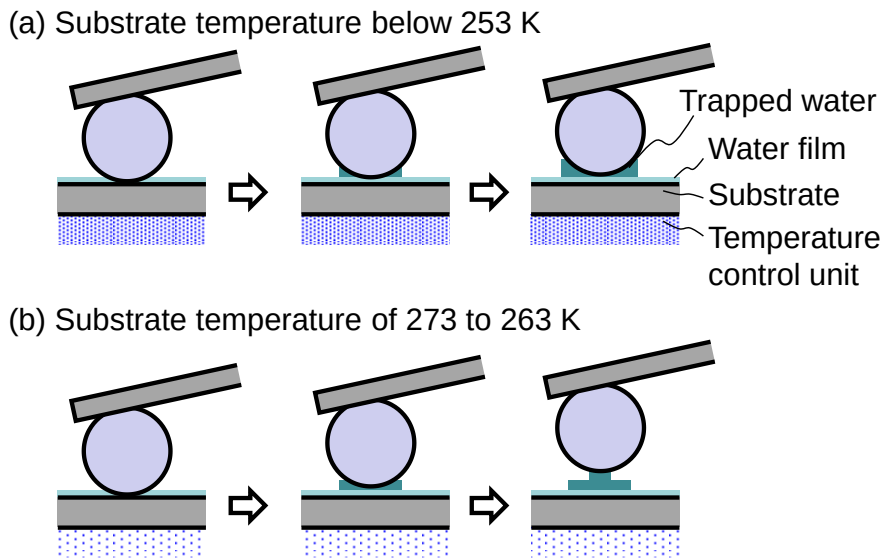


Fig. 4.5 Schematics of the behavior of water molecules on low-temperature substrate surfaces. The adhesion force between the AFM probe and the substrate surface was different due to the growth rate of frozen water. The models correspond to (a) substrate temperatures of 273–263 K, and (b) substrate temperatures below 253 K in this experiment.

4.3.2 Substrate temperature dependence of adhesion force

In the previous section, it was shown that water molecules remaining in high vacuum were supplied to the substrate surface, and these water molecules affected the adhesion force between the small particle and the substrate surface. Based on this, measurement results revealing the dependence of adhesion force on the substrate surface temperature are discussed in this section.

The temperature dependence of the adhesion force between the small particle and the Al substrate surface is shown in Fig. 4.6. The AFM probe with 3.5 μm diameter silica particle and Al substrate surfaces with surface roughness R_q of 0.8 and 2.8 nm were used. The adhesion force was measured 16 times at different positions, with a contact time of 0.37 s under high vacuum of approximately 3×10^{-5} Pa, as the substrate temperature was decreased from 298 to 153 K. The mean values and standard deviations of the adhesion force are shown in the plots and error bars in Fig. 4.6, respectively. First, the evaluation result for the Al substrate with a relatively rough surface roughness R_q of 2.8 nm revealed that the adhesion force of the small particle did not change with decreasing substrate temperature. In contrast, the adhesion force of the small particles changed as the substrate temperature decreased for the Al substrate with a relatively smooth surface roughness R_q of 0.8 nm. The maximum adhesion force was 314 nN when the substrate temperature was decreased from 298 to 273 K. The adhesion force decreased monotonically from 273 to 213 K when the substrate temperature was decreased further. The adhesion force did not change below 213 K.

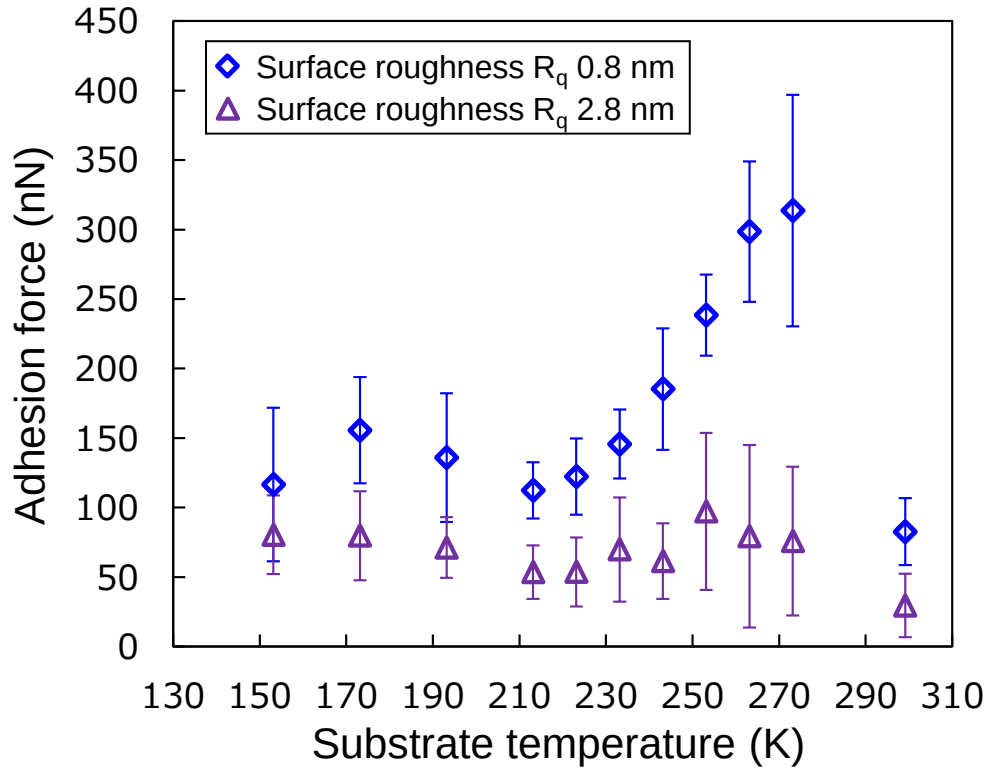


Fig. 4.6 Dependence of the adhesion force on the substrate temperature between the AFM probe and the substrate with surface roughness R_q values of 0.8 nm and 2.8 nm.

The results presenting the substrate temperature dependence of the adhesion forces of small particles on the substrate surface are discussed in detail. First, the van der Waals and capillary forces under the present experimental conditions were estimated by calculation. Moreover, we discuss whether either force contributed to the experimentally measured adhesion forces. In the experiments presented in this chapter, the maximum values of the adhesion force between small particles and the substrate surface were 531 nN for the contact time dependence in Fig. 4.3, 375 nN for the contact frequency dependence in Fig. 4.4, and 314 nN for the temperature dependence of the adhesion force in Fig. 4.6. These values were compared with the van der Waals force on the surface of the Al substrate for silica particles with a radius of 3.5 μm , which was estimated using Eq. (2.10) and the physical properties in Table 2.1. The estimated van der Waals forces depended on the cut-off distance, with values of approximately 60, 350, 720, and 2070 nN for cut-off distances of 1.0, 0.4, 0.28, and

0.165 nm, respectively. As mentioned in Section 2.2.1, the cut-off distance was varied across the range used in previously reported cases. The van der Waals force of 350 nN at a cut-off distance of 0.4 nm was less than the maximum adhesion force in the experimental results. However, the particle and substrate surfaces each had a finite surface roughness, and the effective cut-off distance was considered greater than 0.4 nm. This inference is based on the fact that the surface roughness R_q of small particles and the substrate surface used in this experiment were 6.6 nm and 0.8 nm, respectively, which are larger than 0.4 nm, although the R_q values were analyzed using a general method rather than using the local surface roughness proposed in the previous chapter. The van der Waals force, which is inversely proportional to the square of the cut-off distance, was expected to be even smaller than the above calculated value when a cut-off distance of 0.4 nm was used. Furthermore, the van der Waals force originating from dipole–dipole interactions is independent of the substrate surface temperature within the temperature and contact time range of this study. Therefore, the adhesion forces in the experimental results could not be explained by the van der Waals force and were therefore considered derived from the capillary force.

Next, the magnitude of the measured adhesion force of the small particles was compared with the theoretically obtained calculated value of the capillary force. The capillary force was calculated to be approximately 960 nN according to Eq. (2.25) using 52° and 90° as the contact angles of the silica particles and the Al substrate surface, respectively. The surface roughness was not considered. The estimated capillary force was larger than the magnitude of the adhesion force in the experimental results. As indicated in the previous section, the contact interface between the small particles and the substrate surface was in a non-equilibrium state under the experimental conditions. However, Eq. (2.25) for the capillary force calculation assumes that the water molecules between the small particles and the substrate surface are in an equilibrium state. The equation also assumes contact of ideal spherical small particles on an ideal flat substrate surface and does not consider the effect of surface roughness as in Eq. (2.28). The surface roughness R_q of the small particles and Al substrate used in this experiment were 6.6 and 0.8 nm, respectively. However, it has been reported that the meniscus radius which indicates the capillary size, is a few nanometers at most, suggesting that a capillary was not formed to sufficiently fill the

contact interfaces with water molecules. Therefore, the actual adhesion force due to the capillary force was smaller than the calculated capillary force.

The following is a discussion on the behavior of water molecules, which are the origin of the capillary force. As mentioned above, water molecules, which are the main residual gas in high vacuum, were supplied between the small particles and the substrate surface, and this is thought to have affected the adhesion force under the experimental conditions of high vacuum of the order of 10^{-5} to 10^{-4} Pa.

The adsorption time of water molecules under these experimental conditions was estimated using Eq. (2.33). In the evaluation of a previous report, the activation energy of water molecule adsorption on the Al substrate was approximately 1 eV.⁶⁹⁾ Setting the adsorption time constant as 1×10^{-13} s, which is commonly used,⁶³⁾ the adsorption time of water molecules on the surface was estimated to be 4×10^{11} s. This adsorption time was several orders of magnitude longer than the contact time between the particles and the substrate surface under the experimental conditions.

The surface diffusion rate of water molecules on the substrate surface was calculated. The experiments in this study could not directly evaluate the surface diffusion rate of water molecules. However, it was considered that the activation energy of the surface diffusion of water molecules could be calculated from an Arrhenius plot of the measured substrate temperature dependence of the adhesion force of small particles on the substrate surface under several assumptions.

Without considering surface roughness, the capillary force was estimated using Eq. (2.25). This equation assumes the formation of liquid bridges acting at the interface between ideal spherical particles and an ideal flat substrate in contact under an equilibrium state, as shown in Fig. 2.15. Even if the surface roughness of the small particles or substrate surface is finite, if a sufficient liquid bridge is formed, as shown in Fig. 2.16(a), the capillary force acts as in the ideal case. However, in the absence of sufficient water molecules or in a non-equilibrium state, there may be a case in which liquid bridges are formed only between a single protrusion or multiple protrusions between the small particles and the substrate surface, as shown in Fig. 2.16(b). In this case, the capillary force is the sum of the capillary forces resulting from these small liquid bridges. The size of this small liquid bridge depends on the local radius r of the protrusions, as shown in the expressions for the effective radius

R_{eff} in Eq. (2.29) and the liquid bridge radius r_c in Eq. (2.27), which give expressions for the capillary force. Assuming that the meniscus radius is constant in the non-equilibrium state, the square of the liquid bridge radius r_c is proportional to the effective radius R_{eff} . From Eq. (2.29), the capillary force F_c is proportional to the square of the liquid bridge radius r_c . Therefore, the following relationship can be obtained:

$$r_c^2 \propto R_{eff} \propto F_c. \quad (4.1)$$

Here, the liquid radius r_c is considered proportional to the surface diffusion length L of water molecules. When considering a random walk in two dimensions, the surface diffusion length L becomes Eq. (4.2) with $n = 2$ in Eq. (2.37).⁶⁵⁾

$$L = 2\sqrt{Dt}, \quad (4.2)$$

where D is the surface diffusion coefficient, and t is the diffusion time. Because the square of the diffusion length L is proportional to the surface diffusion coefficient D , the square of the liquid bridge radius r_c is proportional to the surface diffusion coefficient D . Summarizing the above, the following equation is obtained:

$$r_c^2 \propto L^2 \propto D. \quad (4.3)$$

The above equations suggest that the surface diffusion coefficient D is proportional to the experimental results of adhesion force. Using the relational equations based on these assumptions, the surface diffusion coefficient for water molecules under the experimental conditions could be calculated from an Arrhenius plot of the measured substrate temperature dependence of the adhesion force of small particles on the substrate surface. An Arrhenius plot of the measured adhesion force of small particles with the natural logarithm on the vertical axis and $1000/T$ (T : absolute temperature) on the horizontal axis, is shown in Fig. 4.7. Only the adhesion forces at substrate temperatures between 273 and 213 K were considered in the

analysis. As estimated from the fitting curve shown in the figure, the activation energy of the surface diffusion of water molecules between substrate temperatures of 273 K and 213 K was deduced to be 96 meV.

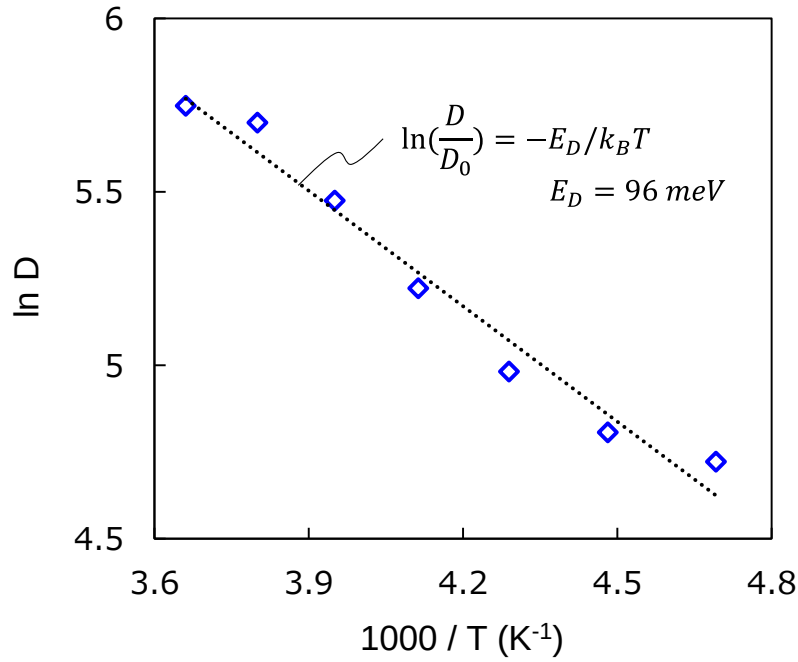


Fig. 4.7 Arrhenius plot of experiment data in the temperature range 273–213 K for the Al substrate with a surface roughness R_q of 0.8 nm. The dotted line is the fitting curve formed using the Arrhenius equation.

The surface diffusion length of water molecules on the substrate surface was calculated using Eq. (4.2) to investigate the behavior of water molecules. The dependence of surface diffusion length on the substrate temperature is presented in Fig. 4.8. Figure 4.8 also present the dependence of adsorption time on the substrate temperature, which was calculated using Eq. (2.33) when the activation energy of water molecule adsorption was 1 eV ⁶⁹⁾ and the adsorption time constant was 1×10^{-13} s.⁶³⁾ As mentioned earlier, the adsorption time was several orders of magnitude greater than the contact time in this experiment.

Using the constant D_0 to estimate the surface diffusion coefficient as $1.4 \times 10^{10} \text{ nm}^2/\text{s}$ ^{70,71)}, obtained from literature values, and the activation energy of surface

diffusion as 96 meV, deduced from the Arrhenius plot of the experiment data, the surface diffusion length of water molecules on the substrate surface with a substrate temperature of 233 K was calculated to be 1.3×10^4 nm at a time of 0.37 s.

Therefore, water molecules adsorbed on the substrate surface near its the contact interface with the particles were considered to diffuse on the surface over a distance that reached the interface. The surface diffusion length calculated using an activation energy of 96 meV for surface diffusion in the substrate temperature range 213–153 K was of the same order of magnitude as, or not more than one order of magnitude smaller than, the surface diffusion length of 1.1×10^4 nm at 213 K. Despite the similar surface diffusion lengths, the adhesion forces were independent of the substrate surface temperature. It has been reported that the structure of water below around 200 K is different compared to temperatures above that.^{72,73)} Therefore, it is considered that no change in the adhesion force occurred below 213 K in this experiment owing to the different behavior of water molecules described above.

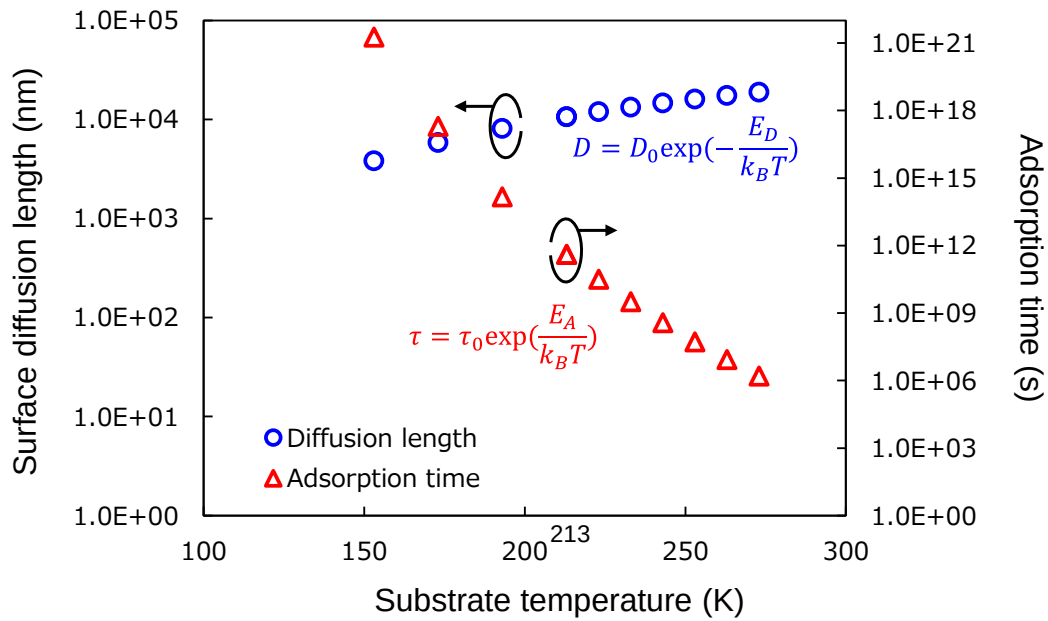


Fig. 4.8 Dependence of the surface diffusion length and adsorption time on substrate temperature.

Under high vacuum, as in the present experimental conditions, the amount of water molecules supplied to the substrate surface is estimated to be of the order of 10^{-5} monolayer/s. Thus, most of the water molecules supplied to the capillary between the small particles and the substrate surface were already on the substrate surface at the time of contact. Therefore, the relationship between the diffusion length of water molecules and the liquid bridge radius is discussed in the following. The volume of water in the capillary was calculated using $0.5\pi r_m r_c^2 (\cos\theta_1 + \cos\theta_2)$, which is the subtraction of the volume of the spherical cap of the particle from that of the cylinder, including the capillary and part of the particle.

The following assumptions were used in the calculations: the thickness of one monolayer of water molecules was 0.3 nm, as deduced from the bulk density of water molecules in water, the diffusion coefficient D_0 was 1.4×10^{10} nm²/s, the diffusion length L was 1.3×10^4 nm for 233 K at a contact time of 0.37 s, and the contact angles θ_1 and θ_2 were 52° and 90°, respectively. Moreover, the meniscus radius of 1 nm was used because this is the typical value and it has been reported that a meniscus radius of 1 nm or larger is formed, even in high vacuum.^{34,74)}

The contact time dependence of adhesion force (Fig. 4.3) was re-presented in Fig. 4.9. The abscissa axis is displayed in linear form. The adhesion force is assumed proportional to the contact time via Eqs. (4.1)–(4.3). Figure 4.9 also shows an approximate line with the proportionality constant of 1×10^1 nN/s. The inset in the figure is the zoomed-in plot of the adhesion force at the contact time of 0.1–1.9 s, showing that the adhesion force were proportional to the contact time around 0.37 s.

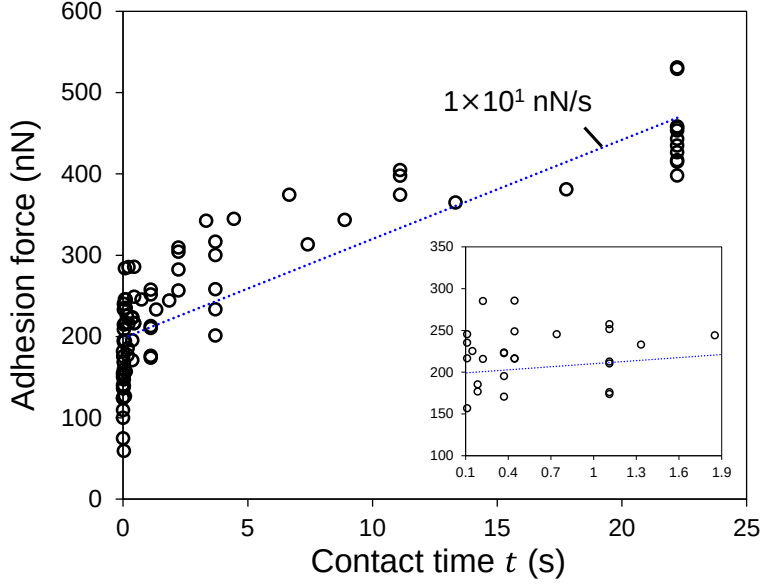


Fig. 4.9 Contact time dependence of the adhesion force between the AFM probe and the substrate with a surface roughness R_q of 0.8 nm. The inset is the zoomed-in plot of the adhesion force at the contact time of 0.1–1.9 s.

First, regarding the results of the contact time dependence of the adhesion force shown in Fig. 4.3 and Fig. 4.9, we may consider that the water molecules in the contact area formed a capillary at the instant when the AFM probe made contact with the substrate surface. Then, part of the water molecules that were diffused into the capillary were adsorbed, and the capillary force increased as the contact time increased via the increase in the liquid bridge radius r_c . The typical values of the liquid bridge radius r_c and the volume of water molecules V_l were estimated as 7×10^1 nm and 4×10^3 nm³, respectively. These were calculated using an adhesion force of 9.7×10^2 nN, assuming an ideal spherical silica particle with a radius of 3.5 μ m and a flat Al substrate surface in equilibrium, and Eqs. (2.25) and (2.27) with a meniscus radius of 1 nm. Within a circle whose radius was the diffusion length L of 1.3×10^4 nm at the time 0.37 s, the volume of water molecules V_l' was 2×10^8 nm³. The ratio of the liquid bridge radius at the moment of contact to the diffusion length was approximately 0.5%, which was calculated using $\sqrt{V_l/V_l'}$. Although a typical volume of water molecules assuming contact between an ideal spherical particle and a flat substrate surface was used, the volume of water molecules estimated by the

experimental data of the adhesion force generated at the moment of contact for approximately 2×10^2 nN was 0.9×10^3 nm³, the order of magnitude was almost the same as that of the calculation.

Next, the increase in the volume of water molecules caused by surface diffusion was considered. Based on Eqs. (2.25) and (2.27) and assuming a constant meniscus radius, the volume of water molecules at the contact interface was proportional to the square of the liquid bridge radius. Furthermore, the square of the liquid bridge radius was considered proportional to the adhesion force, as expressed in Eq. (4.3). Therefore, the increase in adhesion force per unit time of 1×10^1 nN/s was equivalent to the increase in the volume V of water molecules per unit time of 5×10^1 nm³/s, assuming a meniscus radius of 1 nm. At a substrate temperature of 233 K, the increase in the volume V' of water molecules per unit time was 5×10^8 nm³/s within a circle whose radius was the diffusion length L .

The proportionality constant α between the diffusion length and the liquid bridge radius is a sticking probability of diffused water molecules adsorbed in the liquid bridge. Because the volume V of water molecules between the particle and the substrate surface was proportional to the square of the liquid bridge radius, and the volume V' of water molecules within the diffusion area was proportional to the square of the diffusion length, the relation $V = \alpha^2 V'$ was applicable. Using the estimated increase in the volumes V and V' of water molecules per unit time, the sticking probability of diffused water molecules α was 0.03%. This value is consistent with the order of the estimated 0.5%, which was the ratio of the liquid bridge radius at the moment of contact to the diffusion length. It is also consistent with the sticking probability of 0.09% for water molecules absorbed on a stainless steel surface in a high vacuum chamber without annealing, which was shown in the experimental results of a previous report.⁷⁵⁾ Although a thickness of one monolayer of water molecules was assumed in this estimation, the actual thickness of water that could diffuse on the substrate surface may be smaller than one monolayer. As a result, the ratio of liquid bridge radius to the diffusion length of water molecules at the moment of contact is consistent with the ratio of liquid bridge radius to diffusion length, which increased with time.

Here, the behavior of water molecules at the surface is discussed again. It has been reported that water molecules that form the capillary force are adsorbed on the surface under high vacuum, and these water molecules affect the adhesion force unless the temperature of the substrate surface is raised above room temperature.³⁵⁾ Here, the evaluation results of differential scanning calorimetry is explained to describe the analysis of the behavior of water molecules on a low-temperature surface. A differential scanning calorimeter can be used to investigate the phase transition of the state of water molecules adsorbed on surfaces by measuring the temperature difference between a reference material and a target substrate while changing the substrate temperature.

In the case of a silica specimen evaluated using this method, it has been shown that a phase change for water with different interactions with the solid surface occurs at approximately 248 K and 227 K.⁷⁶⁾ It was explained that the lower temperature side corresponds to a phase change of bound water and the higher temperature side corresponds to a phase change of free water. Thus, the behavior of bound water and free water changed in two phases as the temperature of the substrate surface decreased, which may have affected the results of adhesion forces in this experiment.

In the polymer field, a concept has been proposed in which there are intermediate water molecules with properties that are different from those of bound water, which strongly interact with the substrate, and those of free water, which weakly interact with the substrate at the surface of polymers.⁷⁷⁾ This model classifies the properties of water molecules into three types: bound water that does not freeze below 273 K, intermediate water that freezes below 273 K, and free water that melts at 273 K. Thus, there are water molecules on the substrate surface, some of which freeze and remain motionless.

Considering the above reports including the report showing that the structure of water below around 200 K is different compared to temperatures above that^{72,73)}, a model was proposed in which water molecules on the substrate surface partially diffuse in a specific temperature range. That is, water molecules could not surface diffuse below 213 K, but could in the substrate temperature range 273–213 K. In a previous study, the activation energy of the surface diffusion of water molecules deposited on Al₂O₃ to form porous ice molecules was reported to be 308 meV.⁷⁸⁾ In

contrast, calculations have shown that the activation energy of surface diffusion of water molecules on crystalline ice is 108–130 meV,^{78,79)} which is comparable to the activation energy of 96 meV obtained in the present experiment. Therefore, it was considered that the water molecules in the case of surface diffusion were not directly on the surface of the Al substrate. Instead, some of the water molecules adsorbed on the substrate surface froze and then diffused on the surface of the ice layer.

A schematic diagram of the surface diffusion of water molecules at the substrate surface is shown in Fig. 4.10. Figure 4.10(a) is a schematic representing the diffusion of water molecules on the surface of ice, as explained above. Figure 4.10(b) shows the place-exchange diffusion of adsorbed atoms on the surface.⁸⁰⁾ In this case, the diffusion is not of adsorbed atoms but of water molecules, and the ice lattice structure is not a square lattice, as shown in the figure, but a six-membered ring structure. However, this diffusion may have occurred in conjunction with surrounding water molecules as they hopped across the surface. This is because the energy of surface diffusion in this mode is smaller than the energy of surface diffusion when a single water molecule hops while breaking hydrogen bonds with an energy of approximately 300 meV,⁸¹⁾ regardless of the movement of the surrounding water molecules.

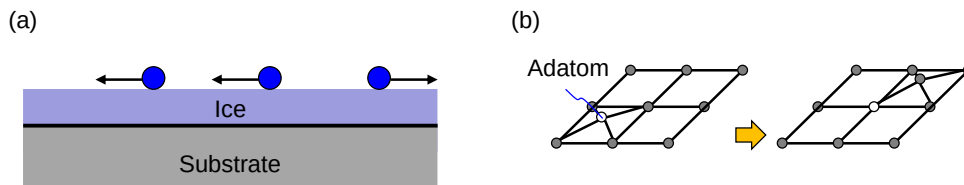
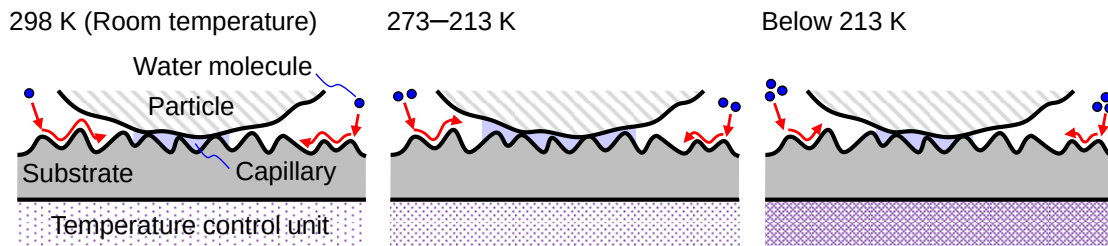


Fig. 4.10 (a) Schematic showing the surface diffusion of water molecules on the substrate surface, which is covered with a layer of ice. (b) Schematic showing surface diffusion model of place-exchange diffusion. While the lattice structure of ice is not tetragonal, water molecules instead of adatoms may diffuse in the illustrated mode.

A schematic showing the behavior of the water molecules in the evaluation of the temperature dependence of adhesion force is shown in Fig. 4.11 based on the above considerations. For the sake of simplicity, the film of water molecules is not shown. First, the behavior of water molecules on a flat surface is described. As shown in Fig.

4.11(a), a liquid bridge was formed by the layer of water molecules on the substrate surface, even in high vacuum, when the substrate temperature was room temperature (298K). As the substrate temperature decreased, the number of water molecules adsorbed on the surface increased. As the substrate temperature was decreased to a certain point, such as approximately 223 K, the water molecules were able to surface diffuse on the substrate, indicating an increased adhesion force between the small particles and the substrate surface. When the substrate temperature was further decreased below 213 K, the number of water molecules adsorbed on the surface increased; however, the adhesion force did not increase because the water molecules could not diffuse on the substrate surface and a sufficient capillary force was not formed at the contact between the small particles and the substrate surface. The behavior of water molecules on the rough substrate surface is shown in Fig. 4.11(b). Although this behavior changed as described above, the area where a liquid bridge was formed between the small particles and the substrate surface was small owing to the limited interaction area of the protrusions on the substrate surface, suggesting that there was little increase or decrease in the capillary force when the temperature was changed.

(a) Smooth surface (Surface roughness R_q 0.8 nm)



(b) Rough surface (Surface roughness R_q 2.8 nm)

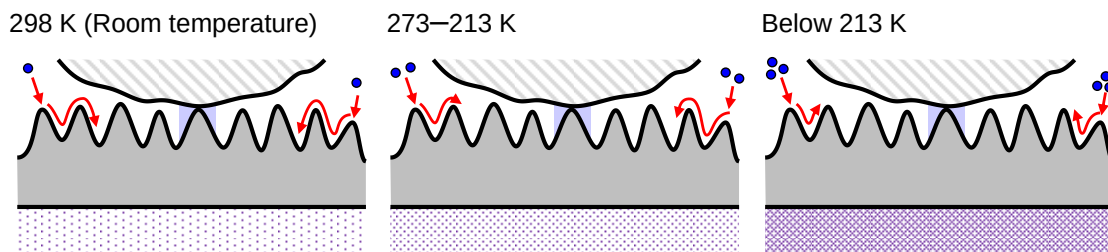


Fig. 4.11 Schematics showing the temperature dependence of adhesion force due to the change in the behavior of water molecules on surface at (a) a smooth surface and (b) a rough surface.

In Sections 1.1 and 4.1, it was shown that some apparatus have industrial applications with components that cool surfaces below room temperature under high vacuum conditions. To control the behavior of small particles in systems containing such surfaces, it is important to consider the surface temperature dependence of the adhesion force of the small particles. The substrate surface temperature dependence of the adhesion force of small particles on low-temperature surfaces under high vacuum conditions was investigated in this study. In particular, it was found that the surface roughness of the wall must be reduced to the nanometer order or less to increase the adhesion force and prevent the scattering of small particles. The results were found under a specific condition or for a combination of small particles and substrate surfaces, which may limit the applicability of the results. However, it was found that the temperature change of surfaces affects the capillary force of small particles on substrate surfaces, even under high vacuum, especially on low-

temperature surfaces. Additionally, there were fluctuations in the adhesion force, which may change the behavior of the small particles. Understanding such phenomena in equipment design and the use of equipment may lead to the control of small particle behavior. Thus, the knowledge obtained in this study is expected to contribute to the industrial field.

4.4 Summary

The adhesion force between an AFM probe and an Al substrate surface was evaluated to investigate the substrate surface temperature dependence of the adhesion force of small particles on surfaces at temperatures lower than room temperature under high vacuum. An AFM probe, which was adhered with a silica particle with a radius of 3.5 μm and a surface roughness R_q of 6.6 nm, and the two different Al substrate surfaces, one relatively smooth (R_q 0.8 nm) and the other rough (R_q 2.8 nm), were used. The findings obtained from this investigation are summarized below.

- Protrusions were grown or formed on the surface of the smooth Al substrate when the temperature of the substrate surface was decreased under high vacuum. Moreover, the adhesion force of the AFM probe on the substrate surface at 233 K was increased with increasing contact time from 0.74 μs to 22 s. The adhesion force also increased with contact frequency when the adhesion force was evaluated repeatedly at the same location. These results indicate that water molecules were supplied and diffused on the substrate surface to change the growth of aggregated water molecules on the substrate surface and the adhesion force between small particles and the substrate surface.

- On the rough Al substrate surface, the adhesion force between the silica particle and the substrate surface was almost constant, independent of the substrate surface temperature. Conversely, on the smooth Al substrate surface, the adhesion force changed with decreasing substrate surface temperature, reaching a maximum at 273 K before monotonically decreasing to 213 K, followed by a nearly constant value between 213 K and 153 K. Considering that the substrate surface temperature dependence of adhesion force was due to the surface diffusion of water molecules, the experimental results of the adhesion force of the silica particle and smooth Al substrate surface in the range 273–213 K were fitted using the Arrhenius equation. As a result, the activation energy of the surface diffusion of water molecules was estimated as 96 meV. This result coincided with the reported activation energy of water molecules on the surface of ice, which was 108–130 meV. It was concluded that the experimental

results of the adhesion force showed water molecules diffusing on the surface of the substrate over the layer of water molecules bound to the substrate surface.

- Based on the experimental result of the adhesion force increase of small particle with increasing contact time, the growth model of a liquid bridge was discussed, considering the surface diffusion of water molecules. The surface diffusion of water molecules adsorbed in the liquid bridge was assumed and its sticking probability was estimated. This value was consistent with the order of the sticking probability of water molecules adsorbed on a chamber wall supplied from high vacuum environment, which was shown in the previous report. Therefore, the mechanism of increase in adhesion force of a small particle on a substrate surface in high vacuum was explained for the first time by the surface diffusion of water molecules, which are adsorbed in liquid bridge.

- One of the findings of this investigation was the observation of the relative increase in adhesion forces between the small particle and the smooth substrate surface when the temperature of which was decreased from room temperature in high vacuum. Therefore, the surface roughness of the wall must be reduced to the nanometer order or less to increase the adhesion force and prevent the scattering of small particles.

5 Conclusion and Future work

In this study, the adhesion force of small particles on the substrate surface was evaluated using AFM to clarify the parameters and mechanisms involved in the adhesion forces of small particles. Furthermore, feedback of the obtained findings in the studies to practical surfaces of the apparatus was considered.

In Chapter 1, the problems caused by small particles in the industrial field are presented, and it is explained that one approach to solving these problems is to control the adhesion force of small particles. The adhesion force of small particles is affected by parameters related to the environment of the contact interface, such as surface roughness, material, humidity, and vacuum pressure. The reasons for focusing this research on the surface roughness and the temperature of substrate are explained. Moreover, the reasons for using silica as the material of the small particles and Al as the material of the substrate surface are also explained, that is, to assume practical surfaces and particles of the semiconductor field.

In Chapter 2, the principle of AFM is explained, followed by a description of the method for evaluating the adhesion force of small particles using AFM. Subsequently, a method for fabricating AFM probes which simulate small particles adhered on the wall surfaces of apparatus, is presented, and a method for evaluating the tip radius of curvature of the AFM probes corresponding to the radius of the small particles, is also described. Furthermore, the methods for calculating the van der Waals force and capillary force, and contact theory, which was used to discuss the contact state between the small particles and the substrate surface, are described to discuss the results of the evaluation of adhesion forces.

In Chapter 3, the surface roughness dependence of the adhesion force of small particles is described. Under the measurement conditions of 20–40%RH at atmospheric pressure, it was shown that the adhesion force between the small silica particles and the Al substrate surface could not be explained by the van der Waals force alone, and the capillary force contributed critically. Moreover, a method of analyzing local surface roughness was proposed based on the size of the region in which the small particles interact with the substrate surface. A correlation between the local surface roughness and the coefficient of variation (standard deviation divided by

the mean value) of the adhesion force of the small particles was found, indicating that the variation in the adhesion of small particles can be predicted for the first time using the proposed method. It was demonstrated that the variation in the adhesion force of small particles could be reduced when the surface roughness of the substrate was reduced to the nanometer order or less, whereas the mean value of the adhesion force decreased for particles of micrometer-order size and did not change for particles of sub-micrometer-order size or smaller. These findings show that reducing the surface roughness of the wall of apparatus to the nanometer order or less is effective in preventing the scattering of small particles due to external forces, which increase as the size of the small particles increases.

Chapter 4 describes the adhesion force of small particles when the substrate surface temperature is below room temperature in high vacuum environment. Two substrate surfaces with different relative surface roughness were evaluated and the capillary force was found to increase the adhesion force, even in high vacuum, for substrate surfaces below room temperature only when the surface roughness of the substrate was of the nanometer order or less. The behavior of the adhesion force was attributed to water molecules diffusing on the substrate surface and contributing to the capillary force. The activation energy of the surface diffusion of water molecules was estimated as 96 meV. Based on the experimental result of the adhesion force increase with increasing the contact time, the mechanism of increase in the adhesion force of small particles on a substrate surface in high vacuum was explained for the first time by the growth of the liquid bridge due to the surface diffusion of water molecules. The findings in this investigation show that the surface roughness of the wall must be reduced to the nanometer order or less to increase the adhesion force and prevent the scattering of small particles.

As a future prospect, it is necessary to verify whether the results of this study can be extended to other systems by conducting evaluations using small particles and substrate surfaces with different materials and surface treatments from those used in this experiment, which interact with water molecules differently. Moreover, it is necessary to analyze the behavior of water molecules using first-principles calculation to determine the surface diffusion mode of water molecules on the substrate corresponding to the system under the conditions of this study, which simulated

practical environments. Furthermore, the range of applicability of a particle with radius in the van der Waals force equation must be investigated through an evaluation in which capillary forces are not affected. The van der Waals force has been shown to be proportional to the first power of the radius of a spherical particle using an approximate formula assuming a smooth sphere-plane interface with a sufficiently large particle radius. However, the influence of protrusions due to the finite surface roughness of particles may be dominant and deviate from that of a particle with a radius to the power of one.

6 Publication lists

1. Peer-Review Paper

(1) Takafumi Miwa, Go Miya, and Seiichiro Kanno, “Effect of Surface Roughness on Small Particle Adhesion Forces Evaluated by Atomic Force Microscopy,” Jpn. J. Appl. Phys. **59**, 076504 (2020).

(2) Takafumi Miwa, and Tomihiro Hashizume, “Evaluation of the Small Particle Adhesion Force on Low Temperature Surface in High Vacuum using Atomic Force Microscopy,” Jpn. J. Appl. Phys. **61**, 085002 (2022).

2. Refereed International Conference Presentation

(1) Takafumi Miwa, Go Miya, and Seiichiro Kanno, “Dependence of Particle Adhesion on Surface Roughness of Chamber Wall Evaluated by Atomic Force Microscopy for Reducing Particles in Semiconductor Apparatuses,” 32nd International Microprocesses and Nanotechnology Conference, Oct. 28–31 (2019).

(2) Takafumi Miwa, Go Miya, and Seiichiro Kanno, “Surface roughness Dependence of Small Particle Adhesion Force Evaluated by Atomic Force Microscopy,” 27th International Colloquium on Scanning Probe Microscopy, Dec. 5–7 (2019).

(3) Takafumi Miwa, and Tomihiro Hashizume, “Evaluation of Small Particle Adhesion Force on Low Temperature Surface using Atomic Force Microscopy,” 29th International Colloquium on Scanning Probe Microscopy, Dec. 9–10 (2021).

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