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RESEARCH ARTICLE

Fabrication of oriented crystals as force measurement tips via focused ion beam and microlithography methods

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Detailed knowledge of the forces between nanocrystals is very crucial for understanding many generic (eg, random aggregation/assembly and rheology) and specific (eg, oriented attachment) phenomena at macroscopic length scales, especially considering the additional complexities involved in nanocrystals such as crystal orientation and corresponding orientation-dependent physicochemical properties. Because there are a limited number of methods to directly measure the forces, little is known about the forces that drive the various emergent phenomena. Here, we report on two methods of preparing crystals as force measurement tips used in an atomic force microscope: the focused ion beam method and microlithography method. The desired crystals are fabricated using these two methods and are fixed to the atomic force microscope probe using platinum deposition, ultraviolet epoxy, or resin, which allows for the orientation-dependent force measurements. These two methods can be used to attach virtually any solid particles (from the size of a few hundreds of nanometers to millimeters). We demonstrate the force measurements between aqueous media under different conditions such as pH.

KEYWORDS

focused ion beam, force measurement, microlithography, tip fabrication

1 | INTRODUCTION

A fundamental understanding of the forces between nanoparticles is essential, not only to reveal the dynamics between a pair of particles involved in self-assembly and aggregation, but also to better understand the complex rheological behavior of colloidal systems in real situations. For nanocrystals, additional complexities, such as crystal orientation, make such phenomena more complicated; more detailed understanding of the forces between nanocrystals is required. However, little is known about the details of forces, including non-Deryaguin-Landau-Verwey-Overbeek (DLVO) forces, due to the currently limited techniques for directly measuring the interaction forces.

Surface-forces-apparatus (SFA) and atomic force microscopy (AFM) have been used frequently to measure the physical forces between surfaces.[1] The (SFA) is difficult to equip with a rotation stage to have continuous rotation angle ranging from 0° to 360° in the force measurement.[2] AFM does not have that drawback. It is one of the most successful techniques for measuring the surface free energy and interactions between surfaces of various materials,[3-8] and it has the capability of scanning the atomic details of surface structures and mapping the topography of various materials. Commercial AFM tips are usually made from Si_3N_4, Si and its oxides, which limit their versatility. To extend the application of AFM, many efforts, such as chemical modification, surface coating, and particles or nanotubes glued on the tips, have been made to functionalize or fabricate AFM tips with new properties.[9-16]

While force measurement between crystal surfaces needs the functionalization of AFM tips with different crystals, it can be also accomplished by direct oriented attachment of crystal particles onto the AFM cantilever. Gluing single crystal particles onto the AFM cantilevers was demonstrated first in 1991[17] and has been broadly used to study the molecular forces and mechanics of biological cells, etc. The ability to probe the orientation dependence between crystal surfaces has been difficult because of the lack of a method of fabricating oriented single crystals as AFM force measurement tips. Here, we first fabricate single crystals with desired orientations

and sizes using two methods. Then, we attach the crystals to AFM cantilevers using Pt deposition and a focused ion beam (FIB) or ultraviolet epoxy/resin glue. Using a FIB enables reproducible and reliable material cutting with high accuracy featuring crystal orientations and dimensions in the micrometer to nanometer range. This technology has been used for the fabrication of AFM probes previously.[18-20] Here, we use FIB to modify single crystals as synthesized or fabricate single crystals with the desired orientation, size, and shape from bulk materials. The second method is to use microlithography to obtain single crystals that have the desired micro size and orientation. Microlithography is a manufacturing process for producing highly accurate, microscopic, 2-dimensional patterns in diverse dimensions.[21] We apply this technique to fabricate arrays of oriented single crystals that will be attached to the AFM cantilever. Force measurements between gibbsite and boehmite crystal surfaces are subsequently provided to demonstrate the reliability and applicability of the fabricated crystal tips.

2 | EXPERIMENTAL

The mounting procedure was performed in a scanning electroscope (Helios NanoLab 600i, FEI, Hillsboro, OR) equipped with a piezo-driven nano-manipulator (Omniprobe, Oxford Instrument). This equipment allows manipulation of two objects with respect to each other with steps of 50 nm and simultaneous observation. A muscovite (mica) single crystal (the highest grade) was commercially obtained from SPI Supplies, West Chester, PA. Boehmite was obtained from Nabaltec (Germany) or synthesized by hydrothermal reaction. Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$; 98%) and NaOH were obtained from Sigma-Aldrich, USA, and Fischer Scientific, USA, respectively. All chemicals were reagent grade or better. Deionized water (18 MΩ) was used as a base for all solutions.

For hydrothermal synthesis of boehmite, rhombic boehmite plates were prepared by modifying the procedure adapted by Chatterjee et al,[22] which involved a 2-step process beginning with the alkaline hydrolysis of $Al(NO_3)_3$ to gibbsite, $Al(OH)_3$, followed by the dehydration of gibbsite to rhombic boehmite. Ten grams $Al(NO_3)_3.10H_2O$ (0.027 mol) was dissolved in 20-ml deionized water at room temperature while being stirred. Ten milliliters of 10 M NaOH was added to the mixture, and stirring was continued for a further 15 minutes. The suspension was transferred to a Teflon-lined autoclave of 50-mL total capacity and heated at 200 ± 2°C for 96 hours. The autoclave was allowed to slowly cool to room temperature over a period of 24 hours. The reaction mixture was allowed to sit in the sealed configuration for a further 24 hours, after which it was transferred to a Teflon beaker. Slow evaporation of the solution resulted in the formation of a white solid. The solid was gravity filtered, washed with excess water and methanol, and stored for further use. The crystal structure of the final product was detected by powder X-ray diffraction (see inset of Figure 1A), which indicates that the product is well-crystallized boehmite.

3 | RESULTS AND DISCUSSION

3.1 | Fabrication of the atomic force microscopy tip with microcrystal (boehmite) using the focused ion beam method

The boehmite microcrystal attached AFM tip was fabricated by milling and Pt deposition using FIB. The detailed fabrication procedure is presented in Figure 1B to I and described as follows.

I. Boehmite microcrystal particles were dispersed into ethanol by sonication, then 1 drop of the mixture was dropped on the surface of silicon wafer. After being dried in air, the Si wafer containing the boehmite microcrystal and the commercial AFM tip were carefully pierced into carbon tape and then transferred into the scanning electron microscope (SEM) chamber.

II. A suitable boehmite microcrystal (Figure 1B) was selected; i.e., it had a clear, perfect crystal and profit size (1.5 to 2 μm) that stood sufficiently free from other particles to allow approach by the Omniprobe in the SEM. A layer of Pt (~1 μm thick) was deposited on the selected boehmite microcrystal as a protective layer to prevent the crystal from being damaged in the following steps. Other materials, such as Al, can also be deposited on the crystals in case the crystals cannot be dissolved by HCl; Al can be easily removed by HCl afterwards.

III. Using FIB cutting in the SEM, two 15 × 10 μm squares beside the protective boehmite crystal were excavated. Excavation created a Si "wall" whose thickness was 1.5 to 2 μm with boehmite on its top (Figure 1C).

IV. After introducing the Omniprobe, the microprobe was placed accurately and carefully on the top of the Si wall beside the boehmite crystal by micromanipulation in SEM. The Si wall attached with boehmite was glued to the Omniprobe, and then it was cut out of the Si substrate. As a result, a small square Si wall was lifted out by the Omniprobe (Figure 1D). The boehmite-attached pillar, 1 × 1 μm in size and 5 to 7 μm tall, was obtained via FIB cutting (Figure 1E).

V. A 2 × 2 μm square hole was produced by the FIB cutting in the commercial Si_3N_4 tip at the apex (Figure 1F).

VI. The pillar attached with boehmite was put into the hole in the tip with the desired crystal orientation. To fix the column rigidly, a Pt layer was deposited around the junction between the tip and the pillar via FIB Pt deposition (Figure 1G). The angle between the pillar and the cantilever can be controlled and is 11° ± 1°, which is required to maintain near parallel face-to-face contact between the AFM tip and substrate.

VII. Afterwards, the pillar was cut off the Omniprobe using FIB cutting (Figure 1H). The Pt protective layer on top of the pillar was carefully removed via FIB milling to expose the boehmite crystal used to form the final tip (Figure 1I); the tip shape can be modified to the desired morphology using FIB milling. Ga contamination and surface damage can be minimized or

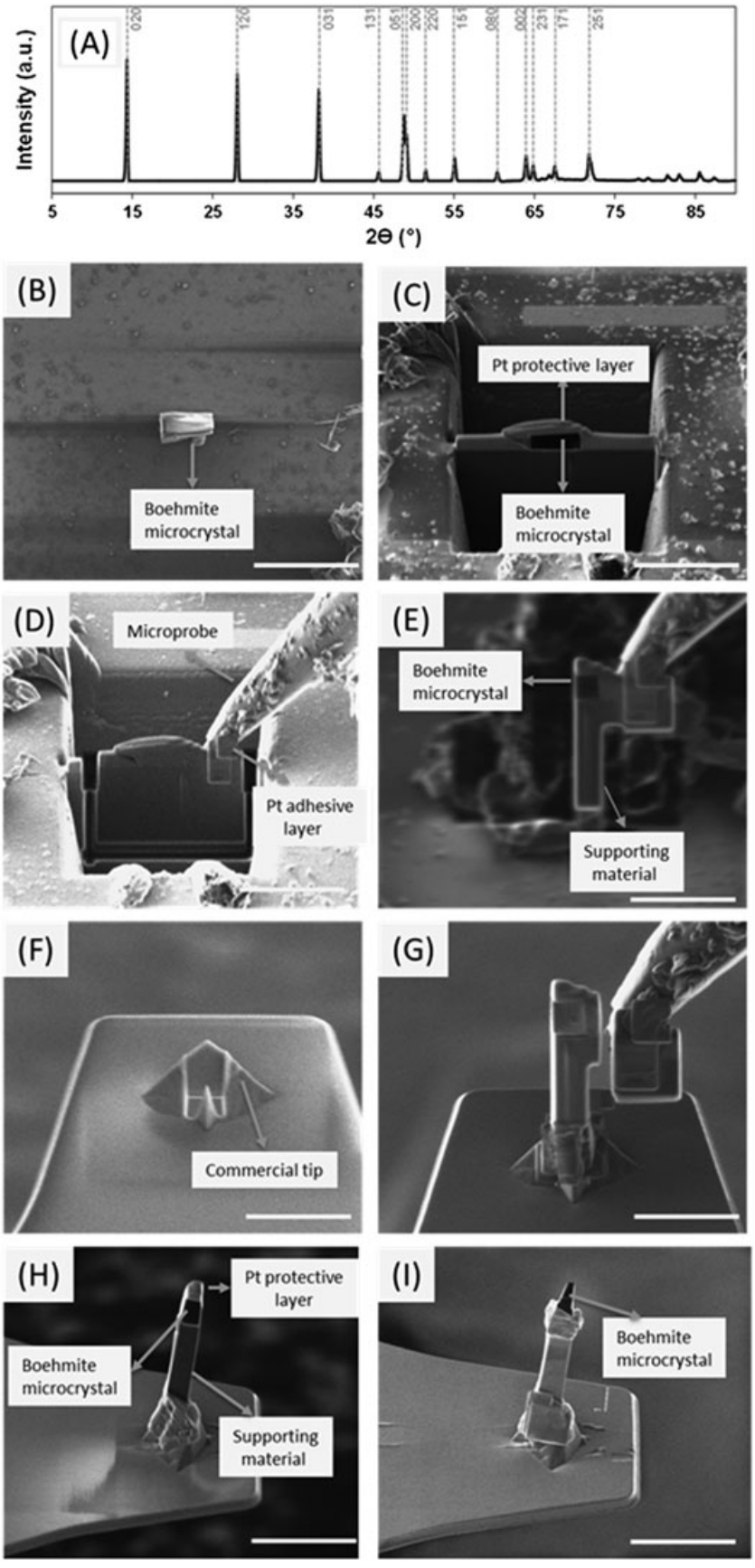

FIGURE 1 Series of SEM images showing the boehmite microcrystal attached AFM tip fabrication procedure; the inset (A) shows X-ray diffraction of the obtained boehmite; the scale bar of (B) to (D) is 10 μm and that of (E) to (I) is 5 μm

avoided by carefully manipulating the beam energy used for milling. Final ion milling was carried out under ion beam voltage of 5 KeV and current of 26 pA. The ion beam is parallel to the crystal surface.

This FIB cutting method can be applied to other crystals, such as TiO_2 and mica of millimeter sizes. In the case of TiO_2, a layer of Al can be deposited as protective layer using an e-beam evaporator and removed via HCl solution afterwards. The exposed rutile (001) surface

has no contamination and is more or less atomic flat.[23] In the case of mica, the tip can be fractured and a fresh cleaved (001) surface is exposed.[24] These exposed surfaces have no Ga contamination and surface damage from the ion beam. Crystal orientation can also be controlled using the Omniprobe and SEM/FIB technique. The preparation step is almost the same as that for the boehmite tip but easier.

3.2 | Fabrication of atomic force microscopy tip with mica microcrystal using the microlithography method

Crystallographically oriented face-specific AFM "mica tips" with a (001) plane for a force probe were fabricated using microlithography assisted by a gluing method. The brief fabrication procedure is described as follows. Arrays of ~5 × 5 μm mica squares (Figure 2B) with a thickness of ~400 nm (Figure 2C) were fabricated on a muscovite mica single crystal (the highest grade commercially obtained from SPI Supplies, West Chester, PA.) via microfabrication at a clean-room facility (Figure 2A). At first, a layer of Cr (150 nm thick) was deposited on the mica surface as a protective layer using an electron beam evaporator (TT-6, Telemark, Battle Ground, WA). A positive photoresist (PR) (1518 Grade, Rohm & Hass, Marlborough, MA) was spin-coated onto the Cr layer. An aligner (NXQ Q4000, Neutronix Quintel, Morgan Hill, CA), in conjunction with a mask, was used to produce PR squares (5 × 5 μm) on the Cr layer. The exposed Cr layer was etched using a Cr etchant (mixtures of perchloric acid ($HClO_4$), and ceric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$), and subsequently the exposed mica was etched for 1 hour by inductively coupled plasma reactive ion etching (Oxford Instruments, Oxfordshire, UK) using CHF_3 under an Ar flow rate of 25 SCCM, a pressure of 10 mTorr, and a power level of 200 W. The remaining Cr layer was removed by the Cr etchant. The fabricated mica square laminas (Figure 2B) were sheared off via (001) plane from the mica single crystal; the thickness of the mica lamina as measured by AFM was ~440 nm (Figure 2C). Finally, the mica lamina was glued to an AFM cantilever tip that had a fresh (001) surface using ultraviolet epoxy or epoxy resin (Figure 2D).

The second method (microlithography) is to fabricate crystals that have a layered structure. The advantage of this method is that the exposed surface is fresh and has no contamination at all. Moreover, we can obtain arrays of single crystals with one fabrication process instead of making one at a time using the time-consuming FIB technique.

3.3 | Demonstration of atomic force microscopy force measurement between the boehmite crystal (010) surface and gibbsite surface

Experimentally, we have obtained reproducible force measurements of a contact model in aqueous solutions under various conditions (pH, ionic species, salt concentration, temperature, etc.) using the fabricated TiO_2 and mica crystal tips.[23,24] Here, we present the results from using the boehmite crystal tip (Figure 3A). A typical force curve (Figure 3B) presents an approaching (red) curve and a retracting (blue) curve. During retracting, the tip jumps off the substrate surface when the attractive forces between surfaces overcome the cantilever spring constant. The "jump-off" deflection is converted to adhesive force (F_{ad}) between crystal surfaces, presuming the tip cantilever as a spring. Our force vs. loading rate (retracting rate) curves (Figure 3C) demonstrate that the F_{ad} increased linearly (pH 5.7 and pure water) or no dependence (pH 9) with the increasing loading rate in the measured range of loading rates indicating the adhesive force was measured near equilibrium region. Therefore, the equilibrium adhesive force F_{eq} can be obtained simply through linear extrapolation. The measured F_{ad} is shown to be affected by pH (Figure 3D). Like many other mineral oxides, boehmite and gibbsite crystals exhibit a pH-dependent surface or zeta potential due to protonation-deprotonation kinetics in oxide groups at the surface.[25] This nature has been represented by an isoelectric point typically defined as a

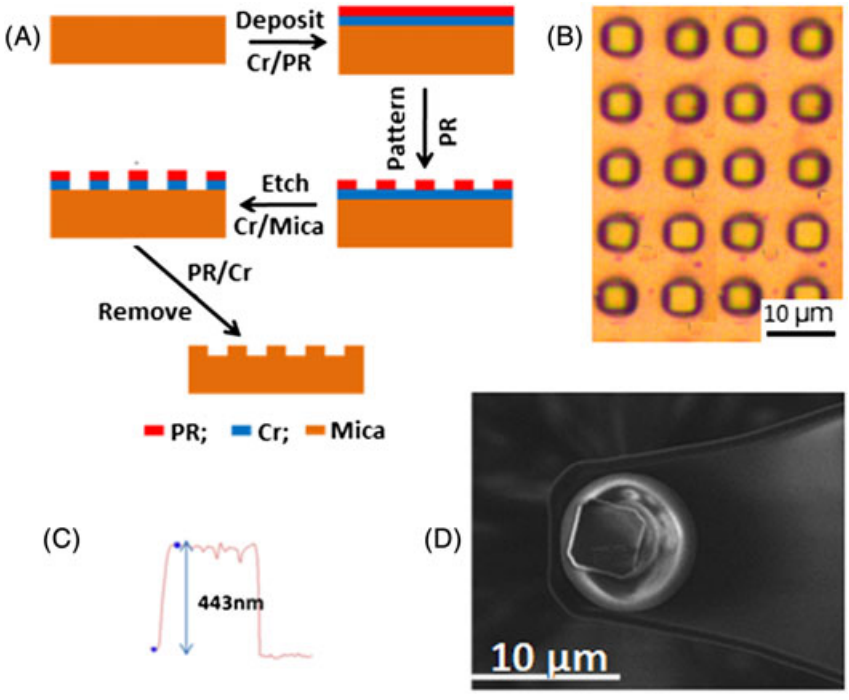

FIGURE 2 (A) Schematic illustration depicting the process for preparing mica laminas. (B) Optical image of mica patterns. (C) AFM profile and height of mica lamina. (D) SEM of the mica tip (top view)

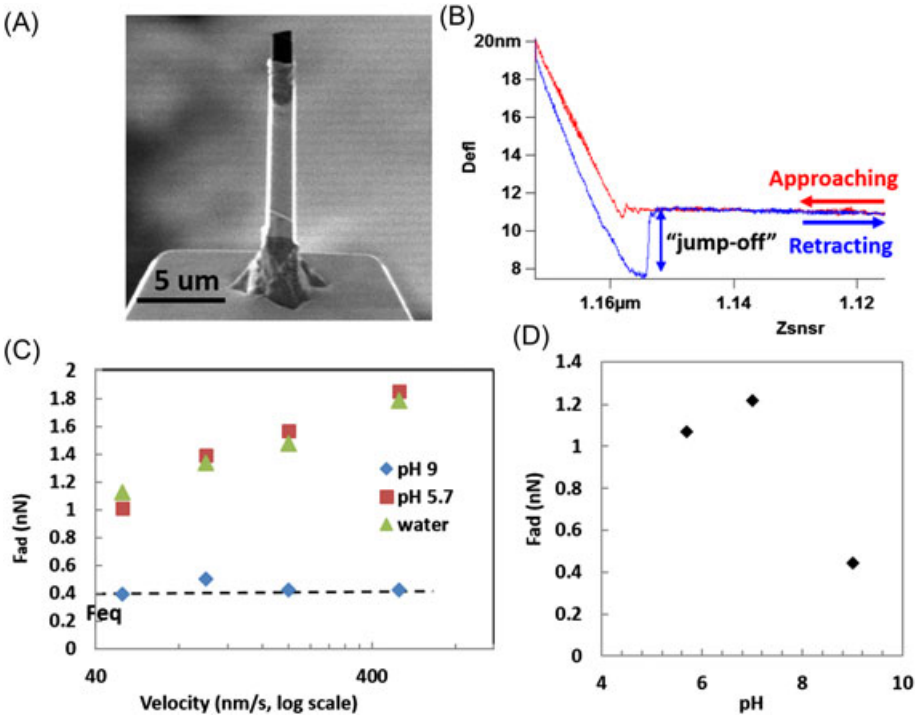

FIGURE 3 Experimental approach to determining adhesive forces between boehmite (010) and gibbsite surfaces. (A) SEM image of customized AFM probe with single crystal boehmite tip presenting (010) faces. (B) Typical force curves in water displaying an approach (red) curve and a retraction (blue) curve. (C) Adhesion force vs log (velocity nm/s) at various pH solutions, showing no rate dependence (pH 9) or linear relationship (pH 5.7 and pure water). (D) pH dependence of adhesive forces measured at retracting rate of 50 nm/s

pH where the zeta potential changes its sign from positive to negative. Therefore, it can be easily deduced that the adhesion forces vary with pH. Considering that isoelectric points for boehmite and gibbsite crystals are pH ~8 to 9 and pH ~5, respectively,[25,26] the forces between boehmite and gibbsite at a pH between those values would be the most attractive or adhesive because the electrostatic force also becomes attractive owing to opposite zeta potentials for both surfaces, in addition to the inherent attractive van der Waals force.

4 | CONCLUSIONS

We have illustrated two well-controlled mounting procedures, using FIB cutting/nano-manipulation and microlithography, to create specific probes that have single oriented crystal terminated AFM tips. The fabricated tips allow the measurement of forces between single crystal surfaces as a function of crystal orientation. The use of modified cantilevers by these two processes for the detection of the interaction between crystals with desired crystal surface has been shown to increase the reliability of the interaction. The two proposed methods for fabricating AFM probes can be used as a force measurement tool to study the interaction force between various mineral nanocrystals and subsequently understand a wide range of emergent phenomena such as oriented attachment and rheology.

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