AFM Study of Forces Between Polyurethane Pads and Ceria Nanoparticles

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INTRODUCTION

Interactions of the ceria particles with polyurethane surfaces are of great interest for polishing processes used in modern semiconductor industry. Specifically, ceria abrasive nanoparticles and polyurethane polishing pads are now broadly used in the process called Chemical-Mechanical Planarization/Polishing (CMP) [1,2,3].

To optimize the process of CMP, various chemicals, abrasives, polishing pads, etc. have been investigated [4,5,6,7,8]. However, due to the large number of parameters that can influence the CMP process, the optimization of CMP by experimental means has been difficult to do. Modeling the CMP process, see, e.g., refs.[9,10] can help to rationalize the CMP optimization. To increase the predictive effectiveness of the models, one needs to know the interaction between the pads and the abrasive particles. The technique that is capable of measuring such information is atomic force microscopy (AFM), see, e.g., [11].

To measure the forces between the ceria particles and the pads with the AFM, we attached the ceria particles to the AFM tip with epoxy. Attachment of large balls to the AFM tip has been reported before, see, e.g., [12], as well as functionalizing the tip surface with various molecules. Here we report the first successful attachment of nanosize (~50-100nm) particles to the AFM tip and the direct measurements of forces using such tips. Specifically, we report study of adhesion and long-range force between nanosize ceria particles and three different polyurethane polishing pads.

EXPERIMENTAL

Ceria Particles and Pads. NanoTek® Ceria abrasive particles by Nanophase Technologies Corp. were used. The ceria was washed a few times by centrifugation, and stored in ultrapure MilliQ water.

The polyurethane pads IC1000™, JR111™ and OXP4000™ by Rohm and Haas Electronic Materials were studied. The material of the pads was put on a highly polished hard-drive disk while casting the pads. After cooling down, the pads delaminated, and created a rather flat surface suitable for study with the AFM.

AFM. A Dimension 3100 Nanoscope AFM (DI/Veeco, CA) with built-in video optical system was used in this work. The AFM operated in contact mode while imaging, and in the force/force-volume modes while measuring the forces. The AFM software v.5.12r4 was employed. Sensitivity of the cantilevers used was determined assuming no deformations of the tip and sample.

AFM Probes Preparation. Standard silicon nitride integrated pyramidal tips fixed on a cantilever with the spring constant k~0.14 *N/m* (it was determined by resonance method using built-in option in the AFM software) were used for attaching ceria particles.

Ceria particles were glued to the AFM tip by using built-in micromanipulator of Dimension Nanoscope AFM. Araldite 10-minute two component epoxy was spread on one part of a glass slide, and the ceria (washed in ultrapure water and dried in ambient conditions) powder was placed on the other part of the same slide. The AFM tip was put in contact with epoxy first, and then with the ceria powder. The tip was placed in incubator at ca. 80^{o}C for 24 hours to completely cure epoxy. After that the cantilever was put in ultrapure MilliQ water and ultrasonicated for 30 seconds to get rid of not strongly enough attached particles.

To be sure that we are dealing with ceria particles, but not epoxy that can be released out and between ceria particles, we did the control experiment as follows. The AFM tip was prepared as above but with no ceria particles, only epoxy. The fabricated tip was used to study the forces between such tip (essentially just epoxy) and a surface of freshly polished silica wafer. We found that the forces of interaction of ceria and epoxy with silica are quite different. We found that the easiest way to distinguish between these materials is to compare the behavior of adhesion with the change of pH 5,7,9 (not shown).

To assure that the AFM tip with the attached ceria does not change during the scanning, and to characterize the geometry of the attached particles, we did the scanning of inverse grid (NT-MDT Inc), which produces inverted image of the AFM tip.

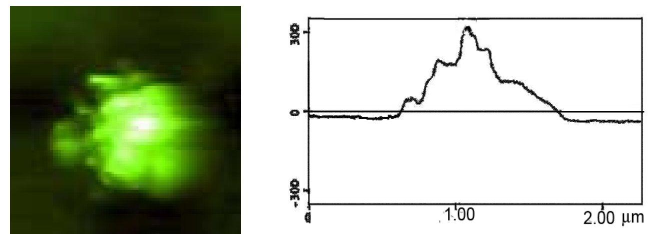

Figure 1. 2x2 µm^2 AFM image of the tip obtained with the inverted grid (left) and corresponding cross-section (right).

An AFM image of such a tip and corresponding cross-section are shown in Fig.1.The typical diameter of the attached particle on the tip apex was ca. 50-100 nm.

Solutions of Different pH. Interaction between the tip and pad surfaces was measured in an aqueous solution of KOH and HNO_3 of various pH, ranging from 5 to 9. The ratio of the base and acid solutions was adjusted to obtain the needed pH. The solutions were prepared to keep the ionic strength to be 10mM. Ultrapure MilliQ water was used.

RESULTS

Using the advanced force and force volume modes of scanning, we measure the force interaction between the ceria particles attached to the AFM tip and the pad surfaces prepared as described above.

Fig.2 shows the forces acting between ceria particles and OXP pad for various acidity. Each force curve is artificially shifted in vertical direction for better visualization. The force values are given as the cantilever deflections, in nanometers. Tog et the force in nano Newtons, one needs to multiply these values by the spring constant, 0.14N/m.

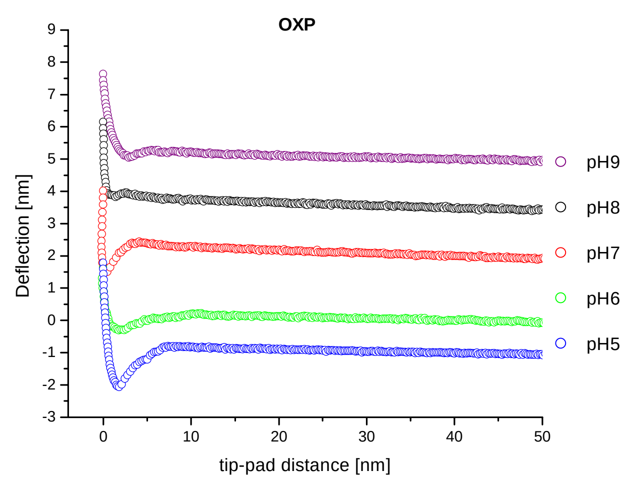

Figure 2.. Interaction between NanoTek ceria and OXP4000 polyurethane pad for various pH.

Each force curve shown is a result of averaging 256 force curves collected over the area of 2x2 μm^2. This was done via processing of 16x16 force measurements done in the Force-Volume mode.

The same type of measurements with <u>the same tip</u> (to assure easy comparison of interaction with different pads) was done for JR111 and IC1000 pads, Fig.3.

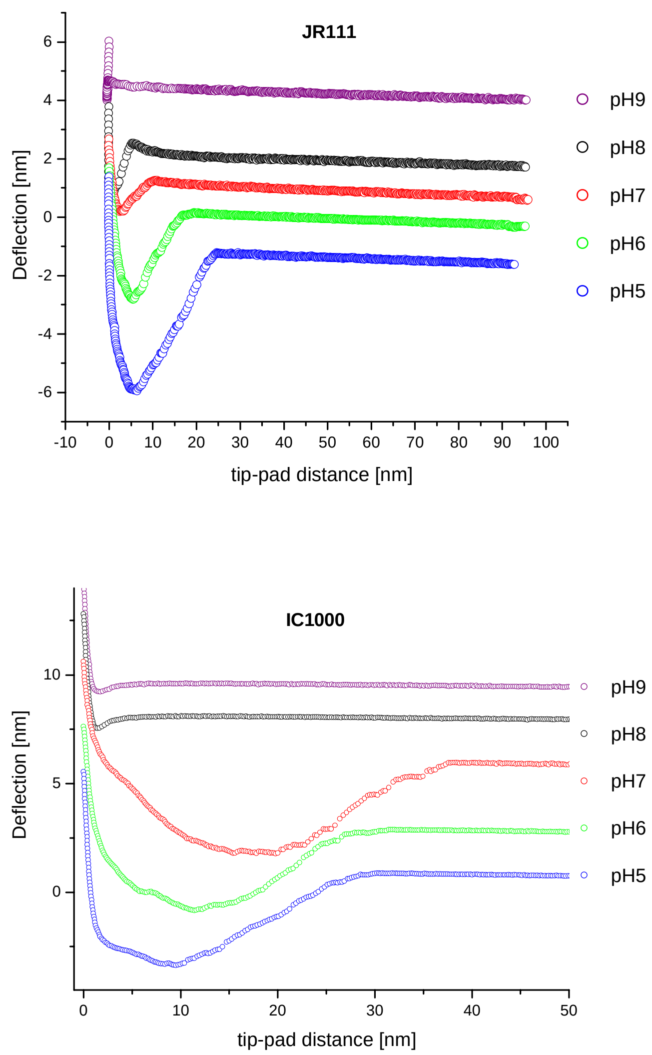

Figure 3.. Interaction between NanoTek ceria and JR111 polyurethane pad (top) and IC1000 (bottom) for various pH.

Somewhat unusual force dependence between ceria and IC1000 pad shown in Fig.3, which demonstrates a rather large long-range attraction.

Adhesion between the ceria particles and the pads is shown in Fig.4. As before, each point is an average of 256 measurements over 2x2 μm^2 area, the error-bar corresponds to one standard deviation.

DISCUSSION

As one can see from the results of the previous section, the forces of interaction of the ceria particles and all three polyurethane pads are quite different. While IC1000 and JR111 have some similarity for pH6, the rest of the data is rather different. The major difference of OXP4000 is small value and short range of the interaction, whereas both IC1000 and JR111 show rather long range attraction for pH less than 7. The list of these differences can be continued.

Let us now look at the results of adhesion of ceria to the pad surfaces. One can see that the adhesion data for ceria are quite similar for JR111 and IC1000 pads for smaller pH5-7, and the adhesion values are higher than for OXP4000 pad. This is in agreement with the measurements of long-range force, Figs.1-3.

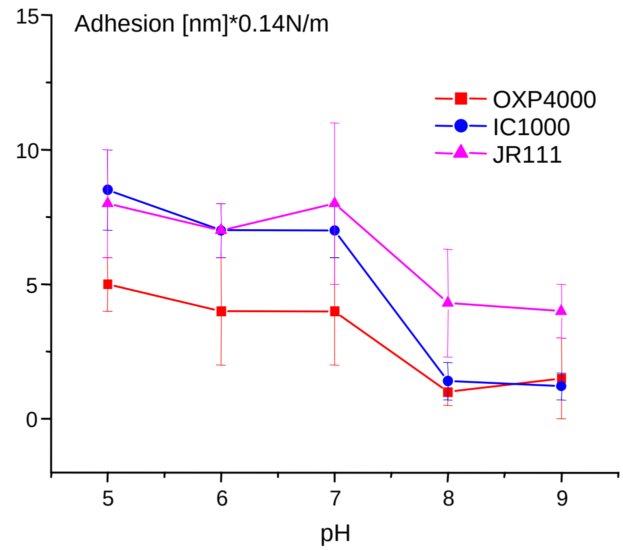

Figure 4. Adhesion of NanoTek ceria to the polyurethane pads

For higher pHs, adhesion to IC1000 pad is similar to the adhesion of OXP4000 and gets smaller than JR111. This correlates with the long-rage force for pH8, but is not obvious for pH9.

In conclusion, we report the first successful direct measurements of forces between various polymeric surfaces and nanoparticles attached to the AFM tip.

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