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Atomic force microscopy study of silica nanopowder compacts

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Nanometer silica powders compacted at different pressures have been studied by atomic force microscopy (AFM). Local elastic moduli measurements made on the powder compacts yield values smaller than that of bulk silica. Loading force-distance curves measured show break points at some critical pressures. AFM images obtained at constant contact forces above and below the critical force at which a break point occured show the break point was a result of AFM tip plowing into the nanometer powder compacts. The applied force required for break points to occur increases with sample density. Such a behavior has been qualitatively explained in terms of adhesion force between nanoparticle and sample surface morphology. © *1999 Kluwer Academic Publishers*

1. Introduction

The invention of atomic force microscopy (AFM) [1] and subsequent development of the related technologies [2] have pushed the study of mechanical properties of materials towards nanometer and atomic scales [3]. It is now possible to study the fundamental atomistic mechanisms governing the macroscopic observables such as elastic modulus, adhesion, and surface energy [4, 5]. These studies have yielded discovery of new phenomena which are absent in macroscopic measurements simply because their effects are averaged out on a macroscopic scale. Among many interesting discoveries, discrete behaviors have been observed in sliding friction, nano-contacts, elastic deformation in crystals when studied on microscopic scale using AFM [6–8]. It has been found that, in general, many aspects of the microscopic mechanical properties of the crystals are quite different from what one observes on a macroscopical scale. Computer simulations and analysis have been used to help understanding these very interesting differences [9, 10].

In the study presented here, we investigated the microscopic mechanical properties of nanometer-sized silica powder compacts using an AFM. Powders or granule materials are the constituents of many objects that are essential to our daily life such as pharmaceutical tablets, gels, concrete, clay, etc. [11]. The properties of powder materials are determined by many factors that include bulk properties of powder particles, grain boundaries between particles, the interactions between particles, and the chemical compositions of the powders. In the experimental studies of powder compacts, most techniques available are for studying the macroscopically averaged effects of these factors [11]. Due to the heterogeneity nature of the powder compacts, especially as the size of powder particles decreases to microscopic scale, the macroscopically averaged properties could be completely different from the local properties probed by microscopic methods [12–14]. The purpose of this study is to examine the mechanical properties of nanopowder compacts as a function of packing ratio using atomic force microscopy. We choose to study oxides because they are relatively inert to exposing to atmosphere, making the experimental control requirements in the study less stringent.

2. Experimental procedure

Silica nanopowders were used as provided by the Dugussa Corporation without further treatment [15]. The powders were produced by the aerosil process under controlled conditions and were in amorphous form as shown by X-ray diffraction studies [15]. The average diameter of the silica powder particle is quoted to be 12 nm with a dispersion factor of about 2 [15].

A compression device, with 10-ton capacity, capable of compressing a large volume of loose powders into a small pellet with a controlled pressure was constructed [16]. Two movable pistons are placed in direct contact with the sample during compression. The contact surfaces were polished using Al_2O_3 powders with an average diameter of 0.05 μm.

A series of samples were prepared, using this device, under ambient laboratory conditions at pressures from 68 to 540 MPa. The process of compressing loose powder into pellet was typically accomplished in a time period of about a few hours. In this study, no effort was directed towards exploring the optimum conditions for

compressing the nanopowders. The final pellets usually broke into pieces with irregular shape when they were taken out of the compression chamber. So a direct measure of sample density from mass and volume measurements becomes difficult. We, thus, use the maximum pressure applied to the pellets during compression to specify the samples in the following discussions.

The local mechanical properties of the samples were investigated by measuring force-distance curves using a commercial AFM [17]. Commercially available AFM tips made of Si_3N_4 and Si were used in the force-distance measurements and in surface morphology imaging [17]. It is crucial, in the study of the microscopic mechanical properties of a material, to characterize the applied force via an AFM tip and the contact area between the tip and the surface. We determined the applied loading force by directly measuring the bending of the AFM cantilever and its spring constant. The bending of the cantilever was measured using the typical reflection method [2]. The spring constants of the cantilevers were determined by measuring their dimensions and the resonant frequencies, and using the known bulk mass densities of Si_3N_4 and Si [2]. To characterize the contact area between a tip and a surface, typically one would measure an AFM tip radius via electron microscopy before and after a measurement to account for tip wear. We do not have constant access to an electron microscope. Thus we take a statistic approach by simply using the manufacturer's quoted tip radius [17] and averaging measured quantities that involve local pressure over many measurements using a group of AFM tips over different spots on the same sample.

In the force-distance curve measurements, the vertical displacement d of the piezotube, where a cantilever was mounted, results in the bending d_c of the cantilever and the local elastic deformation of the sample δd (i.e., $d = d_c + \delta d$). The bending of the cantilever d_c was monitored using the optical reflection technique, as described above. Thus the local elastic deformation δd of the sample was determined from the measured d and d_c. Assuming a constant contact area, the relation between F and δd gives a measure of the local elastic modulus. We tested this method by measuring the elastic modulus of a single crystal lead and obtained an averaged value which agrees with the generally accepted value within 15% [18]. In imaging the surface morphology, contact mode was used and the average force applied was kept to a value typically less than 0.1 nN. No appreciable changes in the surface morphology were observed over time in the course of study.

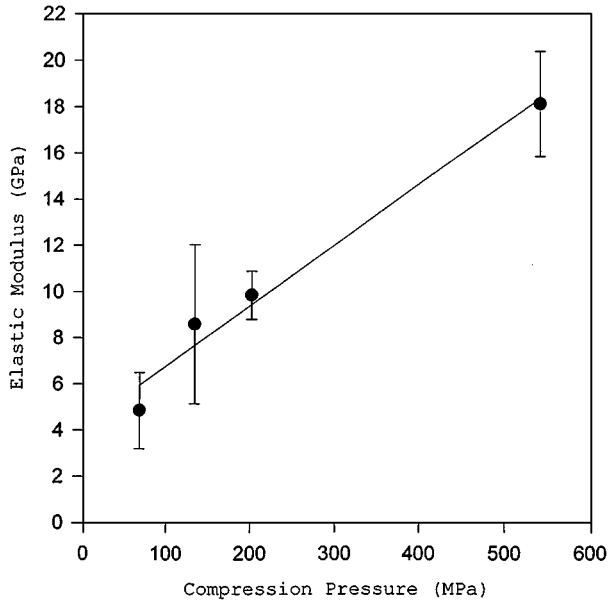

Figure 2 Elastic modulus of the silica compacts, obtained from the loading force-distance cuvres, as a function of maximum compression pressure when the samples were prepared. The solid line is a guide to the eyes.

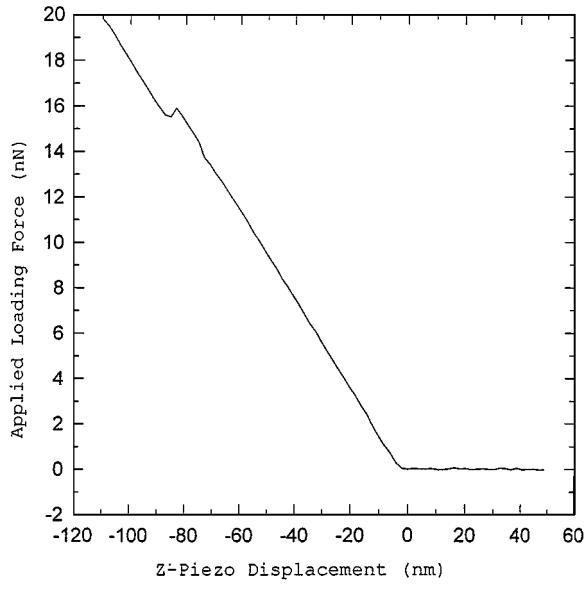

Figure 1 An incoming loading force-distance curve measured on a sample prepared under a compression pressure of 540 MPa. The curve clearly show a jump where the force suddenly decreases as the tip was further pushing against the sample.

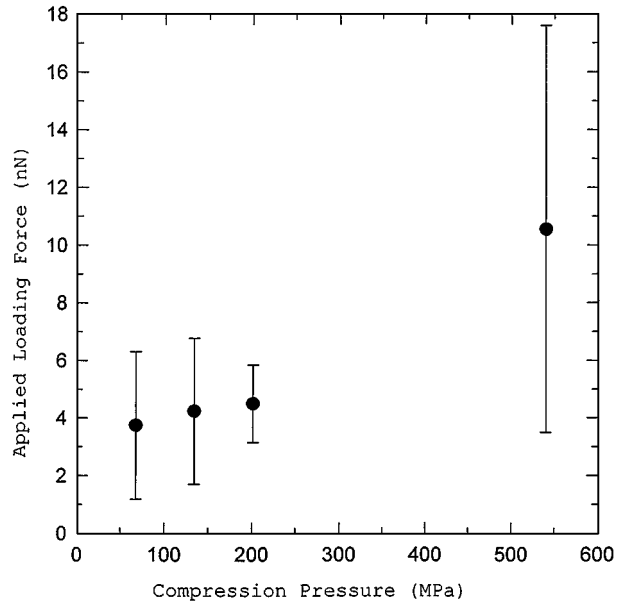

Figure 3 The applied loading force at which the break points occur as a function of the maximum compression pressure applied to the sample when the sample was prepared.

3. Results and discussions

Fig. 1 displays a typical loading force-distance curve obtained on silica powder compacts. Using the method described above, the local elastic deformation δd was derived. A linear fit of F to δd gives the elastic modulus of the sample. Fig. 2 summarizes the average elastic modulus obtained from samples prepared under different compression pressures. The measured elastic modulus is found to be much smaller than that of bulk silica (the Young's modulus for silica glass is 70 GPa) [19].

As shown in Fig. 1, the loading force-distance curve measured with a maximum load on the order of tens of nano-Newtons shows a discontinuity, which we label as "break point". Such a break point indicates a sudden decrease in the surface force as the tip is pressed against the sample. For samples prepared under a higher maximum compression pressure the break point occurs at greater loading force, as shown in Fig. 3. The break point was repeatedly observed on the same sample without changing the AFM tip. This rules out the possibility that break points are caused by tip wearing or tip damage during the force-distance curve measurements. Similar kind of sudden decrease of repulsive force in the loading curve has been observed in a study of metal clusters deposited on flat surfaces [20]. It was explained as due to inelastic deformation of the nanoclusters [20]. In our measurements the pressure applied is much smaller than that required to deform a

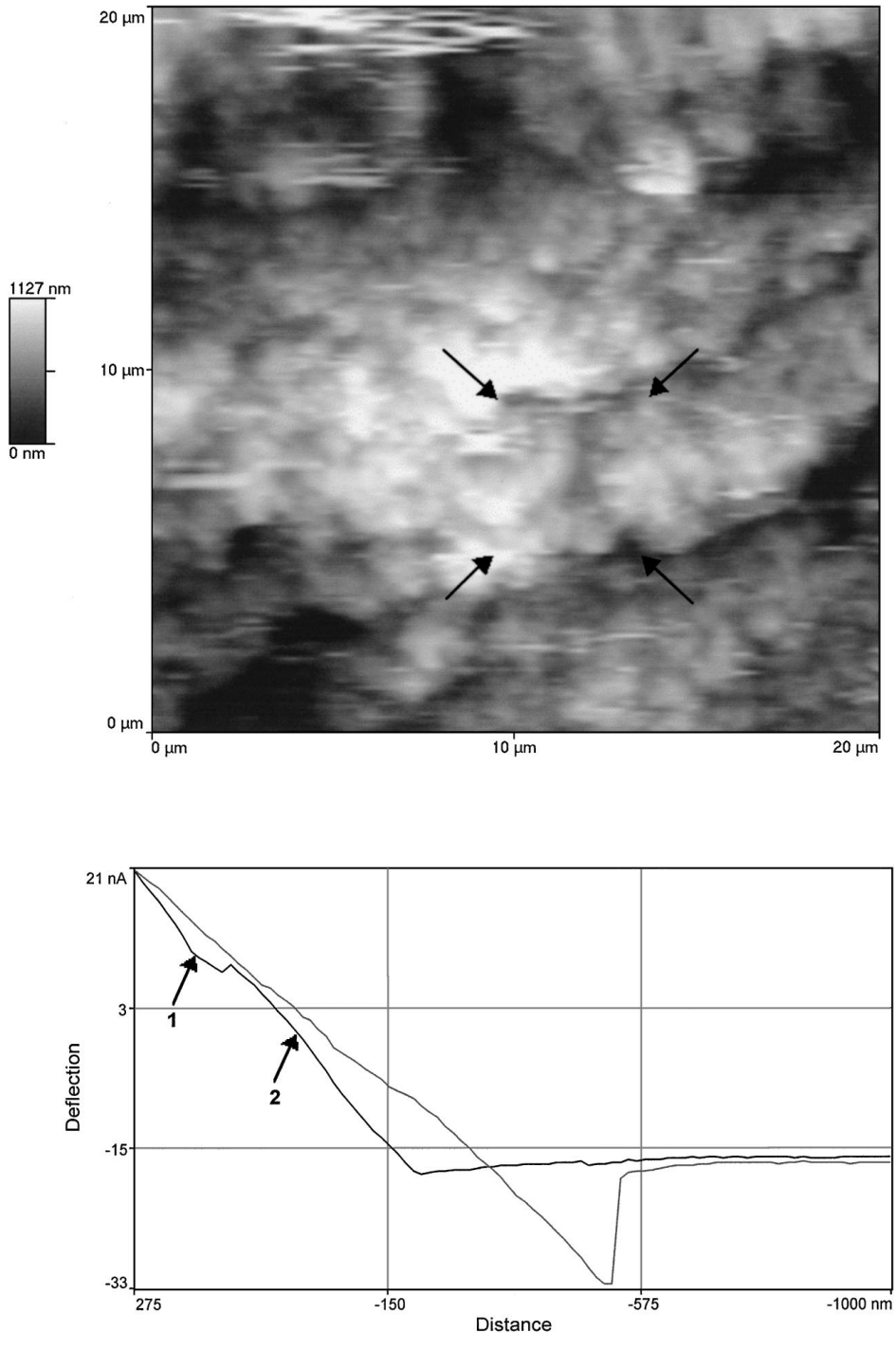

Figure 4 The image of an area first scanned with an applied force stronger and then smaller than that at which a break point occurs in the force-distance curve. The area (5×5 μm^2) indicated by the arrows was first scanned with a force specified by 2 on the force-distance curve. The entire area was then imaged with a force indicated by 1 on the force-distance curve.

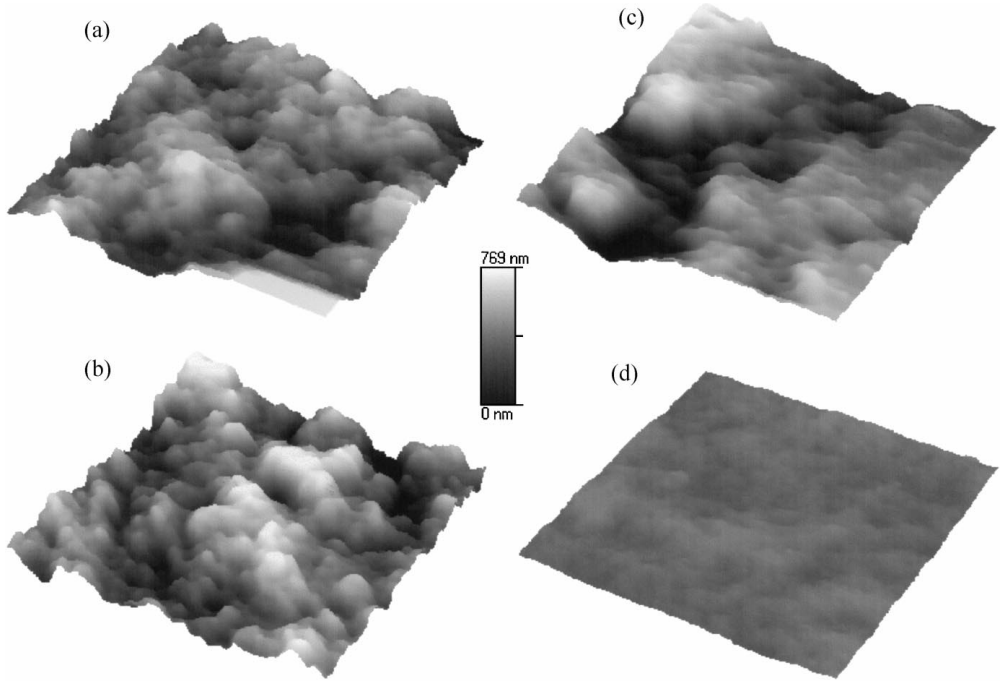

Figure 5 Surface morphology of powder compacts imaged by AFM: (a) compressed at 68 MPa; (b) 134 MPa; (c) 201 MPa; and (d) 540 MPa. The lateral dimensions of all the figures are $20 \times 20\ \mu m^2$.

bulk silica. If we take the measured spring constant and the quoted tip diameter (50 nm) of the cantilevers [17], the pressure applied at the break point is only several MPa. Allowing the tip diameter to vary by a factor of ten still makes the maximum pressure to be considerably lower than the elastic moduli of bulk silica glass [19].

Another mechanism that could cause the break point is the AFM tip plowing into the sample. In fact, this mechanism has been used to modify surfaces of various materials and manipulate atoms or molecules on different surfaces [21, 22]. To check whether this is indeed the cause of the break points one can scratch the surface with a force greater than that where the break point occurs and then identify the scratch from the surface imaging. We therefore first scanned a small area ($5 \times 5\ \mu m^2$) of the sample surface in a contact mode using an average force slightly greater than that where the break point occurred. An image was then obtained using a reduced force on a larger area ($20 \times 20\ \mu m^2$) of the sample surface that containing within its boundaries the small area previously imaged. Fig. 4 includes a typical image and the force-distance curve obtained in this process. We found that when imaging the region with a force greater than where the break point occurred we were be able to resolve the outline of a $5 \times 5\ \mu m^2$ square region in the larger image, indicating the effects of plowing. In the case where forces were kept less than that where the break point occurred we found no evidence of plowing.

The individual nanopowder particles stick together through adhesion force after compression [23]. The total adhesion force should be proportional to the contact area between particles [23]. As was described above, the maximum pressure used in preparing the compacts in this study is much smaller than the bulk modulus of silica. It is then reasonable to assume that the main effect of compression pressure to the nanopowders was to increase the packing ratio of the compacts by forcing more powder particles into a given space. If the powder particles are connected with each other loosely one would expect a heterogeneous distribution of particles in the sample and a rough sample surface [24]. As the packing ratio increases, so does the contact area among powder particles. The distribution of particles would become more uniform and the surface of the sample more smoother correspondingly. When the packing ratio reaches maximum one would expect a homogeneous distribution of powder particles throughout the sample and a correspondingly smooth surface showing height variation on the order of particle size. Therefore, the critical loading force where a break point occurs should be related to the surface roughness of a sample. We imaged surface morphology of the samples using the same AFM tip. Fig. 5 illustrates the images obtained from samples prepared under four different pressures. It is quite obvious that the surface roughness decreases with compression pressure. Fig. 6 shows the surface roughness, which was calculated as the mean deviation from the mean height of the samples. The surface roughness of the pistons, which is also plotted in Fig. 6, is smaller than that of the sample compressed at highest pressure. Thus we think it does not affect significantly the surface roughness obtained. Fig. 7 plots the critical loading forces where the break points occur versus the sample surface roughness. A qualitative correlation between surface roughness and break force seems to exist. However, it should be noted that surface roughness probed by an AFM gives a convolution of surface morphology and the shape of the AFM tip [2]. The height of the tips used in this study is quoted to be about 4 μm [17]. Any abrupt variation on the vertical scale close to or larger than the tip height would be truncated in the image at some length scale related to the tip height. The weak dependence of the surface roughness for samples compressed at low pressure, shown in Fig. 6, might be caused by this effect. A quantitative analysis would

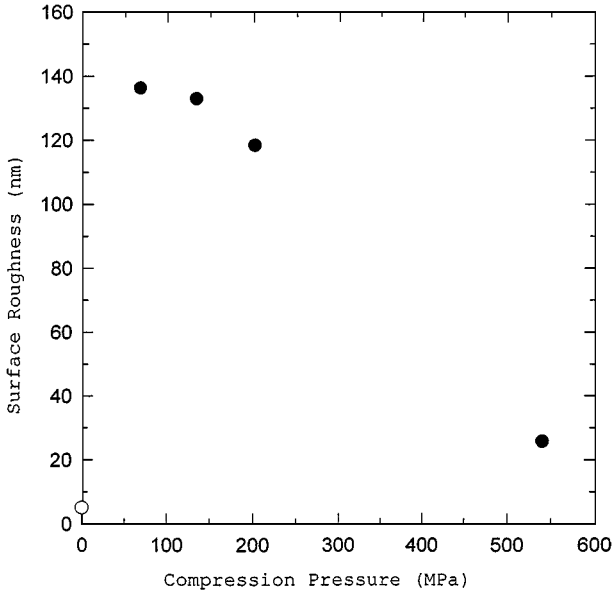

Figure 6 Surface roughness of the silica powder compacts, measured by AFM, versus maximum pressure applied in compression (solid circle). The point indicated by an open circle is the roughness of the piston surfaces in the compression chamber.

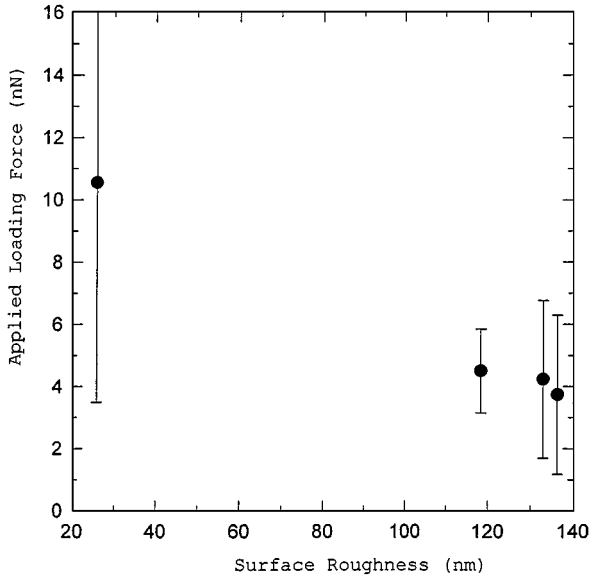

Figure 7 Applied loading force where the break points occur versus sample surface roughness determined from AFM images.

require the imaging of the surface using tips with higher aspect ratio or the use of some other techniques which is able to resolve the true morphology of the surface at various length scales.

4. Conclusion

We have studied mechanical properties of silica nanopowder compacts of silica prepared at different compression pressures by atomic force microscopy. We found that the local elastic modulus of the silica powder compacts increases with sample density, but are significantly lower than that of bulk silica. Sudden decreases of the loading force are observed in the force-distance curves and are interpreted as due to the plowing of the AFM tip into the sample surface. Images obtained by applying a loading force larger and smaller than that where the break points occur verify the interpretation. The critical loading forces where the break points occur have been further related to sample compression pressure and the surface roughness probed by AFM. The results presented here suggest that with better controlled environment and better characterized AFM tips it should be possible to study, directly, the interactions between nanopowder particles.

Acknowledgements

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