Sample preparation

The particles to be tested were two sizes of silica spherical particles, nominally sized 300 nm and 100 nm in diameter, gold spherical particles, nominally sized 60 nm in diameter, and two sizes of gold rods, nominally sized 25×77 nm and 25×66 nm. They were dispersed or embedded (in PMMA) on a silicon substrate.

To test unbound particles, they were dispersed in solution by ultrasonification, pipetted onto the silicon substrate and left to dry.

To embed the particles on the silicon substrate using PMMA, they were dispersed in anisole and ultrasonicated for 15 minutes. After this, with the ultrasonification still running, 2 wt% PMMA was added and left a further five minutes to fully dissolve the PMMA. A drop of this was pipetted onto the silicon on a spinner, which was ramped to 500 rpm and held for 20 s. It was then ramped quickly to 5000 rpm and held for 30 s. 2 wt% PMMA in anisole under these conditions is expected to produce a film slightly under 40 nm in thickness. It was heated on a 160 °C hotplate for 60 s to drive off the solvent and harden the film. The substrate with particles now embedded was placed in 100 W oxygen plasma for 10 s, which stripped the surface of PMMA and exposed the tops while retaining them on the substrate. Imaging in the SEM revealed that the particles had agglomerated and formed spheres of different sizes, as shown in Figure 1a and b, but many single particles had also had large separations from their nearest neighbours. The remaining PMMA layer can be clearly viewed in Figure 1c where some of the layer is missing, exposing the substrate and revealing the thickness of the layer. A single particle is shown in Figure 1a just behind the agglomerate, and a more isolated single particle suitable for testing is in Figure 1d. There were also a few much larger agglomerations on the substrate that could be seen by eye. It is possible that longer ultrasonification would disperse these a bit better.

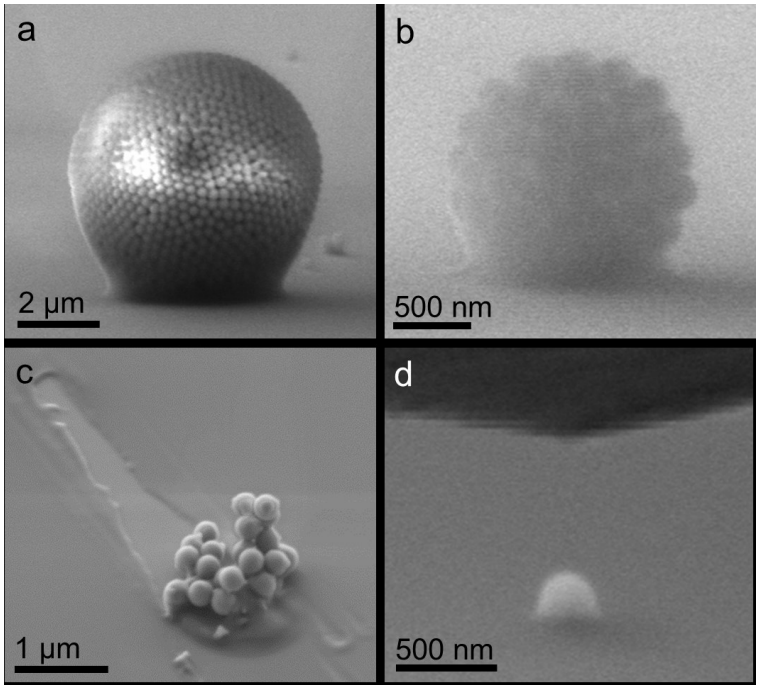

Figure 1: 300 nm particles in PMMA a) in large spherical agglomerate, b) in a smaller spherical agglomerate, c) cluster of particles with the silicon substrate exposed. Imaging conditions: stage tilt 45°, 2 kV, WD 6 mm, d) single particle with indenter positioned above.

The particles were indented with and without the PMMA layer. The purpose of using PMMA was to hold the particles in position so they can be located before and after indentation, however the additional material to the particle and substrate (PMMA) complicated the results due to not fully understanding its properties. Even though the nominal thickness is known, the exact distribution of the PMMA was difficult to image due to resolution even in the SEM. However it can be seen in Figure 1 that there is a meniscus visible at the base of the agglomerates in Figure 1a and b, the single particle in Figure 1d and the thickness in Figure 1c where some of the PMMA has come away from the substrate. By indenting the particle on the substrate without the PMMA layer, a comparison of the two tests can be made to calculate the influence of the PMMA layer on the results.

A sample from each particle size were dispersed and embedded on a silicon substrate starting with the largest. The samples were indented in turn with decreasing particle size until the experiment was no longer possible.

Measurement method

The indenter system used to conduct the tests was an ASMEC UNAT-SEM2 in situ nanoindenter in a Carl Zeiss Auriga 60 FIB-SEM, with a Berkovich tip installed. The nanoindenter was fitted onto the stage in the microscope chamber. The stage was then tilted to 10° in order to view the indenter at the sample surface at an 80° incident angle with the electron beam. The nanoindenter required compliance calibration and load calibration for experiments at non-zero tilt.

To indent a particle, a single isolated particle was located and the indenter manually positioned approximately 1000 nm above it using SEM imaging as a guide. This was done by moving the sample stage on the nanoindenter in X and Y directions. Before positioning over the particle, a test indent is made to the side to check Y positioning is correct before moving to the correct X position. Due to thermal or systematic instabilities, the indenter drifts slightly (approximately 1 nm/s) in the indentation axis. There was also some hysteresis when positioning the indenter in the Z axis. Once the test is running, the piezo stage takes over and the indenter Z displacement is controlled more accurately.

The tests were displacement controlled and the same indentation profile was used for all tests, including the substrate only tests. The total displacement was set at 1000 nm, where the indenter was positioned between 900 nm and 1100 nm above the substrate. It was not possible to position at the exact same height for every test, due to the hysteresis and drift associated with manually positioning the indenter. The indentation rate was 40 nm/s – 25 s to the maximum displacement of 1000 nm, the maximum displacement was held for 30 s, the unload rate was 53 nm/s – 15 s to back off to 800 nm, this displacement was held for 30 s, and the final unload to 0 nm displacement was 5 s. The displacement vs time plot of this for one of the tests is shown in Figure 2.

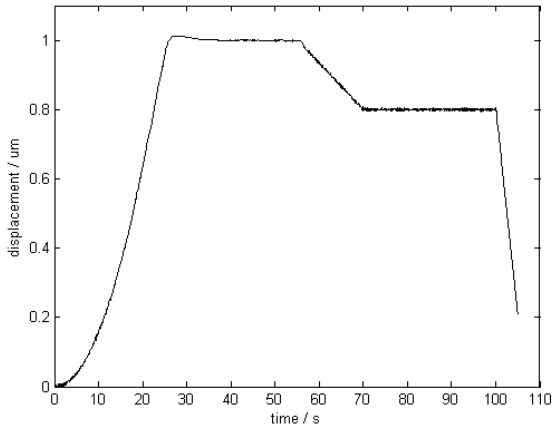

Figure 2: Displacement time graph of the displacement controlled test

Indentation

300 nm particles

The particles were measured as 260±10 nm in the SEM. The indenter was positioned over a particle, such as the one in Figure 3, as described in the previous section, and successful indentations were made. The particle appeared to completely flatten under maximum load, but swelled again slightly when unloaded, leaving a dimple in the middle, as shown in Figure 4 (movies – test B, C, and D). The load displacement curves in Figure 5 show multiple gradients indicating the differences in the four particles reported. The indenter started highest above the substrate in test A (~1100 nm) and was lower for each subsequent test where test D was the lowest (~800 nm). This accounts for different maximum loads. However, loads at different steps on the load-displacement curves differ between tests. Tests A and B show the PMMA layer and silica particle compression stages, test C shows the PMMA layer, silica particle and silicon substrate compression, and test D shows only the silica particle and silicon substrate. For test D, the PMMA layer compression stage was likely present at the start but cannot be seen because the load increased to double the other tests, obscuring the step (as also shown in the load-time curves in Figure 5). All four tests showed the load increasing rapidly and dropping off during holding at maximum displacement. The unloading showed that plastic deformation had taken place, as the load dropped to almost zero. The SEM images after indentation confirm the plastic deformation, as they are now ellipsoids as seen in Figure 4a-c compared to close to spherical as seen in Figure 3. The particles were also imaged at 750 V accelerating voltage to view the surface at the best resolution in Figure 4d-f. All image sin Figure 4 are at the same magnification as the load increased from test A to C, the particles are more flattened with a larger top surface area. The higher loaded particles also have a less pronounced indentation groove, although this may also be affected by the indenter position on the particle which would have not been exactly central in every test.

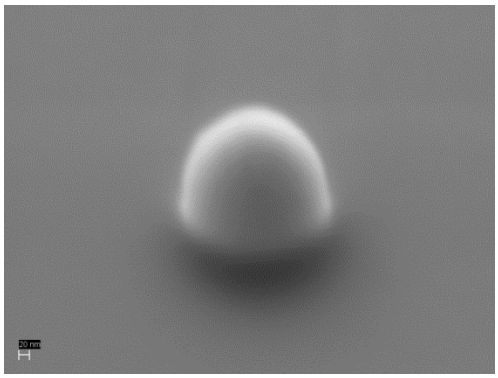

Figure 3: Non-tested particle. Imaging conditions: sample tilt 45°, 2 kV, WD 6 mm

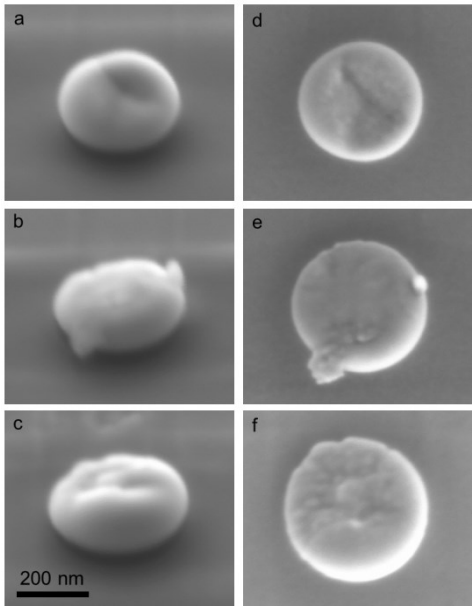

Figure 4: SEM images of indented particles a) test A, b) test B, c) test C. Imaging conditions: sample tilt 45°, 2 kV, WD 6 mm. d) test A, e) test B, f) test C. Imaging conditions: sample tilt 0°, 750 V, WD 4 mm.

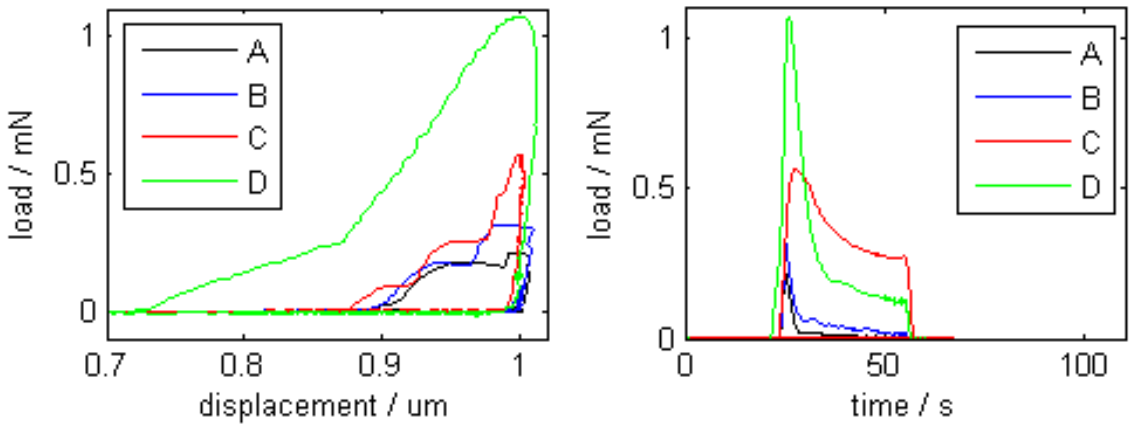

Figure 5: Load against displacement and time plots for indentation of four 300 nm particles in PMMA.

100 nm particles

It is currently not possible to deposit and embed the particles on the substrate using the same method for the 300 nm particles.

Substrate

By testing the substrate, the gradient on the full tests can be compared to distinguish between indentation of the nanoparticle and of the substrate. The test conditions for indents on the substrate were the same as with previous indentation of the particles. Also similarly, the position of the indenter above the substrate could not be finely controlled, leading to different maximum loads for each test. There was some plastic deformation, as hysteresis was observed in the load-displacement graph in Figure 6, and an indent was left behind in the substrate after testing. During the hold at maximum displacement, there was a small drop in load in some tests as seen in the load-time graph in Figure 6, but did not show the dramatic drop as with the particles in Figure 5.

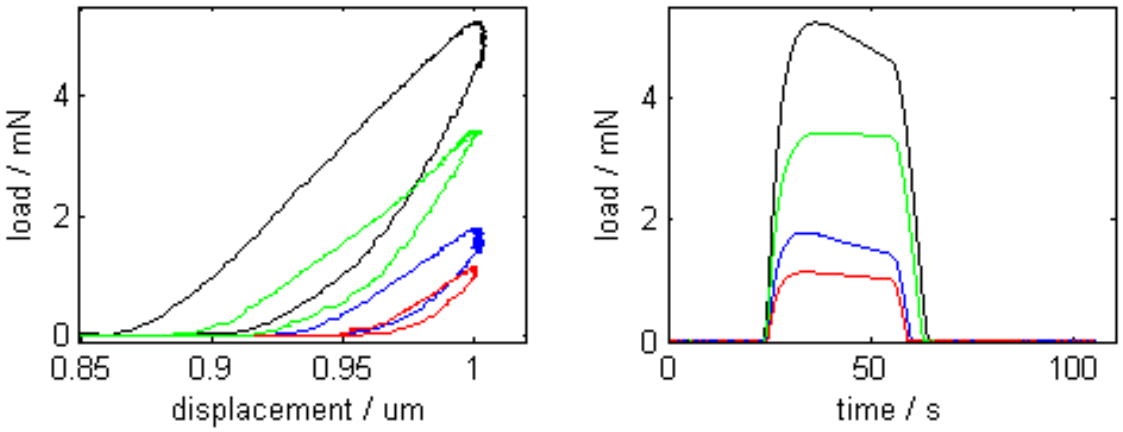

Figure 6: Load against displacement and time plots for four indents on substrate with PMMA layer

Discussion

The measured size of the particle depends on SEM conditions, where the observed difference in value compared to the original stated size (AFM), dispersed, and embedded in PMMA sizes is due to the variance in image noise depending on the technique.

It was not possible to measure the thickness of PMMA using SEM technique, as PMMA at this thickness is electron transparent. It was deduced that it is nominally 40 nm on the top of the substrate, thinner underneath the nanoparticle, and none on top of nanoparticle. The PMMA layer was also not uniform around the particle, showing build-up around the bottom. It also should be noted that the PMMA may cause apparent hardening due to prevention of expansion at the sides of the nanoparticle.

Indentation of embedded 300 nm nanoparticles is possible using a Berkovich indenter and force-displacement curves can be obtained. These showed multiple stages where the PMMA layer, nanoparticle and substrate all have different properties and therefore indented at different rates. By using an *in situ* technique in the SEM, it is possible to observe the test in real time, making it easier to locate the nanoparticles and position the indenter correctly.