Fabricating Vitreous Silica Micropillars for Uniaxial Compression with *in situ* Raman Spectroscopy

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Primary CNF Tools Used: Autostep i-line stepper, PT770 etcher, Oxford 100 etcher, Oxford 81 etcher

Abstract:

In silicate glasses, the interplay between glass structure and plastic deformation is not well understood. To address this, high-quality SiO_2 micropillars were fabricated through a reactive-ion etching based method which were then tested in compression while characterizing the structure of the glass *in situ* using Raman spectroscopy. These experiments provide direct observation of how the structure of the glass changes in response to a well-known uniaxial stress and strain state. The SiO_2 micropillar fabrication process, as well as considerations for optimizing pillar geometry are described.

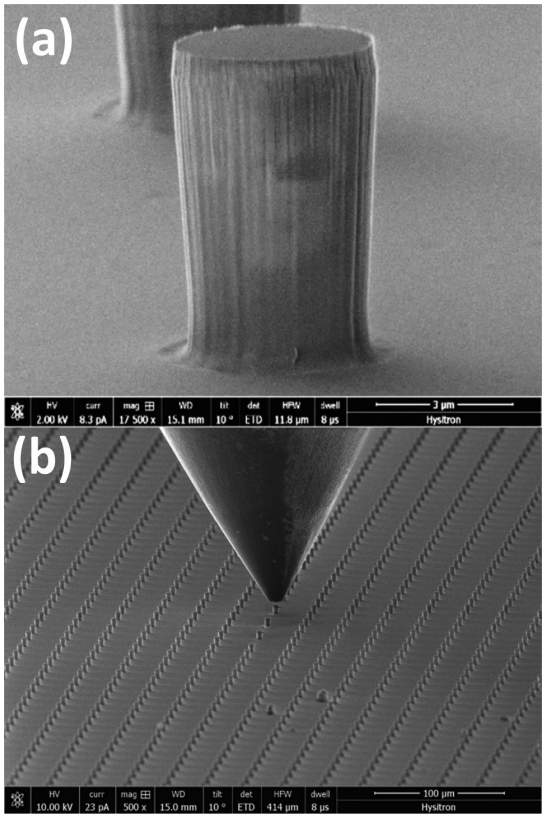
Summary of Research:

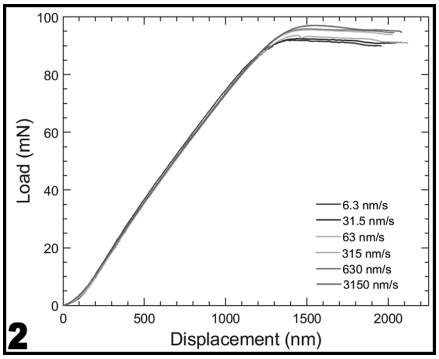
Silicate glass is a vital component in countless applications such as display screens, solar panels, and vehicle windshields and as such its fabrication has become a near trillion-dollar industry. Although silicate glasses are macroscopically brittle materials, in small volumes they can undergo extensive plastic deformation. The character of this deformation influences the stress field evolution and crack nucleation around mechanical contacts, ultimately dictating the bulk fracture of the glass. Despite this, very little is known about the underlying atomistic mechanisms leading to silicate glass plasticity.

A popular method of probing these mechanisms is to perform Raman spectroscopy of residual indentations *ex situ*. A basic understanding of how the glass network reconfigures during deformation can be acquired by associating spectral peaks with known glass network features and then observing the spectral shifts between a pristine and an indented region. However, the quantitative analysis of data acquired through this method is limited due to the poorly known and highly heterogeneous stress/strain states of the probed volumes underneath the indentations. Additionally, these *ex situ* tests only characterize the nature of the glass network due to residual deformation, rather than during deformation. To rectify this, we developed a novel experimental method in which Raman spectra are recorded *in situ* during uniaxial micropillar compression of SiO_2.

This testing enables us to probe the structure of a glass that is being subjected to well-known, homogeneous, and easily tunable stress and strain-states.

The success or failure of this method is entirely dependent on the ability to fabricate numerous high-quality SiO_2 micropillars with highly vertical side walls and minimal structural damage. To accomplish this, a new reactive-ion etching based process was developed at CNF. In this process first a thick (> 1.25 μm) chromium film is sputtered onto a standard SiO_2 wafer using the CVC 601 sputtering tool. An anti-reflective coating (ARC) followed by photoresist is then spun coat on top of the chromium. A reticle with a grid of circles with various diameters is then used for the resist exposure on the Autostep 200 stepper tool. After development (and oxygen plasma etching of the uncovered ARC), the residual discs of resist are used as a mask for a chlorine-based reactive-ion etch through the chromium film in the Plasma-Therm 770 etcher. After removal of the remaining resist, the residual discs of chromium are used as a mask for an extremely deep (6-10 μm) fluorine-based reactive-ion etch of the underlying SiO_2 wafer on the Oxford 100 etcher. The remaining chromium caps are dissolved with a chemical chromium etchant, and the passivating fluropolymer layer left on the pillar sidewalls is stripped with an EKC solvent.





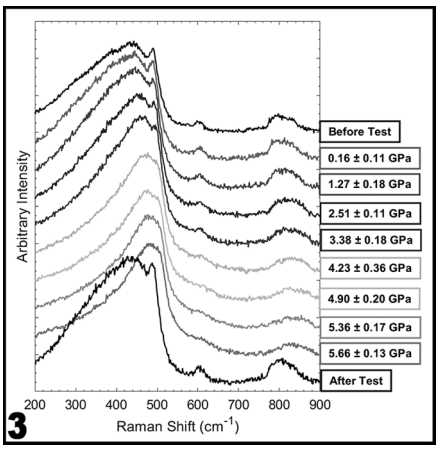


Figure 1, above: left (a) Scanning electron images of one typical silica micropillar and (b) a wide view of an array of micropillars as well as the diamond flat punch used to compress them. Figure 2, top right: Schematic of the utilized testing setup for micropillar compression with in situ *Raman spectroscopy. Figure 3, bottom right:* Ex situ *and* in situ *Raman spectra taken during micropillar compression at various applied engineering stresses. Spectrum peaks are associated with specific, known SiO_2 network features.*

This process leads to the creation of millions of pristine SiO_2 micropillars such as the one shown in Figure 1. Other SiO_2 micropillar compression studies made through analogous fabrication procedures have struggled with highly uneven pillar cross-sections [1,2]. This study's pillars are extremely dimensionally uniform and have only a slight negative taper angle of 1.8°. The tapering observed in other studies is largely caused by slanted side walls in the initial photoresist side walls, which transmits into the chromium (and then later into the SiO_2) when the resist is used as a mask. To mitigate this, a stepper exposure tool (as opposed to a contact exposure tool) using carefully optimized exposure parameters was used. During the etching stages, obtaining a very high etch selectivity was also critical for mitigating the transmission of a taper from the masks to the substrates.

To compress these pillars, the wafers were cleaved into pieces which were then mounted on a nanoindenter system (Bruker) equipped with a diamond flat punch tip. The nanoindenter system was then incorporated into a confocal Raman microscope (Renishaw InVia) such that micropillars near the cleaved edges could be probed by the Raman laser while simultaneously being compressed by the indenter punch as shown in Figure 2. By repeatedly raising the applied stress and then pausing to acquire a Raman spectrum, we can observe *in situ* Raman spectra as a function of a well-known uniaxial stress and strain for the first time ever (Figure 3).

From the dramatic peak shifts in these Raman spectra we can see that significant structural rearrangements occur with increasing applied stress, but surprisingly it is also observed that a large portion of these structural changes recover upon unloading of the pillar. This provides strong evidence that elastic deformation in SiO_2 significantly alters the glass network structure and provides a physical justification for silica's highly non-linear elastic behavior. By connecting the observed Raman peaks with SiO_2 network features, future quantitative analysis of these spectra will enable us to illuminate the fundamental atomic mechanisms of silicate glass deformation in a way that has never been possible before.

References:

[1] Kermouche, G., et al. (2016). "Perfectly plastic flow in silica glass." Acta Materialia 114: 146-153.

[2] Lacroix, R., et al. (2012). "Plastic deformation and residual stresses in amorphous silica pillars under uniaxial loading." Acta Materialia 60(15): 5555-5566.