In situ Analysis of Materials Under Mechanical Stress: A Novel Instrument for Simultaneous Nanoindentation and Raman Spectroscopy

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Abstract: An instrument that allows the simultaneous measurement of the mechanical deformation and Raman spectra of materials under contact loading is described. The instrument consists of a custom nanoindenter that operates on a laser-scanning Raman microscope.
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1. Introduction

Instrumented indentation is a method that is widely used in the study of the mechanical deformation of materials on small length scales (~μm). Raman spectroscopy is a technique that provides insight into the molecular or crystallographic level processes involved in the mechanical deformation of materials, such as strain build-up, phase transformations and variations in crystallinity. Typically these approaches have been used separately wherein the spectroscopic analysis of the material might take place at the beginning and end of a mechanical transformation. Of course, there is significant interest in *in situ* analyses of materials during mechanical transformation as such an approach promises a richer understanding of the underlying physics than is likely possible with analysis limited to pre- and post-transformation. Consequently significant effort has been directed toward the coupling of indentation instruments with various in situ analysis capabilities.

This talk describes the design, calibration, and operation of an indentation instrument that is coupled with a laser scanning Raman microscope to conduct *in situ* spectroscopic analyses of mechanically deformed regions of optically transparent materials under contact loading. The force transducer of the device allows adjustment of crucial experimental parameters, such as indentation strains and strain rates. An incorporated displacement sensor allows for collection of force-displacement curves comparable to conventional instrumented indentation instruments. The device is mounted on the sample stage of an inverted optical microscope that is configured for Raman microscopy, allowing optical access to the mechanically deformed regions of transparent samples. The capabilities of this novel instrument are demonstrated by *in situ* studies of the indentation-induced phase transformations in an epitaxial silicon-on-sapphire (SoS) thin film, in both a microspectroscopy and a laser scanning Raman imaging configuration.

2. Experimental

A comprehensive description of the Raman nanoindentation system is beyond the scope of this paper but can be found elsewhere [1]. Several improvements have been made to the instrument since publication of reference 1, most notably, the addition of laser scanning capability to allow *in situ* Raman imaging of materials held under constant contact loads. Two galvanometer scan mirrors (X,Y) are co-located at a plane conjugate to the microscope objective pupil in a conventional 4f imaging system. This configuration is unusual for spontaneous Raman microscopy as the scanning speed advantage of laser scanning over sample scanning is rarely relevant given the long spectral acquisition times typical of spontaneous Raman spectroscopy. However, in this instrument it is quite difficult to perform sample scanning as this would require moving the relatively large nanoindenter as well, undoubtedly compromising the quality of the force and displacement measurements. This issue was one of the principal motivations for the use of a custom Raman apparatus as opposed to attempting to couple the nanoindenter to a commercial Raman microscope as these are generally based on sample scanning. The Raman images are acquired by raster scanning the laser focus over the mechanically deformed region of the sample and measuring a spectrum at each location of the laser focus. Images based on various spectral features can then be assembled from the hyperspectral Raman data cube (*e.g.*, amplitude or width of a particular spectral feature).

3. Results

Silicon (Si) can be transformed to different crystallographic phases through mechanical stress. Given its importance to electronic devices and microelectromechanical systems and given that modification of the Si crystallographic structure is connected to its performance properties, phase transformations of Si have been intensively studied,

particular by indentation techniques. However, the full path of Si phase transformation induced by mechanical deformation cannot be determined by conventional indentation techniques and thus this material provides an attractive opportunity for evaluating the Raman nanoindentation system as the phases of Si have distinctive Raman signatures. This instrument was used in the first direct observation of the phase transformation cycle induced by indentation in Si thin films [2]. Figure 1 shows a sequence of 785 nm Raman spectra taken from the mechanically deformed region of a SoS thin film under increasing levels of contact pressure from a 50 μm, conospherical diamond indenter. During loading, the initial diamond cubic Si-I phase transforms gradually to *β*-tin Si-II, confirming previous assumptions. Simultaneously, the formation of an additional phase, which was identified as bct-5, is observed. This marks the first experimental evidence of the existence of this phase and its position in the phase transformation sequence of Si. [2] During unloading, (not shown here) a sudden change from the body-centered tetragonal crystal structures of the phases generated during loading to the rhombohedral and subsequently cubic structures of Si-XII and Si-III, respectively, occurs. Furthermore, the transition pressure for the different phases were determined and found in good agreement with theoretical calculations.

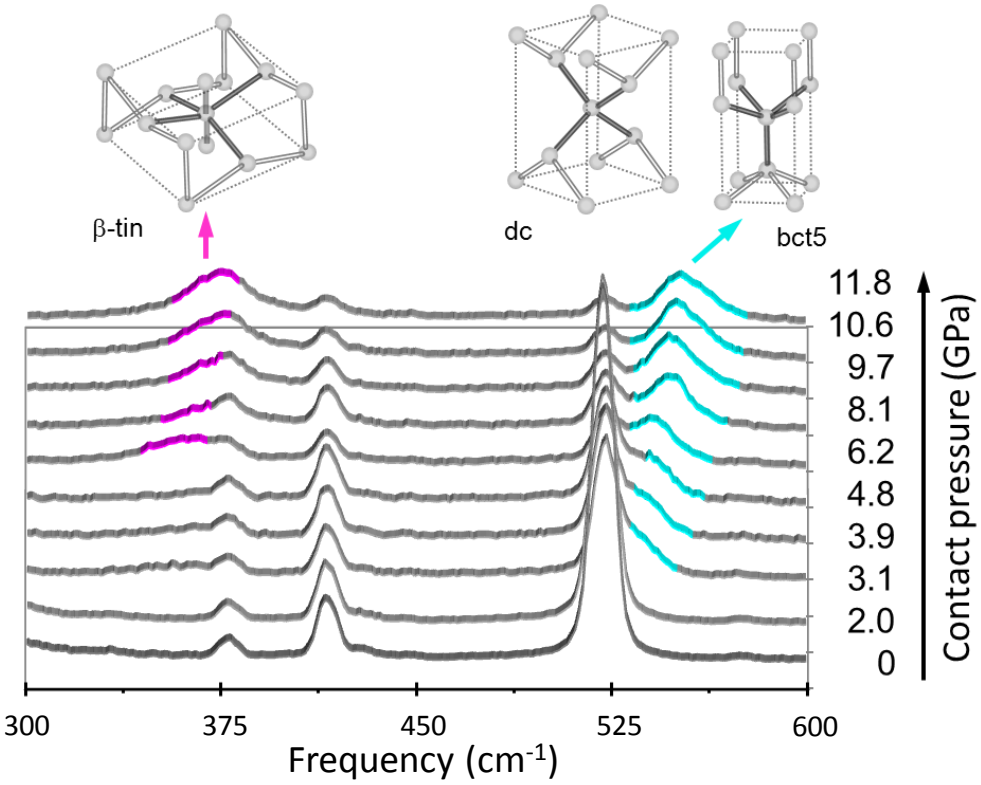

Figure 1. Sequence of 785 nm spectra of the mechanically deformed region of an SoS thin film taken as function of increasing contact pressure showing the phase transformation path.

It is also possible to image the spatial extent of the phase transformed region by measuring a laser scanning Raman image while holding the sample under constant contact pressure. Although these images may take several hours to acquire, tests of the displacement and force stability have been performed that indicate the system is sufficiently robust to perform such measurements. Figure 2 is a 10 x 10 μm image showing the bct5 Raman band area (~550 cm^{-1}) at a contact pressure near 10 GPa with the gray scale bar shown below the image. The areas of high intensity indicate where the phase transformation has taken place to the greatest extent as they are also correlated with the loss of intensity in the band due to the diamond cubic phase. This is, to our knowledge, the first report of a Raman image of a material held under contact pressure and undergoing a phase transformation induced by mechanical deformation. Further imaging measurements aimed at understanding the spatial progression of the phase transformation as a function of contact pressure are ongoing.

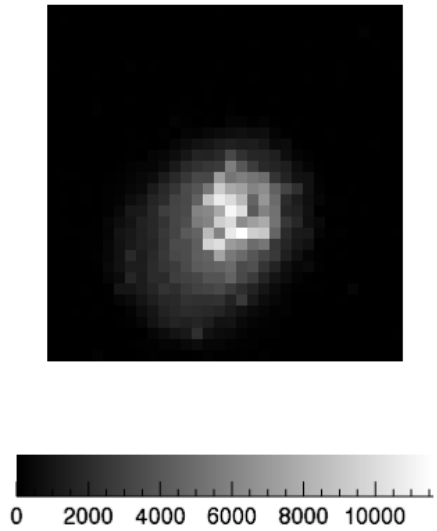

Figure 2. Laser scanning 785 nm Raman image of a SoS thin film held under contact pressure of approximately 10 GPa wherein the spectral band area of a peak due to the bct5 phase of Si is plotted.

4. Conclusions

A new indentation instrument that couples the ability to measure the mechanical deformation of transparent materials under contact loading with the ability to probe molecular or crystallographic level changes via Raman spectroscopy and imaging has been discussed. The application of this instrument in the study of mechanically induced phase transformations in a thin film SoS has been reported. Future work is focused on extending this approach to other classes of materials, including other semiconductors, polymers and fibers.

5. References

[1] Y.B. Gerbig, C.A. Michaels, A.M. Forster, and R.F. Cook, "In situ observation of the indentation induced phase transformation of silicon thin films," Phys. Rev. B **85,** 104102 (2012).

[2] Y.B. Gerbig, C.A. Michaels, A.M. Forster, J.W. Hettenhouser, W.E. Byrd, D.J. Morris, and R.F. Cook, "Indentation device for in situ Raman spectroscopic and optical studies," Rev. Sci. Instr. **83,** 125106 (2012).