

# UV Raman Scattering in 6H-SiC Indents

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## Introduction

While there have been many studies of the mechanical properties of single crystal silicon, the lack of similar research on single crystal SiC may limit the application of this high temperature, refractory material. In this study, ultraviolet (UV) micro-Raman spectroscopy is employed to investigate the effects of plastic flow and induced stresses in single crystal 6H-SiC subjected to high-pressure indentation. Indentation provides a method to study a material's resistance to plastic deformation under high pressure. The pressures that are achieved at the contact points between the indenter tool and the material can cause the structure of the material's lattice to distort, change form, or fracture. In some cases a small amount of stress, or strain in the lattice, can enhance a device [1]. However, a large amount of stress can directly lead to the formation of voids and cracks in areas extending outward from the point of highest stress. This effect can lead to eventual mechanical failure in devices [2].

UV Raman spectroscopy allows for the nondestructive investigation of materials, and with micro focusing optics the information can be obtained for a small collection volume. Moreover, the short absorption depth of light allows accurate probing of the surface of the indented region. Many other methods of material analysis, which are destructive to the sample, can cause stress relaxation and present misleading results.

## Experiment

A Berkovich diamond indenter tip shaped as a three-sided pyramid is used to create triangular shaped indentations. The tip is brought into contact with the material at a constant loading rate of 5mN/sec under a load of 200 mN and 400 mN. Various conditions can affect the resulting plasticity of the material from the indenter. These conditions include the loading and unloading rates, the geometry of the indenter, the indenter size, annealing conditions, and the load amount. All indents were performed on the (0001) surface of the 6H-SiC. This surface corresponds to the Si-face of an ideally terminated structure.

The Raman spectra are collected in a 180° backscattering geometry. The laser power into the microscope is measured as ~50 mW. The laser light is focused with a 40x objective lens to a spot size with a diameter of 600 nm. Visible light is not a good choice of wavelengths for Raman measurements of the surface of this material because it has a photon energy less than that of the bandgap SiC, and the SiC is, therefore, transparent. A UV wavelength of 244 nm is chosen to reduce the laser probing depth to 87.6 nm (where the penetration depth is determined at the point of 10% of the incident intensity), and therefore, reduce the collection volume to .025  $\mu\text{m}^3$ . The Raman peaks (center frequency shift and full width at half maximum) are analyzed by fitting to a Lorentzian function or a mix of Lorentzian and Gaussian function for the most accurate fit.

## Results

Raman spectroscopy uses monochromatic radiation to detect a difference in energy between incident and transmitted light. The interaction of the electric field component of light with a material can create or annihilate lattice vibrations. The amount of energy absorbed or emitted in a vibration is specific to a material and its bonding structure.

According to quantum mechanics, a vibration is Raman active if the polarizability of the solid changes during vibration [3]. The first-order Raman selection rules for 6H-SiC (uniaxial crystal structure) allow for indirect

observation of lattice vibrations corresponding to the  $k \approx 0$  optical phonons. These vibrations include doubly degenerate transverse optical modes (TO), which are derived from atomic displacements perpendicular to the  $c$ -axis, and a nondegenerate longitudinal optical mode (LO), which is derived from atomic displacements parallel to the  $c$ -axis [4].

In this study, the intense TO frequency at  $789.77 \text{ Rcm}^{-1}$  ( $E_2$  symmetry) and the LO frequency at  $966.79 \text{ Rcm}^{-1}$  ( $A_1$  symmetry) are analyzed. (We employ the notation,  $\text{Rcm}^{-1}$ , to represent the wavenumber shift of the observed mode from the incident laser frequency. In all measurements the Stokes shifted spectra are presented.)

Local stress in a material will typically cause the frequency of the  $k \approx 0$  optic phonons to shift to a higher value under compression and a lower value under tension. Figures 1a and 1b present the Raman spectra for the TO and LO modes of vibration of the indented 6H-SiC sample. In comparison to the reference spectrum, which is collected far from the indent, the Raman peaks are shifted to higher frequencies inside and surrounding the indent indicating compressive stress. A maximum shift in the center of the indent signifies that the region of the contact point of the diamond tip and the 6H-SiC is the zone of maximum stress. The stress decreases outward from the center as is indicated by the decrease in frequency shift of the Raman peak.

## Discussion

According to prior studies of hexagonal SiC, the mechanical stress can be calculated from the measured shift in the corresponding TO and LO Raman peaks with the following power-law approximation [5],

$$\begin{aligned}\omega_{\text{TO}} (\text{cm}^{-1}) &= 789.77 + 3.11\sigma - 0.009\sigma^2 \\ \omega_{\text{LO}} (\text{cm}^{-1}) &= 966.79 + 3.83\sigma - 0.013\sigma^2,\end{aligned}$$

where  $789.77 \text{ Rcm}^{-1}$  and  $966.79 \text{ Rcm}^{-1}$  are the relaxed values in the TO and LO modes respectively and stress,  $\sigma$ , is measured in stress GPa. In the center of the indent obtained with an indenter load of 400 mN, the Raman peak shifts correspond to a stress as high as 2.899 GPa as determined from the TO mode and 1.093 GPa as determined from the LO mode frequency. The stresses calculated from the measured TO and LO optic mode shifts under indenter loads of 200 mN and 400 mN are graphed in Figure 2.

The elastic/plastic contact of a sharp indenter results in a plastic deformation zone of hemispherical symmetry. Tensile stress outside the plastic zone permits outward extension of lateral, median, and radial cracks. Within the plastic zone, compressive stress can terminate crack formation [6]. The detection of compressive stress indicates that the probing depth of the UV Raman measurements is within the plastic zone.

The stress deduced from the LO and TO Raman modes is not equal, however, the difference in the deduced stress becomes closer in the zones of greater stress. The non-uniformity in deduced stress indicates that this material exhibits biaxial compressive stress. Similar experiments that were performed by Liu et al., on 6H-SiC subjected to high hydrostatic pressures in a diamond anvil cell indicate that the splitting reaches a saturation point at  $\sim 60$  GPa. The TO and LO Raman modes were observed to pressures as high as 95 GPa demonstrating the structural stability of this material. It is also reported that the transverse effective charge increases with pressure, reaching a maximum at  $\sim 40$  GPa, and then decreases, suggesting changes in the electronic structure of the material with compression [5].

It is interesting to note that in addition to a peak shift, the peaks show broadening in areas inside and close to the indent. This broadening is attributed to a gradient of stress found within the laser collection volume, and each peak can be fitted to a distribution of Lorentzian peaks. It is possible that a component of the broadening of the TO mode is due to splitting on the double degeneracy of the mode. However, this would require non uniformity in the plane of the substrate, which may be unlikely for the indents. In the stress determinations, the center value of the broadened peak was employed and the possible mode splitting was not considered.

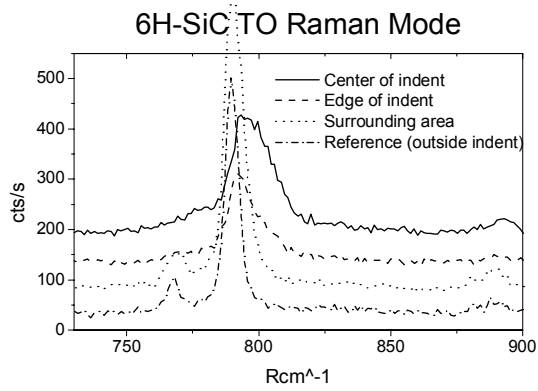
## Conclusions

Indentation allows for the study of material plasticity under high pressure. As the demand for products of higher precision is increasing, it is becoming essential to understand the surface deformation of materials on a nanometer scale. Micro-Raman spectroscopy has proven to be a convenient tool for obtaining information about the structure of a material. In this study, the small probing depth of UV light allowed for investigation of the plastic zone caused by indentation. It was found that 6H-SiC subjected to indentation exhibits biaxial compressive stress in regions close to the indentation surface. Stress and stress gradient is greatest near the center of the indent and in the direction perpendicular to the c-axis.

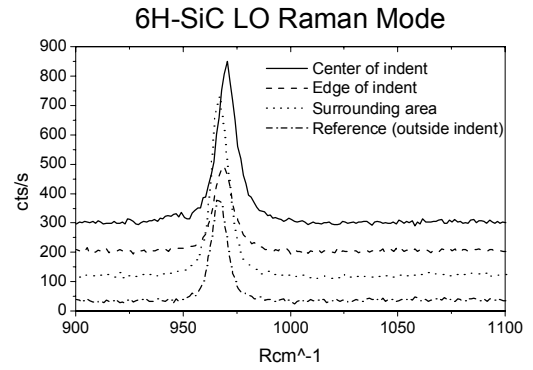
## References

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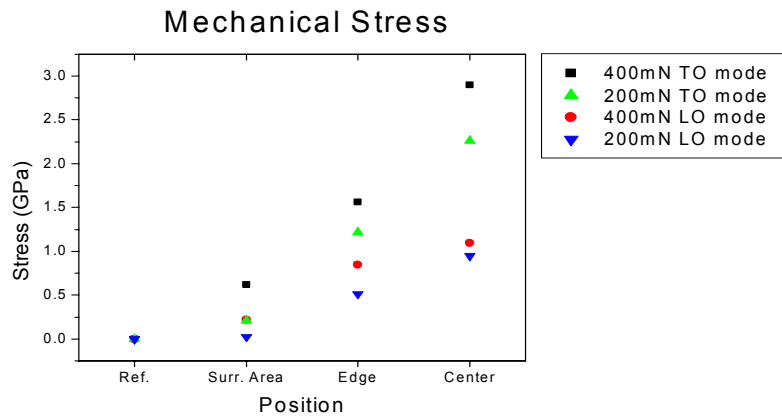
(a.)



(b.)



**Figure 1:** UV micro Raman spectra which display the (a.) TO and (b.) LO modes of vibration for different regions around an indent produced with a load of 200 mN. The reference data is obtained from outside the indent and represents unstressed 6H-SiC. The spectra shifted from this value are collected in regions in and surrounding an indent.



**Figure 2:** The local stress (in units of pressure) in regions in and surrounding an indent for the transverse (TO) and longitudinal (LO) Raman modes. The results were obtained from indents produced from loads of 200 mN and 400 mN.