Indentation Induced Structural Changes Probed by Raman Spectroscopy

Introduction

Raman spectroscopy is a widely-used nondestructive chemical analysis method which can detect changes in the stress state, molecular orientation, crystallinity and phase transformations in materials. Combining Hysitron’s nanomechanical test instruments with Raman spectroscopy enables in-situ analysis of mechanical properties and corresponding physiochemical changes.

In-Situ Indentation and Raman for Pharmaceutics

In the pharmaceutical industry, detection of different polymorphs of drug materials is critical as any changes in the composition or structure may lead to a different clinical response. The present study investigates mechanical anisotropy and stress induced structural changes in single crystal β-form piroxicam (anti-inflammatory drug). The variation of mechanical properties in the (0T1) and (011) crystallographic planes and the associated chemical changes under indentation were studied in detail. Hysitron’s TI 980 TriboIndenter® platform system was used for mechanical characterization and a custom-built indentation device was used for in-situ Raman. Anisotropy in mechanical behavior was observed along (0T1) and (011) crystallographic planes.

In-situ Raman spectra recorded from the contact region detected changes in the chemical bonding. The main building block of the piroxicam crystal is acentrosymmetric dimer of piroxicam molecules connected by two N−H···O (3.055Å) hydrogen bonds. Each molecule in the dimer interacts with neighboring dimers via six C−H···O hydrogen bonds to form infinite corrugated two dimensional layers that are parallel to the (010) plane. The interactions between separate two dimensional layers comes from one C−H···O hydrogen bond and one π···π stacking interaction. Thus, the principal slip planes are along the (010) planes, which was reflected by lower hardness on (011) surface (Figure 2) during indentation. In-situ Raman spectra recorded during indentation on (0T1) face showed a shift in 1334 cm⁻¹ band, corresponding to SO₂ asymmetric stretching, over a normal load variation from 3 to 20mN (Figure 2). In case of (011) face,
the in-situ Raman spectra did not show a shift in $SO_2$ stretching modes; instead a small peak shift is observed at 990cm$^{-1}$ which corresponds to C-O stretching. At higher loads (15, 20mN) the 990cm$^{-1}$ band shifted to 995cm$^{-1}$; this red shift in the C-O stretching vibration indicates a break in O-H··O intermolecular interaction during indentation. It is reasonable to conclude that the deformation resulted in a different bonding re-arrangement for (0T1) and (011); an intra-layer interaction modification (C−H···O interactions) observed for (011) as compared to an interlayer interaction modification seen in case of (0T1). Furthermore, the observed mechanical anisotropy is not solely related to the alignment of crystal planes but also the interlayer chemical interactions contributed to the enhanced hardness of the (0T1) surface. The results demonstrate the capability of the in-situ Raman indenter to collect the chemical as well as mechanical information real time, which can be correlated to gain deeper understanding of material behavior.

**Indentation Induced Phase Transformation in Monocrystalline Silicon**

Combining Hysitron’s TI 950 or TI 980 system with Raman spectroscopy enables mechanical and chemical mapping of the sample of interest. Indentation induced phase transformation in silicon is one of the most studied phenomenon for the last few decades. Figure 3 demonstrates the capabilities of the combined indentation and Raman system, where combined high resolution SPM imaging and Raman mapping enables local topographical and chemical variation characterization. The Raman map in Figure 3 shows an indentation induced phase transformation zone in monocrystalline silicon. A Raman line scan profile generated across the indent showed a variation in diamond cubic 520cm$^{-1}$ band, where compressive stresses at the edges shifted the dc peak to higher wavenumbers. In the phase transformation zone corresponding to amorphous silicon, r8 and bc8 phases of silicon were observed.

**Conclusion**

Hysitron’s TI 980 combined with Raman spectroscopy enables chemical and quantitative ultra-high speed nanomechanical property mapping in a single platform. Hysitron’s 2D capacitive transducer technology enables friction and wear testing at nanoscale which can also be combined with Raman mapping to help researchers gain further insight on interfacial phenomenon and thus develop new advanced coatings or materials. Hysitron preserves the concept of modularity with Raman instruments; therefore, almost any laser source and spectrometer can be used with Hysitron’s Raman solution.

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