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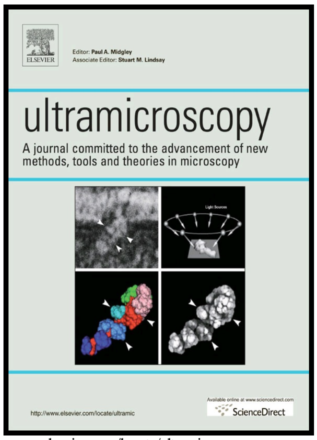

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In situ TEM Raman spectroscopy and laser-based materials modification

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Abstract

We present a modular assembly that enables both *in situ* Raman spectroscopy and laser-based materials processing to be performed in a transmission electron microscope. The system comprises a lensed Raman probe mounted inside the microscope column in the specimen plane and a custom specimen holder with a vacuum feedthrough for a tapered optical fiber. The Raman probe incorporates both excitation and collection optics, and localized laser processing is performed using pulsed laser light delivered to the specimen via the tapered optical fiber. Precise positioning of the fiber is achieved using a nanomanipulation stage in combination with simultaneous electron-beam imaging of the tip-to-sample distance. Materials modification is monitored in real time by transmission electron microscopy. First results obtained using the assembly are presented for *in situ* pulsed laser ablation of MoS_2 combined with Raman spectroscopy, complimented by electron-beam diffraction and electron energy-loss spectroscopy.

Keywords: *in situ* TEM, Raman spectroscopy, pulsed laser ablation, MoS_2

1. Introduction

Raman spectroscopy is a versatile tool for the characterization of molecules and condensed matter, probing inelastic scattering interactions of photons with vibrational, rotational and other low-frequency modes. In materials science, Raman spectroscopy is thus used to probe plasmons, phonons, and magnons, providing information on chemical composition, temperature, stress/strain, and magnetization[1]. The laser beam used for the excitation can be scanned across a sample to generate Raman spectra pixel by pixel. Through integration onto a microscope platform, these Raman images can then be correlated directly with the information yielded by various other imaging techniques. For example, integrated assemblies for confocal microscopy[2], scanning electron microscopy (SEM)[3], and atomic force microscopy (AFM)[4] have been developed, thereby combining Raman spectroscopy with different flavors of surface imaging at various spatial resolutions. The focus of the work presented here is on a new approach for combining Raman spectroscopy with transmission electron microscopy (TEM), paving the way to rich datasets in which Raman signals can be correlated directly with structural features and chemical compositions in small volumes imaged at the nanoscale.

A major challenge in Raman spectroscopy is the limited signal strength, since the cross sections for Raman scattering are inherently low. Therefore, efficient methods for coupling light to and from the sample are required. If the *in situ* experiment is to take place in vacuum, as is the case with SEM and TEM, then a low-loss means to couple optics to the sample in the vacuum chamber of the microscope is needed. In addition, in the case of TEM, the Raman assembly must be designed to meet the stringent height requirements imposed by the pole-piece gap in the objective lens, which is at most ~10 mm. In the *in situ* TEM Raman approaches developed thus far[5, 6], optical access is achieved through a viewport installed on the microscope column. A parabolic mirror mounted near the specimen is then used to focus the incoming light and to collect the outgoing optical signals that pass back through the viewport to the spectrometer. *In situ* TEM Raman spectra have been acquired for diamond[5], silicon[6], and carbon nanotubes[6], employing optical illumination in the far field with spot sizes of several microns. Picher *et al.*, whose setup is integrated into a microscope optimized for environmental TEM, have also demonstrated the measurement of sample temperature via the downshift of Raman peaks[6].

Here we introduce a novel modular system for *in situ* TEM Raman comprising a lensed Raman probe with optics for excitation and collection, and a nanomanipulation sample holder with a vacuum feedthrough for a tapered optical fiber. The assembly is installed on an electron microscope equipped with an energy filter, hence enabling electron energy-loss spectroscopy (EELS) to compliment the Raman spectra. Since the Raman probe is installed inside the microscope column and collects optical signals from the sample directly, mirrors and an optical viewport are not required. The direct coupling of an optical fiber to the sample chamber via the sample holder follows a method developed previously and enables localized laser illumination (pulsed or continuous wave) through close approach of a tapered fiber to the specimen for nanoscale *in situ* investi-

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