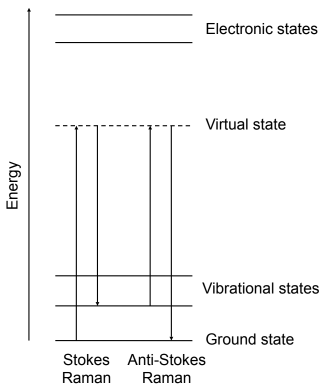
Femtosecond laser-nanostructured substrates for surface enhanced Raman scattering

Eric D. Diebold and Eric Mazur
Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA

Introduction: Raman Scattering



Raman scattering is an inelastic process in which an incident photon is scattered by a molecule. By detecting the energy of the emitted photons, a spectrum is obtained which corresponds to the quantized vibrational energy levels of the molecule. Since each molecule has a unique vibrational spectrum, Raman scattering can be used for detection and identification spectroscopy.

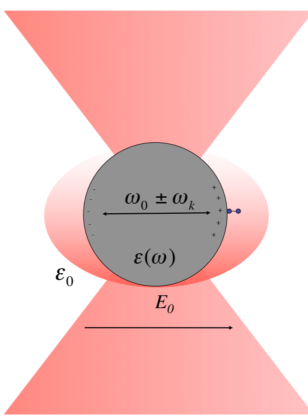
The difference in energy between the incident and scattered photon is measured in wavenumbers, given by:

$$\Delta \upsilon\ (\mathrm{cm}^{-1}) = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}$$

Surface enhancement

Raman scattering cross sections are extremely small (~10^{-30} cm^2). However, the cross section can be increased by several orders of magnitude if the molecule is placed in the near field of a plasmonic resonant surface. For an example of the surface enhancement process, we examine the Raman scattering of a molecule adsorbed on the surface of a sphere of radius *r* in the Rayleigh limit ($r < 0.05\lambda$).

1. An applied optical field polarizes the sphere, resulting in an enhanced electric field, spatially confined to the surface.
2. The enhanced field excites a Raman transition
3. The Raman scattered field causes a polarization of the sphere at the Raman frequency
4. The sphere polarization radiates into the far field



The electromagnetic enhancement of the Raman scattering cross-section for a molecule located at a distance *d* from the sphere surface can be described by

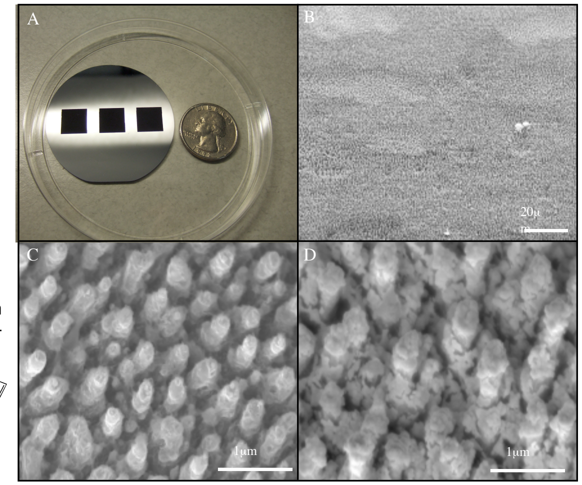
$$\sigma' \propto \sigma \left|\frac{\varepsilon(\omega)-\varepsilon_0}{\varepsilon(\omega)+2\varepsilon_0}\right|^2 \left|\frac{\varepsilon(\omega)-\varepsilon_0}{\varepsilon(\omega)+2\varepsilon_0}\right|^2 \left(\frac{r}{r+d}\right)^{12}$$

where σ is the molecular Raman scattering cross section.

Femtosecond laser-structured substrates

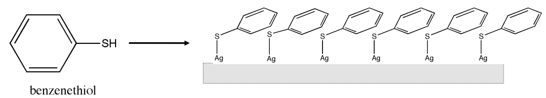
Substrates are fabricated using a frequency-doubled, amplified Ti:Sapphire femtosecond laser. The resulting nanostructured surfaces are coated with silver via thermal evaporation.

Right: Femtosecond laser nanostructured silicon substrates. A. Silicon wafer after processing B,C. SEM images of structured surfaces D. Surface after coating with silver



Experimental procedure

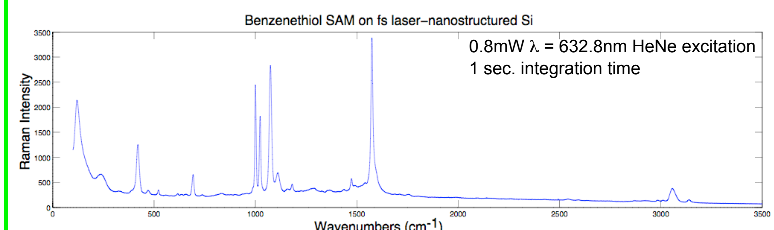
In order to quantify the Raman scattering cross-section enhancement of the surfaces, we apply a benzenethiol self-assembled monlayer (SAM) to the silver-coated substrates.

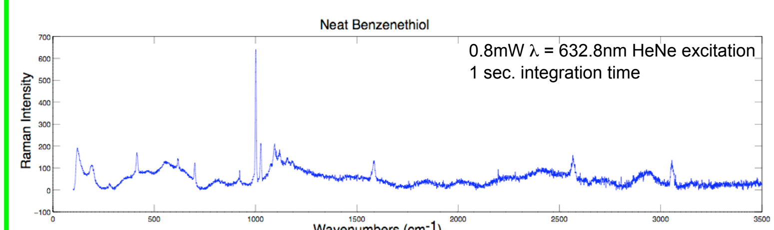


Experimental results

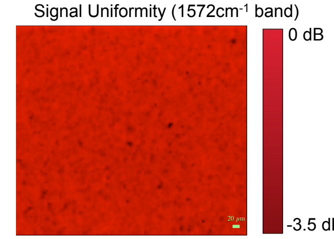
By collecting spectra from both the SAM sample and from a neat sample of benzenethiol, we can normalize the integrated intensity of the bands to calculate the Raman enhancement factor

Enhancement factor (1000 cm^{-1} band) 1.9×10^{10}
Enhancement factor (1572 cm^{-1} band) 1.5×10^{11}

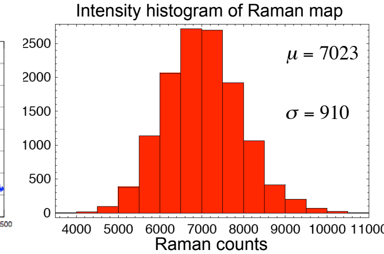




Signal Uniformity (1572cm^{-1} band)



Intensity histogram of Raman map



Acknowledgements: This work is supported by the NDSEG fellowship, Army Research Office, and the Center for Nanoscale Systems at Harvard University

http://mazur-www.harvard.edu