Near-field Raman spectroscopy has opened a way for molecular analysis and identification of various materials with true nanoscale resolution. It enables advances in areas of biophysics such as characterizing tissues to studying physical and chemical properties of today’s electronic devices. The most popular tool for near field Raman spectroscopy is tip-enhanced Raman spectroscopy (TERS) [1] because of its nondestructive capability for high spatial resolution beyond the diffraction limit. TERS uses surface plasmon resonance (SPR) in metallic nanoparticles when illuminated with visible light [2]. A sharpened metallic tip (usually silver, Ag, or gold, Au, coated tips) is used which acts as a point surface enhancement. The spatial resolution, comparable to the size of the tip, has been successfully demonstrated. In TERS, detecting signal from a very small scattering volume is still a challenge because scattering signal rapidly vanishes below the background level. Moreover, collecting high signal in the presence of strong background field from the total illuminated area and underlying thick substrate makes it even harder to obtain high-contrast Raman signal. Strong background signals are observed for opaque, bulk and multilayered samples because the same objective lens is used for illumination and detection [3-4].

In this work, we demonstrate several techniques to obtain high contrast Raman signals in strained silicon (ε-Si) assembled on silicon germanium substrate (SiGe) in the visible range. We present ways to overshadow strong far-field background signals from Raman active materials by utilizing the results obtained from depolarized surface-enhanced Raman scattering (SERS) experiments in conjunction with silicon Raman tensor calculation to quantify at which polarizer, analyzer and sample azimuth combination gives the minimum far-field signals for background suppression [5]. Unlike most TERS studies, we utilize the s-polarization instead of p-polarized light in conjunction with polarization properties of ε-Si to obtain high contrast Raman signal. The utilization of edge filter for shorter collection time, specialized tip for higher field enhancement, shorter wavelength, sample orientation relative to probing polarization, and depolarized configuration for higher Raman signal contrast are presented. Both the field enhancement effect and depolarization effect were considered to obtain a high contrast TERS signal [6].

Figure 1 shows the reflection mode TERS used in the experiment. The laser beam is introduced at $\phi=60^\circ$ relative to the ε-Si normal (z-axis). The sample azimuth is varied to obtain the maximum and minimum Raman intensity level for both p- and s-polarization of incident light. The p-polarized Raman spectra is detected and recorded using the CCD camera. The laser power was set at 9.8mW with collection time of 3min. We used 442nm (HeCd) excitation light with silver coated Si3N4 tip. The inset shows the 50nm Ag coated tip by evaporation at the rate of $\sim0.5\AA/s$ and under the $\sim10^{-6}$ Torr vacuum pressure. To demonstrate background signal reduction in TERS, we compared experimentally the TERS spectra between P-P-max and S-P-min whose only difference is the incident polarization. P-P-max means, polarizer is P, analyzer is P, and “max” is the sample orientation where “max” denotes maximum far-field intensity level. P-P-max gives the maximum while S-P-min provides the minimum far-field intensity level. The far-field (blue) and
TERS (red) spectra obtained from P-P-max and S-P-min configurations are shown in Fig. 2(a) and 2(b), respectively. Each spectrum is decomposed into two Lorentzian function (dashed lines) for analysis. The relative contrasts, ratio between e-Si and SiGe were calculated from the ratio area under the Lorentzian curves. The contrast for each photon mode is indicated in the plots (e.g. 15x and 1.6x for e-Si in S-P-min and P-P-max, respectively). TERS experiments suggest that P-P-max gives the highest signal intensity and good for faster data acquisition in microscopic Raman studies. The S-P-min shows the highest contrast at 15.7 between e-Si and SiGe layers. Results show that S-P-min condition strongly reduces the background signal but also reduces the tip-enhancement effect due to s-polarized incident. On the other hand, P-P-max condition shows higher tip-enhancement effect due to p-polarized incident light but the presence of strong far field background reduces the contrast between strained Si and SiGe. The contrasts difference between P-P-max and S-P-min is not only due to depolarization effect from tip but also due to the minimum far-field Raman intensity level offered by s-polarized light. The strong far-field Raman signal that comes from the focus with high transmittance at the surface in P-P-max is mostly p-polarized and allowed to pass through P-analyzer setting, and thus, strong SiGe Raman signal. The depolarized TERS signals, which are converted from p- to s-polarization, cannot pass through the P-analyzer setting. On the other hand, for the S-P-min configuration, both the s-polarized incident light and far-field Raman signal are depolarized into p-polarized light by the tip. The depolarized TERS Raman signal can pass through the analyzer while the s-polarized far-field signal is blocked. Since we blocked the s-polarized far-field Raman signal, we suppressed contributions from strong unwanted SiGe signals. Hence, for imaging Raman active and bulk crystalline materials such as silicon, background signal suppression (s-illumination) is more important than the field enhancement with strong far field Raman signal level (p-polarization).

参考文献