Raman spectroscopy using a fiber optic probe with subwavelength aperture

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Raman spectroscopy with subwavelength spatial resolution of a diamond sample was recorded using a tapered fiber optical probe in conjunction with a conventional Raman spectrometer. The experiment demonstrates the potential of suboptical wavelength resolution analytical spectroscopy. The tapered fiber optical probe with an aperture of around 100 nm, served as the means for delivering pump radiation while simultaneously collecting the Stokes radiation from the diamond specimen. Comparing the magnitude of the Raman scattering measured with the submicron single mode fiber probe to similar signals obtained with a nontapered probe made of the same type of fiber, illustrates the potential increase in effective optical aperture resulting from the close approach of the fiber to the surface.

Near-field optical scanning microscope has attracted considerable interest as an instrument for imaging topographic and surface relief details of optical samples with spatial resolution below the diffraction limit.[1,2] Lateral resolutions of λ/20 and vertical resolutions of λ/100 have been claimed as achievable from the various near-field microscopes.[3–6] It is achieved in practice by scanning a miniature light collection or emission aperture of suboptical wavelength dimension over the observing sample surface.

Although the earliest applications of the near-field microscopes were concerned with surface imaging, it subsequently became evident that the use of the instrument could be extended to an analytical function. For example, information about the surface could be obtained by spectroscopic analysis of the light which the nanoprobe collects when the surface layer is illuminated to produce photoluminescence, fluorescence, or Raman signals. Such spectroscopic information would enable nondestructive chemical, physical, or biological analysis of the sample surface to be achieved on a subwavelength scale.[7]

In this letter we describe the use of a tapered submicron size fiber optic probe as a means of both conveying laser radiation to the surface of an optical sample material and then collecting light scattered from the sample. The tapered fiber allows the detection of Raman spectroscopy from regions of the sample surface that are an order of magnitude smaller in size than the core of a typical single mode fiber. Our investigation is motivated by the eventual realization of a nanometric resolution spectroscopic optical analytical microscope.

A schematic of the experimental setup is shown in Fig. 1. This consists of a Krypton ion laser which provides the light source for Raman scattering, a 2×2 single mode fiber optic coupler with a 1:1 coupling ratio, a viewing microscope, a Triplemate 1877 Spex spectrometer, and a silicon charge coupled device (CCD) cooled at liquid nitrogen temperature. Light at a wavelength of 530.8 nm from the Krypton laser was focused into port A of the fiber directional coupler. The fiber at port C of the coupler is a tapered fiber end terminating in a submicron delivery/collection aperture. Fiber port D was terminated with a cleaved end with the diameter of the fiber core at 4 μm. Positioning of the fiber on the sample surface was controlled by a three-axis translation stage with a positioning accuracy of 100 nm. The separation between the tip and sample surface is estimated to be less than 100 nm based on the near-field signal. Light collected from the sample using the fiber probe was directed into the monochromator for spectral analysis by the objective lens *L* of the viewing microscope. This lens collected and collimated light exiting from fiber port B of the coupler. Basically, the experimental arrangement can be described as the introduction of a special fiber optic "extension" to a conventional laser Raman microscope to allow remote submicron Raman analysis to be performed.

The tapered fiber tips were fabricated by pulling a quartz

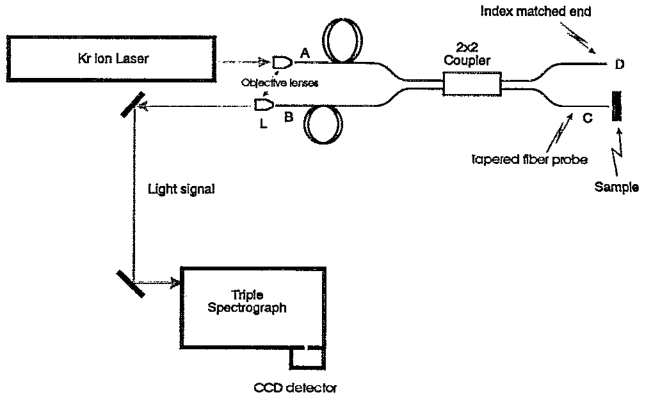

FIG. 1. Schematic of the experimental setup.

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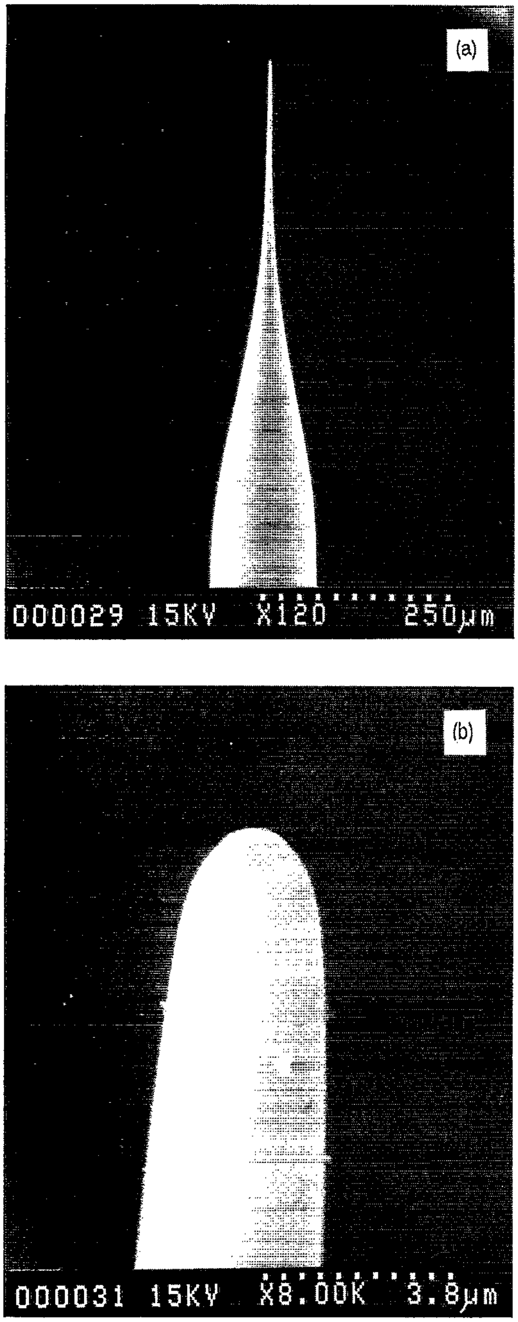

FIG. 2. (a) SEM photographs of a tapered fiber tip. (b) The tip region at higher magnification. Calibration bars are at the bottom right of figures.

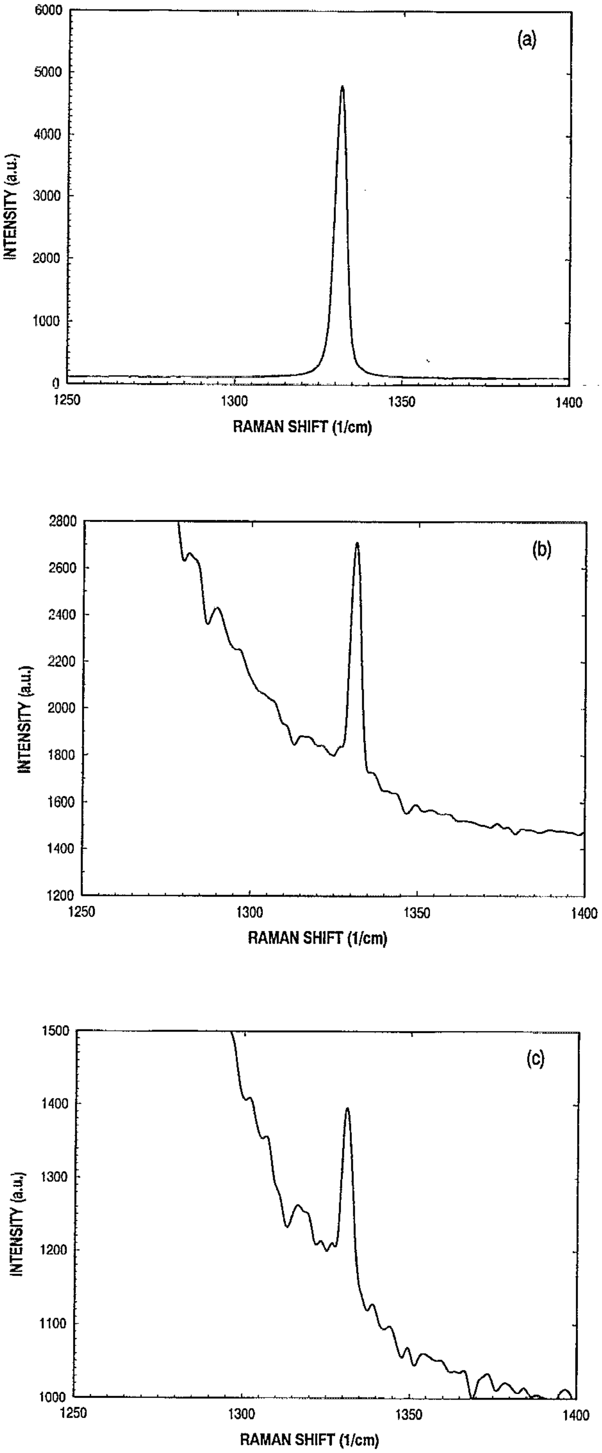

FIG. 3. (a) Raman spectrum generated from a diamond sample using a conventional Raman microprobe. (b) and (c) are the Raman spectra generated from the same diamond sample by using a flat end and a tapered fiber, respectively, as emitter and collector.

single mode step index fiber with 4 and 125 μm diam of core and cladding, respectively, from a 2×2 coupler, at constant force while locally heating it in the discharge produced by the arc electrodes of a commercial fiber splicer. Figure 2 shows SEM photographs of a tip we used. The flat end shown in the high-magnification inset of Fig. 2(b), is characteristic of most tips we produced in the melting and pulling process. Its 1.2 μm diam includes both the cladding and core. Although the contraction ratio of the cladding and core cannot be determined separately, we found[8] that fibers sharpened in the manner used in this study, have effective optical apertures of approximately 100 nm. Moreover, the taper angle of the end of the probe in Fig. 2 is approximately 40°. This should result in a probe with numerical aperture approximately equal to 1 for far-field collection, substantially greater than the original numerical aperture of 0.1.

The system was initially tested by observing the light which was scattered back into the detection system from the fiber itself. Two sources of such light scattering can be identified. The first is the light scattered into the collection fiber port B from scattering within the fused region of the directional coupler and from the tapered region in the probe fiber (the fiber end D was dipped into an index matching oil to minimize reflections). Light generated in silica fibers through the Raman effect has a broadband Stokes signal with components at Raman shifts of 450, 800, 1055, and 1195 cm^{-1} (due to SiO_4 vibrations), 491 and 604 cm^{-1} (due to defects), 970 cm^{-1} (due to Si-OH vibrations). Raman signals generated from the sample at the above wave numbers will, therefore, be concealed by the Raman signals generated from within the fiber unless suitable compensation techniques involving mathematical processing of the spectra are utilized when analyzing the return signals. In our initial investigations, such compensation techniques were avoided by using a sample material whose Raman spectrum has a peak outside the range of Raman values produced from the fibers. The material used was a 2 mm×2 mm×3 mm polished industrial diamond (Stokes shift at 1332 cm^{-1}), which is also known for its generation of strong Raman signals.[9]

Figure 3(a) shows the Raman spectrum generated from the diamond sample using the conventional Raman microprobe and a 40× objective lens both to focus and to collect light from the sample surface. Figure 3(b) shows the Raman spectrum with the characteristic phonon peak at 1332 cm^{-1}, generated from the same diamond sample by using a flat-end fiber as emitter and collector (i.e., the port D of Fig. 1). Similarly, Fig. 3(c) shows the Raman spectrum of the same sample collected using the tapered fiber probe. The intensity ratio of the diamond phonon band obtained with the flat-end fiber to that of the tapered fiber is approximately 4:1, as compared to the core diameter ratio that is approximately 40:1. The larger than expected intensity ratio can be explained by the smaller high numeric aperture of the tapered probe as compared to the flat-end fiber conditions which offsets the reduced diameter of the fiber.

The factor of 10 increase is, in fact, in accord with what is expected for an increase in numerical aperture by approximately a factor of 10. However, arguments based on far-field optics are not strictly applicable in this case. For a small enough probe, the optical response of tip and surface must be solved. Likewise it would be more fruitful to consider the tip as a dipole radiating into a light guide rather than as an aperture passing incident radiation, Shalaev *et al.*[10,11] to be published.

In summary, we have demonstrated the use of a submicron diameter fiber as a means for illuminating a sample and collecting Raman scattering light. Such a probe, when used in conjunction with conventional Raman spectrometers, will form the basis of a suboptical wavelength resolved analytical instrument for high resolution surface analysis.

[1] W. Denk and D. W. Pohl, J. Vac. Sci. Technol. B **9**, 510 (1991).
[2] M. Isaacson, J. A. Cline, and H. Barshatzky, J. Vac. Sci. Technol. B **9**, 3103 (1991).
[3] T. L. Ferrell, S. L. Sharp, and R. J. Warmack, Ultramicroscopy **42–44**, 408 (1992).
[4] E. Betzig and J. K. Trautman, Science **257**, 189 (1992).
[5] D. W. Pohl, U. C. Fischer, and U. T. Durig, J. Microsc. **152**, 853 (1988).
[6] R. C. Reddick, R. J. Warmack, D. W. Chilcott, S. L. Sharp, and T. L. Ferrell, Rev. Sci. Instrum. **61**, 3669 (1990).
[7] M. A. Paesler, P. J. Moyer, C. J. Jahncke, C. E. Johnson, R. C. Reddick, R. J. Warmack, and T. L. Ferrell, Phys. Rev. B **42**, 6750 (1990).
[8] D. P. Tsai, Z. Wang, and M. Moskovits, Proc. SPIE **1855**, 93 (1993).
[9] S. A. Solin and A. K. Ramdas, Phys. Rev. B **1**, 1687 (1970).
[10] V. M. Shalaev, R. Botet, D. P. Tsai, J. Kovacs, and M. Moskovits, Physica A (to be published).
[11] D. P. Tsai, J. Kovacs, M. Moskovits, J. S. Suh, R. Botet, and V. M. Shalaev (unpublished).