Spectroscopy and Imaging Using the Photon Scanning-Tunneling Microscope

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Introduction and Background

Despite the diffraction-limited resolution of optical microscopes, it is evident that their low cost, convenience, kinship to vision, and compatibility with optical spectroscopy have maintained them in broad use in modern laboratories and industry. Many refinements are available (confocal microscopes, for example), but the best resolution is roughly half the wavelength of the light that is employed because diffraction limits the performance of lens and mirror elements. When parallel imaging (as in a photographic process) is not the best form, there are scanning systems available although there are an increase in cost and some sacrifice of time and convenience. The advent of high-speed personal computers has made serial imaging (as in forming an image line-by-line) more attractive and less costly. The photon scanning-tunneling microscope (PSTM) is a new form of optical microscope which acquires its image serially, but performs much better than the diffraction limit.[1-4] Before describing it, we present some background information offered below.

Vastly improved spatial resolution is typically available when electrons are used in lieu of photons. This is true because the electrons used, say in scanning electron microscopes (SEMs) and transmission electron microscopes (TEMs), have much shorter wavelengths than visible photons. The disadvantages are that samples have to be placed in vacuum and considerable sample preparation efforts, such as slicing or coating with a conductor in a vacuum evaporator, have to be used in these forms of lens-based microscopy. The diffraction limit still obtains, and it quickly becomes very expensive to reduce the electron wavelength by going to higher energies in order to obtain atomic-scale resolution.

In the past decade the electron scanning-tunneling microscope (STM, or ESTM) has become available for imaging in either vacuum or air at atomic resolution on electrically conducting samples at a cost lying between that of optical microscopes and that of electron microscopes. This invention by G. Binnig and H. Rohrer overcomes the diffraction limit by acquiring its signal from tunneling electrons.[5] The electron waveform at a sample's surface has a steep exponential which decays over a distance of the order of 2 wavelengths. The ESTM uses a sharp metal probe to sense this decay. (A bias voltage is set between the probe and the sample and a tunneling current is engendered when the probe is positioned by a piezoelectric crystal to within reach of the exponential.) A change in tip-to-sample distance of 0.1 nm can cause a signal change of a factor of 10. The resolution of the ESTM on crystal surfaces is thus limited mainly by how accurately the exponential curve can be measured amid the noise that is invariably present.

The images produced by the STM are three-dimensional so that resolution must be specified in the normal direction as well as the more usual lateral direction. The exponential decay not only provides exquisite normal resolution but also limits the laterally sensed area around a given point so as to provide atomic-scale lateral resolution. The PSTM also detects a decaying exponential signal and is in fact the true optical analogue of the ESTM. Exactly how the analogy arises is described in the next section. The niche filled by the PSTM can be understood by noting the characteristics of other scanning-probe microscopes.

The ESTM can be operated in air, but does well at this stage of development to obtain 2-nm lateral resolution on even a thin layer of an electrically insulating sample placed on a conducting substrate. In fact, subatomic resolution is thus far limited to atomically-flat conductors and semiconductors. The ESTM has revolutionized microscopy, but at present there remains much research to be done on sample preparation methodology and on tunneling theory in order to facilitate diversification of its uses. Alternatives, such as the atomic force microscope (AFM),[6] have found a place in ultrahigh-resolution microscopy of insulators, but neither the ESTM nor the AFM offers spectroscopic resolution comparable to that obtainable with photons. The AFM is of considerable benefit when imaging electrically insulating samples, but its atomic resolution is also limited to flat surfaces. For DNA molecules, there are tip effects which usually make the biomol-

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(5) Binnig, G.; Rohrer, H. *Rev. Mod. Phys.* **1987**, *59*, 615.
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ecules appear 3–5 times larger than their true dimensions. This can be improved with better tips. The form of spectroscopy carried out with an ESTM is that of determination of the local electrical conductance of samples. For the AFM there are friction and elasticity measurements that help in identifying target compounds. But the best form of spectroscopy invariably involves photons for a host of reasons. If one is willing to give up some spatial resolution, the PSTM can be used to advantage spectroscopically. Moreover, there are many important optical measurements that can be made on various samples only by using a local optical probe. For example, measurements of the energy flux in optical waveguides as a function of location can be carried out without touching the sample if one uses a PSTM. Measurement of local optical properties extending over a broad range of the electromagnetic spectrum, studies of electromagnetic scattering from small objects, studies of holes and pits, and studies of fiber-optic sensors and optical waveguides provide a range of uniquely suitable areas of PSTM application. Moreover, unlike any other type of microscope, the PSTM can rather easily be extended to the X-ray regime where atomic resolution is possible. The PSTM does not need apertures, lenses, or mirrors, and its resolution normal to the surface is an unambiguous function of the wavelength used. Finally, the PSTM can be easily combined with standard optical microscopes to obtain a zoom capability.

The attractiveness of photons being significant for many reasons, it is not difficult to imagine that an STM using photons instead of electrons would be of benefit to microscopy. Indeed, quantum mechanics tells us that the tunneling of electrons can be described in the same way as the frustrated total internal reflection of photons. If one calculates electron transmission through a potential barrier, the results are formally identical to those of photon transmission through a barrier that presents a change in the index of refraction (if one considers photons in a beam polarized perpendicular to the plane of incidence). This is a key to the original concept of the PSTM, as discussed in the next section.

Basic Concepts for the PSTM

When a light beam inside a medium with index of refraction n encounters a plane boundary beyond which lies air (index of refraction essentially unity), the beam will be partially reflected and partially refracted. If θ is the angle that the beam makes with respect to the boundary normal inside the medium, increasing θ gives more reflected light. Beyond $\theta = \theta_c$, where

$$\sin \theta_c = 1/n$$

the light is totally internally reflected. The index n can be taken to be λ_0/λ, where λ_0 is the wavelength of the light in air. The wavelength in air is longer than the wavelength λ of the light in the medium. For quartz, $n = 1.457$ and θ_c is about 43°. Of considerable interest, however, is the fact that the electric field of the light, which is now traveling along the boundary, penetrates into the air with a decaying exponential dependence. Moreover, if a second plane-bounded medium is brought face-on to within a wavelength of the boundary in air, the light is no longer totally internally reflected and, instead, a portion will be observed propagating inside the second medium in a direction parallel to that of the beam in the first medium. The light is said to have suffered "frustrated total internal reflection".

Mathematically, the transmission coefficient for photons polarized perpendicular to the plane of incidence (s-polarized) is identical with that for electron tunneling provided one properly defines the relative index of refraction in terms of relative wavelengths instead of relative velocities. In order to understand this, image an electron of wavelength λ, say a free electron in a metal, normally incident on a plane boundary beyond which lies a potential energy barrier. If the electron's energy is greater than the height of the barrier, then the electron will be transmitted through the barrier. Within the barrier region let its wavelength be λ_0 and let the analogous index be $n = \lambda_0/\lambda$. Then an electron of this energy incident at or above $\theta_c = \sin^{-1}(1/n)$ will be totally internally reflected unless the barrier is of finite width. For a finite barrier the electron tunnels through, the dominant term in its wave function in the barrier region being a decaying exponential (unless the barrier width is small compared to λ_0, in which case there is also a significant positive-argument exponential). The transmission coefficient both for this case and for s-polarized photons across a planar gap separating two identical media is

$$T = \frac{1 - \cos \alpha}{\cosh 2b - \cos \alpha}$$

where $\cos(\alpha/2)$ is $[n^2 \cos(2\theta+1)]/(n^2-1)$ and for barrier width h the signal decay is controlled by

$$b = 2\pi hs/\lambda$$

with

$$s = (n^2 \sin^2 \theta - 1)^{1/2}$$

being a real number for $\theta \geq \theta_c$. For $h \geq 2\lambda/\pi$ the hyperbolic cosine is approximately $e^{2b}/2$, and this is the usual working regime of the PSTM wherein

$$T \approx \frac{8s^2n^2 \cos^2 \theta}{(n^2-1)^2} e^{-2b}$$

which explicitly shows the exponential nature of the signal.

Description of the PSTM

A diagram of the PSTM is shown in Figure 1. Light from a stable source such as a HeNe laser is directed into a hemicylinder so that the beam strikes the flat surface internally at an angle larger than the critical angle. A sample is mounted on a microscope slide, and the slide is optically coupled to the flat surface with an index matching gel. The surface of the sample effectively becomes the surface at which the internal reflection occurs. Curvature of the sample surface on a scale larger than the wavelength can cause some oblique transmission, but this is generally not a problem for samples of interest for PSTM imaging. Even for micron-sized optical gratings, accurate profiles can be obtained with the PSTM.

An optical fiber can be etched to a sharp point on one end to serve as a probe tip. The fiber is mounted inside a metal-coated hollow cylindrical piezoelectric tube with

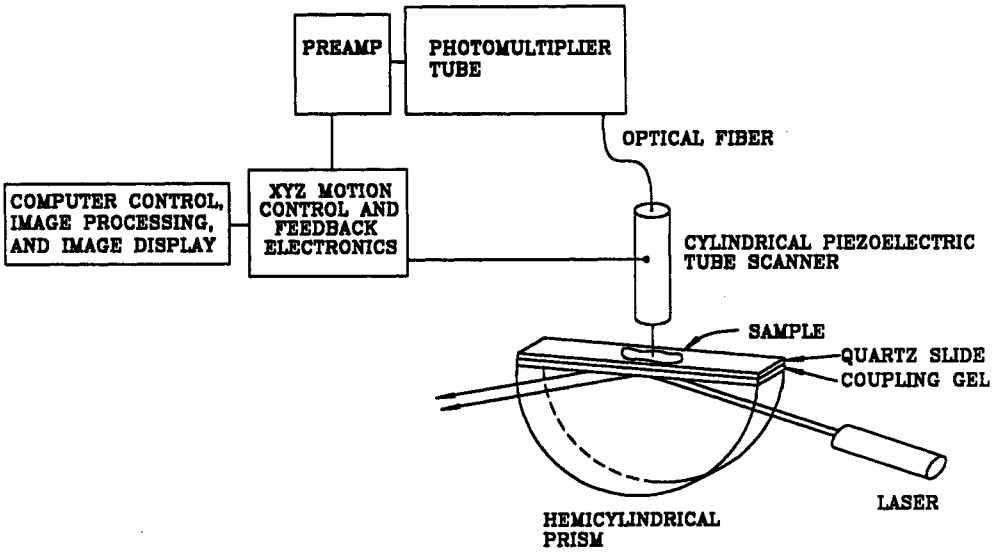

Figure 1. Block diagram schematic of the photon scanning-tunneling microscope (PSTM). An acid-etched fiber-optic tip is positioned above the sample and is scanned and lowered in the exponential electric field of the light by using a piezoelectric tube. The electronics is the same as used for electron scanning-tunneling microscopy.

electrodes scribed on the walls. The tip is mounted rigidly and barely extends outside the tube. The other end of the fiber is directed into a photomultiplier (PM) tube. In operation the tip is placed within a wavelength of the sample surface using first a micrometer and then the piezoelectric tube. The tunneling exponential can then be readily detected even with a low-power source.

The output of the photomultiplier tube is amplified by a preamp, and the resulting signal may be directed to a feedback circuit that produces a high-voltage control for the piezoelectric crystal. As the tip is rastered across the sample by the piezoelectric crystal, it is thereby also raised or lowered so that the signal current is held constant. The voltage necessary for this is monitored at each point in the scan. This means one obtains a data stream that consists of the voltages for the lateral coordinates (x, y) and normal coordinate (z). This signal represents a topographical image which can be analyzed, interpolated, and displayed on a computer. The piezo and electronics are essentially the same as are used for ESTMs.

Performance of the PSTM for Imaging Purposes

The fact that the PSTM reads an exponential signal allows it to exceed the diffraction limit. The z coordinate can be read on a scale down to whatever level is determined by noise. Without extra measures beyond use of a simple vibration-isolation platform, one can measure z to an accuracy of a few nanometers. With reduced noise from the electronics, from scattered light, and from intensity variations in the source, it is possible to improve the z accuracy considerably.

The decay of an exponential wave function originating on a flat surface helps the lateral, or x-y, resolution as well as the z resolution. For example, suppose the tip is a cone of opening half-angle β. Then a reasonable modification of the transmission coefficient T is

$$T_c \approx \frac{8s^2n^2\cos^2\theta}{(n^2-1)^2}\sin\beta e^{-2b(1+\cos\beta)}$$

which gives the power transmitted into a normal elemental area of the cone divided by the incident intensity at the sample, i.e., the power density per incident intensity at $z = h_0 + R\cot\beta$. Here z is the height of a point on the cone at radius R, and h_0 is the distance from the tip to the sample. Integration over the area then gives the total power transmitted into the probe divided by the incident intensity. Note that $T_c = 0$ for $\beta = \pi/2$. (The coefficient is evaluated at $\beta = \pi/2$ *prior* to the integration if the planar limit is examined.)

With the above result one can see that the normalized power density falls dramatically with radius. As an example, if the tip is 50 nm from the surface, $\theta = 60°$, $\beta = 30°$, and $\lambda = 442$ nm, then T_c at $R = 22$ nm is one-tenth of T_c at $R = 0$. The lateral resolution is thus about one-tenth of the wavelength of the light.

Figure 2 shows a PSTM image of a polished diamond surface.[6] The polishing marks are clearly visible on a subwavelength scale. The diamond was furnished by Doubledee-Harris.[7]

For a surface with abrupt features, even the best probe tips are expected to produce distorted images. However, good images can still be obtained under certain conditions. A PSTM image of an optical grating with a rectangular profile is shown in Figure 3. The width of the top of each grating line is known to be 200 nm. Despite the fact that the tip used was not one of the best possible, and was produced by a simple acid etching procedure, the PSTM gives the correct dimensions. It is a surprisingly accurate image, especially considering that the feedback electronics was not used and a constant-height scan was performed.

The PSTM as an Optical VOM (Volt-Ohm-Milliammeter)

Due to the high information-carrying ability of optical fibers and a variety of other advantages of optical circuits, considerable research on a worldwide scale is now being carried out on integrated optical circuits. Thin-film optical waveguides confine visible light, and

(7) Doubledee-Harris Corp., 100 Stierli Court, Mount Arlington, NJ 07856.

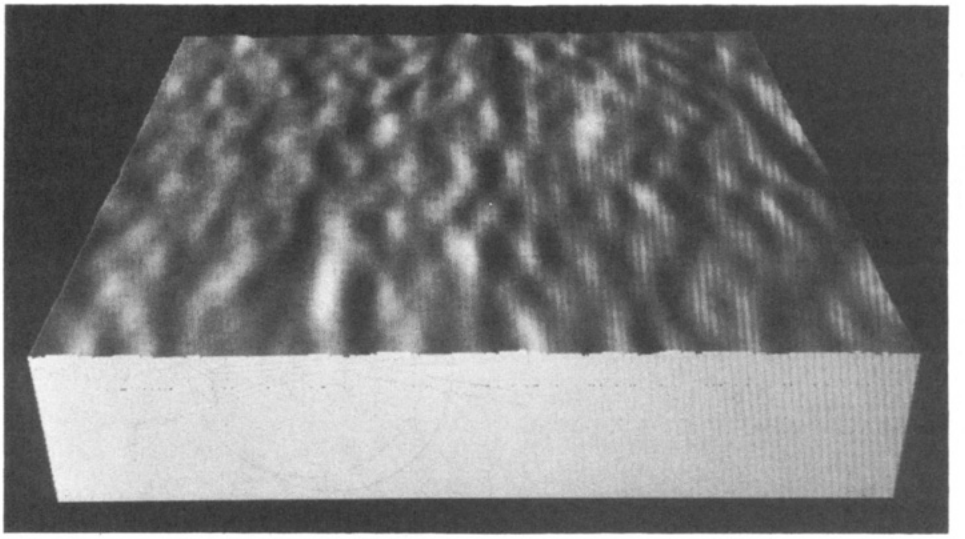

Figure 2. The surface of a polished diamond cylindrical lens measured topographically at subwavelength resolution by the PSTM. The scan region is 5 μm square.

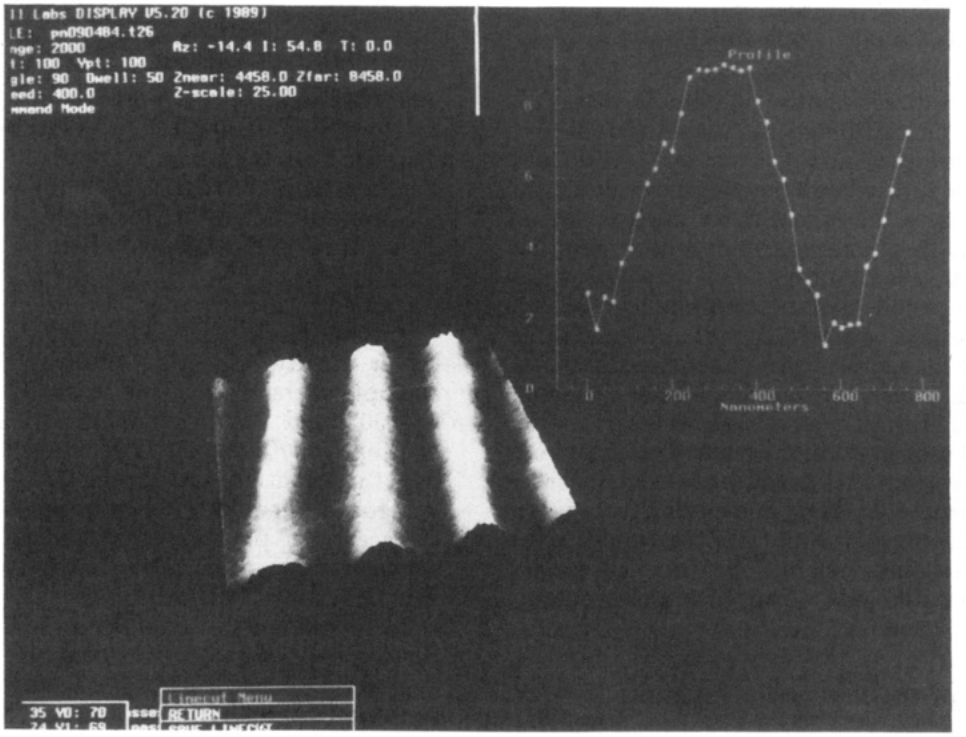

Figure 3. PSTM image of a quartz diffraction grating known to have a rectangular profile with the top of each line 200 nm in width. The cross-cut profile shown as an inset reveals a flat top of the correct dimension when a constant height scan is performed.

their index of refraction can be altered for various purposes. It is desirable to measure the spatial distribution of the propagating energy in such elements, and the PSTM offers a unique, nondestructive means of doing this. Moreover, by modulating the z position of the tip and using a lock-in amplifier to fix upon the oscillating data, stray light can be eliminated and the local index of refraction can be recovered from the measured exponential decay length. Research we have done on this application is described in the references,[8] but since the PSTM can nondestructively measure the optical analogues of voltage, current, and resistance, it clearly is likely to be of value for much more than imaging purposes.

Fluorescence and Raman Spectroscopy with the PSTM

The fluorescence signal from single molecules in droplets has been the subject of recent investigations.[9,10] Also, fluorescent tags for biological samples have been developed which offer sensitivity to local environmental conditions and do not have the deleterious effects of staining.[11] Other current work involves fluorescent tags for DNA-sequencing purposes. Indeed, because of the many relevant applications of fluorescence spectroscopy

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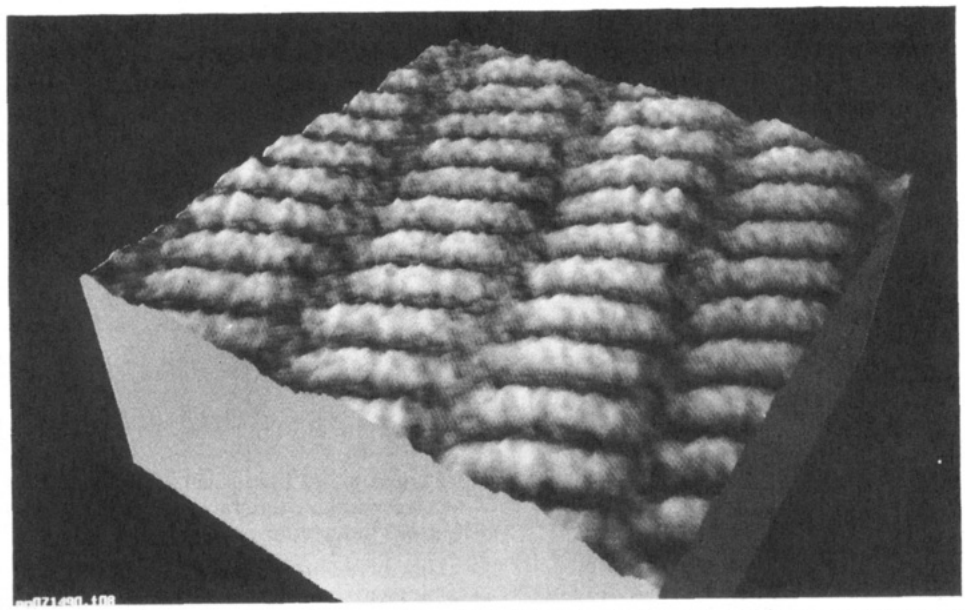

Figure 4. Photolithographically produced angular crossed grating etched in quartz. This PSTM image shows roughness structures on each particle in the array, which is 14 μm square. When coated with silver the sample makes an effective substrate for surface-enhanced Raman scattering (SERS) from adsorbed compounds.

it was a natural choice for the first form of PSTM spectroscopy.

Our initial research was devoted to imaging stress patterns in chromium-ion-implanted sapphire and detecting the shift in the Cr^+ doublet as a function of the stress patterns.[12] This permitted us to measure a fluorescent signal from highly localized sources for a sample in which simultaneous imaging is critical. A split fiber was used in this case with one arm of the fiber directed to a spectrometer and the other to the usual imaging system. The results for this specialized sample showed a distinct shift of the spectral peaks as a function of stress across a region much smaller than can be accessed by diffraction-limited spectroscopic tools such as micro-Raman systems. The signals collected by the fiber, and induced by a low-power laser, were easily detected by an inexpensive photomultiplier tube with a monochromator.

To test the ability of the PSTM to collect sufficient spectroscopic signal intensity with a less specialized sample and a relatively weak scattering cross section, we turned to surface-enhanced Raman spectroscopy.[13] Using a standard Raman spectroscopy system with a diode-array detector and an argon-ion laser, we targeted several compounds on a dry, open-air, microstructured array of silver particles. The use of a crossed-grating array (made photolithographically) was valuable for imaging purposes; a PSTM image of a typical such array etched in quartz is shown in Figure 4. Silver was deposited at oblique incidence on this sample in a vacuum evaporator, and a solution of 10^{-3} M cobalt phthalocyanine was then spin-coated onto the substrate. In a separate experiment we also used a similar solution of benzoic acid.

Figure 5 shows both the Raman signal from (a) cobalt phthalocyanine and (b) benzoic acid collected through the fiber tip of the PSTM.[14] A split fiber was used with

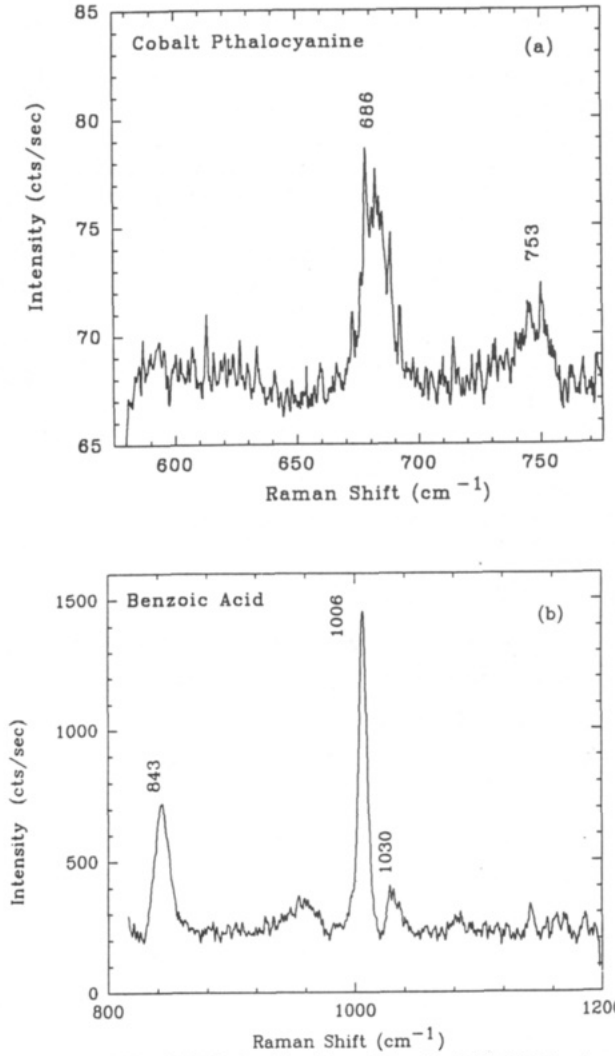

Figure 5. The SERS signal collected by the PSTM tip above the silvered substrate of Figure 4 coated with (a) cobalt phthalocyanine and (b) benzoic acid.

one arm directed to the spectrometer and the other arm providing the imaging signal. The spectral in-

(12) Paesler, M. A.; Moyer, P. J.; Jahncke, C. J.; Johnson, C. E.; Reddick, R. C.; Warmack, R. J.; Ferrell, T. L. *Phys. Rev. B* **1990**, *42*, 6750.
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tensity was adequate for unambiguous identification despite the well-known relative weakness of Raman scattering. Currently, we are investigating the possibility of using a silver-coated tip to detect the Raman signal from compounds on a bare quartz slide. This would permit better localized spectroscopy that may be expected to provide high-resolution chemical maps of complex samples under ambient conditions.

Among the applications of the research described above is detection of fluorescent tags on DNA base pairs. Separation of DNA fragments by electrophoresis in microgels can be carried out more quickly than in standard gels, and diffraction-limited spectroscopy instruments may well be displaced by the PSTM for rapid reading of microgels in improved sequenators.

Other Forms of PSTM Spectroscopy/ Microscopy

Since the light source for PSTM imaging can be entirely separate from the source used for acquiring a spectroscopic signal with the PSTM, high-resolution imaging can be carried out even when using infrared spectroscopy. Moreover, we have recently employed an inexpensive flashlight as the source and were able to obtain the exponential decay curve resulting from the average curve of a range of wavelengths. With a quartz-halogen lamp as a more intense source one can naturally expect that even the reduction in level introduced by a monochromator can be used to give sufficient strength at a variety of wavelengths. This then permits optical absorption spectroscopy with the PSTM.

The demonstration of the ability of the PSTM to detect small spectroscopic signals offers a number of new opportunities in many forms of spectroscopy extending even into the X-ray regime. A phosphorescent coating on the probe tip allows conversion of X-rays to visible light, and we are presently preparing a PSTM for installation on a synchrotron port. This should permit high-resolution imaging extending possibly down to the atomic scale. The advent of laser-plasma X-ray sources may permit more convenient X-ray PSTM instruments.

Other PSTM Capabilities

The use of monomode optical fibers allows the polarization state of the detected light to be maintained.

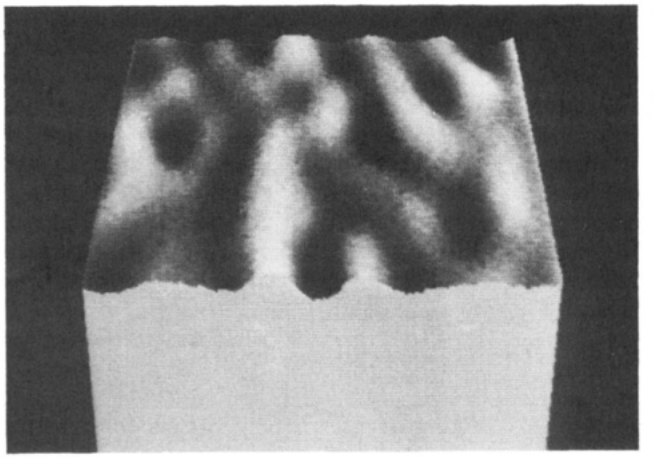

Figure 6. A 1-μm-square PSTM scan of the surface of a polycarbonate membrane filter containing a random distribution of 100-nm micropores.

Use of polarized light with samples examined by a PSTM with a monomode fiber and a polarization analyzer offers several new opportunities. For example, it should be practicable to image microstresses which rotate the polarization state (at subwavelength resolution).

Using an intensity-threshold bleach coated with photoresist it is possible to carry out microlithography with an exponential exposure profile using the PSTM. In this case the region exposed by the tip is limited because the intensity threshold is exceeded only at the location of the tip (where transmission occurs). The exposed region drops off exponentially in both the lateral and normal directions. A particularly interesting PSTM image is shown in Figure 6. This sample is a polycarbonate membrane filter (Costar, Inc., Kennebunk, ME) containing 100-nm micropores. We have recently imaged this sample with the tip and sample immersed in distilled and deionized water, an important result for potential biological applications.

The PSTM can also be used to study electromagnetic scattering from individual microscopic particles while imaging the particles.[15] In this case the standing-wave patterns are imaged where the reflected and incident surface waves interfere.

In the future we can expect higher spatial resolution with the PSTM using vacuum ultraviolet photons and X-ray photons. Additionally, a broader range of spectroscopies will be introduced to operate during imaging.

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