A Review of Near-Field Laser Ablation for High-Resolution Nanoscale Surface Analysis

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Abstract: Traditional laser ablation is a well-known method of solid sampling for surface characterization, but the resolution of the technique has been limited by the diameter of the incident laser beam and is typically on the order of 100–200 μm. Unfortunately, this microscale resolution can be too low to characterize isolated surface features that have submicron dimensions. Near-field laser ablation is an emerging analytical tool for nanoscale, high-resolution surface analysis. In this review, applications of near-field laser ablation for solid sample introduction are explored. Also, a descriptive overview of the near-field region is given, and methods of generating a near-field region and several processes for tip manufacture are described.

Keywords: Near-field region, laser ablation, nanoscale analysis, resonant laser ablation, high resolution, surface characterization, direct solid sampling, tip manufacture

INTRODUCTION TO THE NEAR-FIELD OPTICAL REGION

There exists a growing demand across a number of scientific fields, ranging from analytical chemistry to materials science and cell biology, for the characterization and microanalysis of surfaces on the nanometer scale (1). Optimally, a microanalytical characterization technique must provide an analysis of the surface of interest that is high in both spatial resolution and
sensitivity, but at the same time, it is desirable that the technique be nondestructive or minimally destructive to preserve the sample surface. Traditional surface characterization techniques, such as conventional far-field optical microscopy, are unsuitable for the study of nanoscale properties of surfaces due to limited resolution as a result of diffraction that takes place in the microscope lens. When light or material waves are incident on a surface, two kinds of optical fields are generated. The first type is a propagating wave field that is related to objects on the surface with details that have dimensions that are greater than the wavelength of the illuminating source. This is the premise for traditional far-field optical spectroscopic probes. The second type of field is a non-propagating wave field that is related to surface details that have dimensions that are smaller than the wavelength of the illuminating source. These confined waves are the premise for near-field optical spectroscopy and will be described later.

The standard experimental arrangement for far-field optical microscopy consists of a system of lenses that focus the light or material waves that are scattered from the sample surface into a virtual, magnified image. The virtual image is created by the interference of the scattered waves that are propagating from the sample surface, but since interference is required for image formation, there exists a fundamental limit on the dimensions of features on the surface of interest that can be resolved by the detector. If the features of interest on the sample surface have dimensions that are smaller than the wavelength of the source, then the images of those features cannot be resolved and become smeared out into Airy functions. In other words, the virtual image of the surface feature would appear as a series of concentric ripples, rather than an ideal point image due to the wave nature of light. The images of two surface features can be considered resolved if the maximum of one Airy function lies on the first minimum of its neighbor. It turns out that the resolution of conventional far-field optical microscopy is limited to no better than one half of the wavelength of light being used to interrogate the sample. Indeed, cutting-edge far-field optical microscopes that use vacuum-based ultraviolet wavelengths, for which the shortest available wavelength is 200 nm, can achieve lateral resolution no better than 100 nm (2). This resolution is insufficient for many microanalytical problems. For example, important structures on the surfaces of cell membranes, such as pores and protein channels, which have features on the order of 1 nm (3), are not accessible by far-field optical microscopy.

However, as previously mentioned, there exists a second type of optical field that can be generated when light or material waves are incident on a surface. In special cases, non-propagating local electromagnetic interactions, or confined evanescent fields, occur. These evanescent fields contain the sub-wavelength information about the sample surface, and the collection and study of that information has been termed near-field spectroscopy. Near-field spectroscopy is an interaction-based imaging technique that has been shown to overcome the fundamental diffraction limitations imposed by lenses, and it
is capable of spatial resolution that is vastly superior to the relatively high resolutions that can be obtained by detection of interfering optical fields.

At this point, it is useful to define the “optically near systems” that produce evanescent fields. When two atomic-scale objects, X and Y, are isolated as an electronic system, three distinct light-scattering processes are possible. These processes are shown in Figure 1, which was adapted from Ohtsu (4). In an optically far system (Figure 1A), objects X and Y are separated by a distance that is greater than or equal to the wavelength of the incident light source. A light source impinges on object X, and propagating light that is scattered from the surface of object X then impinges on object Y. Light that is scattered from the surface of object Y is then collected by a detection system. In this system, the interaction between objects X and Y is such that unidirectional photons that are propagating from X to Y satisfy the dispersion relation, so the resultant scattering can be observed as two separate scattering events from two separate sources. In other words, the images of X and Y would be fully resolved by an optical detector, and can be viewed as two separate objects.

A second scenario is an optically close system (Figure 1B), where objects X and Y are electromagnetically tightly coupled by intrinsic internal interactions, such as van der Waals forces. There is no separation between X and Y, so the optical response received by the detector is scattering from a kind of molecular state of the electromagnetically coupled XY system.

Figure 1. Definition of optically far, close, and near systems. There exist three different light-scattering scenarios for two atomic-scale objects X and Y that are isolated as an electronic system. This figure was adapted from Ohtsu (4). See text for details.
In the third possible situation (Figure 1C), the separation distance between objects X and Y is greater than 0 but less than the wavelength of the incident light, and this has been termed a near optical system. Here, objects X and Y are considered to be separate objects with respect to their electronic states, and there exist no intrinsic internal interactions between X and Y. Upon illumination of a near optical system, there arises an electromagnetic interaction between X and Y that is multidirectional. Scattered light from X impinges on Y, and scattered light from Y hits the surface of X. This is opposed to the unidirectional interaction that occurs in a far optical system. The multidirectional waves give rise to an effective quasi-static localized electromagnetic field between X and Y. This type of confined field has been termed an evanescent wave. Evanescent waves are non-propagating electromagnetic phenomena that have field amplitudes that decay exponentially with increasing distance from their source, so a reduction of the distance between objects X and Y results in an increase in the strength of the confined evanescent field. Also, the intensity and size of the evanescent field are maximized when objects X and Y are of equal size (4). The region between objects X and Y where evanescent waves exist has been termed the near-field region, and the onset of an evanescent field has been termed the near-field effect.

It has been shown that it is possible to optically image nanoscale features on surfaces of interest if the tip of an illuminated probe with nanoscale dimensions is made to interact directly with the effective evanescent field at a small distance from the surface feature (4). For example, Gerton et al. (5) coupled near-field optical microscopy with fluorescence detection to resolve structures with a spatial resolution of just 10 nm, and Frey and coworkers (6) used fluorescence detection to image single dye molecules with a spatial resolution of 15 nm. In this way, the probe tip acts as object X, and the nanoscale surface feature acts as object Y. In other words, when the probe is placed in proximity to a nanoscale surface feature, and within the near-field region, the probe interacts with a fixed volume of the surface feature as a function of position over the sample surface. The typical separation distance between the probe and the surface feature is on the order of a nanometer.

As previously mentioned, nanoscopic information about the surface of interest is inherently present in the confined waves that arise between the probe tip and the surface feature in the near-field region. Since the localized evanescent waves are interaction based and do not propagate, the frequency information present in the light scattered between near objects X and Y is not limited by diffraction and is not lost by interference (4). The confined waves are later converted, by scattering off either the probe tip or the sample surface, into propagating waves that can then be detected either in the far-field or directly in the near-field with any conventional optical detection method. Detection of the evanescent waves can be performed under ambient, non-vacuum conditions in either the near- or far-field, but the method of collection of signal from evanescent waves must be inherently
sensitive, since only a small surface volume is probed. Regardless of the method of detection, nanoscopic features on a sample surface can be imaged by rastering the probe tip over the entire surface, and the resolution that is attainable is a function of the size of the tip of the probe (7).

In near-field spectroscopic applications, two primary types of probes, namely apertured and apertureless, have been used to optically generate nanoscale information about the surface of interest. These probe types are discussed here briefly in order to enable a context for the approaches used with near-field laser ablation (NF-LA) that are reviewed later. In the apertureless probe approach, a sharp metal tip is placed in the focus of an incident laser beam and in the near field region with respect to the sample surface. An electrostatic lightning rod effect, which consists of the enhancement of the localized electric field between the surface and the probe, occurs (8, 9). The intensity of that enhanced field can be significantly greater than the intensity of the incident laser light (10–12). For example, Mosbacher and coworkers calculated that an 11-fold enhancement in the field intensity of the incident laser intensity occurred in the near-field region at the sample surface (13). Martin and Girard observed extremely strong field gradients just below the tip apex, and the intensity of the field was 183 times the intensity of the incident field (12). It turns out that the diameter of the enhanced field is equal to the dimensions of the probe tip, so the resolution of apertureless near-field work is limited to the dimensions of the tip of the probe (8).

In the apertured probe approach, source light is introduced through a miniature, tapered aperture with sub-wavelength dimensions (14). The tip of the aperture is placed in the near-field region. When a beam of light is incident on a small hole, the portion that passes through the hole will at first be confined to the dimensions of the aperture (15). If the aperture is of sub-wavelength dimensions, then the exiting light will rapidly diffract in all directions, but the beam retains the approximate dimensionality of the hole in the near-field region, as shown in Figure 2, which was adapted from

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Origin of the near-field region using an aperture. A beam of light incident on an aperture with sub-wavelength dimensions will remain collimated in the near-field region. This figure was adapted from Betzig et al. (16).
Betzig et al. (16). Therefore, the collimated region of the light beam illuminates only the small volume of surface molecules present in the near-field, and a portion of the electric and magnetic fields of the incident light penetrates the aperture to form an evanescent wave in the near-field (17). The resultant evanescent wave can then be used to locally excite an optical response, with nanometer resolution, from those few molecules. The entire sample surface can be studied by rastering the light source, and this is the premise for near-field scanning optical microscopy (NSOM) technique. Near-field scanning optical microscopy has received considerable attention because in principle, any conventional optical spectroscopic technique could be adapted for use with an NSOM probe to perform nanoscale chemical analyses (18), and detection can take place in the far-field after diffraction has occurred without any loss of information (2). For example, Butter and Hecht observed emission signals of single molecules of terrylene in p-terphenyl crystals using NSOM (19). Vanden Bout and coworkers (20) used NSOM to visualize functional organic thin-films, and Takahashi et al. (21) coupled an NSOM probe with Raman detection to produce high-resolution Raman spectra of copper phthalocyanine. The NSOM probe has also been coupled to fluorescence detection for biomedical applications (22).

APPLICATION OF THE NEAR-FIELD EFFECT TO NANOSCALE LASER ABLATION SOLID SAMPLING

By extension, just as surface features that are significantly smaller than the operating wavelengths cannot be imaged by exploiting propagating waves, craters with sub-wavelength dimensions cannot be created by laser ablation with propagating waves. However, recently, it has been shown that solid sampling can be performed on the nanoscale by use of NF-LA. Laser ablation is a well-known sample introduction technique for surface microanalysis (23), but the resolution of LA has traditionally been limited by the diameter of the incident laser beam. For example, in recent work performed by us (24–26), the ablation laser spot size was on the order of 100–200 μm. Significantly smaller sample volumes can be liberated from the surface of interest by use of an apertured or apertureless probe with nanoscale dimensions.

In the case of apertured NSOM probes, the sub-wavelength laser light beam that is emitted from the tip of the probe can be used to ablate small volumes of analyte from the surface of interest. Likewise, apertureless probe tips can be used to significantly enhance the intensity of the incident laser light in the near-field region and to subsequently use the enhanced field to remove material from the solid surface (9). While the exact nature of material removal from a solid sample surface during near-field laser ablation has not been agreed upon, it has been suggested that the ablation mechanism is photothermal in nature when NSOM probes are used (27–30), and the result of radiation intensity singularities when sharp metal tips are used (8, 9).
The liberated molecules or atoms can be analyzed with separate trace analytical methods, such as mass spectrometry or fluorescence detection. So far, the sensitivity of NSOM reached has permitted the detection of fluorescence from single molecules with a high signal-to-noise ratio (31). Therefore, it might be possible to use NF-LA solid sampling to liberate a single atom, molecule, or particle from the surface of interest. Only a limited number of NF-LA studies have been performed to date using an NSOM probe, and still fewer laser ablation studies have been performed using an apertureless near-field approach. Recently, probeless methods that use layers of nanoparticles have also been investigated for NF-LA. The following paragraphs are arranged by probe types and review the literature applications of near-field laser ablation for nanoscale surface analysis.

Probe Methods of Near-Field Laser Ablation

Applications of Near-Field Scanning Optical Microscopy Probes for Near-Field Laser Ablation

Stöckle et al. (32) coupled near-field laser ablation to mass spectrometric detection (NF-LA-MS) for the nanoscale analysis of anthracene and bis(phenyl-N,N-diethyltriazene)ether crystals under ambient conditions. The authors used an NSOM probe to ablate small volumes of sample from the crystal surfaces. The laser light exiting the tip of the NSOM probe was estimated to have a pulse energy of 2 nJ, 200 nm beam diameter, and a power density of $10^{11}$ W cm$^{-2}$. A suction tube was used to transmit the ablated particles to a quadrupole mass spectrometer. A spatial resolution of less than 200 nm and a sensitivity below 2 amol was demonstrated. The results suggested that NF-LA-MS had sufficiently high sensitivity to detect individual near-field ablation events.

Zeisel and coworkers (27, 28) performed pulsed laser-induced desorption and precise surface modification of a polyvinylbutyral film on the nanoscale using an Nd:YAG-pumped OPO laser coupled into a single-mode optical fiber. The optical fiber had a nanometer-sized aperture with dimensions that were estimated to be below 50 nm. The authors used an ablation laser wavelength of 450 nm, and the sample was scanned under the NSOM tip with a fixed scan rate of 5 μm s$^{-1}$. The craters produced in the film surface were then imaged using shear force topographic imaging and were observed to have a FWHM of as little as 70 nm, with pronounced rims around the outer edges. The absolute depth of the craters ranged from 5 to 20 nm, depending on the incident energy of the laser pulse. The same experiment was performed using an anthracene crystal as the solid sample. The shear force images of anthracene showed nanometer-sized craters without any apparent rims or material deposited in the vicinity of the hole, while the absolute
crater depths ranged from 15 to 75 nm. In similar work (29), the authors observed near-field ablation of rhodamine dye films.

Hwang et al. (33) investigated NF-LA as a potential method of the precise nanoscale modification of electronics materials. The authors used an NSOM near-field probe to deliver sub-wavelength laser radiation to chromium and gold thin films that had been deposited on a quartz substrate. The authors compared the use of nanosecond and femtosecond lasers and found that smaller features and less melting of the films occurred via use of a femtosecond laser pulse. In other work, Hwang and coworkers (34) monitored the evolution of the laser-induced plasma during near-field laser ablation studies of a chromium thin metal film. A 532-nm nanosecond Nd:YAG laser was fiber-coupled to an optical near-field fiber (NSOM) probe. The authors observed the formation of an intense plasma in the near-field region between the solid surface and the probe tip, and optical spectra of the laser-induced plasma were recorded using an intensified CCD spectrometer. The plasma occurred within the laser pulse duration and decayed temporally after several nanoseconds. Material ejection from the solid surface was observed to be highly directional and jet-like, while the ablation craters had diameters of the order of 800 nm. Emission lines corresponding to the electronic transitions of chromium were observed using the CCD spectrometer, and the authors felt that these observations supported the idea that near-field laser ablation might be applied to laser-induced breakdown (LIBS) spectroscopic studies.

Masaki and coworkers (35) evaluated the analytical utility of near-field laser ablation for the treatment of atherosclerosis. The authors used a free electron laser coupled to an NSOM probe to dissociate a thin film of cholesteryl oleate. Atomic force microscopy was used to evaluate nanoscale changes in the molecular structure of the cholesteryl oleate. The authors were able to decompose the cholesteryl oleate to cholesterol and oleic acids and to reduce the thickness of the cholesteryl oleate thin film by one half using NF-LA.

Near-field laser ablation has also been used to study diamond sample surfaces. Smolyaninov and Davis (36) directed a 1060-nm Nd:YAG laser beam, with a power density of 100 MW cm\(^{-2}\) into a tapered, NSOM fiber-optic probe. Shear force microscopy was used to track changes in the surface morphology of the sample. At that laser power density, ablation spots with diameters less than 500 nm were achieved in the surface of the diamond.

Samek et al. (37) coupled femtosecond laser pulses into an NSOM fiber-optic probe to perform nanoscale LIBS analysis of brass samples. The authors directed a slightly focused 755-nm, 10-Hz femtosecond laser beam with an energy of 15 \(\mu\)J per pulse into the fiber-optic probe, which had a tip diameter of approximately 200 nm. A very weak emission was visible to the naked eye under the fiber tip, and submicrometer craters were observed in the brass surface. Unfortunately, an analytical signal could not be detected using standard LIBS light collection optics.
The analytical utility of NF-LA for the repair and production of photolithographic masks for chip production was tested by Korte and coworkers (38). A 260-nm femtosecond titanium:sapphire laser was directed through a tapered NSOM fiber-optic probe with a 100-nm diameter. The probe tip was brought into the near-field region and held at a constant height of 50 nm above a chrome sample surface. A laser ablation crater that was produced in the chrome surface was imaged by atomic force microscopy and found to have an approximate diameter of 500 nm and a 100-nm depth. The authors demonstrated that nanoscale grooves could be produced in the sample surface by rastering the probe position across the sample surface. In similar work, Lieberman and coworkers (39, 40) demonstrated that surface defects could be removed using femtosecond near-field laser ablation. A pulled micropipette with a 690-nm diameter was positioned 150 nm above a chrome substrate that had been coated with chromium, and the beam of a femtosecond titanium:sapphire laser was directed into the pipette. The sample was scanned beneath the micropipette aperture, and the authors were able to successfully modify the sample surface.

The local chemical compositions of meteorite, basaltic rock, and sea salt samples were investigated by Kossakovski and Beauchamp (41). The authors delivered pulsed nitrogen laser radiation through a tapered fiber-optic (NSOM) probe. The optical emission in the laser-induced plasma was collected with a standard microscope objective and transmitted via a fiber-optic probe to a miniature spectrometer. Several emission lines of constituents in the samples, including iron, magnesium, and calcium, were observed.

Applications of Apertureless Probes for Near-Field Laser Ablation

Only a few papers applied NSOM probes for nanoscale solid sampling, and to the best of our knowledge, only one paper has used an apertureless probe experimental arrangement for near-field laser ablation. Becker et al. (9) analyzed biological samples with single-shot near-field laser ablation using a 532-nm Nd:YAG laser, coupled to inductively coupled plasma sector field mass spectrometric detection. Argon carrier gas was used to transport the ablation plume to the mass spectrometer. The near-field enhancement effect was created by use of a thin silver needle that was placed in proximity to the sample using an XYZ positioner and illuminated with a defocused laser beam. Samples included a leaf from an African violet, a rose petal, and a small piece of a 2-D electrophoresis gel that had been used to separate human brain proteins. The samples were doped with uranium and copper and zinc isotopic tracers, and small pieces were placed into the ablation cell where the authors performed single shot LA measurements. Craters were observed in the sample with approximately same diameter as probe tip, and the authors compared the signal size for uranium in an inductively coupled plasma mass spectrometer (ICP-MS) when the needle was far from the surface to the ICP-MS signal size for when the needle was brought into
proximity of the sample surface. A 60-fold enhancement in the intensity of the uranium signal was observed when the needle was in the near-field region, compared to the signal obtained when the needle was far away from the surface. The authors felt that the signal enhancement demonstrated the near-field enhancement effect for LA-ICP-MS. Further experiments investigated the quantification capabilities of NF-LA-ICP-MS by measurement of isotope ratios for $^{65}\text{Cu}/^{63}\text{Cu}$, $^{67}\text{Zn}/^{66}\text{Zn}$, and $^{235}\text{U}/^{238}\text{U}$ and the construction of a calibration curve.

Fabrication of Near-Field Scanning Optical Microscopy Probes for Apertured Near-Field Laser Ablation

One of the technical difficulties in developing the NSOM-based laser ablation technique lies primarily in fabricating a tapered probe that has an aperture with sub-wavelength dimensions. The resolution of NSOM probe techniques is determined mainly by the aperture size, but an aperture cannot be made arbitrarily small in an effort to improve resolution. The amount of light transmitted by a small aperture poses a limit on how small it the aperture can be before no light can pass through the opening. In other words, it is increasingly difficult to force light through an aperture that is considerably smaller than the wavelength of the incident light. As the dimensions of the aperture are reduced, the optical power of the light source must be increased to permit transmission of light through the aperture. However, as the aperture diameter is reduced to 50 nm and smaller, the transmitted optical power is rapidly reduced and extinguished. At 50 nm, only one part in $10^8$ of the total incident power is transmitted through the aperture (42). Further, the input power cannot be arbitrarily increased without regard for damage to the tip of the optical probe. However, some improvement in photon transmission has been observed with the use of sharply tapered optical probe tips (43). Also, nanoscale changes in surface morphology are best tracked when the probe has a sharply pointed tip, and a smooth taper assists in the prevention of light leakage from the probe. Several methods have been used to prepare sharply tapered NSOM probes for optical spectroscopy, including chemical etching (18–21, 44–46), focused ion beam milling (47), heat-pulling (15, 16), micromachining (48, 49), and hybrid heat-pulling/chemical etching combinations (50). Only two methods, namely heat-pulling (33, 34) and chemical etching (27–29, 32, 37, 41), have been specified in the literature as methods for fabricating apertured probes for near-field laser ablation, and these methods are described in the following paragraphs.

Heat-pulled tapered tips have been produced for NF-LA by heating a regular, bare optical fiber with a CO$_2$ laser. The heated region of the fiber was then quickly, mechanically pulled apart to produce a tapered, sharp tip. The pulled fibers were then coated in thin metal coatings, which were applied by sequential evaporation, to prevent light leakage. The pulling
Self-terminating chemical etching procedures have been the most common technique for preparation of sharply tapered NSOM probes used for high-resolution laser ablation studies. Etching procedures produce shorter tapers, which increases light transmission through the tip. The etching process can be carried out on bare or cladded optical fiber. The etching process has been referred to as the Turner method (51), or the protection layer method, when bare fibers are used, and as the tube etching method (52) when cladded fibers are used. Both types of chemical etching processes use a two-component liquid mixture, composed of 40% hydrofluoric acid etching fluid and a protecting overlayer. The liquid that makes up the overlayer is less dense than, and not miscible or reactive with, the aqueous etching solution so that the overlayer floats on top of the HF. Various organic overlayers, including iso-octane, oils, and p-xylene, have been used to protect the non-submerged portion of the fiber optic from corrosive HF vapors. It has been shown that the identity of the overlayer has no influence on tip formation (32), and the etching process can be accelerated by application of heat.

During the Turner etching process (51), a bare optical fiber is inserted into the two-component etching mixture for 90 min. As the fiber is gradually etched, its diameter decreases, and following the laws of superficial tension, the height of the meniscus formed by the acid along the fiber decreases until the tip is fully formed. The etching process then self-terminates as the meniscus height of the etching fluid drops below the finished taper, and the tip is left exposed only to the protective overlayer. This method offers high reproducibility and allows for precise control over tip angles. The fiber can then be metallized to suppress light leakage and to obtain a defined aperture. Unfortunately, the etching process can leave the surface rough, which can lead to light leakage along the taper.

In the tube etching method (32, 52), the protective cladding is left on the fiber-optic as it is submerged into the two-component Turner etching mixture. The cladding resists degradation by the hydrofluoric acid, so in this way, the entire etching process occurs inside the hollow cylinder formed by the cladding. The method of tip formation during the tube etching process is different than the mechanism of the Turner method since during tube etching, the tip forms even though the height of the meniscus never changes. During tube etching, the acid diffuses through the cladding to etch the glass. As the acid ions react with the quartz fiber, new ions have to diffuse from the liquid to the surface of the quartz. In the upper part of the meniscus, the layer of etching liquid is very thin, so the ions saturate more rapidly, and this slows down the etching rate. As the depth of the etching fluid increases, the concentration of ions close to the fiber remains higher, since diffusion of ions is more efficient from a larger, deeper reservoir. After 35 min, a sharp tip is formed, and the fiber is removed from the
etching solution and rinsed in water, trichloroethylene, and acetone. The cladding is removed by mechanical stripping or by dissolution in hot sulfuric acid, and the fiber can then be metallized as desired to reduce light leakage. The tube etching method is thought to offer better control over the etching process by providing a more stable meniscus, and this reduces surface roughness and irregularities. Therefore, tube etching combines the smooth fiber surfaces that are provided by heat-pulling and the large taper angle and high optical transmission provided by chemical etching.

Fabrication of Thin Silver Needle Probes for Apertureless Near-Field Laser Ablation

As previously described, Becker and coworkers (9) used an etched thin silver needle as an apertureless probe for near-field laser ablation studies. The probe was lab-prepared using a two-part electrolytic etching method proposed by Gorbunov et al. (53). In the first part of the procedure, the main taper of the probe tip was formed by self-limited etching in an electrochemical cell. A cold-drawn 0.5-mm 99.9% silver wire was immersed 2 mm into a 40% (w/v) aqueous citric acid solution. In this electrochemical cell, stainless steel was used as the counterelectrode. A 100-V AC voltage was applied to the cell, and the silver wire was slowly withdrawn from the citric acid solution at a rate of 1 mm min\(^{-1}\). After one minute had elapsed, the remaining portion of the wire that was still immersed in the citric acid dissolved, and the withdrawn portion had been formed into a tapered cone shape. In the second part, the very end of the main taper was electropolished to a fine point. A 5-mm stainless steel loop with a drop of citric acid electrolyte was mounted on an XYZ positioner. This loop and the horizontally positioned silver wire formed an electrochemical cell, which was placed in view of an optical microscopy with 100× magnification, to allow for observation of the electrochemical shaping process. A microswitch was then used to apply short pulses of 100–200 V DC voltage to the cell. The probe was sharpened to the desired diameter using slight movements of the loop against the silver needle tip. After polishing, the tip was immersed in dilute nitric acid to remove etching products and then rinsed in deionized water.

Technical Considerations for Performing Near-Field Laser Ablation with Probes

In addition to probe fabrication, several additional factors must be taken into consideration when the probe methods of NF-LA are performed. First, the tip of the probe must be accurately positioned over the surface of interest. In the case of NSOM probes, the tip must be situated close enough to the sample surface that the emitted light remains collimated, so that the sample is located in the near-field region. Also, the near-field region typically extends no farther in space than the dimensions of the probe tip itself (2), so the
distance between the surface and both types of probes must be held constant to within a few percent of the extent of the near-field. Therefore, a feedback mechanism is required to control the tip-to-sample separation distance, prevent the probe from crashing into the sample surface, and maintain a constant ablation laser spot size and intensity. Some feedback systems that have been used with NSOM probes for optical spectroscopy have included electrical tunneling, ion conductance, damping from atomic forces, and the monitoring of evanescent waves (2). For near-field laser ablation, only the atomic force damping approach has been specified so far in the literature (27, 29, 33, 37, 41).

It should be noted that some distortion of the field distribution by the probes has been noted (54). Also, since the probes are placed in the middle of the laser-induced plasma during near-field ablation, spurious signals can occur if the tip of the probe is not cleaned between ablation measurements (41). However, the requirements for feedback mechanisms, proper tip-to-sample spacing, and probe cleaning, as well as the possible distortion of the field distribution, have been overcome by use of the probeless method, which is described in the next section.

probeless methods of near-field laser ablation with nanoparticles

Several authors have applied an alternate incarnation of apertureless near-field laser ablation, where the NSOM or thin needle probes were replaced with metal or dielectric nanoparticles, which were scattered over the surface of the sample of interest. When laser radiation was incident on a nanoparticle, a local near-field enhancement occurred at the location of the particle, and laser-induced ablation occurred on the nanoscale. For example, Ou and coworkers (55) used a random metal-dielectric composite Sb-SiN film as a source of nanoparticles. Small metal antimony particles, with diameters ranging from 1 to 50 nm, were randomly embedded inside the silicon nitride film. The composite film was then layered on top of a GeSbTe sample and irradiated with 690 nm laser radiation. The pulse of the laser was varied in temporal length from 500 ns to 5 μs and in power from 4.5 to 8.2 mW. The ablation spots that appeared on the GeSbTe sample layer were observed by scanning electron microscopy, and the location and onset of ablation was compared for GeSbTe samples covered and not covered with the Sb-SiN thin film. On the sample without the nanoparticle composite film, ablation occurred only when the laser pulse length was at a maximum 5 μs and the energy was maximized at 8.2 mW. Also, ablation of the uncovered sample occurred primarily at the center of the irradiated region. For the GeSbTe sample covered with the nanoparticle film, ablation was observed to be a violent process that occurred at multiple points along the surface of the sample, and it occurred at a much lower laser power and with a reduced laser pulse length (6.4 mW and 1 μs, respectively) compared to
ablation of the sample without the nanoparticle film. The authors observed that the maximum intensity of the local enhanced field was approximately six times greater than that of the incident field and postulated that the local near-field enhancement may have been due to scattering by the antimony particles embedded in the composite film.

Nedyalkov and coworkers (56) demonstrated the precise fabrication of nanostructures on a silicon surface using a near-field enhancement in the vicinity of gold nanoparticles. Gold nanoparticles with sub-wavelength dimensions were spun-coated onto a silicon sample, and then the sample was irradiated with an 820-nm, 100-fs laser pulse. It was observed that when the laser fluence was reduced below the ablation threshold of silicon, craters were produced in the silicon surface at the location of the gold nanoparticles. In similar work, Boneberg and coworkers (54, 57) spun-cast polystyrene nanospheres with sub-wavelength dimensions onto a smooth silicon surface. The sample was then irradiated by pulses from a slightly focused femtosecond titanium:sapphire laser, and the resulting topographies of the silicon were imaged by atomic force microscopy or scanning electron microscopy. The incident laser energy was attenuated so as to not affect parts of the substrate that were far away from the ablation area. Ablation of the silicon substrate was observed in areas around and near the locations where the nanoparticles had been deposited. Also, gold metallic triangles with sub-wavelength dimensions were deposited on the silicon substrate and then irradiated by a single laser pulse. The authors noted that craters were produced in only two corners of each triangle, and the craters had the same dimensions as the corners of the triangles. Ablation did not occur at the tip that was pointing in the direction of the field of the polarized laser radiation.

CONCLUSIONS

Near-field laser ablation solid sampling is a promising method for surface analysis, as indicated in this review. The primary advantages of NF-LA include that it provides a very high-resolution picture of the composition of the solid sample surface and that it is readily coupled to traditional detection systems, such as mass spectrometry. Alternative detection methods such as fluorescence or emission detection might be employed in the future to maximize sensitivity (58). Also, since only a few isolated atoms are ablated from the solid surface, near-field ablation significantly reduces collateral damage to the sample surface. Ultimately, with continual improvement in probe fabrication, and with the use of probeless approaches for generating the near-field region, ablation measurements might approach single atom detection (SAD) (31, 59). For example, the thought that superresolution measurements might be made using NF-LA to extract single atoms or molecules in biological tissues or cells is attractive (60).
REFERENCES


Near-Field Laser Ablation Solid Sampling


