Near-field second harmonic generation from a rough metal surface

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Local second-harmonic generation (SHG) from a rough metal surface has been measured using a near-field optical microscope. The dependence of the SH signal on the tip-surface distance for excitation with *S*- and *P*-polarized light shows the presence of evanescent SH field components. With excitation by *S*-polarized light the SHG over the rough surface is found to be strongly related to surface topography. For *P*-polarized light excitation, local enhancement of SH emission have been observed that may be attributed to SH field localization. [S0163-1829(97)07040-9]

I. INTRODUCTION

In recent years there has been increasing interest in linear and nonlinear optics of disordered media, particularly rough surfaces.[1] Because second-harmonic generation (SHG) is known to be surface sensitive on an atomic scale[2] (especially when the nonlinearity itself is due to the presence of the surface, as is the case for isotropic materials[3]), studies of the nonlinear optical response are particularly suitable for improving our knowledge of the relationship between optical properties and morphology (roughness, defects, impurities, adsorbates) of metallic and semiconductor surfaces.[4,5]

Second-harmonic generation from very flat surfaces has been extensively studied.[2,6] However, real surfaces always have different degrees of roughness. The inclusion of roughness leads to several phenomena affecting SHG (such as relaxation of polarization selection rules and an enhancement of the electromagnetic field by the roughness). Less obvious is the strong influence of weak-localization effects on the SHG from rough surfaces[7] that result in significant changes of the angular spectrum of SHG observed in the far-field region.[8] Even more pronounced changes should be expected in the near-field region close to the surface.

Until now, SHG from rough surfaces has been studied only in the far-field region without exact knowledge of the surface topography. Information provided by the usual (far-field) optical studies of surfaces is derived from data averaged over a surface region limited, in the best case, by diffraction of the probe light. However, the usual sizes of these regions is much larger: from several square micrometers to several square millimeters. Thus, optical data obtained from linear and nonlinear spectroscopy are valid for very large defect ensembles. At the same time, the lateral distribution of the electromagnetic field over a surface is not uniform and depends itself on the surface defect structure. The local-field intensity can vary by several orders of magnitude on a scale less than half a wavelength along the surface.[9,10] Therefore, investigation of the averaged optical response in many cases does not result in an understanding of the underlying physics (especially in nonlinear spectroscopy where optical response depends on the driving field in a nonlinear manner).

The recent development of near-field optical microscopy (NFOM) has opened the possibility for study of numerous optical phenomena with a resolution well below the diffraction limit.[11] Most near-field optical studies have concentrated on the investigation of the linear optical response of materials. The possibility of studying nonlinear optical processes (especially, wave mixing) with near-field optical characterization methods has been discussed recently,[12,13] but only phase-conjugation experiments were experimentally realized in the near-field region.[14] This slow progress in nonlinear near-field optics stems from numerous experimental difficulties caused by the small optical throughput of conventional metal-coated near-field apertures. This small throughput enters quadratically into the measured SH optical signal. Another disadvantage of metal-coated fiber tips in nonlinear optical measurements is a strong perturbation introduced by a tip into the local surface field distribution. For example, in SHG experiments SH light intensity is proportional to the fourth power of the local field. Hence, by using a metal-coated fiber tip one can study only the properties of a microresonator formed between the tip and the sample, but not the true local SH field distribution. Uncoated fiber tips (used in Ref. 14) introduce much smaller perturbation into the local field near the sample, since the dielectric constant ϵ of a fiber is much less than ϵ of a metal. However, the decrease in optical confinement does lead to somewhat lower resolution.

The combination of second-harmonic generation techniques with near-field optical microscopy has significant potential for probing the nonlinear optical response of a surface locally with subwavelength lateral resolution while simultaneously measuring surface topography using shear-force feedback. The data obtained in such a way may allow comparison of experiment and theory in sufficient detail to understand the essential features of SHG at rough surfaces and provide better understanding of the underlying microscopic electrodynamics. Since SHG is sensitive to any asymmetry of the sample, it is sensitive to surface magnetic or electric dipole moments. Near-field SHG microscopy can be used to image magnetic or electric domains and is an alternative to magnetic and electric force microscopies in this regard. Near-field SHG microscopy of a rough metal surface is an important first step in this direction.

In this paper we report the observation of second-harmonic light generated at a rough silver surface using a near-field optical microscope. The SH signal dependence on the tip-surface distance has been measured for *S* and *P* polarization of the excitation light. The spatial distribution of

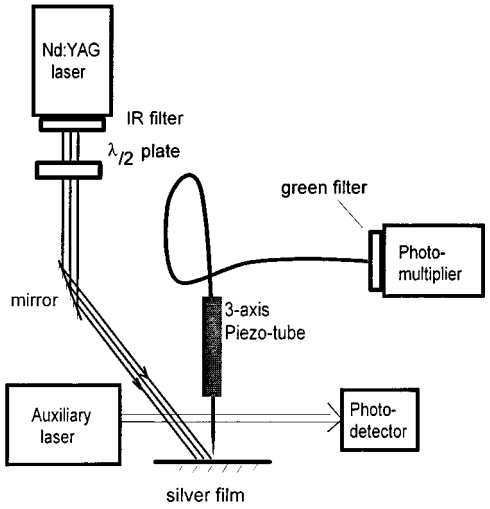

FIG. 1. Schematic view of the near-field optical microscope for second-harmonic light studies.

SHG over the surface has been imaged. Such images demonstrate that different mechanisms affect surface SHG at rough metal surfaces for *S*- and *P*-polarized excitation light. Our data clearly show near-field features inaccessible in the usual far-field measurements.

II. EXPERIMENTAL SETUP

Our experimental setup for near-field microscopy of second-harmonic generation is shown in Fig. 1. A 400-nm-thick silver film was prepared by thermal evaporation on a glass substrate and was used as the sample in our near-field optical microscope. The local SH field distribution has been probed with an uncoated adiabatically tapered fiber tip, which is drawn at the end of a single mode fiber by heating it with a CO_2 laser in a micropipette puller. The fiber tip can be scanned over the sample surface with a constant tip-surface distance of a few nanometers using shear force feedback control. Therefore, surface topography can be imaged with a resolution on a nanometer scale, while simultaneously recording the SH near-field image. The SHG has been excited at an angle of incidence of 60° with a Nd:YAG (yttrium aluminum garnet) laser operating at 1064 nm (repetition rate 10 Hz, pulse duration 20 ns, pulse energy 10–15 mJ). The excitation power at the sample surface is estimated to be about 1 MW/cm^2. The SH signal has been measured with a photomultiplier and gated electronics. The SH signal at every point of the image has been averaged over 70 or 100 laser pulses for *P*-polarized and *S*-polarized light excitation, respectively. The characteristic SH photon counting rate was on the order of one photon count per 3–5 laser pulses. The main source of noise in our data is statistical fluctuation ($N^{1/2}$) of the number of photon counts detected. The measured SH intensity depends quadratically on the fundamental light power. The spatial resolution of the microscope in the SH light collection mode has been determined to be better than 150 nm (this is the size of the smallest features visible in the SH images of piezoelectric ceramics and the sharpness of magnetic domain walls observed in SH images of a Ni surface[16]). The fiber tip itself did not contribute to the SH signal: we measured zero SH signal when the sample was far from the tip.

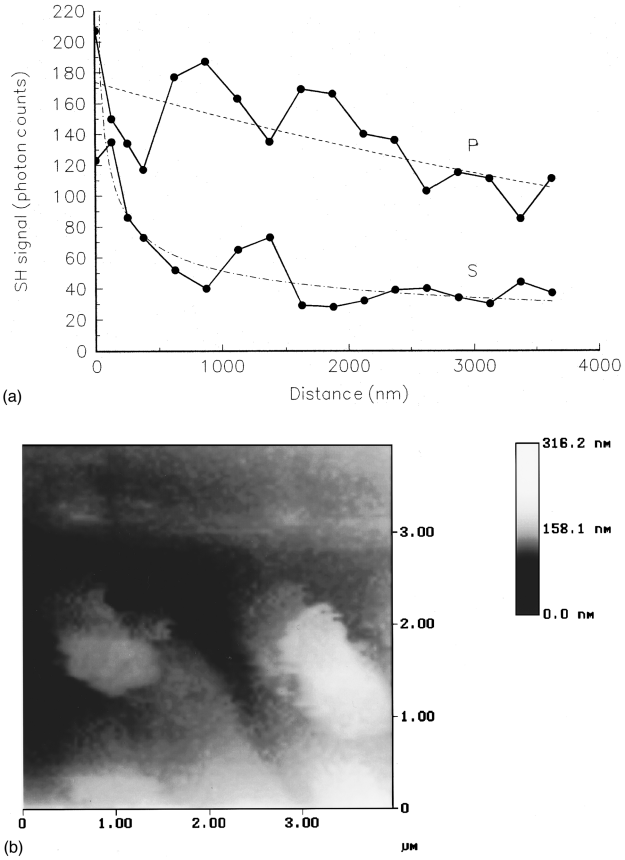

FIG. 2. (a) Variation of SH signal on the tip-sample distance for *S*- and *P*-polarized excitation. These variations have been measured in the center of the silver film region imaged in (b). The noise level in these data is determined by the statistic fluctuations ($N^{1/2}$). Dashed lines are simple power-law curves drawn as a guide to the eye.

III. RESULTS AND DISCUSSION

To determine the contribution of near-field processes to the SH generation, we have studied the dependence of the second-harmonic signal on the tip-sample distance for *S*- and *P*-polarized excitation light [Fig. 2(a)]. These measurements were made near the center of the silver film surface shown in Fig. 2(b). A rather strong decrease in the signal occurs about 500 nm from the surface. This behavior is especially pronounced for *S*-polarized excitation. This initial drop in the signal is followed by a number of oscillations for both polarizations. Note that each maximum for *P*-polarized excitation corresponds to a minimum for *S*-polarized excitation and vice versa. Similar oscillations have been observed at every point on the sample surface. We believe that this behavior results from the standing waves of the 1064 nm fundamental light formed between the glass tip and silver film surface. The phase shift of π between the distance dependencies can be explained by the phase shift of π between *P*- and *S*-polarized fundamental waves reflected between tip and metal at angles larger than the Brewster angle.

The ratio of the SH signals induced by *P*- and *S*-polarized

light changes substantially in the near-field region. This ratio falls from 3.1 at a distance of 3600 nm from the surface to 1.5 near the surface. This is a nontrivial near-field phenomenon. In the dipole approximation the nonlinear polarization $\mathbf{P}(2\omega)$ induced by incident laser light $\mathbf{E}(\omega)$ is equal to

$$P_i(2\omega)=\chi^d_{ijk}E_j(\omega)E_k(\omega)+\cdots. \quad (1)$$

Here χ^d_{ijk} is an electric dipole related source of the nonlinear susceptibility. Symmetry considerations show that this contribution is absent in centrosymmetric media and in this case the only remaining source of nonlinearity is a surface interface where inversion symmetry is broken. SHG from a perfectly flat metal surface can be excited mainly with *P*-polarized light while the much smaller *S*-polarized-light-induced SHG is a measure of the roughness of the surface.[17] In the near-field region there is a substantial contribution from evanescent fundamental and second-harmonic fields. Phase-matching condition and polarization selection rules are meaningless in the near-field region of a rough surface. Both are defined with respect to the plane of incidence by the direction of propagation and the normal to the surface. There is no direction of propagation for an evanescent wave. The normal direction depends on the scale of observation and does not coincide with the average normal to the sample surface. As a consequence there is a substantial increase in *S*-polarized-light-induced evanescent SH field in the vicinity of a rough surface.

Simultaneously measured topographical and near-field second-harmonic images of the silver film are shown in Figs. 3 and 4. For these figures characteristic data acquisition time was 4–6 h. The power of the 1064 nm light has been selected in a trade off between signal magnification and the rate of thermal drift of the image. The noise in the topographical image is due to the laser pulses striking the sample surface. The noise in the SH image results from statistical variations in the number of photons counted in individual pixels.

Near-field images in Figs. 3(b) and 3(d) have been measured using *S*-polarized excitation light. It appears that the main contrast mechanism for the *S*-polarized-light-induced near-field SH image is topography variation. The surface topography in Fig. 3(a) can be described as essentially flat regions at the top and at the bottom of the image separated by a narrow groove. The SH image [Fig. 3(b)] looks almost like a ''negative'' of the topographical image. The SH signal measured in the flat regions is much smaller than the signal measured near the groove. In Fig. 3(c) one can see generally flat regions at the left and at the right sides of the image divided by a step. Again, the SH signal measured near the step is much larger than the signal measured in the flat regions [Fig. 3(d)]. In both cases the enhancement of SH generation induced by *S*-polarized excitation occurs near the places on the surface where inhomogeneities are present. This effect has the same origin as the growth of the ratio of *S*-polarized- to *P*-polarized-light-induced SH signals near the rough surface discussed above.

Generally, *P*-polarized-light-induced SH images are much more complicated. The topographical image in Fig. 4(a) shows a rather usual picture of different crystalline grains randomly distributed over the silver film surface. In the SH image these grains have different brightness: the

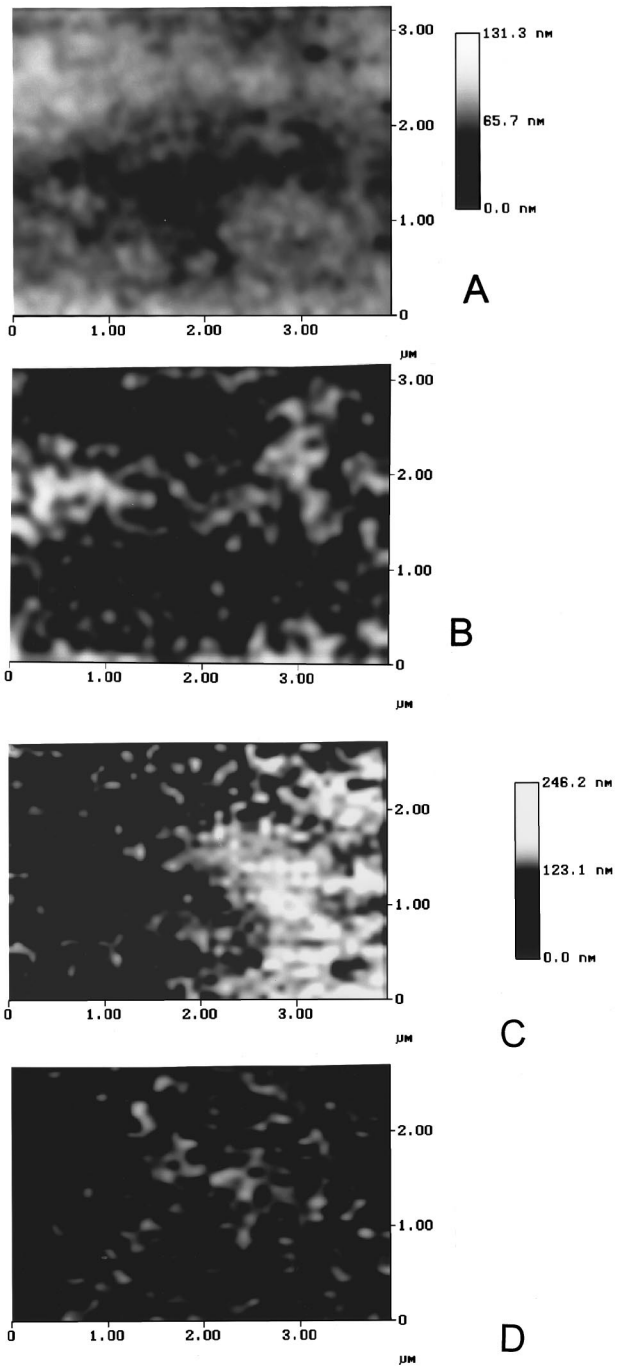

FIG. 3. Topography (a),(c) and SH light distribution (b),(d) measured for *S*-polarized excitation light.

grain in the bottom right corner looks much darker than the grain in the top right corner. This contrast may be due to the different crystalline orientation of different grains. SH generation is known to be sensitive to the atomic structure of the surface,[2] since in an isotropic metal such as silver the SH light is generated within the top few atomic surface layers. In addition, our experiments have been conducted under ambient conditions. Although we have used freshly prepared silver films, surface oxidization could have affected our results. The rate of surface oxidization depends on crystalline orientation. Thus, we may see a contrast that is related to surface chemistry of the silver film. It will be necessary to conduct further experiments in ultrahigh vacuum to clarify this issue.

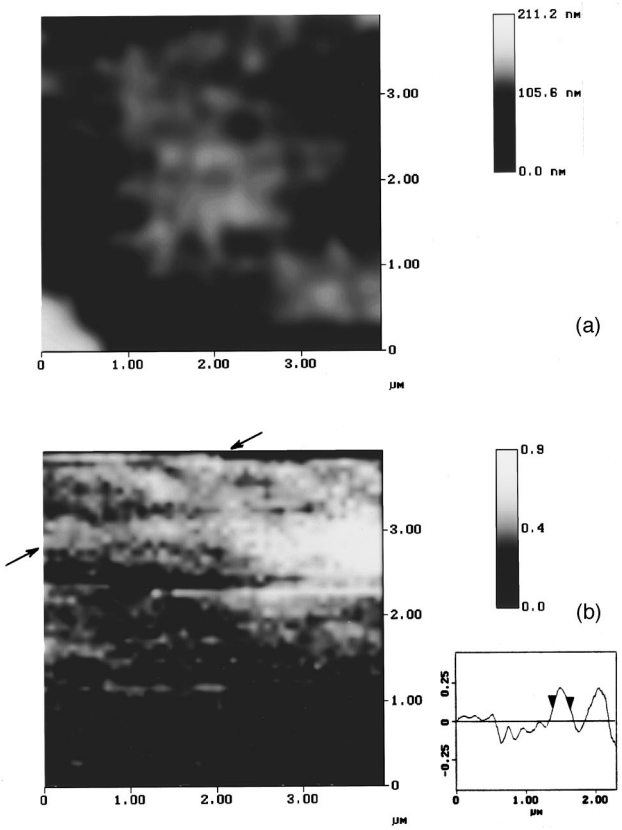

FIG. 4. Topography (a) and SH light distribution (b) measured for *P*-polarized excitation light. The cross section of the SH image along the line determined by the arrows is shown in the inset.

An interesting feature of Fig. 4(b) is the presence of small bright spots in the top part of the image. The cross section through two of these spots is shown in the inset. The width of the spot shown by the markers is equal to 240 nm, or about half of the wavelength of the SH light. Bright spots with similar sizes have been detected in the surface near-field distribution with surface plasmon-polariton (SPP) excitation.[10] These spots have been identified as the result of optical field localization.

In fact, SH generation at a rough surface and SPP excitation are closely related phenomena since any surface defect is a source of a surface wave.[15] Localization effects in the SH generation from rough metal surfaces have been predicted by McGurn, Leskova, and Agranovich.[7] It has been shown that multiple scattering leading to light localization gives a contribution to the SH generation. Both fundamental and second-harmonic wave localization contributes to the effect giving rise to components of SH light propagating perpendicularly to the average sample surface and in the reverse direction to the fundamental wave propagation, respectively. The latter process results in a local surface enhancement of the SH field. The spots observed in Fig. 4(b) may correspond to this localization. Previously, the SH field localization has been observed indirectly by measuring weak changes in the far-field angular distribution of the SH lights.[8]

IV. CONCLUSION

In summary, we have presented images of SH light emission taken in near-field proximity to a metal surface together with corresponding images of surface topography. Differences in the mechanisms of SH generation for different polarizations of the excitation light have been demonstrated. For *S*-polarized excitation the observed local SH generation is related mainly to the topology of the surface. For *P*-polarized light excitation, local enhancement of SH emission have been observed that may be attributed to SH field localization. We believe that these results are important for further development of SH near-field microscopy, which may become a useful tool in magnetic and electric domain imaging and has the potential for accessing the microscopic electrodynamics of rough surfaces.

ACKNOWLEDGMENTS

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