Second-harmonic generation from individual surface defects under local excitation

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Enhancement of optical second-harmonic generation (SHG) at individual defects on metal surface has been studied. SHG has been excited locally at chosen defects using a near-field optical microscope with an uncoated fiber tip. SH intensity enhancement up to ten times has been observed at the apex of micron size defects on a gold surface while the average enhancement is of about 1.2 times. Observed SHG enhancement has been described by lightning rod effect. Specific features of SHG enhancement due to local excitation are briefly discussed.

I. INTRODUCTION

Surface enhanced optical phenomena such as surface enhanced Raman scattering (SERS) and surface second-harmonic generation (SHG) have attracted continuous interest over the last decade as they provide a possibility for probing electrodynamics at rough surfaces and are sensitive tools for surface studies.[1–6] The intensity of related processes is enhanced by many orders of magnitude at metal surfaces with nanometer size features.

To account for SERS and SHG enhancement, electromagnetic mechanisms have been adopted in numerous theoretical studies that have given rise to detailed description of electromagnetic field properties close to rough metal surfaces. First models have considered a rough metal surface as an ensemble of noninteracting spheroids placed on ideally flat surface.[3,4] Enhancement of the electromagnetic field due to surface curvature (pure geometrical effect) as well as excitation of local surface plasmons at spheroidal particles have been taken into account. The total optical response from a surface is then calculated by averaging the field over spheroids with random distributions in size and shape. Next, the electromagnetic interaction between individual particles has been introduced that leads to a shift of the localized surface plasmon resonances and the establishment of a strong electromagnetic field between closely placed metallic particles.[5,6] Different models of collective mode of surface enhancement and an influence of propagating surface plasmon polaritons (SP's) have also been discussed.[1,7,8]

Nevertheless, up to now the exact verification of the existing models of the electromagnetic enhancement is far from being conclusive due to experimental difficulties in obtaining information which is free from uncontrollable factors such as surface structure parameters. In classical experiments on surface enhanced second-harmonic generation one has a possibility to measure only the intensity and the angular distribution of the SHG originated from the relatively large surface area (determined by the illuminating spot) and therefore averaged over a large number of defects without an exact knowledge of the surface morphology. The only approach has been to change by one or another way the distribution of defect size and shape and compare the measured tendencies of average SH enhancement with model predictions obtained for an average random defect ensembles. In an ideal experiment one would like to know exactly the size and shape of defects where second-harmonic light is generated. In the experiments on SHG from diffraction gratings, a long-range periodical structure of the grating plays major role as the resonant excitation of propagating SP's is the dominant enhancement mechanism while small-scale roughness and grating irregularity are assumed to affect the quantitative agreement between theory and experiment.[7]

Scanning near-field optical microscopy (SNOM) has opened a possibility for local optical studies.[9] With SNOM one can measure optical properties over the surface while simultaneously imaging its topography. Thus the detected optical signal can be related to the exact morphology of a surface. Linear optical measurements of the electromagnetic field distribution at different metal surfaces have demonstrated the field enhancement related to single defects as well as to defect ensembles.[10–12] Nevertheless, the data obtained with linear optical measurements of local field enhancement cannot always be directly extrapolated to nonlinear processes for which electromagnetic responses of a surface at both fundamental and second-harmonic wavelengths are important[3,6] and often coupled together (e.g., via nonlinear excitation of surface polaritons[13]).

Direct measurement of the second-harmonic generation in the near-field proximity to rough surfaces has been achieved recently showing strong presence of the inhomogeneous SH component in the vicinity of surface defects.[14,15] The correlation between near-field SHG and surface defect structure has been demonstrated for appropriate cases when field enhancement occurs at the pits or protrusions on a metal surface.[14–16]

In this paper we have studied far-field second-harmonic generation at individual surface defects excited locally at a chosen defect. In contrast to previous studies of second-harmonic generation from metal surfaces with SNOM, we have collected SH light in far field (as in conventional SHG measurements) while knowing exactly the origin of this SHG. This gives the possibility to identify a source of SHG enhancement which is related to different kinds of local excitations at rough surfaces.

II. EXPERIMENTAL SETUP

To achieve a local excitation of second-harmonic generation,[17] we have used a near-field optical microscope built on top of an inverted optical microscope. The sample was illuminated through an uncoated adiabatically tapered fiber tip with light of a picosecond Ti:sapphire laser ($\lambda = 790$ nm, 82-MHz repetition rate) which was coupled into a polarization preserving single mode fiber. Pulse duration after the fiber was about 5 ps. The polarization of the excitation light was controlled by rotating the output end of the fiber. The diffuse SH radiation from the sample was collected through the inverted microscope using a CP-Achromat objective with numerical aperture of 0.8 corresponding to an acceptance angle of about 106°. The SH light was then separated from the pump beam with a band-pass filter and measured with an avalanche photodiode connected to a photon counter. The SH signal at every point of the image was averaged over 30 ms. Typical count rates were of the order of one SH photon count per 100 excitation laser pulses. The measured SH intensity was verified to depend quadratically on the fundamental light intensity.

The distribution of the SH enhancement over a surface was imaged by moving the excitation position. Image acquisition (128×128 pixels) was achieved by scanning the sample mounted on a two-dimensional-piezoscanner against a fiber tip. To ensure constant tip-surface separation (of the order of a few nanometers) during scanning and, as a result, simultaneous topography imaging, shear-force distance regulation conventional in SNOM was used.[9] For this purpose a fiber tip was fixed on a resonantly excited quartz tuning fork which is mounted on a piezotube. The piezotube keeps constant tip-surface distance compensating the deviation of the shear-force signal detected by a tuning fork which arises due to the tip-surface interaction.

Thus described technique allows us to obtain high-resolution information about the topography of the sample and to excite second-harmonic generation at the specifically chosen surface defects. With uncoated fiber tips one can achieve a good spatial localization of the excitation and avoid strong perturbation of the field distribution close to the surface that is always introduced by metal coated tips.

III. RESULTS AND DISCUSSION

We have studied second-harmonic generation from the surface of a gold film thermally evaporated onto a polished amorphous glass substrate. The nominal mass thickness of the film was 30 nm as determined by the quartz sensor during evaporation. Topographical images of the surface reveal large areas with topography variations less than 10 nm and occasional bumps and pits with lateral dimensions of about one micrometer. In the surface region shown in Fig. 1 one can see ~30-nm-high bumps exhibiting nearly conical shape. Second-harmonic images show a strong (up to ten times) enhancement of SHG at these defects compared to the ''flat'' surface on which they are placed. Other surface defects, which are more flat, also reveal themselves in the SH images but the corresponding SHG enhancement is much lower. Average enhancement of second-harmonic at this surface region recalculated from the data of local measurements is of about 1.2 times while local enhancement reaches values up to 10 times at the apex of the defects (Fig. 2).

Rotating the polarization of the fundamental light by 90°, the overall distribution of SHG remains the same but the value of the enhancement is three to four times lower (Fig. 1). The latter is probably related to the fact that the fiber tip is not parallel to the axis of the cone-shaped defects. Therefore the component of the electric field parallel to the cone axis changes during the rotation of the excitation light polarization leading to a different degree of SHG enhancement. From the changes of the SH intensity for different excitation polarizations, the angle between the SNOM tip axis and the normal to the mean surface of the sample has been estimated to be not less than 10°.

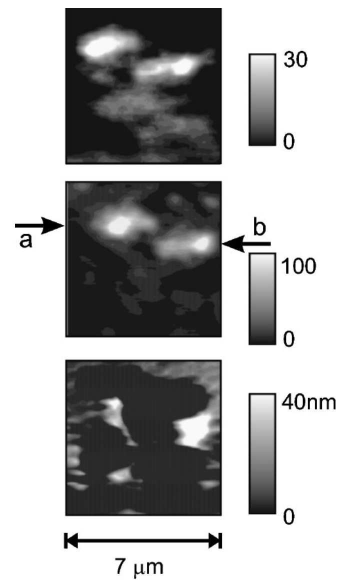

FIG. 1. Topography (bottom) and corresponding SH images of a gold film for two orthogonal polarizations of excitation light (relative grey scales). Please note that the upper image has been recorded after the others and is slightly shifted with respect to them. Arrows indicate the defects shown in Fig. 2.

In the general form an enhancement of the second-harmonic generation excited and detected in the far-field of a surface defect can be expressed by[3,4]

$$I_{SH} \sim b^4 |L(2\omega) L^2(\omega)|^2, \quad (1)$$

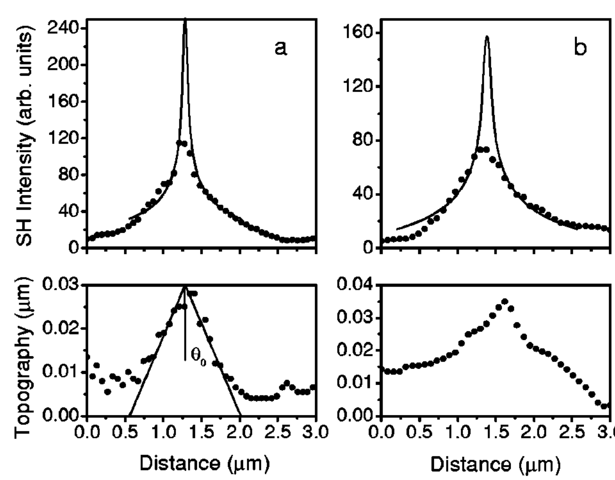

FIG. 2. Topography and SH intensity cross sections [(a) and (b)] indicated by arrows in Fig. 1. Symbols represent the experimental data, solid lines are the model calculations for lightning rod effect.

where b is a characteristic size of a defect, $L(2\omega)$ and $L(\omega)$ are field enhancement factors at fundamental and second-harmonic wavelengths, respectively, that describe enhancement due to the geometrical shape of a defect and the localized surface plasmon excitation. Local field enhancement factors can be easily calculated analytically for simple shape defects like spheroids on a conducting surface.[1–4] Factor b^4 in Eq. (1) describes the surface area that contributes to SHG and the fact that SH light propagating into the far-field region is originated by coherent radiation of the nonlinear dipoles at a surface of a defect. (The latter condition is relaxed for the second-harmonic observed in the near-field of a defect where both homogeneous and inhomogeneous SH waves are present.[14])

In contrast to the excitation with a single plane wave for which Eq. (1) is derived, under the local excitation with a SNOM tip one should take into account both homogeneous and inhomogeneous components of the fundamental field. To adopt the above-described SHG enhancement for the near-field excitation, Eq. (1) should be averaged for all possible **k** vectors present in the near field of a tip. From the physical point of view an illumination with a SNOM tip leads to an effective excitation of the higher multipoles and the excitation of propagating surface polaritons.

A geometrical factor b^4 in Eq. (1) depends on the excitation mode as well. If the lateral resolution of a SNOM (described qualitatively by the tip size a) is better than the particle size b, then the only $\sim(a/b)^2$ part of the particle surface is excited. Nevertheless, if the surface plasmon localized at the particle (an excitation of the particle as a whole) is excited the whole surface of the particle will contribute to the SHG. In a case when the localized surface plasmons are not important and only geometrical enhancement plays a role, only surface area under excitation is important. In the opposite limit, when surface particle is much smaller than the illuminated area, $a \gg b$, obviously, the whole particle is excited.

Local field enhancement factor $L = L_{LR} L_{SP}$ reflects both electromagnetic field enhancement at the surfaces of large curvature (lightning rod effect) and localized surface plasmon excitation.[3,4] In our case (Fig. 1, defect A), dipolar localized surface plasmon related to the major axis of the oblate spheroid[18] of volume $V \approx 0.03\ \mu\mathrm{m}^3$ is estimated to be at about 0.9 eV which is much lower than the fundamental and second-harmonic photon energies. Surface plasmons related to higher multipoles are expected to be at even lower energies. Therefore an enhancement related to localized surface plasmons is not important for such defects.

Thus the lightning rod effect seems to be the only important mechanism in our case. To estimate this geometrical field enhancement we have considered the surface defects (Fig. 1) as particles of conical shape. The field enhancement close to the apex of such particles can be easily estimated in the electrostatic model according to[19]

$$E \sim 1/r^{1-\nu}. \tag{2}$$

Here, r is a distance to the cone apex, and ν is a first root of $P_\nu[\cos(\theta_0)] = 0$, where P_ν and θ_0 are Legendre function and the cone angle, respectively.

For the calculation of the SHG dependencies in this model, the cone angles have been taken from experimental topography images. The resolution of the microscope is assumed to be better that the size of the defects, so that the geometrical factor in Eq. (1) is determined by the resolution and is the same for both defects under consideration. Finally, background SHG intensity at the ''flat'' regions of a film and a factor dependent on the polarization of the excitation have been used as fitting parameters.

Comparison of the SHG enhancement according to this model and the experimental data for different defects are shown in Fig. 2. The observed SH intensity depends on the position of the tip over defects and reaches its maximum at the apex of the defects as it is expected for the lightning rod effect. This simple model gives a fairly good agreement for the shape of the SH intensity distribution but leads the divergency of the field at the apex of the ideal cone [Eq. (2)]. When taken into account, the finite size of a cone apex will eliminate this problem resulting in the smaller local enhancement. In turn, the finite resolution of a SNOM will lead to an averaging of the signal over the excitation area and to the subsequent reduction of the observed enhancement at the cone apex. The considered model of the lightning rod effect is formulated here for a perfect conductor, the smaller absolute value of the enhancement should be expected if the dielectric constants of gold are taken into account. Moreover, the small height-to-base ratio of the defect may lead to the strong influence of an additional decay channel, namely, into propagating surface polaritons, that will reduce the local enhancement as well.

Finally, resemblance should be noted between the experiments with SP excitation on diffraction gratings[7,8] and local excitation using a SNOM tip. In the latter case, propagating SP's can be effectively launched on a surface by light passing through a SNOM tip as was discussed above. The SP-related effects take place on the length scale determined by the SP propagation length which is much greater than the image size. Thus it could turn out that in our experiments the SH light distribution is observed on the SHG background related to surface polaritons. The off-SP-resonance SH signal from diffraction gratings has also been anticipated to reveal the enhancement due to small-scale roughness of the grating[7] that has been recently observed with SNOM.[15] Since the measurement of the absolute value of the enhancement is beyond the scope of this work, we cannot conclude about the presence and nature of possible background.

IV. CONCLUSION

We have studied second-harmonic generation at individual surface defects using a scanning near-field microscope working in the second-harmonic excitation mode. This provides the data on the local SHG enhancement together with an exact knowledge of the topography of a surface where this enhancement occurs. Although the mechanisms of SHG enhancement at surface defects are commonly accepted in general, without simultaneous local measurements of topography and SHG there has been no possibility to see and study this enhancement directly at one individual defect of known size and shape.

Simultaneously recorded optical and topography images reveal the correlation between the lateral distribution of the second harmonic signal and the defect morphology. Local enhancement of the SHG up to ten times at the defects of micron size lateral dimensions has been observed at the rough gold films while the average SHG enhancement is only of about 1.2 times. This enhancement has been described by pure geometrical effects. As the value of the enhancement depends on polarization of the excitation light with respect to the conical defect axis, at the different excitation geometries providing polarization of the fundamental light collinear to the cone axis, the SHG enhancement is expected to be stronger.

Usually, the second-order nonlinear susceptibility $\chi^{(2)}$ of small metallic particles is considered to be independent on the particle size. This assumption breaks down for really nanoscopic particles where quantum size effects play significant role. Additional changes of effective $\chi^{(2)}$ is also predicted in the near field of a SNOM tip.[20] Investigations of local second-harmonic generation are inevitable to examine these issues experimentally.

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[1] M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).

[2] *Nonlinear Surface Electromagnetic Phenomena*, edited by H.-E. Ponath and G. Stegemann, (North-Holland, Amsterdam, 1991).

[3] G.T. Boyd, Th. Rasing, J.R.R. Leite, and Y.R. Shen, Phys. Rev. B **30**, 519 (1984).

[4] C.K. Chen, T.F. Heinz, D. Ricard, and Y.R. Shen, Phys. Rev. B **27**, 1965 (1983).

[5] J.I. Gersten and A. Nitzan, Surf. Sci. **158**, 165 (1985).

[6] V.M. Shalaev and A.K. Sarychev, Phys. Rev. B **57**, 13 265 (1998); E.Y. Polyakov, V.A. Markel, V.M. Shalaev, and R. Botet, *ibid.* **57**, 14 901 (1998); **60**, 2127 (1999).

[7] A.C.R. Pipino, R.P. Van Duyne, and G.C. Schatz, Phys. Rev. B **53**, 4162 (1996).

[8] H.J. Simon and Z. Chen, Phys. Rev. B **39**, 3077 (1989).

[9] *Near Field Optics*, edited by D. W. Pohl and D. Courjon, (Kluwer, Dordrecht, 1993).

[10] S.I. Bozhevolnyi, I.I. Smolyaninov, and A.V. Zayats, Phys. Rev. B **51**, 17 916 (1995); S.I. Bozhevolnyi, B. Vohnsen, I.I. Smolyaninov, and A.V. Zayats, Opt. Commun. **117**, 417 (1995).

[11] D.P. Tsai, J. Kovacs, Z. Wang, M. Moscovits, V. Shalaev, J. Suh, and R. Botet, Phys. Rev. Lett. **72**, 4149 (1994).

[12] S.I. Bozhevolnyi, V.A. Markel, and V. Coello, Phys. Rev. B **58**, 11 441 (1998).

[13] Y.R. Shen and F. de Martini, in *Surface Polaritons*, edited by V. M. Agranovich and D.L. Mills (North-Holland, Amsterdam, 1982), p. 629.

[14] I.I. Smolyaninov, A.V. Zayats, and C.C. Davis, Phys. Rev. B **56**, 9290 (1997).

[15] A.V. Zayats, I.I. Smolyaninov, and C.C. Davis, Proc. SPIE **3732**, 81 (1999).

[16] I.I. Smolyaninov, C.H. Lee, C.C. Davis, and S. Rudin, J. Microscopy **194**, 532 (1999); A.V. Zayats, I.I. Smolyaninov, and C.C. Davis, Opt. Commun. **169**, 93 (1999).

[17] Schematic diagram of a near-field second-harmonic microscope working in the SH excitation mode employed here can be found, e.g., in Ref. 15.

[18] Depolarization factor used for this estimation has been calculated from the topography image to be ~ 0.025.

[19] L.D. Landau and E.M. Lifshits, *Electrodynamics of Continuous Media* (Pergamon, London, 1984).

[20] J.M. Vigoureux, C. Girard, and F. Depasse, J. Mod. Opt. **41**, 49 (1994); A. Liu and G.W. Bryant, Phys. Rev. B **59**, 2245 (1999).