Feasibility Study for Near-Field Optical Sum-Frequency Generation Spectroscopy Using a Metal-Coated Fiber

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A near-field optical spectroscopy technique has been developed that collects the nonlinear sum-frequency signal from the surface adsorbed monolayer sample. The sum-frequency signal generated at the surface was collected with a silver-coated multi-mode fiber probe. The metal coating of the fiber effectively eliminates the far-field stray light that enters the core fiber from the outer edge, passing through the clad region. As the tip was pulled away from the sample surface, the sum-frequency signal from the GaAs crystal sample decreased rapidly with increasing tip–sample distance, indicating that the signal is essentially due to the near-field generated by the sum-frequency process. By using the metal-coated multi-mode fiber probe, information about the vibrational structure of the adsorbed molecules at the surfaces is studied. [DOI: 10.1380/ejssnt.2013.76]

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I. INTRODUCTION

Molecules adsorbed at or near a surface dramatically influence the surface properties in applications such as corrosion inhibition, catalysis, electronics, wettability, and biocompatibility [1, 2]. For investigation of the surface and interfacial structure, second-harmonic generation (SHG) and sum-frequency generation (SFG) are powerful techniques in material analysis. SHG and SFG processes occur only at the surface of such media, where the symmetry is broken, and appear to be highly surface-specific for interfaces between centrosymmetric media, since they are based on a second-order nonlinear optical process. Especially, SFG spectroscopy is widely used for the study of surfaces and interfaces and is applicable to a wide range of samples. In general, the spatial distribution of the molecules on the surface cannot be taken into account in SFG, because SFG spectroscopy yields a macroscopic signal from the interface without any spatial resolution. To obtain information about the vibrational information of molecules at the surface, an SFG micro-spectroscope is also able to spectroscopically and spatially investigate surfaces since it has surface specificity, a high sensitivity, a high chemical selectivity, and a potential spatial resolution of approximately a few μm [3–6].

On the other hand, sub-wavelength lateral spatial resolution can be reached by using near-field optical microscopy (SNOM) [7]. The fine resolution offered by SNOM helps to resolve the local features on a nanometer scale and obtain a better understanding of relationships between microscopic and macroscopic molecular structures and configurations, which may, in turn, supply additional insight into molecular engineering for nanometer-scale devices. However, the drawback of the near-field optical Raman experiment is that the recorded signals correspond to a probed depth of about a quarter of the wavelength [8]. Consequently, it would then be extremely fruitful to couple the interface-sensitive SFG spectroscopy with near-field optical microscopy to obtain the vibrational structure at the interface with spatial resolution of about 100 nm. Several attempts to combine near-field optical microscopy with SFG have been made. In these previous studies on combining the near-field technique with SFG, several groups tried to probe the near-field SFG signal using an optical shear-force microscope integrated with the SFG system. Shen and co-workers first demonstrated near-field imaging of the SFG signal from a small nonlinear organic crystal using visible and near-IR beams [9]. Schaller and Saykally, and Humbert et al. probed the near-field IR–VIS SFG signals from noncentrosymmetric materials [10, 11]. Although their spatial

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FIG. 1: (a) Schematic diagram of the experimental configuration. (b) Photograph of the SNOM apparatus on the SFG sample stage.
resolution results are excellent as compared with that of a far-field SFG microscope, they have not tried to provide any information about the vibrational structure of molecules at the surfaces. One significant drawback of high-resolution aperture SNOM probes is their low energy throughput. The origin of this low throughput lies in the fact that narrow cylindrical dielectric waveguides with a metallic coating have a cutoff beyond which only evanescent fields exist. Therefore, Schaller and Saykally, and Humbert et al. used a non-coated fiber for the collection of the near-field SFG signal [10, 11]. However, as discussed below, use of a non-coated fiber has a risk to collect the far-field stray light together with near-field light. Therefore, the development of high-throughput near-field optical devices, which effectively eliminates the stray light, is required for collection of the weak near-field signal from targeted regions of a material’s surface.

The aim of this paper is to present the results of preliminary experiments on coupling SFG and near-field optical microscopy for the detection of the vibrational signal of molecules which transcends the far-field diffraction limit on spatial resolution. We also perform finite-difference time-domain (FDTD) calculations on the optimization and the characterization of the metal-coated fibers.

II. EXPERIMENTAL

A previously described laboratory-made near-field microscope [12], equipped with a shear-force scanning microscope, was employed for the collection of the near-field light of SFG. Figure 1 displays our experimental device. The near-field optical signals were collected by the fiber probe, which was kept close to the surface by means of a feedback loop measuring the damping of the lateral vibration amplitude of the tip. The tips were laboratory-made optical fiber tapers, obtained commonly by the heating-and-pulling technique. For the fiber probe, single-mode (Newport, F-SMF-28, NA = 0.13, mode field diameter = 9.3±0.5 μm) and multi-mode fibers (Newport, F-MLD, NA = 0.29, core diameter = 100±4 μm) were used for this study. A thin silver layer was deposited on the tapered fibers from the oblique direction. The thickness of the silver coating was about 30 nm.

The SFG system employed in this experiment has been described in detail in a previous publication [13]. Tunable IR laser beam was generated by the optical parametric generator/amplifier (OPG/OPA, Ekspla, PG401 VIR/DFG) pumped by a mode-locked Nd:YAG laser at 1064 nm (Ekspla, PL-2143D, 25 ps, 10 Hz). The second-harmonic of the YAG laser was used for the visible pump beam of the SFG. As shown in Fig. 1, the 532 nm pulse was incident on the sample at 70° normal and was focused to a 50 μm spot by the fused silica lens (f = 800 mm) for simplicity of alignment. The polarization of the 532 nm light was controlled with a zero-order half-waveplate and checked with a polarizing cube. The p-polarized IR pulses were focused on the sample by the ZnSe lens (f = 100 mm) at a 50° angle to a 150 μm spot size. The overlap of the two spots was spatially coincident with the point at which the SNOM probe investigated the sample. The near-field optical configuration used was the external reflection collection mode. All SFG data were collected using p-polarized visible and p-polarized IR pulses. The prism-monochromator (PF-200, Bunkoukeiki Co., Ltd.) and holographic notch filter were used to remove scattered excitation light, and the SFG light was detected by a photomultiplier (PMT, Hamamatsu, R649).

III. RESULTS AND DISCUSSION

First, we simulated the scattering of electromagnetic radiation from the metal-coated and non-coated multi-mode fiber tips using the FDTD method [14]. Simulations were performed for tip–sample separations of 0 and 1000 nm.
with the sample assumed to be glass with a refractive index of 1.46. The electric field was polarized perpendicular to the plane of incidence. The refractive indices of the clad and of the core of the tip are 1.46 and 1.49, respectively. For the FDTD calculation, the diameter of the tip apex aperture was set to 125 nm, and the core area is assumed to be 71%. The angle and the diameter of the first and second cones of the tip are 90° and 53°, and 1.94 µm and 4.52 µm, respectively. For the metal-coated tapered model tip, the thickness of the silver was 50 nm. The simulated electric field distributions are illustrated in Figs. 2(a) and (b). Figure 2(c) shows the simulated field intensity collected by the tip versus the sample-tip distance. We also simulate the electric field propagation for the different kind of the core shape of the tapered tips, and we have found that the tapered shape does not seriously affect the propagation of the near-field light. Instead, significant effects from the far-field stray light are always propagated in the case of the non-coated fiber even in the case when the tip position is far from the surface, as shown in Fig. 2(c). This far-field light comes from the outside of the fiber and passes through the clad region. In contrast, the silver-coated fiber tips effectively eliminate the effect of the far-field light as shown in Fig. 2. On the other hand, the electric-field intensities are not changed significantly by the silver coating when the sample-tip distance is much smaller than λ/4. Thus, we conclude that the metal coating is necessary both in the case of the tapered fiber for the collection of the near-field light from the surface.

Based on the above calculation results, we tried to collect the near-field SFG signal by using the metal-coated multi-mode fiber. Figure 3 displays the SFG intensity of the GaAs sample collected by the 30 nm silver-coated multi-mode fiber tip versus the sample-tip distance. The SFG signal is generated by the 532 nm visible laser and the 3472 nm infrared laser. In order to avoid irradiation damage, the fluence of the visible beam was kept below 3 µJ per pulse. The signal was averaged over 300 pulses by a gated integrator for every data point. The distances are estimated from the voltage applied to the Z-piezoceramic. As shown in Fig. 3, the SFG signal decreased rapidly when the fiber was pulled away from the sample surface. At the sample-tip distance from 500 to 2000 nm, the intensity of the sum-frequency signal gradually decreased, and we found that it is completely disappeared at the sample-tip distance of about 10000 nm. Thus this residual sum-frequency signal must be derived from the far-field sum-frequency light, because the thickness of the silver coating is 30 nm. After the subtraction of the residual signal, a sample-tip distance of about 100 nm is necessary in order to reach half the peak intensity. The observed sum-frequency response is fitted by an exponential curve exp(−d/dp) with dp = 135 nm. Such evolution indicates that the signal recorded by the tip is essentially due to the near field of the electric field generated by the sum-frequency process. It should be noted that such a trend was not observed when we used the non-coated single-mode fiber tips for the SFG collection. In the case of the non-coated single-mode fiber tip, the decrease of the sum-frequency response against the sample-tip distance is much weaker than that of the silver-coated multi-mode fiber. This must be caused by the far-field SFG light that comes from the outer edge of the taper and passes through the clad, as mentioned above. Furthermore, no SFG signal was observed using the silver-coated single-mode fiber, probably due to the small NA of the single-mode fiber (NA=0.13) as compared to the multi-mode fiber (NA=0.29). Another plausible reason why the silver-coated single-mode fiber could not collect the near-field SFG signal is because the smaller core diameter of the single-mode fiber than that of the multi-mode fiber. Near-field light, which is localized on the sample surface, is scattered by the tip in all directions when the sample-tip distance is smaller than λ/4. When it comes into the tip from the small aperture, the scattered light is converted into propagating light in the fiber. In this sense, the propagating light can be more effectively propagated by the large cross-sectional cylindrical dielectric waveguides of the multi-mode fiber than in the case of the small core diameter of the single-mode fiber.

Next, we demonstrate the detection of the near-field SFG vibrational signal of the gold sample coated with octadecanethiol (ODT). The Au substrates were prepared by thermal evaporation on Si(110) under high vacuum conditions (ca. 10⁻⁶ Pa). The thickness of the Au film was about 100 nm. The substrate was immersed into an ethanol-diluted ODT solution at a concentration of 1 mM for 24 h at room temperature. After removal from the solution, the samples were rinsed with pure solvent for removal of weakly adsorbed molecules on the ODT monolayers. Figure 4(a) shows the near-field SFG spectrum taken by the silver-coated fiber tip. For comparison, we also measure the far-field SFG spectrum of the ODT-coated Au sample in Fig. 4(b). The far-field SFG spectrum of the ODT adsorbed on the Au is dominated by the nonresonant SFG signal from the gold surface on which resonant signals from adsorbate molecules appear as inverted peaks. Three dominant peaks are observed at 2882, 2940, and 2970 cm⁻¹ in the far-field SFG spectrum of the ODT adsorbed on the Au, which can be attributed to the symmetric stretching mode of the methyl group, the Fermi resonance between the methyl symmetric stretching and a bending overtone, and the asymmetric stretching mode of the methyl group, respectively [15].
dominance of the methyl resonances reflects the conformational order of the film and agrees with previous work for a close-packed alkanethiolate monolayer on gold. The near-field SFG spectrum of the ODT adsorbed on the Au were taken from 2850 to 2900 cm$^{-1}$. The dip centered at 2880 cm$^{-1}$ derived from the symmetric stretching mode of the methyl group is clearly detected by the fiber probe. Although it is hard to see the whole range spectrum due to the irradiation damage of the Au sample, we succeeded in obtaining the near-field vibrational information from the surface.

In conclusion, we have shown the preliminary results of the near-field sum-frequency optical micro-spectroscopy for studying molecular vibrational information at a surface. Using the silver coated multi-mode fiber probes, we succeeded in collection the near-field signals generated at the surface, and the silver coating effectively eliminates the far-field light. This experiment is a first step in coupling SFG spectroscopy with near-field optical microscopy. However, submicronic lateral spatial resolution and near-field imaging were not demonstrated in this experiment. We have noted that it takes a fairly long time to obtain the near-field SFG image using a 10 Hz laser system. One advantage of the SNOM system is that it can obtain the AFM image, which can be used for the same near-field probe. Although the usually accepted surface coverage limit for detecting far-field SFG signals is around 10%, one could hope to use the near-field SFG microscope to obtain the vibrational spectrum of these localized molecular aggregates in the case of molecular aggregates with a high local density. While the scanning near-field images at the surface adsorbed molecules are not demonstrated here, this paper is the first step toward a microscopic device of sum-frequency generation spectroscopy. Coupled SFG and near-field microscopy can certainly be applied to numerous heterogeneous interfaces relevant to various fields of surface sciences.

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