Time-gated scanning near-field optical microscopy

S. K. Sekatskii,[a] G. T. Shubeita, and G. Dietler
Institut de Physique de la Matière Condensée, Université de Lausanne, BSP, CH-1015, Lausanne-Dorigny, Switzerland

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A time-gated scanning near-field optical microscope (SNOM) has been developed. The optical signal was recorded at the precise moment during the fiber tip oscillation period when it made contact with the sample surface. The use of such an approach substantially improves the signal-to-noise ratio for common SNOM applications such as frustrated total internal reflection, surface plasmon imaging, and fluorescence resonance energy transfer-based SNOM. The observed dependence of the frustrated total internal reflection optical signal on the gate delay time confirms that repetitive bumping is the mechanism responsible for the shear force tip–sample interaction. © *2000 American Institute of Physics.* [S0003-6951(00)01340-1]

Scanning near-field optical microscopy (SNOM) is becoming a widely used method in nanotechnology, surface and material physics, biology, and other fields (see, e.g., Refs. 1 and 2, for a recent review). Nowadays, sharpened optical fibers are the most commonly used near-field probes, and the shear-force method, first proposed in 1992,[3,4] is normally chosen to regulate the tip–sample distance. The method is based on driving the fiber tip into lateral dithering and detecting damping in its oscillation when approaching the sample surface.

Although some ambiguity about the nature of the shear force persists,[1,2] recent reports tend to hint at ''repetitive bumping'' or ''knocking'' as the mechanism for such forces, at least for the most common experimental conditions: the laterally vibrating SNOM tip, which is rarely precisely vertical to the sample surface, bumps into the surface at one specific moment of each oscillation period. Mathematically, this mechanism can be expressed as follows: the equation describing the tip vibration under the action of an external force F_{ext}, is $m_{\text{eff}}\ddot{x}+\gamma\dot{x}+kx=F_{\text{ext}}$, with m_{eff} being the effective oscillator mass. The damping coefficient γ and the spring ''constant'' k are not constant throughout the whole oscillation period. Instead, after the tip bumps into the surface at some critical point x_{crit}, during its oscillation period, an additional spring constant k_{add}, and damping coefficient γ_{add}, appear because part of the kinetic energy of the tip is imparted into its mechanical deformation. Thus, terms like $\theta(x-x_{\text{crit}})k_{\text{add}}(x-x_{\text{crit}})$, where $\theta(x-x_{\text{crit}})$ is a step function, should be added to the left-hand side of the equation above.[5] This leads to the simultaneous increase of the resonance frequency and quality factor of the oscillation.[5–7]

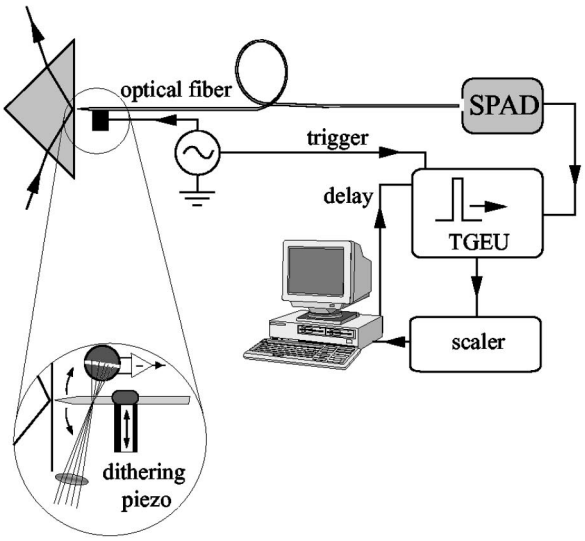
The same conclusions about the character of the tip–sample interaction were obtained using combined scanning tunneling microscope–SNOM devices. The shear-force signal appears always in synchronization with the electric current pulses, which implies that the tip and the sample are in contact.[8]

In usual SNOM detection schemes, photons are collected during the many approach–retraction cycles of the fiber dithering, i.e., the optical signal is the average over the corresponding range of the tip–sample distances. The amplitude of the lateral oscillations of the fiber is usually smaller than the fundamental limit of the microscope's resolution (typically, 50–100 nm governed by the probe's aperture), hence, the fact that it oscillates while raster scanning the object under study posed no problems in many cases. Nevertheless, it is possible to name some applications where this averaging can lead to an essential decrease in the signal-to-noise ratio and, hence, in the sensitivity and spatial resolution of the method. Such applications include ''interface-related'' phenomena, such as, frustrated total internal reflection, surface plasmons,[1,2] and, most crucially, fluorescence resonance energy transfer (FRET) between fluorescence centers located on the sample surface and those on the tip apex.[9]

In the FRET case, a donor chromophore on the apex of the tip is optically excited and its excitation is transferred to an acceptor chromophore on the sample surface (or vice versa), which in turn emits light to be registered. When imaging via collection of the acceptor fluorescence, the spatial resolution, as well as the sensitivity, are ameliorated relative to conventional SNOM,[9] due to the fact that the energy transfer is effective only when the chromophores are separated by distances not larger than about 1–5 nm—the Förster radius. The energy-transfer probability decreases as the inverse sixth power of the distance separating the chromophores (see, e.g., Ref. 10, for a review). Imaging under these circumstances means that the collected light is mostly due to the acceptor fluorescence only when the tip is closest to the sample and, thus, the contact–selective light collection should increase the signal-to-noise ratio.

Recent observations of the nanolocal contact-dependent FRET processes and the demonstration of the FRET SNOM (Refs. 11 and 12) make the development of a SNOM capable of contact–selective light collection timely, and in this letter we report the realization of such a time-gated SNOM. To demonstrate the utility of the time-gated SNOM, we used the frustrated total internal reflection scheme (FTIR) (see Fig. 1) because the strong exponential dependence of the FTIR optical signal on the tip–sample distance is well established.[1,2] Uncoated fibers, sharpened by chemical etching in a HF so-

[a]Electronic mail: sergey.sekatskii@ipmc.unil.ch



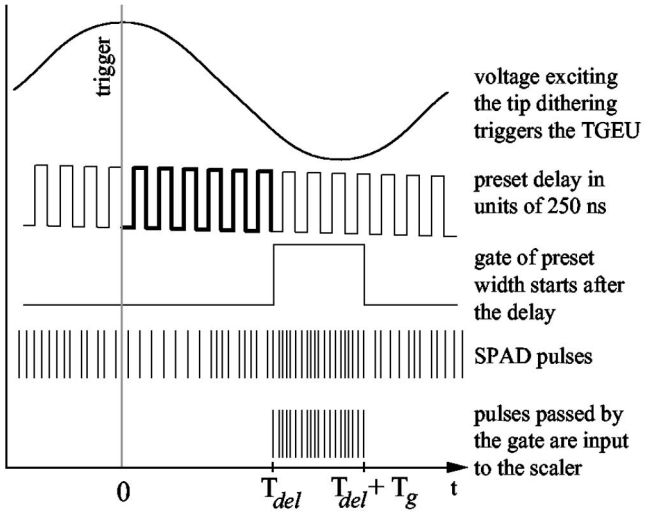


FIG. 1. Schematic of the experimental setup and time diagrams illustrating the operation of the time-gating electronic unit (TGEU).

lution to a radius of curvature below 200 nm, were used as the near-field probe of the homemade SNOM described earlier.[11]

The optical shear-force detection scheme[3,4] (see the inset of Fig. 1) was used to control the distance between the tip and the prism surface. Light collected by the sharpened fiber was detected by a single-photon avalanche diode (SPAD) with the noise level of $\sim 80\,s^{-1}$ (EG&G, Canada). Usual SPAD (or photomultiplier tube) -based photon detection schemes, designed to measure very low-light levels (e.g., single-molecule fluorescence), imply the use of a scaler (frequency-to-voltage converter) which counts the SPAD pulses during a preset integration time T_0 (typically, 100–200 ms) and converts the counted number into a proportional voltage which is then used as the SNOM signal.[1,2] An analogous scaler has been constructed and used by us earlier when measuring the contact-dependent FRET phenomena in the geometries of SNOM and atomic-force microscope.[11] To realize the time-gated version of the detector, we combined this scaler with an additional independent computer-controlled electronic unit,[13] which we will refer to as a time-gating electronic unit (TGEU) below.

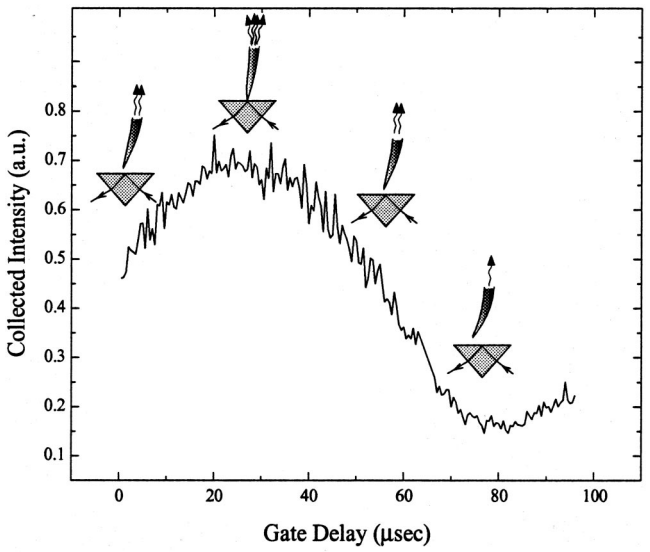


FIG. 2. Dependence of the optical frustrated total internal reflection signal on the delay time. Relative tip–prism surface positions are shown to illustrate the dependence.

Time diagrams illustrating the operation of the TGEU are depicted in the lower part of Fig. 1. Briefly, this electronic unit enables the time-gated registration of the SPAD pulses with the manually preset gate width T_g ranging from 250 ns to 32 μs, with a very large repetition rate (up to hundreds of kHz) using the full range of the delay time T_{del} (from 250 ns until the period minus 250 ns, controlled via a personal computer). It should be noted that these requirements (high-repetition rate, very short input pulses, and the necessity to work with delay times covering the whole oscillation period) are not provided by most standard boxcar integrators.

The same sine-wave generator which excited the lateral vibrations of the tip was used to trigger the TGEU [in our experiments we used the Stanford Research Systems lock-in amplifier (SR850) both to excite the tip vibration and to detect the shear-force amplitude used as the SNOM feedback signal]. The phase shift between the trigger signal and the moment of the oscillation period when the tip–sample contact occurs is not known beforehand and, thus, the moment of the contact should be found as corresponding to the maximum of the optical signal with respect to the delay time T_{del} with a fixed gate width T_g.

The TGEU output as a function of the delay time T_{del} is shown in Fig. 2 for the optical shear-force detection scheme with the gate width set to 1 μs. It is clear that the amplitude of the collected signal does depend on the delay time T_{del},[14] which is consistent with the known strong dependence of the frustrated total internal reflection light intensity on the distance between the tip and the prism surface,[1,2] as well as with the repetitive bumping model of the shear force. The experimental data can be described by the known exponential z-coordinate (normal to the surface) dependence of the intensity of an evanescent wave:[15] $I = I_0 \exp(-kz)$, where

$$k = \frac{4\pi}{\lambda}(n^2 \sin^2 \vartheta - 1)^{1/2}. \tag{1}$$

Here, n is the refraction index of the glass prism at the wave-

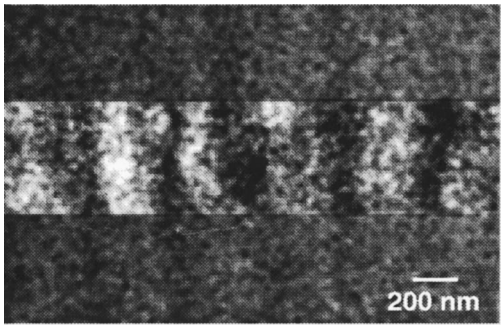


FIG. 3. Low-contrast standing wave imaged by the time-gated frustrated total internal reflection SNOM. The delay time is adjusted on the signal maximum (the moment of the tip–sample contact) for the central part of the scan. The gate width is 1 μs.

length λ, and θ is the incidence angle with respect to the surface normal. Using the values $n=1.517$, $\lambda=650$ nm, and $\theta=45°$, one gets $k^{-1}=130$ nm and, thus, the observed difference between the maximum and the minimum of the optical signal (a factor of 3–4) corresponds to the normal fiber dithering amplitude of ~ 80 nm. It is of the same order of magnitude as the total dithering amplitude (which is estimated as ~ 100 nm for our case) and, thus, formal application of the repetitive bumping tip–sample interaction model requires an unrealistically large inclination of the tip with respect to the sample to explain the data. However, this discrepancy is rather common for shear-force experiments[16,17] and probably can be explained by additional normal movements (''tapping'') of the piezotube–tip combination itself during the dithering,[16] or probably more complicated models to describe the light collection by the tapered fiber are required.[18]

Control experiments were performed measuring not the frustrated total internal reflection but fluorescence photons from a submonolayer of DCM dye molecules[19] spin coated onto the prism surface (see, e.g., Ref. 11 for details). Fluorescence was excited by the 488 nm cw argon-ion laser line; a holographic notch filter for the excitation and a number of red- light-transmitting filters were used to suppress the excitation light. The measured dependence of the signal on the gate delay time was very weak and practically unobservable, as it should be for such a *fluorescence* (not FTIR) signal.

To illustrate the performance of the time-gated SNOM, in Fig. 3 we present a SNOM image of the standing wave on the surface of the prism obtained when using the time-gating electronic unit in the geometry of frustrated total internal reflection shown in Fig. 1. The central part of the image was recorded when the gate delay was set to coincide with the tip–surface contact, while in the first and last portions the delay was changed to correspond to the position when the tip is far from the contact. No special mirrors to reflect the light and form a highly contrasted standing wave were installed, but only the small back-reflection of the laser light from the side surface of the prism was used to form a low-contrasted standing wave. When obtaining the image, we also used a low-intensity unfocused laser diode light and installed a relatively large integration time of the scaler (100 ms), which accounts for the fuzziness of the image in Fig. 3. This was done specially to mimic the conditions of the future single-molecule FRET SNOM experiments. It can be seen that the standing wave can be clearly discerned against the background for the central region of Fig. 3 (optimal TGEU adjustment) while it is practically indistinguishable in its upper and lower parts (''bad'' adjustment).

Thus, an operational time-gated scanning near-field optical microscope has been demonstrated. Any SNOM can be easily equipped with the TGEU described in the letter to work as a time-gated SNOM. This improves the signal-to-noise ratio and other related SNOM characteristics for such common SNOM applications as frustrated total internal reflection SNOM (also referred to as scanning tunneling optical microscopy[1,2]), surface plasmon imaging, and also fluorescence resonance energy transfer-based SNOM.

To conclude, it is also worthwhile to emphasize that the observed dependence (the existence of a single pronounced maximum) of the frustrated total internal reflection optical signal on the delay time constitutes an additional confirmation of the repetitive bumping mechanism of the tip–sample shear-force interaction,[5–8] rather than the shear-force model involving the dissipative tip interaction with a ''contaminant'' water layer covering the sample.

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