

Review

Development of femtosecond time-resolved scanning tunneling microscopy for nanoscale science and technology

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Abstract

‘Smaller’ and ‘faster’ are the key words in the progress of current nanoscience and technology. Thus, a method of exploring the ultrafast transient dynamics of the local quantum functions in organized small structures is eagerly desired. Ultrashort optical pulse technology has allowed us to observe transient phenomena in the femtosecond range, which, however, has the drawback of a relatively low spatial resolution due to the electromagnetic wavelength used. In contrast, scanning tunneling microscopy and its related techniques, although having a time resolution limited by the circuit bandwidth (~ 100 kHz), enable us to observe spatial dynamics at the atomic level in real space. Our purpose is to combine these two techniques to achieve a new technology which will advance the pursuit of future nanoscale scientific research in terms of the ultimate temporal and spatial resolutions.

We proposed a promising new design for achieving ultimate spatial and temporal resolution, by combining a short-pulse laser and STM. Using this method, time-resolved tunneling current measurement in the subpicosecond range was successfully demonstrated, this is shaken-pulse-pair-excited STM (SPPX-STM) satisfies the requirements for exploring the ultrafast dynamics of the local quantum functions occurring in organized small structures. We hope this new technology will promote the development of future research on the nanoscale.

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Keywords: STM; Ultrashort-pulse laser; Pump-probe technique; Nanotechnology; Femtosecond laser

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1. Introduction

With the progress of nanoscale science and technology, barriers between different research fields have been eliminated and interdisciplinary fields have been emerging. The ability to work at the molecular level, atom by atom, to create large structures with fundamentally new properties and functions is leading to unprecedented understanding and control over the basic building blocks and properties of all natural and man-made things. However, as the size of the components in the integrated structures is reduced to

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nanoscale order, there appears a growing and urgent need to develop a new technique for analyzing the local electronic dynamics, which determines the major device characteristics as well as fundamental functions.

At present, for example, the single-molecule observation is performed by several techniques. However, in order to understand and realize functional materials at the single-molecule level, detailed study of the intramolecular structure is important even for the single-molecule case. Fig. 1 shows a scanning tunneling microscopy (STM) image of a Si nanoparticle, and its cross sections obtained at different bias voltages. Since the Si nanoparticle is emissive, it is expected to be a future nanoscale optical element. The figure indicates that a Si nanoparticle is not homogeneous and has various internal structures depending on the bias voltage. Since STM images at different bias voltages reflect the local density of electronic states of different energy levels, the observed results indicate that the distributions of the local electronic structures are very complicated even in a simple single molecule.

In the case of more complex materials such as functional polymers, understanding the functions on the basis of the molecular structures becomes more difficult despite their importance. Fig. 2 shows the STM image and schematic structure of an optically active π -conjugated polymer, phlyphenylacetylene bearing menthoxycabonylamino groups [(–)-poly(MtOCAPA)] [1]. Its high chiral hierarchical structure was clearly observed. If the π -conjugated polymer chain can be controlled in the higher order structure, novel functions at the molecular level will become possible due to the characteristic π -electron systems. In order to realize this, however, we must characterize the local molecular and electronic structures with respect to the macroscopic functions.

Another observation technique involves surface photovoltage (SPV), which reflects the characteristics of local carrier dynamics. Fig. 3 shows an STM topographic image of a Ag/Si(100)- 2×3 surface (left) and its SPV map (right) obtained by light-modulated STM [2]. Line profiles of the SPV image obtained at different bias voltages are also shown. The characteristic length of the spatial variation is

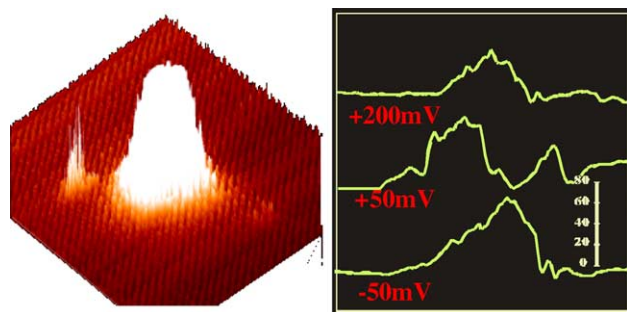


Fig. 1. STM image of Si nanoparticle and its cross sections at different bias voltages.

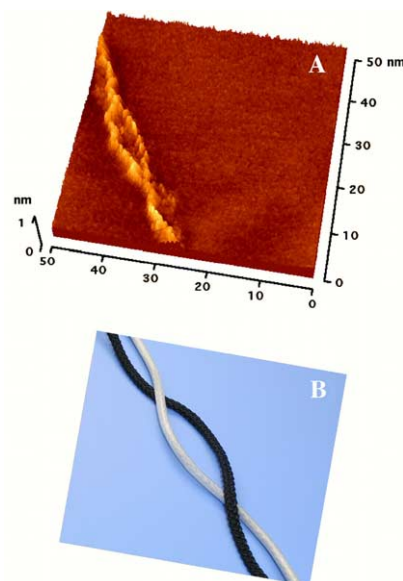


Fig. 2. STM image of optically active π -conjugated polymer, phlyphenylacetylene bearing menthoxycabonylamino groups [(–)-poly(MtOCAPA)].

5–10 nm, indicating the importance of the dynamical analysis of the electronic structure on the nanoscale.

These important local phenomena, observed in electronic devices, signal transfer in biosystems and chemical reactions, occur in the subpicosecond time range. However, resolutions in space and time have not yet been realized simultaneously. Therefore, in order to explore this intriguing world, the development of a new technique is urgently needed.

In this paper, we introduce our recent efforts in developing a new microscopy method, laser-combined STM, which enables us to explore the ultrafast dynamics of quantum functions with atomic resolution.

Near-field scanning optical microscopy (NSOM) may be a complementary approach to the analysis of the dynamics on the nanoscale in the future, the details of which will not be discussed in this paper. We here concentrate on the work of laser-combined STMs which can realize the ultimate spatial resolution through the measurement of the tunneling current.

2. Previous studies in this field

Ultrashort optical pulse technology has allowed us to observe transient phenomena in the femtosecond range, which, however, has the drawback of a relatively low spatial resolution due to the electromagnetic wavelength used. In contrast, scanning tunneling microscopy and its related techniques, although having a time resolution limited by the circuit bandwidth (~ 100 kHz), enable us to observe spatial dynamics at the atomic level in real space. Therefore, one of the most challenging and exciting tasks is to combine these two techniques to achieve unprecedented simultaneous

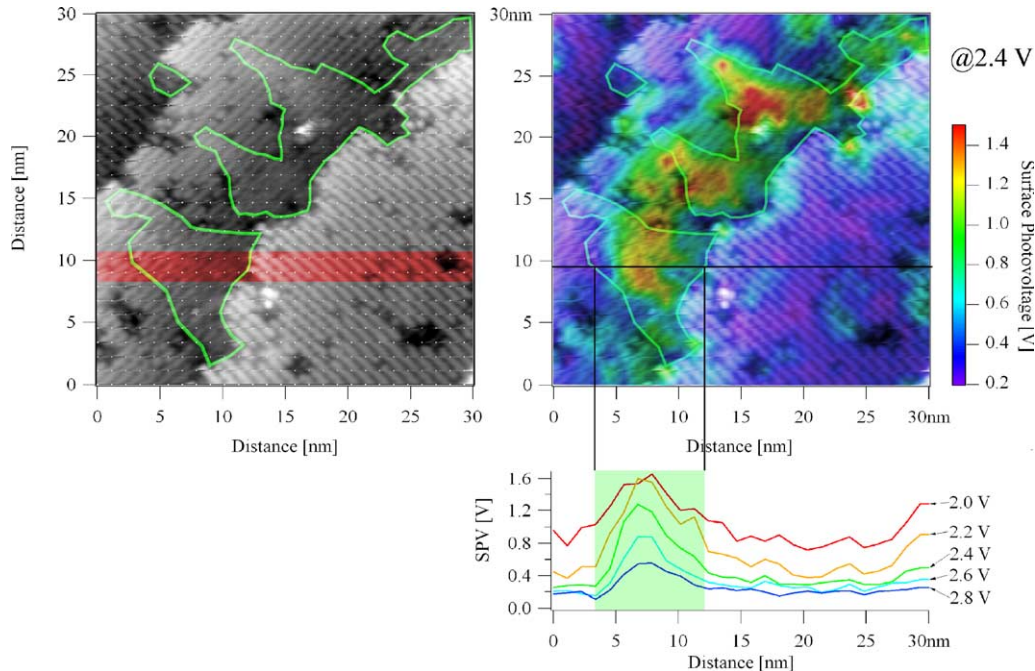


Fig. 3. STM topograph of Ag/Si(100)- 2×3 surface observed with the sample bias voltage of -2.0 V (left). SPV map for the sample voltage of 2.4 V and cross sections obtained at different bias voltages (right).

spatial and temporal resolution, i.e. femtosecond-angstrom technology. In fact, since the development of STM, many researchers have been making efforts to accomplish this task [1–6]. The ultimate goal is to analyze the electronic and structural dynamics of materials on a femtosecond time scale with atomic resolution.

There have been two major concepts proposed for achieving this goal. One is to introduce an ultrafast photoconductive gate into the current detection line of STM, as shown in Fig. 4. This type of microscopy is called ‘photoconductively gated STM’ [3,4]. Two laser beams consisting of a train of laser pulses are used to excite a sample and switch the photoconductive gate, respectively, as shown in Fig. 4. The photoconductive gate enables the sampling of instantaneous tunneling current induced on the sample by the excitation laser pulses. When the current value is recorded as a function of the delay time between excitation and gating, the transient tunnel current is presumed to be reproduced in a real-time scale. However, the detected signal was primarily due not to the tunneling current, but to the displacement current generated by the coupling of two stray capacitances, one at the tunneling junction and the other at the photoconductive gate [5]. When a signal arises from the displacement current, the lateral resolution of measurement is given by the geometric dimension of the capacitance at the tunneling junction, typically about $1\ \mu\text{m}$, and is much worse than that of STM. Up to now, several attempts have been made to improve this type of STM [6]. However, since the time resolution of this type of STM, in principle, cannot overcome the response

time of the photoconductive gate, typically about $1\ \text{ps}$, this method is of rather limited application.

In another approach, the tunneling junction is excited by a sequence of laser pulses and the induced tunneling current is measured as a function of the interpulse spacing, t_d (Fig. 5).

As a pioneering work, the carrier relaxation time at the Si(111)- 7×7 surface was determined with about a $10\ \text{ns}$ time resolution and $1\ \mu\text{m}$ spatial resolution [7]. The sample surface just below the STM tip was irradiated by a train of laser pulses. Since the surface potential is modulated by the irradiation due to the surface photovoltage effect, the displacement current can be probed by the STM tip, when the irradiation is switched from on to off and vice versa. As the amount of displacement current depends on the change in band bending during the interpulse period of the laser pulses, the signal as a function of the repetition time of the

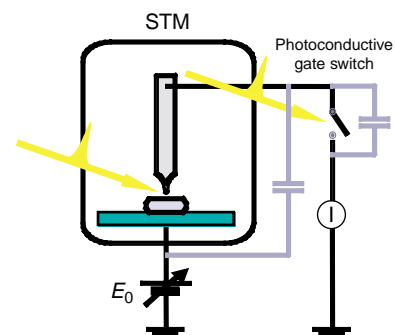


Fig. 4. Schematic of a photoconductively gated STM.

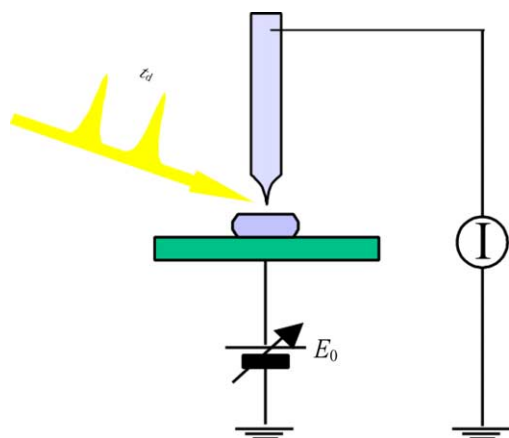


Fig. 5. Schematic of a pulse-pair-excited STM.

laser pulses provides information about the band relaxation mechanism. This technique is applicable, but the spatial resolution is limited to $\sim 1 \mu\text{m}$, since the signal is the displacement current. Moreover, since the repetition rate of laser pulses is changed by thinning out laser pulses from the original pulse train, the time resolution is limited by the repetition rate of the original pulse train, $\sim 100 \text{ MHz}$ (10 ns).

In order to obtain a time resolution higher than the repetition rate, a new method, called ‘pulse-pair-excited STM’ was proposed. Tunneling current measurement by STM yields us the atomic resolution simultaneously.

3. Pulse-pair-excited STM

In this method, the illumination is composed of a sequence of pulse pairs and the tunneling current is measured as a function of the delay time of the pulse pair. The signal obtained by this process is complicated compared with signals obtained by the straightforward approaches such as photoconductively gated STM, but it is free from the drawback of the slow response of the electronic circuit. Furthermore, since the time resolution is determined by the delay time between the two pulses in pulse pairs, instead of the repetition rate of the original laser, it can be improved by shortening the laser pulse width without any other limitation. Thus, in principle, pulse-pair-excited STM has the potential to achieve both the femtosecond and angstrom resolutions.

However, in the measurement by pulse-pair-excited STM, we must devise a way to detect the small component of tunneling current that is dependent on the delay time. For such a purpose, in general, the lock-in detection technique is used to realize the sensitive measurement. As a reference signal for the lock-in detection, for example, the modulation by a mechanical chopper or the repetition rate of the laser pulses is used [6]. In both cases, the output from the lock-in

amplifier corresponds to the photoinduced tunneling current $I_{\text{diff}}(t_d)$ as

$$I_{\text{diff}}(t_d) = I_{\text{illum}}(t_d) - I_{\text{dark}}$$

Here, $I_{\text{illum}}(t_d)$ and I_{dark} are the tunneling current with and without illumination, respectively. T_d is the delay time of the two pulses in pulse pairs. The lock-in detection method reduces the broad-band noise from the current–voltage converter of STM. Thus, the delay-time dependence of the photoinduced current is expected to be clarified. However, the delay-time-dependent component is quite small compared to the large background of the delay-time-independent component. For example, when the laser intensity is modulated at low frequency, thermal expansion and shrinking of the STM tip at the modulation frequency increases the background. Displacement current due to the photovoltage effect, in the case of a semiconductor sample, also increases the background. Thus, an unrealistic dynamic range is required for the lock-in amplifier. What is worse is that the large background fluctuates with the unavoidable small fluctuation in the laser intensity at low frequency. The lock-in amplifier does not eliminate this fluctuation.

Here, we summarize the requirements that must be satisfied for the development of the time-resolved STM.

1. High signal-to-noise ratio.
2. Reduction of noise from the fluctuation of laser intensity.
3. Removal of the thermal expansion effect of the tip and sample.

These requirements are the difficulties that remain unresolved.

4. Shaken-pulse-pair-excited STM [8–11]

To satisfy the requirements listed above, we proposed a new technique, ‘shaken-pulse-pair-excited STM (SPPX-STM)’. Fig. 6 shows the schematic of the setup. The tunneling junction is directly illuminated by a sequence of

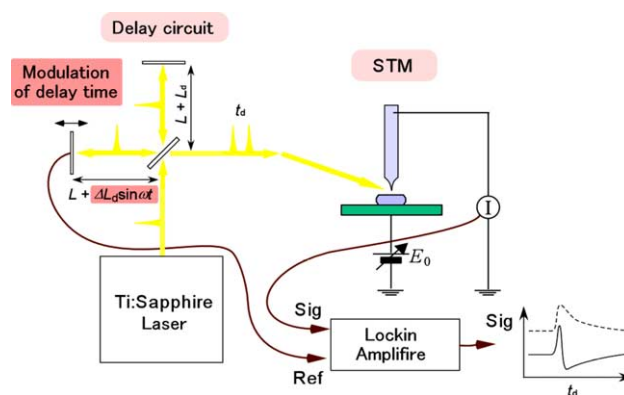


Fig. 6. Schematic of the shaken-pulse-pair-excited STM system.

laser pulse pairs and average tunneling current, $I_t(t_d)$, is measured as a function of the delay time between the two pulses, t_d . To decrease the broadband noise, the delay time t_d is modulated with a small amplitude Δt_d at a frequency ω , and the tunneling current is detected by a lock-in amplifier. Since, the tunneling current I_t responds to the modulation as

$$I_t(t_d + \Delta t_d \sin \omega t) = I_t(t_d) + \Delta t_d \sin \omega t \frac{dI_t}{dt_d} + O^2,$$

the coefficient $\Delta t_d (dI_t/dt_d)$ of the term $\sin \omega t$ is obtained by lock-in detection. Since, the laser intensity is not modulated in this system, neither thermal expansion nor shrinking of the STM tip occur. Then, with the numerical integration of the dI_t/dt_d signal, $I_t(t_d)$ can be obtained, conserving the spatial resolution of STM.

In the pulse-pair-excited STM measurement, the first laser pulse in each pulse pair acts as the pump pulse to excite and modulate the electronic structure of the sample surface, which causes deviation in the tunneling current. Then, the tunnel current is again deviated by the second laser pulse, as shown in Fig. 7. In the case of a short delay time, the excited state induced by the first pulse partially remains when the second pulse impinges on the sample. Thus, the amount of tunneling current deviation due to the second pulse can be different from that caused by the first pulse and dependent on the delay time. Although such ultrashort spikes in the tunneling current cannot be resolved by any amplifier of the present STM systems, this change can be detected as the average value of the tunneling current, if the deviation also changes the total amount of tunnel current for each pulse pair (Fig. 8). Thus, we can observe the ultrafast transient

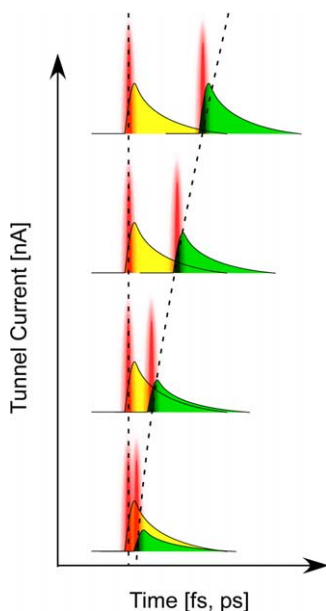


Fig. 7. Relationship between the change in tunneling current and the delay time of two laser pulses.

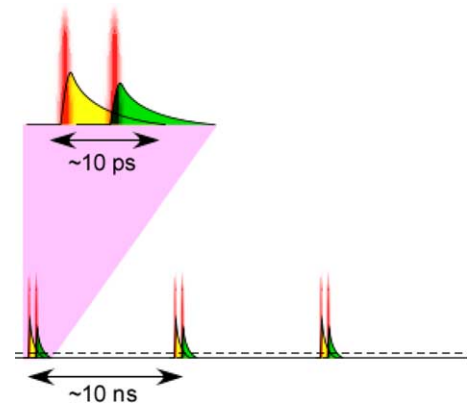


Fig. 8. Relationship between the average tunneling current (dotted line) and the current photoinduced by the pulse pairs.

phenomenon by measuring the time-averaged tunnel current as a function of the delay time.

In such measurement, the relationship between the excitation/relaxation phenomena of interest and the time-resolved signal in the tunnel current is rather complex. However, this method combines and conserves the ultimate temporal resolution of the optical pump probe approach and the ultimate spatial resolution of STM. Namely, SPPX-STM satisfies the requirements for exploring the ultrafast dynamics of the local quantum functions occurring in organized small structures.

5. Experimental and results [8–10]

Here we show some experimental results. Experiments were performed on $\text{GaN}_x\text{As}_{1-x}$ ($x=0.36\%$), which is an excellent candidate for future fast information transfer systems and highly efficient solar cells, similar to other III-V-N compound semiconductors [11,12].

For comparison, we first examined the dynamics of the $\text{GaN}_x\text{As}_{1-x}$ sample by the conventional optical pump-probe method. The system setup was similar to that shown in Fig. 6; Ti:sapphire excitation laser of 300 mW, central wavelength of 800 nm, bandwidth of 30 nm, pulse width of 25 fs and oscillation frequency of 80 MHz.

The sample was first excited by an intense pump pulse and the reflectivity just after pumping was measured by the probe pulse with six times lower intensity of the pump pulse (Fig. 9). The intensity of the reflected probe pulse was measured as a function of the delay time between pumping and probing.

Fig. 10 shows the result. From the analysis of fitting by exponential functions, two exponential components with decay times of 0.8 and 10 ps were obtained. These were respectively attributed to the lifetimes of the intraband (faster one) and interband (slower one) carrier relaxation processes, similar to the case of GaAs [12,13].

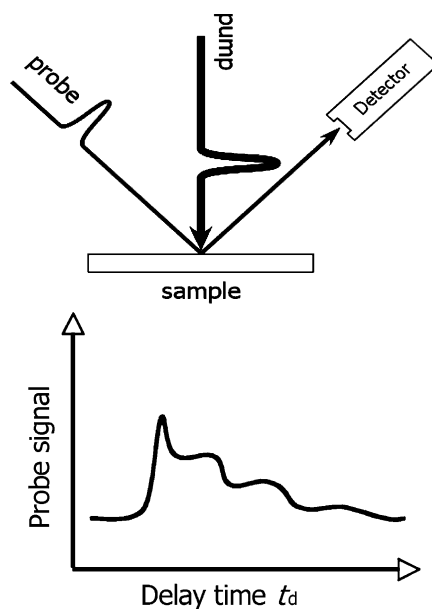


Fig. 9. Schematic of the conventional optical-pump-probe method.

Fig. 11 shows a result obtained by SPPX-STM for the $\text{GaN}_x\text{As}_{1-x}$ sample. The raw signal and the fitting result are plotted as a function of the delay time. The vertical axis represents the amount of change in the tunneling current. Here, the left-hand side of the graph is adjusted to the zero point for simplicity, since the absolute value cannot be determined by this experiment. The asymmetry of the graph for the negative and positive delay times is due to the difference between the light intensities of the two pulses (1: 2 in this case; intense pulse impinging first for $t_d < 0$ region). The curves for $t_d < 0$ and $t_d > 0$ were confirmed to have similar shapes at various intensity ratios. The experimental curve for each side of the x -axis was well reproduced by the same function of two exponential components with fast (~ 1.0 ps) and slow (~ 50 ps) decay times. The difference between the baselines for the positive and negative sides indicates the existence of a long-time-scale physical process in the system, the origin of which is not yet clear.

The two decay times obtained by the SPPX-STM

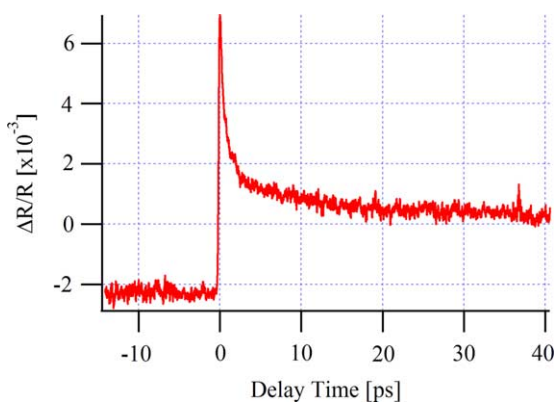


Fig. 10. Result obtained by the optical-pump-probe technique for a $\text{GaN}_x\text{As}_{1-x}$ ($x=0.36\%$) sample.

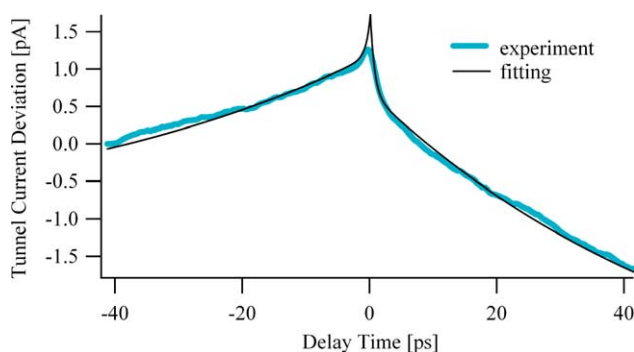


Fig. 11. Result obtained by SPPX for a $\text{GaN}_x\text{As}_{1-x}$ ($x=0.36\%$) sample.

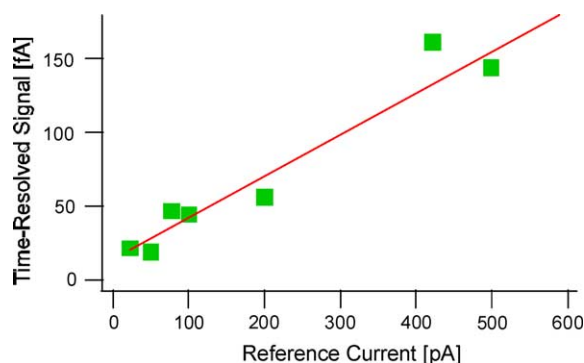


Fig. 12. Relationship between time-resolved signal intensity and average tunnel current, measured while varying of the tip-sample distance.

measurement are in similar ranges as those obtained by the conventional pump-probe reflectivity measurement, which suggests that this system is probing the same ultrafast transient phenomena [14,15].

In the development of the time-resolved STM, what is always questioned is whether the time-resolved signal is related to the tunnel current, because this is the key issue that determines whether the method can have the same superior spatial resolution as STM or not [4–8]. Fig. 12 shows the time-resolved signal intensity of SPPX-STM as a

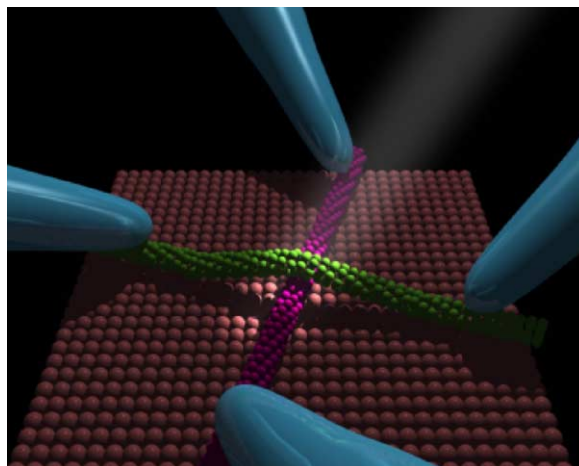


Fig. 13. Schematic of the pulse-pair-excited-multiprobe STM.

function of the average tunnel current (reference current), which was measured while varying the tip-sample distance. There is a strong linear relationship, indicating that the time-resolved signal is indeed produced by tunneling current. In other words, we are observing the transient phenomena induced by photoexcitation just below the STM tip. Thus, the result shown in Fig. 11, actually is the first successful demonstration of probing subpicosecond dynamics using pulsed-laser-combined STM.

In order to make the system more practical and efficient, we are now constructing a shaken-pulse-pair-excited-multiprobe STM, with which ultrafast electronic dynamics at different points can be detected simultaneously (Fig. 13). Studies on nanoscale materials for the application of our new technique are also in progress [16–22].

6. Conclusion

A promising new design for achieving ultimate spatial and temporal resolution, by combining a short-pulse laser and STM, was proposed. Using this method, time-resolved tunneling current measurement in the subpicosecond range was successfully demonstrated. Namely, shaken-pulse-pair-excited STM (SPPX-STM) satisfies the requirements for exploring the ultrafast dynamics of the local quantum functions occurring in organized small structures. We hope this new technology will promote the development of future research on the nanoscale.

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