

Development of Time-Resolved Scanning Tunneling Microscopy in Femtosecond Range

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A promising design for achieving the ultimate spatial and temporal resolution is proposed. With modulation of the time delay between two femtosecond laser pulses repeatedly illuminating a scanning tunneling microscope junction, the induced component of the tunneling current is detected as a function of the delay time. With this method, a high signal-to-noise ratio, stable measurement free from fluctuation of laser intensity, and removal of the thermal expansion effect can be achieved. Using the photovoltage effect of GaAs, the high performance of the newly developed system is demonstrated in the femtosecond range. [DOI: 10.1143/JJAP.41.4994]

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The emerging fields of nanoscale science, engineering, and technology—the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new properties and functions—are 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 shrinks to the nanoscale order, there appears a growing and urgent need to measure the local electronic structures and their dynamics, which determine the major device characteristics as well as fundamental functions.

The recent improvement of measurement techniques has resulted in extremely high spatial and temporal resolutions. On the one hand, scanning tunneling microscopy (STM) allows us to observe individual molecules and atoms with angstrom resolution. On the other hand, currently, the state of the art in quantum optics offers ultrashort laser pulses on the order of several femtoseconds, which enables terahertz bandwidth measurement based on the pump-probe technique. However, these spatial and time resolutions were not established simultaneously; the measurement bandwidths of scanning probe microscopes are typically limited by the external electronics to ~ 100 kHz and the spatial resolution of the laser technique is generally limited to its wavelength. Therefore, one of the most challenging and exciting tasks is to combine these two techniques to achieve unprecedented simultaneous 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 and control the electronic and structural dynamics of materials with atomic resolution on a femtosecond time scale. There have been two major concepts for achieving this goal.

One is to utilize ultrafast photoconductive gates to adjoin the time resolution to STM. Weiss *et al.* presented photoconductively gated STM with a time resolution of 1 ps, in which an ultrafast photoconductive gate was inserted on the tunneling current detection line.¹ This was based on the idea that the photoconductive gate enables the sampling of instantaneous tunneling current immediately after laser pulse excitation of the sample. The sampled current is then recorded as a function of the delay time between excitation and sampling,

just as in other pump-probe techniques. If this were indeed the case, the system would be a femtosecond STM. However, Groeneveld and van Kempen pointed out that the detected signal was primarily due, instead of to tunneling current, to the displacement current generated by the coupling of two stray capacitances, one at the tunneling junction and the other at the photoconductive gate.⁷ When the signal arises from the displacement current, the lateral resolution of measurement is given by the geometric dimension that defines the capacitance at the junction and is much worse than that of STM; it is typically about $1 \mu\text{m}$. Up to now, several attempts have been made to improve this type of STM.^{2,3} Junction mixing STM has exhibited 1 ps time resolution with 1 nm spatial resolution. However, this spatial resolution originates from the nanoscale variation of the current–voltage dependence of the sample while the ultrafast phenomenon itself does not have an atomic-scale structure. Thus, it is of rather limited application. Moreover, the time resolution of this type of STM, in principle, cannot overcome the response time of the photoconductive gate, which is typically about 1 ps.

The other approach relies on the direct excitation of the tunneling junction by a sequence of laser pulses and the detection of the induced tunneling current as a function of interpulse spacing. Hamers and Cahill, in their pioneering work, determined the carrier relaxation time at the Si(111)- 7×7 surface with about 10 ns time resolution and $1 \mu\text{m}$ spatial resolution by this approach.⁴ In order to measure the small current variation due to surface photovoltage, they used a lock-in amplifier with the laser intensity modulated by a mechanical chopper. The difference in the time-averaged tunneling current with and without illumination of an optical pulse train was recorded as a function of the repetition rate of laser pulses. To obtain a time resolution better than the repetition rate, pulse-pair-excited STM is also proposed, where the illumination is composed of a sequence of pulse pairs and the tunneling current is measured as a function of delay time of the pulse pair. The signal from this kind of setup is determined by individual physical systems; thus it is complicated compared to more straightforward approaches such as photoconductively gated STM, but is free from the drawback of slow response of the electronic circuit. In addition, the time resolution is determined by the time delay between the two pulses, instead of the repetition rate of the original laser, and can be improved

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without limit by shortening the laser pulse width. Thus, in principle, pulse-pair-excited STM has the potential of achieving femtosecond and angstrom resolution. Although several attempts to realize this concept have been made, its applicability has not yet been demonstrated.

In this study, we reconsider the difficulty in the development of a pulse-pair-excited STM and propose a promising new design to surpass the critical requirements. The basic performance of the system is clearly demonstrated. Temporal resolution is achieved up to the femtosecond range with the spatial resolution of STM remaining unchanged.

In the development of pulse-pair-excited STM, we must devise a way of detecting the small component of tunneling current that depends on delay time. For the purpose, the detection must be sensitive. It is common to use lock-in detection with light intensity modulation. For instance, Hamers and Cahill used a mechanical chopper,⁴⁾ while Gerstner *et al.* mentioned locking to the repetition rate of the laser pulse.⁶⁾ In both cases, the output from the lock-in amplifier corresponds to the illumination-induced tunneling current difference, $I_{\text{diff}}(t_d)$, as

$$I_{\text{diff}}(t_d) = I_{\text{illum}}(t_d) - I_{\text{dark}}. \quad (1)$$

Here, $I_{\text{illum}}(t_d)$ is the tunneling current under illumination, which is delay time dependent, and I_{dark} is that under dark condition. On account of the lock-in detection, the broadband noise from the current-voltage converter of STM is reduced. Thus, the delay time dependence in the induced-current difference can be obtained precisely. In practice, however, the delay-time-dependent component is expected to be quite small compared to the large background of the delay-time-independent component. In addition, when the laser intensity is modulated at low frequency such that the STM current-voltage converter can respond, the change in the heat delivered by laser pulses causes the thermal expansion and shrinking of the STM tip at the modulation frequency, which increases the background. Other undesirable signals, such as the displacement current due to the photovoltage effect in the case of the semiconductor sample, also increase the background. Thus, an unrealistic dynamic range will be required for the lock-in amplifier. What is worse is that this large background fluctuates with the unavoidable small fluctuation of laser intensity at low frequency. The lock-in amplifier does not eliminate the fluctuation. When each of the two pulses in the pulse pair is chopped independently at different frequencies and the amplifier is locked at the difference frequency, the signal proportional to

$$I_{\text{signal}} = (I_{12} + I_{\text{dark}}) - (I_1 + I_2) \quad (2)$$

would be obtained, where I_{dark} , I_1 , I_2 and I_{12} are the tunneling currents with no laser pulse, with laser pulse 1, with laser pulse 2, and with both laser pulses, respectively. Thus, only the nonlinearity of the tunneling current with respect to the laser intensity can be retrieved. This method reduces the dynamic range required to the lock-in amplifier as well as the fluctuation of the background component. However, since it also modulates the laser intensity, thermal expansion and shrinking of the STM tip cannot be avoided. Measurement with high intensity of the exciting laser, which generally gives larger nonlinearity in the tunneling current, will crash the STM tip into the sample.

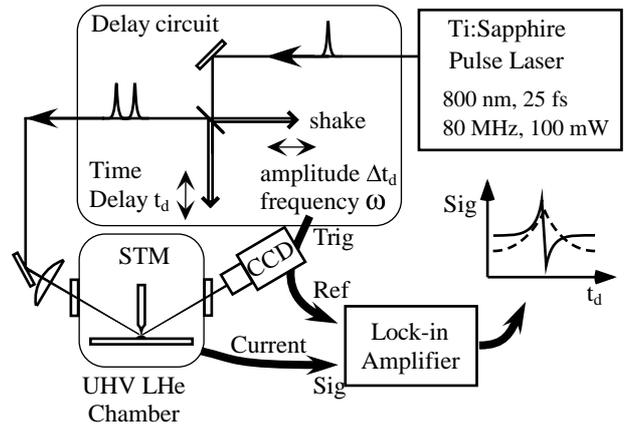


Fig. 1. Schematic of our shaken-pulse-pair-excited STM system.

Here, we summarize the requirements that have to be met for the development of 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 tip and sample.

These requirements are difficulties that had not been surpassed until now.

To overcome the difficulties listed above, we propose the shaken-pulse-pair-excited STM system. Figure 1 shows the schematic. The optical source is a Ti:sapphire laser that routinely generates 25 fs pulses centered at 800 nm at 80 MHz repetition rate. The pulse pairs are generated by an interferometer-type delay circuit. A half-mirror splits the laser beam into two delay arms with slightly different path lengths. Those beams are reflected by retro-reflectors at the end of the delay line and remixed by the half-mirror. The delay time is determined by the difference between the path lengths of the delay arms, which can be precisely adjusted using piezoactuators. Finally, a sequence of pulse pairs is focused onto the STM tip-sample junction, and the tunneling current is measured using an STM electronic circuit with 10 kHz bandwidth.

In our system, the repetition rate of the excitation laser is chosen to be high in order to minimize the thermal expansion effect of the STM tip. Furthermore, we do not use the mechanical chopper. Instead, what is noteworthy is that it modulates the delay time between two laser pulses by periodically shaking one of the two end reflectors on delay arms and detects the component of the corresponding tunneling current using a lock-in amplifier. Our two delay lines are capable of shaking the end reflector at a maximum frequency of 10 Hz or 100 Hz up to 150 ps or 0.7 ps, respectively.

When the time delay of the two pulses t_d is modulated with a small value Δt_d around the center position t_d at frequency ω , the tunneling current can be represented as

$$I_t(t_d + \Delta t_d \sin \omega t) = I_t(t_d) + \Delta t_d \sin \omega t \frac{dI_t}{dt_d} + O(\Delta t_d^2). \quad (3)$$

With the use of a lock-in amplifier, the coefficient of the term $\sin \omega t$, dI_t/dt_d , can be obtained. In this system, when the tunneling current is independent of the delay time, the output is zero. There is no background at all. Thus, the signal-to-background ratio is maximized. The fluctuation of laser

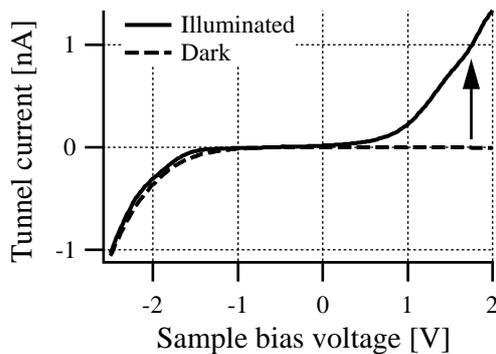


Fig. 2. I - V curves obtained for n-type GaAs(100) with and without laser illumination.

intensity can be reduced by lock-in detection. Finally, since the laser intensity is not modulated, thermal expansion and shrinking of the STM tip does not occur. All the requirements listed above can be satisfied by this technique.

In order to confirm the validity of the idea, the performance of our system was examined using a surface photovoltage effect. A nondoped n-GaAs(001) was used as the sample (carrier density $\sim 1 \times 10^{15} \text{ cm}^{-3}$). Figure 2 shows the I - V curves obtained with and without laser illumination (set point $V_s = -2.5 \text{ V}$, $I_s = 0.10 \text{ nA}$). Because of the low doping level, when a positive sample bias voltage is applied, the wide depletion layer formed at the tunneling gap prevents the tunneling current under a dark condition. With illumination, however, the photoinduced carriers decrease the depletion layer, allowing the tunneling current to flow. The tunneling current increases with the intensity of the excitation laser. Since the sample is nondoped, small changes in the photoillumination intensity at the tunneling junction can be sensitively detected as changes in tunneling current. According to the independence of the current difference between illuminated and dark conditions on the frequency of switching, the displacement current component is determined to be negligible. In addition, no current difference at negative sample bias voltages indicates the thermal expansion effect of the tip is also negligible in our experiments. Thus, almost all of the current change at positive sample bias voltage is attributed to a change of the tunneling current.

Figure 3 shows an experiment for evaluating the temporal resolution of our system. The tunneling current was recorded during sweeping of the temporal delay of the paired laser pulses with a static tip-sample separation. When the delay time is small compared to the pulse width and the two pulses are temporarily overlapped, sweeping the delay time causes the oscillation of the effective laser intensity at the periodicity of the carrier wave owing to the interference between the two pulses. The oscillation decreases as the portion of overlap decreases, and when the two laser pulses separate, the oscillation vanishes. The oscillation of illumination intensity at the tunneling junction can be detected as an oscillation in tunneling current as shown in Fig. 3. The wavelength of the laser pulse is centered at 800 nm, and the pulse width is 25 fs. As is shown in Fig. 3(a), the tunneling current oscillates at 2.6 fs, which corresponds to the periodicity expected from the wavelength of 800 nm.

Similar measurement was performed by Gerstner *et al.*⁶⁾

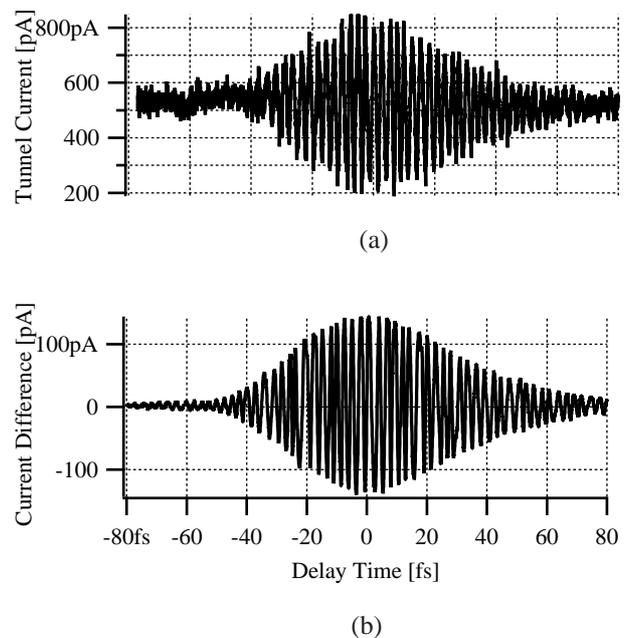


Fig. 3. Results of the temporal resolution of our system; (a) delay-time-dependent tunneling current, (b) shaken-pulse-pair-excited STM signal.

However, in their case, thermal expansion of the STM tip was used for the analysis. In our case, by using a nondoped n-GaAs(001) as the sample, the laser intensity could be kept low so that the thermal expansion effect could be avoided. As a result, the laser intensity precisely at the tunneling junction could be obtained.

Now let us examine the performance of the shaker method which we introduced. Figure 3(b) shows the lock-in amplifier signal (time constant = 30 ms) plotted versus delay time, where the delay time was modulated by 0.5 fs around the center value at 400 Hz. The derivative of the graph in Fig. 3(a) was successfully obtained with a lower noise level, indicating the expected performance of our time-resolved STM. Its temporal resolution is limited by the pulse width, in the range of femtoseconds. In the actual experiment, one has to maintain a delay time longer than the pulse width to avoid the interference effect shown here.

So far, we have demonstrated that our method can measure the dependence of tunneling current on the delay time of an excitation pulse pair with good sensitivity and precision. The question "which system causes the dependence of tunneling current on the delay time?" or "to which system can your microscope be applied?" may arise. One of the easiest cases of using this method is when the dependence of the tunneling current on laser intensity in the specific system is nonlinear. In this case, the average tunneling current with excitation by the sequence of pulse pairs with long delay time is different from that with excitation by a sequence of completely overlapped pulse pairs, in other words, a single pulse with double intensity. Therefore, when the delay time is swept, the decay time of the state excited by the first pulse can be obtained. For example, let us assume that each of the laser pulses generates a change in the tunneling current of 10 nA during 1 ps, and the tunneling current due to the second pulse changes 10% depending on the delay time. The resultant change in the av-

eraged tunneling current is

$$10 \text{ (nA)} \times 1 \text{ (ps)} \times 80 \text{ (MHz)} \times 10\% = 0.08 \text{ (pA)}. \quad (4)$$

This is in the range of realistic values.

There is another issue to be considered for spatial resolution. Owing to the exponential dependence of tunneling current on tunneling distance, when the tunneling current is detected by precision electronics and mechanics of STM apparatus, acquisition of localized information in the angstrom order is guaranteed. However, when the detected signal arises from photoexcited electron emission, displacement current or field emission, the spatial resolution can be much worse. Thus, as discussed with photoconductively gated STMs,¹⁻⁴⁾ the origin of the signal must be examined carefully for individual systems. Thermal drift of the STM tip relative to the sample surface can also affect the spatial resolution, especially when the time-resolved tunneling current detection takes a long time. Our method discussed above keeps the averaged laser power constant so that the thermal drift is minimized. However, current detection with an extremely long acquisition time might require active drift correction combined with the atom-tracking technique,⁸⁾ where the velocity and direction of thermal drift are determined by the atom-tracking technique and compensated.

In conclusion, a promising new design for achieving ultimate spatial and temporal resolution, by combining a short pulse laser and STM, is proposed. Using the photovoltage effect of GaAs, high performance of the newly developed system is demonstrated in the femtosecond range. Further experiments are now in progress.

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