Chapter 120
Time-Resolved Scanning Tunneling Microscopy

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Keywords STM · Ultrashort pulse laser · Ultrafast phenomena
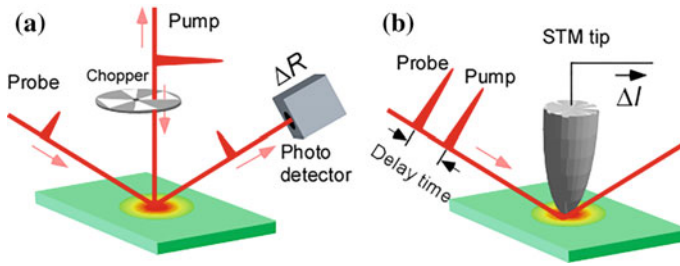Optical pump-probe STM · THz-STM

120.1 Principle

Since the invention of scanning tunneling microscopy (STM) in 1982, the addition
of high time resolution to STM has been the most challenging issue, and various
time-resolved STM (TR-STM) methods have been considered and developed [1, 2].
The most successful approach is to combine STM with quantum optical techniques
based on the optical pump-probe (OPP) method [3–5]. In the OPP method [6], a
sample is illuminated by a train of pulse pairs with a delay time as shown in
Fig. 120.1a. To use the OPP method for time-resolved analysis, the first (pump)
pulse is used as a pump to excite the sample surface and the second (probe) pulse is
used as a probe to observe the relaxation of the excited states induced by the pump
pulse. When carriers excited by the pump pulse, for example, remain in the excited
states, the absorption of the probe pulse is suppressed by an amount depending on
the delay time, which is called absorption bleaching. Therefore, if the reflectivity of
the probe pulse, for example, is measured as a function of delay time, we can obtain
information on the relaxation of the excited states induced by the pump pulse
through the change in the reflectivity of the probe pulse, ΔR. In this case, the time
resolution is limited only by the pulse width, i.e., the femtosecond range
(the attosecond range is now available).

   In time-resolved scanning tunneling microscopy (TR-STM), the sample surface
below the STM tip is similarly excited by a train of pulse pairs as shown in
Fig. 120.1b, which are also called pump and probe pulses here. However, instead of
measuring the change in the reflectivity of the probe pulses, the tunneling current is
measured as a function of delay time. Namely, since the tunneling current induced

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Fig. 120.1 Schematic diagrams of **a** optical pump-probe (OPP) method and **b** optical pump-probe STM (OPP-STM) for time-resolved measurement

by the probe pulse depends on the delay time due to absorption bleaching, the change in the total tunneling current ΔI provides the dependence of the carrier dynamics on the delay time. Instead of absorption bleaching, when the tunnel current depends on the delay time, such as in the case of a photostimulated phase transition, in which conductivity changes, a similar measurement is possible.

120.2 Features

- STM images can be obtained with atomic resolution.
- Information about time-resolved carrier dynamics can be measured using the tunnel current with the spatial resolution of STM.
- The temporal resolution is determined only by the laser pulse width, similarly to OPP method.
- Using circularly polarized light, spin dynamics can be measured.
- Using THz laser pulses, a high bias voltage can be applied between the STM tip and sample using the tip-induced enhancement of a single-cycle electric field, which enables snapshots of nanoscale dynamics to be obtained.

120.3 Instrumentation

Since TR-STM signals are weak, it is necessary to use the lock-in detection method, in which the excitation is oscillated at a certain frequency and the corresponding change in the signal is measured [3]. In general, the laser intensity is modulated in the OPP method, which, however, causes thermal expansion of the STM tip and sample. Since a 0.1 nm change in the tip-sample distance produces a one-order change in the tunneling current, it is difficult to detect a weak signal under this condition. A promising approach is to modulate the delay time t_d between the pump
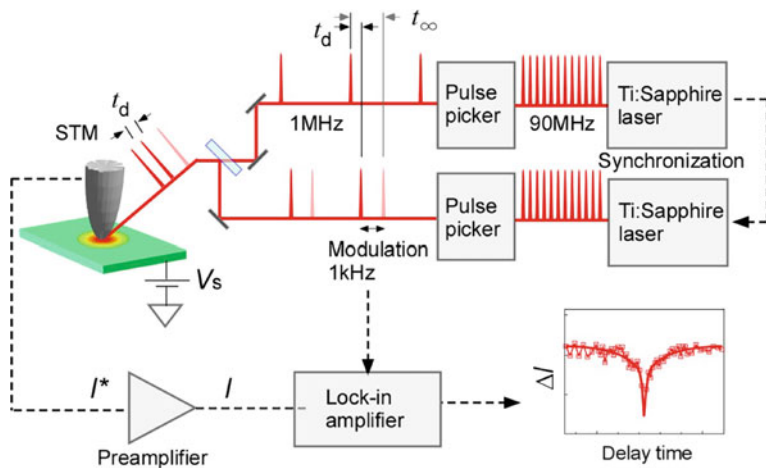
Fig. 120.2 Schematic view of optical pump-probe STM (OPP-STM) system. Here, two Ti: sapphire lasers (90 MHz) are used to produce pump and probe pulses. The delay time t_d between the pump and probe pulses is modulated using two Pockels cells (pulse pickers) for lock-in detection. I^* and I indicate the raw tunnel current and that temporally averaged in the preamplifier

and probe pulses instead of the intensity. In this modulation technique, the laser intensity is not changed and we can choose a modulation frequency independent of the noise frequency originating from thermal expansion. As shown in Fig. 120.2, for example, pulse trains are generated by two synchronized Ti: sapphire lasers at a 90 MHz repetition rate (11 ns intervals) with a pulse width of 150 fs. The relative timing of the two pulse trains is controlled by a synchronizing circuit, which provides a delay time that ranges from 0 to 11 ns with a time jitter. Each train is guided to a pulse picker that can selectively transmit one pulse per 90 pulses, resulting in a reduced repetition rate of 1 MHz. The selection of the pulse enables the production of a longer delay time that can be adjusted in multiples of 11 ns. Consequently, the delay time can be adjusted continuously from zero to a large value as needed. This control of the delay enables the probing of nanometer scale structures with a wide range of relaxation lifetimes. For spin detection, circularly polarized light is used for excitation and probing, and the mixture ratio between left and right circularly polarized light is modulated as a reference for lock-in detection [5]. When THz pulses are used for excitation, problems associated with thermal expansion can be neglected because of their low photon energy [4, 7, 8] and intensity modulation for lock-in detection becomes possible, enabling easier measurement.
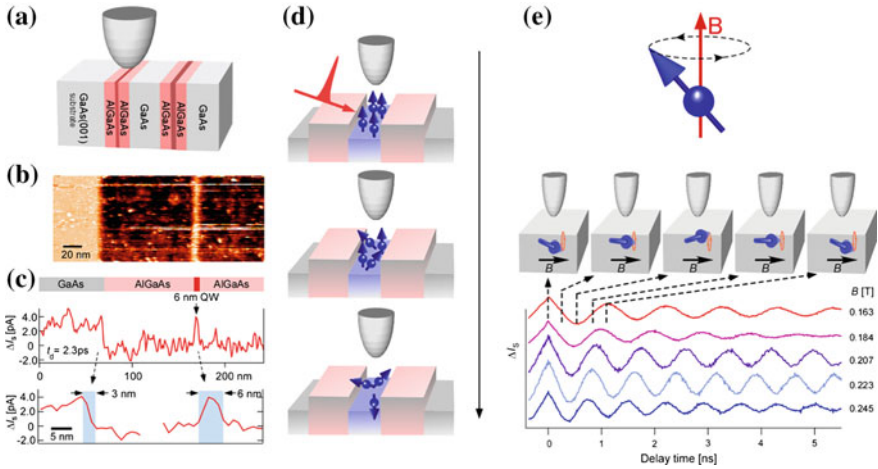
Fig. 120.3 **a** to **d** OPP-STM signals showing the relaxation of spins optically oriented in a quantum well of 6-nm width as schematically shown in **d**. **a** Measurement setup, **b** STM image of the quantum well, **c** spin signal at 2.3 ps after photoexcitation obtained by scanning the STM tip across the quantum well. **e** Schematic of the relationship between the directions of the spins with precession in a magnetic field *B* and the magnetic field *B* (*upper*), and the change in the spin precession frequency with the variation of the magnetic field (*lower* graphs). *Dotted arrows* show the relationship between the spin direction and the OPP-STM signal

120.4 Applications

Figure 120.3 shows two examples of spin dynamics obtained by OPP-STM with circularly polarized light showing the relaxation of spins optically oriented in an AlGaAs/GaAs/AlGaAs quantum well with 6-nm width [(a) to (d)] and (e) the change in the Larmor frequency of spin precession with the applied magnetic field [5]. For the former case, the STM tip was scanned across the 6-nm quantum well shown in (a) and (b) with the delay time fixed at 2.3 ps. Figure 120.3c shows the degree of spins oriented at 2.3 ps after spins were optically oriented in a single quantum well by photoexcitation as illustrated in the top figure in Fig. 120.3d. In the latter case, absorption bleaching is related to the directional correlation between the spins excited by the pump pulse, which rotate around the axis of the applied magnetic field *B*, as schematically shown in Fig. 120.3e, at the Larmor frequency ($\omega_L = g\mu_B B/\hbar$, g: electron g factor, μ_B: Bohr magneton, B: applied magnetic field, $\hbar$: Dirac constant), and the spins excited by the probe pulse. Therefore, the signal intensity decreases with oscillation at the Larmor frequency. When the laser repetition rate coincides with the Larmor frequency, oscillation is resonantly enhanced. Namely, the oscillation intensity increases and decreases with the change in the magnetic field, as shown in Fig. 120.3e. From the analysis of the lifetime of spin orientation and its resonance, information such as the local g factor and environmental conditions of electrons around defects can be obtained [5, 9]. Regarding the

carrier dynamics in a semiconductor, single atomic level analysis, for example, a comparison of the hole capture rate among (Mn, Fe, Co)/GaAs sites, can now be realized [10].

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