The modulation of carrier dynamics in a GaAs–PIN junction after photoexcitation by an ultrashort-pulse laser was probed by shaken-pulse-pair-excited scanning tunneling microscopy (SPPX-STM), which enables nanoscale mapping of time-resolved STM images. The effect of the built-in potential on the carrier dynamics, diffusion and drift, which cannot be probed by the optical pump-probe technique, was successfully visualized in real space.

Study of the nonequilibrium transport of carriers in semiconductors is of great importance not only from fundamental viewpoints but also as a basis for the development of electronic devices. With the size reduction of structures in current electronic devices, differences in the electronic properties caused, for example, by the structural nonuniformity of each element have an ever increasing effect on macroscopic functions. The direct observation of device characteristics provides us with a basis for the macroscopic analysis of results.

In a previous work, the doping characteristics and carrier transport properties in a GaAs p–n junction were visualized with ~10 nm spatial resolution by light-modulated scanning tunneling spectroscopy (LM-STM). The characteristic properties under the operating conditions, which had previously been analyzed on the basis of empirical electric properties, were directly visualized on the nanoscale. The obtained results provided a solid basis for elucidating the mechanism of the carrier transport properties predicted by the macroscopic analysis. However, LM-STM enables the imaging of only stationary states. Therefore, to achieve further advances in characterization, a method of exploring the transient dynamics of local quantum functions in small organized structures is highly desirable.

STM has an excellent spatial resolution on the subangstrom scale. However, since its temporal resolution is limited by the circuit bandwidth (~100 kHz), increasing its potential by, for example, combining its characteristics with those of other techniques is desired. A promising approach is to control the material conditions in STM measurement using optical techniques. Ultrashort-optical-pulse technology has enabled the observation of transient phenomena with femtosecond duration, i.e., the optical-monocycle region, although this has the drawback of a relatively low spatial resolution limited by the electromagnetic wavelength. Therefore, realizing the measurement of time-resolved tunneling current in the sub-picosecond range by combining STM with an ultrashort-pulse laser is a challenge that will lead to the simultaneous realization of ultimate spatial and temporal resolutions.

In their pioneering work, Hamers and co-workers analyzed surface photovoltage. By changing the repetition rate of laser pulses, they observed a corresponding change in the surface photovoltage (SPV), which they considered to be proportional to the photocarrier density. Through the comparison of experimental and calculated results, they successfully determined the carrier lifetime in Si to be 1 μs. Another approach to obtaining a better time resolution is to use the pump-probe method. Recently, a new microscopy technique, shaken-pulse-pair-excited STM (SPPX-STM), was developed and the real-space imaging of nanoscale transient carrier dynamics with a wide range of lifetimes was realized. Since the probe in SPPX-STM is tunneling current, the effect of local electronic structures on carrier dynamics can be observed; the effect of gap states on the hole capture rate was visualized for a Co nanoparticle/GaAs system on the nanoscale.

In this paper, we present results obtained by SPPX-STM for the carrier dynamics in a GaAs–PIN junction. Variation in local potential essentially influences carrier dynamics in small organized structures; therefore, understanding this effect on the nanoscale is extremely important for the future development of semiconductor devices. Here, we demonstrate the first real-space imaging of carrier dynamics modulated in the built-in potential of a GaAs–PIN junction.

First, we briefly explain SPPX-STM and its basic mechanism. Fig. 1 shows a schematic illustration of SPPX-STM. In the conventional optical pump-probe reflectivity (OPPR) method, a sample is illuminated with a train of paired laser pulses with a certain delay time between the pulse pairs. The first pulse is used to excite the sample surface, and the reflectivity of the second pulse is measured as a function of delay time. Thus, the signal is the change in the reflectivity of the second pulse, and the information is averaged over the photoilluminated area. In SPPX-STM, on the other hand, the sample surface below the STM tip is similarly excited by a paired-pulse train, but the signal is the tunneling current as a function of delay time. Namely, the tunneling current is measured by changing the delay time. How does this work?

Fig. 2 shows the relationship between the tentative raw tunneling current $I$ induced by a pair of laser pulses and the delay time $t_d$. The...
between the two pulses (Fig. 2, left). When the delay time is large, the change in the tunneling current induced by each of the two laser pulses independently contributes to the signal, i.e., the temporally averaged tunneling current $I$ (right).

Fig. 2 Relationship between the tentative raw tunneling current induced by a pair of laser pulses $I^*$ and the delay time between the two pulses (left), producing the delay-time dependence of the signal, i.e., the temporally averaged tunneling current $I$ (right).

modulated in the form of a sine wave and the differential value $dI/dt$ was measured. In the second-generation system, as shown in Fig. 1, the pulses are selectively transmitted using a pulse picker, and the delay time is controlled digitally. With this system, repetitive switching (rectangular modulation) between two delay times whose difference is larger than the relaxation time of the photocarriers is possible. The modulation frequency for lock-in detection was 20 Hz when the optical length was mechanically changed by controlling the mirror position, which can be increased to 1 kHz or more through the electronic control of the delay time. Therefore, the measurement is hardly affected by low-frequency fluctuations in the laser intensity and tunneling current. In addition, the modulation becomes free from mechanical noise, which causes a critical problem in the case of optical-length control by moving the mirror position, thus providing a high signal-to-noise ratio. Furthermore, in the case of rectangular modulation, we can carry out accurate measurement and directly obtain the absolute value of the signal instead of the differential value, which is obtained by sine-wave modulation, i.e., $\Delta I = I(t_d) - I(\infty)$, where $I(t_d)$ and $I(\infty)$ are the average tunneling currents for a delay time $t_d$ and that sufficiently long for the excited state to be relaxed, respectively (Fig. 1(b)).

The nonlinearity between two excitations by paired pulses depends on the material under observation. In SPPX-STM on a semiconductor, a nanoscale metal–insulator–semiconductor (MIS) structure is formed by the STM tip, the tunneling gap and the sample. Under a reverse bias voltage, tip-induced band bending (TIBB) is induced owing to the leakage of the bias voltage. With photoexcitation, the redistribution of photocarriers reduces TIBB, i.e., SPV, which subsequently relaxes to the original state through two processes. One is the decay of the photocarriers on the bulk side via recombination, drift and diffusion (bulk-side decay). Absorption bleaching on the bulk side, similar to that observed in the conventional OPPR technique, produces a change in the SPV, resulting in a change in tunneling current that depends on the delay time, thereby, we can probe the decrease in the density of photoexcited carriers in a semiconductor sample, i.e., bulk-side decay. The other is the decay of carriers trapped at the surface (surface-side decay) that appears following the bulk-side decay, which was discussed in detail in the analysis of the gap state effect observed for the Co nanoparticle/GaAs system.
In this study, we analyzed carrier dynamics through the probing of the bulk-side decay. We first carried out OPPR measurement and SPPX-STM on three different samples, GaAs, low-temperature-grown GaAs (LT-GaAs) and GaNAs, and compared the results. Then we applied SPPX-STM to the analysis of a GaAs–PIN junction to probe the effect of the local potential landscape on carrier dynamics, which cannot be obtained by the conventional optical pump-probe technique. OPPR measurement was carried out in air, while for SPPX-STM measurement, samples were prepared by cleaving them in a vacuum (~5 x 10⁻⁷ Pa), and experiments were carried out under an ultra high vacuum (UHV) condition (~2 x 10⁻⁸ Pa).

Fig. 3 shows the spectra obtained by the OPPR technique and SPPX-STM for LT-GaAs, GaNAs and GaAs. Since the intensities of pump and probe pulses were adjusted to be the same, the SPPX-STM signal has a symmetry with respect to the longitudinal axis at \( t_d = 0 \). The value of 500 ns was chosen as \( t_d \) to obtain \( I(\infty) \). The decay constants for each sample were obtained by single exponential curve fitting of the SPPX-STM spectra to be 2.4 ps, 440 ps and 4.8 ns for LT-GaAs, GaNAs and GaAs, respectively. The derived decay constants are: (a) 1.5 ps, (b) 2.4 ps, (c) 410 ps, (d) 3.3 ns and (f) 4.8 ns. \( t_d = 500 \) ns was chosen for \( I(\infty) \), which is not considered here, has a decay constant much larger than that of bulk-side decay for these materials, the signal does not decrease to zero in this time range.

Next, we applied SPPX-STM to the GaAs–PIN junction with a different potential landscape. Fig. 4 shows schematic diagrams of the GaAs–PIN junction that we used as the sample and its built-in potential. A p-type GaAs buffer layer (Be doping concentration: 2 x 10¹⁸ cm⁻³, thickness: 250 nm), p-type GaAs (Be doping concentration: 1 x 10¹⁸ cm⁻³, thickness: 500 nm), n-type GaAs (i-GaAs, 400 nm) and an n-type GaAs substrate (Si doping concentration: 1 x 10¹⁷ cm⁻³, thickness: 1000 nm) were deposited on a p-type GaAs(100) substrate (Be doping concentration: 5 x 10¹⁸ cm⁻³). Au was deposited on both sides of the sample to form an ohmic contact to enable the application of bias voltage to the sample. In this experiment, we used a short-circuit condition and, as shown in Fig. 4(b), a built-in potential was induced in the sample, which was confirmed by measuring the SPV.

Fig. 5(a)–(d) show four images from a series of 2D maps of time-resolved signals. Instead of obtaining the full spectrum by changing the delay time, the STM tip was scanned with the delay time fixed at (a) 0, (b) 2, (c) 4 and (d) 11 ns. Namely, the images show the carrier density at each delay time after photoexcitation at \( t = 0 \). As described above, since a reverse bias voltage between the STM tip and the sample is necessary to produce TIBB and its relaxation by photoexcited carriers (SPV), which are both required for the measurement of the time-resolved signal, only the left half of each figure is considered here because measurements were carried out under the conditions of \( V_S = -2.2 \) V (sample bias voltage) and \( I_t = 100 \) pA (set point current). Namely, the photoexcited electron density in the conduction band was probed since a negative sample bias voltage was applied in this experiment. To observe the dynamics in the right half of the figures, it is necessary to change the sign of the bias voltage. Since the combination of TIBB and SPV is the basic mechanism for bulk-side decay in this case, the depth information originates from the area where the drift of photocarriers is influenced by TIBB depending on the bias voltage applied between the tip and sample, i.e., several tens of nanometres in the present case.

The decay constant \( \tau_d \) is obtained from the full series of 2D maps by fitting the change in the carrier density at each point, a map of which is shown in Fig. 5(e). Fig. 5(f) shows the cross-section along the line in Fig. 5(e). The variation observed in the cross-section is partly caused by the low signal-to-noise ratio owing to the probing of the weak signal.

As described above, absorption bleaching is the mechanism for providing the SPPX-STM signal for the bulk-side decay. The number of photocarriers excited by the second optical pulse (probe pulse)
These results clearly indicate that what is observed by SPPX-STM is the change in the carrier density in the region where nanostructures are probed, including the effects of diffusion and drift in the local potential, rather than the ordinary lifetime observed by OPPR measurement. In such a case, the spatial resolution is determined by the physical processes in the observed sample. As has been reported in our previous paper, local dynamics can be probed with atomic resolution when the surface-side decay is analyzed.\textsuperscript{29} By using one of these two analysis methods depending on the target processes, we can obtain more detailed information on the carrier dynamics in semiconductors. Since SPPX-STM is applicable if nonlinear interference exists between the two excitations induced by the two laser pulses, the probing of other physical processes of various materials is possible, which is currently being investigated.

We have carried out SPPX-STM measurements on a GaAs–PIN structure. The direct observation of the effect of built-in-potential on the carrier dynamics, which cannot be probed by the OPPR technique, was clearly and directly observed, showing the high potential of this microscopy technique.

**Acknowledgements**

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

**Notes and references**