

Femtosecond Transient Reflecting Grating Methods and Analysis of the Ultrafast Carrier Dynamics on Si(111) Surfaces

Tomohiro MORISHITA,* Akihide HIBARA,* Tsuguo SAWADA,* Isao TSUYUMOTO,**
and Akira HARATA***

*Department of Applied Chemistry, School of Engineering, The University of Tokyo,
Hongo, Bunkyo, Tokyo 113-8656, Japan

**Department of Environmental Systems Engineering, Kanazawa Institute of Technology,
Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

***Department of Molecular Science and Technology, Graduate School of Engineering Science,
Kyushu University, Kasugakoen, Kasuga, Fukuoka 816-8580, Japan

The femtosecond transient reflecting grating (TRG) method was developed and applied to monitor the ultrafast dynamics of photo-excited carriers on Si(111) surfaces. TRG responses were measured as a function of the pump beam intensity and fringe spacing, and two relaxation components were observed. An analysis of the results has suggested that the slow component corresponds to carrier diffusion and that the fast component corresponds to a combined process between ballistic transport and carrier-carrier scattering of non-equilibrium carriers.

(Received October 6, 1999; Accepted January 31, 2000)

The ultrafast carrier dynamics of semiconductor surfaces on a sub-picosecond time scale has become a significant area for study from the viewpoints of basic science and technological innovations^{1,2} because of the explosive development of the large-scale integration of semiconductor circuits. Among surface materials, Si is one of the most important for electronic devices, and many studies on its surface ultrafast carrier dynamics have been performed using such methods as the two-photon photo-emission method^{3,4} and the transient-reflectivity (TR) method.^{5,6} The time-resolved two-photon photo-emission method has provided useful information about the carrier thermalization process *via* carrier-carrier scattering, and the TR method has elucidated the multi-body effect of photo-excited carriers. However, ultrafast carrier dynamics has not yet been clarified. For instance, the time evolutions of a distribution of photoexcited carriers and of the Coulomb interaction should be taken into account under a strong excitation condition on a femtosecond time scale; the validity of the random-phase approximation has already been investigated under such a condition.⁷ Experimental difficulties are derived from the fact that most of the ultrafast phenomena are non-radiative processes, and thus band-to-band relaxation cannot be directly observed. For such a case, photothermal spectroscopy, which measures any heat or refractive-index change due to photo-excitation, would be a powerful tool. As a photothermal method, we have developed a transient reflecting grating (TRG) method with a time resolution of 80 ps, and have applied it to semiconductor surfaces.^{8,9} The TRG method has many advantages, such as surface selectivity, high sensitivity, background-free detection, and providing directional information. We can expect to observe carrier thermalization and carrier transport dynamics by raising the time resolution to the femtosecond time region of the TRG method.

In this study, we developed a femtosecond time-resolved TRG (fs-TRG) method and applied it to measure Si(111) surfaces.

We want to use it to clarify the behavior of photo-excited carriers at these surfaces. We present results suggesting the ballistic transport of non-equilibrium carriers, and the Auger recombination and carrier diffusion of equilibrium carriers.

Experimental

Since the experimental setup for the TRG method was the same as that described in our previous report,¹⁰ only an outline is presented here based on Fig. 1. Two pump pulses of the same wavelength, λ_{pump} , were crossed on a sample surface to form an optical interference pattern with a fringe spacing (Λ) of $\Lambda = \lambda_{\text{pump}}/2\sin\theta$, where θ is the pump beam incident angle normal to the surface. This interference pattern induced a periodic refractive-index change, which acted as a transient diffraction grating. The probe pulse was incident normal to the grating, and diffracted light was observed. The intensity of the diffracted light was monitored as a function of the delay time of the probe beam. The TRG signal reflected dynamic information about the surfaces, such as a refractive-index change by carrier excitation and heat generation.

The light source was a regeneratively amplified Ti:sapphire laser system which had an auto-correlation of 150 fs, a wavelength of 800 nm and a repetition rate of 1 kHz. The output beam (800 nm wavelength) was partly reflected by a half mirror to generate the probe beam, which passed through a computer-controlled optical delay line. The residual beam was frequency-doubled by a BBO crystal to generate a 400 nm beam, which was split into two parts. Each pump pulse had a spot size of 600 μm and *p*-polarization. The polarizations of the pump and probe beams were perpendicular to each other. The diffracted light was detected by a PIN photodiode. The output of the photodiode was fed into a fast-gated-integrator, and its

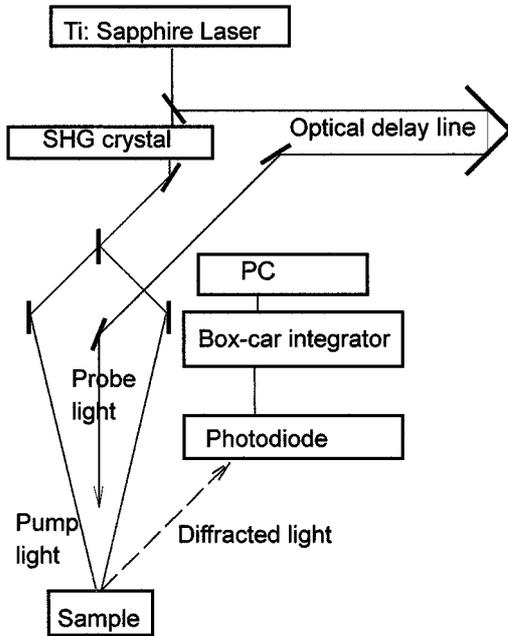


Fig. 1 Schematic of the experimental apparatus of the femtosecond TRG method.

average signal was recorded as a TRG response.

In order to examine multi-body effects of photo-excited carriers, the photo-excited carrier density was controlled by changing the pump beam intensity. Furthermore, in order to differentiate information parallel to the surface and perpendicular to it, the dependence of the TRG responses on the fringe spacing was measured by changing the incident angle of the pump beam.

A single crystal of Si(111) was used for the measurements. The oxidized layer on the Si surface was 100 nm thick. All experiments were performed in air at 296 K.

Results and Discussion

Analysis of the TRG signals

Typical TRG responses are shown in Fig. 2. We first discuss how to analyze them. The TRG responses reflect the change in the refractive index (Δn) on the Si surface, as induced by the pump beam. Δn is evaluated as $\Delta n = \Delta n_N + \Delta n_{\Delta T}$, where Δn_N and $\Delta n_{\Delta T}$ are the carrier and temperature contributions to Δn , respectively. For small N and ΔT , Δn_N and $\Delta n_{\Delta T}$ are given by $\Delta n_N = (\partial n/\partial N)N$, $\Delta n_{\Delta T} = (\partial n/\partial T)\Delta T$ with $\partial n/\partial N$ and $\partial n/\partial T$ being constant, where N is the density of the photo-excited carriers and ΔT is the temperature rise on the Si surface.

To discuss Δn_N due to the carrier effect, we need to calculate the proportional constant, $\partial n/\partial N$, by applying the Drude model for the optical properties of quasi-free carriers to the photo-excited electron-hole pairs.¹¹ The change in the refractive index (Δn) is given by

$$\Delta n_N = \frac{\partial n}{\partial N} N = - \frac{Ne^2}{2n_0 m_{\text{ch}}^* \epsilon_0 \omega_p^2} \leq 0, \quad (1)$$

where N is the photo-excited carrier density, e the fundamental electron charge (1.60×10^{-19} C), n_0 the absolute refractive index of Si at 800 nm (3.69^{12}), ϵ_0 the dielectric constant (8.85×10^{-12} F m⁻¹), m_{ch}^* the effective reduced mass of the electron-hole pair (1.17×10^{-31} kg¹³) and ω_p the radial frequency of the probe light (2.36×10^{15} s⁻¹). From Eq. (1), the change due to the carrier

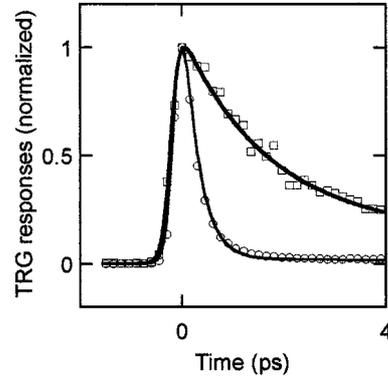


Fig. 2 Typical TRG responses with a constant fringe spacing of 1.2 μm . The symbols \square and \circ correspond to pump beam powers of 0.75 (mJ/cm²) and 3.74 (mJ/cm²), respectively. The solid lines are best fits of the bi-exponential function.

effect (Δn_N) becomes negative. In this experiment, the calculated value of $\partial n/\partial N$ is -6.0×10^{-22} cm³.

We next discuss $\Delta n_{\Delta T}$ due to a temperature rise on the Si surface through a variety of effects, including electron-phonon coupling or Fermi smearing. The change in the refractive index induced by the temperature rise ($\Delta n_{\Delta T}$) is given by

$$\Delta n_{\Delta T} = \frac{\partial n}{\partial T} \Delta T + \frac{\partial k}{\partial T} \Delta T,$$

where n and k are the real and imaginary parts of the refractive index, respectively. Based on a previous report,¹⁴ the temperature dependence of $\partial n/\partial T$ and $\partial k/\partial T$ can be neglected. At a probe wavelength of 800 nm, we estimate the temperature coefficients as $\partial n/\partial T = 5.1 \times 10^{-4}$ K⁻¹ and $\partial k/\partial T = 5.2 \times 10^{-5}$ K⁻¹ from literature values.^{15,16} Because the effect of $\partial n/\partial T$ on Δn is minor,⁶ Δn induced by the temperature rise is approximated as $\Delta n_{\Delta T} \approx \partial n/\partial T \Delta T \geq 0$. The temperature rise (ΔT) at equilibrium is estimated to be 144 K.¹⁷

Δn_N is given by

$$\Delta n_N = \frac{\partial n}{\partial N} N = (-6.02 \times 10^{-22}) \times (7.25 \times 10^{20}) = -0.437$$

and $\Delta n_{\Delta T}$ is given by

$$\Delta n_{\Delta T} = \frac{\partial n}{\partial T} \Delta T = 5.1 \times 10^{-4} \times 144 = 7.34 \times 10^{-2}.$$

Thus, the contributory ratio, $\chi = \Delta n_N/\Delta n_{\Delta T}$, is calculated as $\chi = -5.95$. Because the intensity of the TRG responses is proportional to $(\Delta n)^2$, the dominant component in the TRG responses is the carrier effect. This result is supported by our previous report, in which we measured the negative change in the refractive index from the transient reflectivity responses on a Si surface on a picosecond time scale.⁶ We can thus regard the change in the refractive index as being mainly due to the carrier effect.

The decay curve ($R(t)$) is fitted with a summation of some exponential functions. A bi-exponential model provides the best fitting with the TRG responses. The decay curve ($R(t)$) is formalized as

$$R(t) = C \exp\left(-\frac{t}{\tau_f}\right) + (1 - C) \exp\left(-\frac{t}{\tau_s}\right),$$

where τ_f and τ_s are the relaxation-time constants of the fast-decay component and of the slow one, respectively, and C is a pre-exponential factor. We discuss ultrafast carrier dynamics by analyzing these two relaxation processes below.

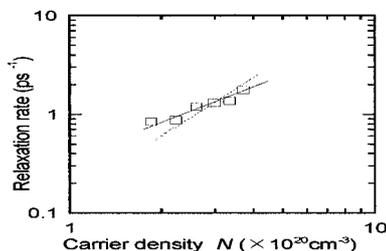


Fig. 3 Dependence of the relaxation rate of the fast component (τ_f^{-1}) on the carrier density (N). The solid line is an eye-guide; the dotted line has a slope of 2.

Dependence on the photo-excited carrier density

As shown in Fig. 2, the TRG responses were drastically influenced by the photo-excited carrier density (N), which was calculated from the light-absorption volume, reflectivity¹⁸ and intensity of the pump beam. For a detailed analysis, the carrier density (N) vs. the relaxation rate is plotted in Fig. 3. The relaxation rate of the fast component increased with increasing photo-excited carrier density, whereas that of the slow one was independent of the carrier density (N).

Here, we focus on the fast-relaxation component. The decay of the photo-excited carrier density with time is given by¹⁹

$$\frac{\partial N}{\partial t} = -\gamma_1 N - \gamma_2 N^2 - \gamma_3 N^3 + D \frac{\partial^2 N}{\partial x^2} + I(t=0),$$

where N is the photo-excited carrier density; γ_1 , γ_2 and γ_3 are the carrier-recombination rates of linear, two-body and three-body processes, respectively. D is the carrier-diffusion coefficient and I is the intensity of the pump beam at time zero. Considering the experimental condition of the high carrier density ($\approx 10^{20}$ cm⁻³) and a previous report,⁵ the Auger-recombination process is expected to be the dominant process for the fast component. In this case, the above equation is approximated as $\partial N/\partial t \approx -\gamma_3 N^3$ and the relaxation time (τ_f) is given by $\tau_f = I/\gamma_3 N^2$; the slope in Fig. 3 would thus be 2 cm³/ps. However, the experimental slope was clearly smaller than 2. This result suggests that the fast-decay component includes another ultrafast multi-body process as well as the Auger-recombination process. The one- and two-body recombination processes are 10⁶-times slower than this result. We thus consider that another ultrafast multi-body effect, the energy-dissipation process *via* carrier-carrier scattering, called the carrier-thermalization process, occurs. It is known that the carrier-thermalization process occurs on a sub-picosecond time scale following the generation of hot carriers, which don't equilibrate with the phonon system. Actually, the calculation for the effective mass¹⁴ indicates that the contribution of the non-equilibrium state to the TRG response is 36-times stronger than that of the equilibrium state. This also supports our result. This result suggests that the fast-decay component contains the thermalization process *via* carrier-carrier scattering, and that the TRG responses are strongly affected by the carrier-thermalization process.

Dependence on the fringe spacing Λ

The dependence of the relaxation rates of the fast and slow components on the fringe spacing (Λ) was measured with a pump beam power of 3.4 mJ/cm². The fringe spacing (Λ) was changed by controlling the incident angle (θ) of the pump beam. The dependence of the relaxation rates of the fast and slow components on the fringe spacing (Λ) is shown in Fig. 4. Both the fast and slow relaxation rates increased with decreasing the

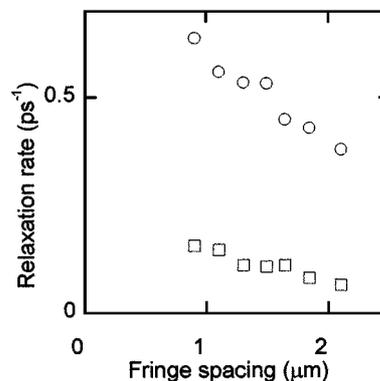


Fig. 4 Dependence of τ_f^{-1} and τ_s^{-1} on the fringe spacing (Λ). The symbols \circ and \square correspond to τ_f^{-1} and τ_s^{-1} , respectively.

fringe spacing. If the phenomenon corresponding to the components occurred perpendicular to the surface, no dependency on the fringe spacing should be observed. The dependency of both components on the fringe spacing indicates that both decay components can be regarded as a phenomenon parallel to the surface. We estimated the diffusion coefficients of photo-excited carriers from this result using the transient grating theory,²⁰ and found that the values of the slow and fast components are 20 cm² s⁻¹ and 60 cm² s⁻¹, respectively.

First, we discuss the slow component. Since the slow component is over 10 ps, this is probably due to diffusion of the carriers after equilibrium with phonons. We estimated the carrier mobility from Einstein's relation, $D/\mu = k_B T/e$, by substituting the experimental diffusion coefficient of the slow component and the estimated temperature ($T = 440$ K) on the Si surface, which was calculated assuming that all surplus energy given to carriers is used for the temperature rise of the equilibrium carrier and phonon systems. The obtained value is 530 cm² s⁻¹ V⁻¹, which agrees with the previously reported value of 572 cm² s⁻¹ V⁻¹.²¹ Therefore, we conclude that the slow-decay component corresponds to diffusion of the photo-excited carriers after equilibrium with phonons.

We next discuss the fast-decay component. For the fast component, the transport of non-equilibrium carriers and equilibrium carriers is probable. However, from an earlier discussion, the fast component cannot be explained by diffusion of the equilibrium carriers. This suggests that the fast component is mainly due to diffusion of the non-equilibrium carriers, *i.e.*, there is little carrier scattering with phonons during fast decay. We thus propose the ballistic transport of non-equilibrium carriers occurring before the carrier-thermalization process *via* carrier-carrier scattering, in which there is no scattering process during several hundred femtoseconds.

Details can be added by an analysis of the non-equilibrium carrier condition. By approximating the photo-excited carriers on the Si surface as quasi-free carriers in a metal, we obtain the theoretical Fermi velocity, $v_F = 2.8 \times 10^7$ (cm/s). On the other hand, the velocity of the photo-excited carriers is estimated by using the following equation from this experiment:

$$\frac{\partial N}{\partial t} = V \frac{\partial N}{\partial x},$$

where N is the carrier density and V is the transport velocity. We obtain an experimental value of 1.2×10^7 cm/s for V_F . This value agrees with the theoretical one in terms of the time scale. We believe that this result suggests the ballistic transport of non-equilibrium carriers. Considering the results for the

dependence on the photo-excited carrier density, we conclude that the fast-relaxation component corresponds to a process of ballistic transport and carrier-carrier scattering of non-equilibrium carriers.

In conclusion, we have developed a femtosecond time-resolved transient-reflecting grating (fs-TRG) method, and have successfully measured the ultrafast carrier dynamics on Si surfaces. An analysis of the TRG responses as a function of the pump beam intensity and fringe spacing suggests that the slow component corresponded to the carrier diffusion, and that the fast component corresponded to a combined process of ballistic transport and carrier-carrier scattering of non-equilibrium carriers. We believe that the fs-TRG method will provide significant information about the relation between the electric property and the photo-excited carriers, especially non-equilibrium carriers in the ultrafast time region, and that it will be a powerful tool for evaluating defects on semiconductor surfaces.

Acknowledgements

This work was supported by Grand-in-Aids for Specially Promoted Research (No. 07102004) and for Scientific Research on Priority Areas of Electrochemistry of Ordered Interfaces (No. 09237219) from the Ministry of Education, Science and Culture of Japan.

References

1. Z. C. Ying and W. Ho, *Phys. Rev. Lett.*, **1988**, 60, 57.
2. Z. C. Ying and W. Ho, *Phys. Rev. Lett.*, **1990**, 65, 741.
3. N. J. Halas and J. Bokor, *Phys. Rev. B*, **1989**, 62, 1679.
4. S. Jeong, H. Zacharias, and J. Bokor, *Phys. Rev. B*, **1996**, 54, 17300.
5. F. E. Doany and D. Grischkowsky, *Appl. Phys. Lett.*, **1988**, 52, 36.
6. T. Tanaka, A. Harata, and T. Sawada, *J. Appl. Phys.*, **1997**, 82, 4033.
7. L. Banyai, Q. T. Vu, B. Mieck, and H. Haug, *Phys. Rev. Lett.*, **1998**, 81, 882.
8. A. Harata, N. Adachi, and T. Sawada, *Phys. Rev. B*, **1998**, 58, 7319.
9. K. Katayama, Q. Shen, A. Harata, and T. Sawada, *Phys. Rev. B*, **1998**, 58, 8428.
10. A. Harata, H. Nishimura, T. Tanaka, and T. Sawada, *Rev. Sci. Instrum.*, **1993**, 64, 618.
11. J. J. Kasinski, L. A. Gomez-Jahn, S. M. Gracewski, and R. J. D. Miller, *J. Chem. Phys.*, **1989**, 90, 1253.
12. D. F. Edwards, in "Handbook of optical constants of solids", **1985**, Academic Press, 565.
13. M. Cardona, in "Landort-Bornstein 17-a", ed. K. H. Hellwege, **1982**, Springer-Verlag, Berlin, 45.
14. M. Cardona, in "Landort-Bornstein 17-a", ed. K. H. Hellwege, **1982**, Springer-Verlag, Berlin, 70.
15. M. Cardona, in "Landort-Bornstein 17-a", ed. K. H. Hellwege, **1982**, Springer-Verlag, Berlin, 387.
16. H. H. Li, *J. Phys. Chem. Ref. Data*, **1980**, 9, 561.
17. C. M. Li, *Appl. Sur. Sci.*, **1996**, 104/105, 57.
18. M. Cardona, in "Landort-Bornstein 17-a", ed. K. H. Hellwege, **1982**, Springer-Verlag, Berlin, 67.
19. T. Tanaka, A. Harata, and T. Sawada, *J. Phys. IV*, **1994**, C7, 171.
20. H. J. Eichler, P. Gunter, and D. W. Pohl, in "Laser-Induced Dynamics Grating", ed. T. Tamir, **1986**, Springer-Verlag, Berlin, 59.
21. F. J. Morin and J. P. Maita, *Phys. Rev.*, **1954**, 96, 28.