

## *Chapter 8*

### MASK PATTERN TRANSFERRED TRANSIENT GRATING TECHNIQUE FOR MOLECULAR-DYNAMICS STUDY IN SOLUTIONS

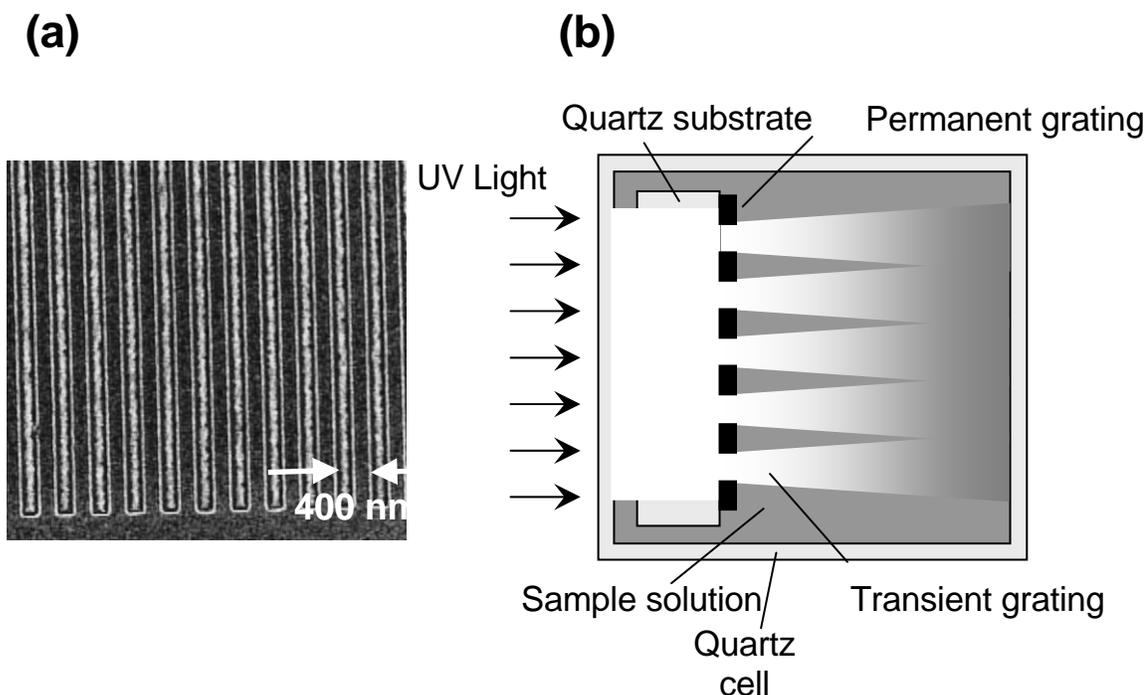
#### 8.1 Introduction

The transient grating (TG) technique [1, 2], which is one of the third-order nonlinear spectroscopies, has been a powerful tool to monitor several photonics and photochemical processes in solutions since its outset. For a brief history, solutions were photoexcited by an optical interference pattern generated by two crossing pump beams. As parameters, several properties of a solution were spatially modulated according to the interference pattern and were detected through the diffraction of the probe beam. The time-varying profiles of the diffracted signal indicate the many processes in solution, such as electron transfer, molecular dynamics, heat dynamics, ultrasonics, volume/structure change, clustering/aggregation, and chemical reaction [3-8]. The optical heterodyne detected-TG (OHD-TG) technique [9-16] was also developed later to improve sensitivity. The reference beam, which has the same direction, polarization, and wavelength as the signal beam, was superimposed on the signal beam to amplify the signal intensity. The experimental setups of the OHD-TG were very difficult because the probe and reference beams need to be aligned and tuned within submicron meter scale to meet the phase-matching condition. Very recently, Katayama et al. developed a lens-free OHD-TG technique [17, 18] by using a transmission grating structure in a 3 mm glass. This technique was easier than the traditional OHD-TG technique. In this chapter, we describe a more convenient and easy

well aligned technique; the mask pattern transferred—TG (MPT-TG) technique—by using a metal film grating fabricated in our laboratory.

## 8.2 Experimental setup

Figure 8.1a shows the scanning electron microscope (SEM) image of the smallest metal grating film (400 nm metal width and 1  $\mu\text{m}$  period). Chromium layer (100 nm) was created by vacuum evaporation on the quartz substrate. A fine grade resist was deposited on a Cr layer by spin coating. Nano or micrometer scaled patterns are written by the lithography

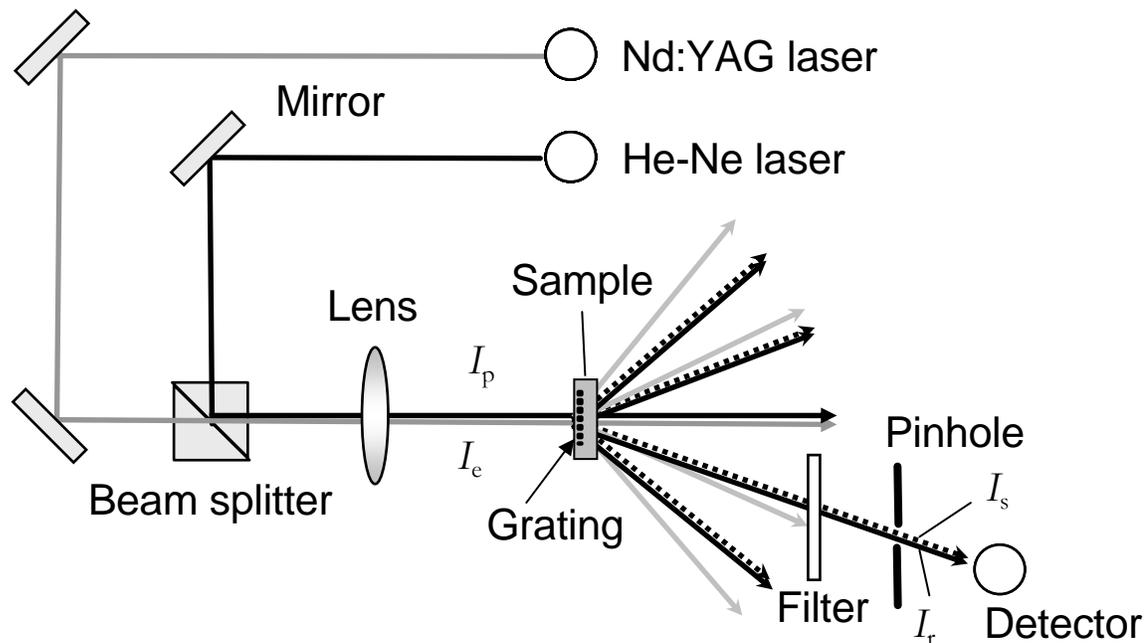


**Figure 8.1 (a) Scanning electron microscope (SEM) image of the smallest fabricated nano metal grating. (b) Schematic diagram of the pattern transfer from the metal grating film to the solution**

of an electron beam or a direct writing laser. Finally, metal grating structures are engraved by chemical etching. The principle of the MPT-TG is depicted in Figure 8.1b. A finished metal grating film is suspended into the sample solution and the excitation UV pump beam

( $I_e$ ) is incident at the grating in solution. Thus the grating pattern is transferred from the metal film to the sample solution under near-field condition (Fresnel diffraction). This is similar to traditional photo-lithography but, in this case, the sample material is liquid solution. The solute molecules were excited by this special transient grating (TG) structure. A part of the probe beam ( $I_p$ ) irradiated on the grating in the solution is diffracted under the far-field condition (Fraunhofer diffraction) and was detected by the photodetector.

The experimental setup of the MGT-TG is schematically shown in Figure 8.2. A



**Figure 8.2** Experimental setup of the MGT-TG technique with metal grating and the optical configurations of irradiated pump ( $I_e$ ) and probe ( $I_p$ ) beams and diffracted reference ( $I_r$ ) and signal ( $I_s$ ) beams

frequency-tripled Nd:YAG laser ( $\lambda_e = 366$  nm,  $I_e = 0.3$  mJ/pulse) was used as a pump beam. The pulse width and repetition rate are 10 ns and 3 Hz, respectively. A cw-He-Ne laser ( $\lambda_p = 633$  nm,  $I_p = 0.05$  mW) is used as a probe beam. Both beams are focused by a lens on the

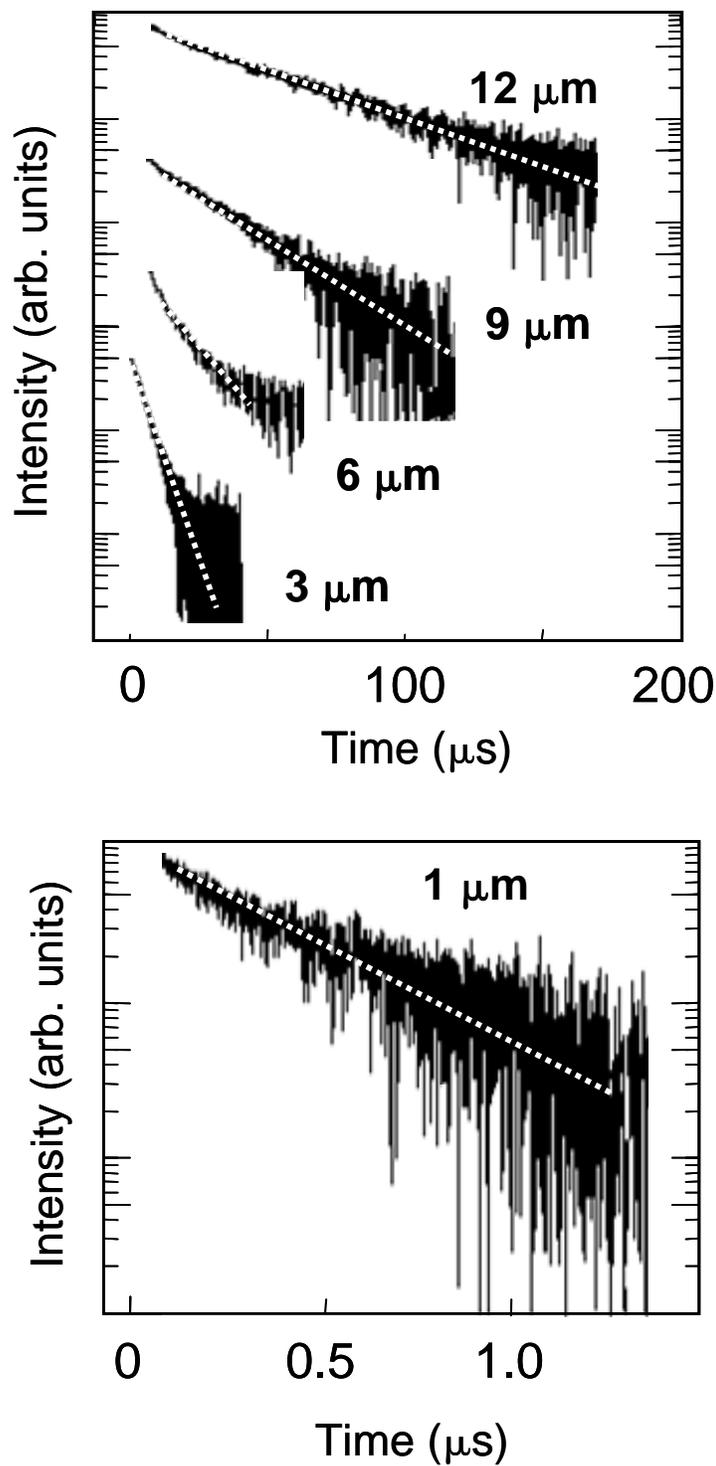
sample solution in a quartz cell (10 mm spacing). A limited diffraction beam passes through a pinhole and a glass filter and is registered with an InGaAs photodetector. Two types of signals, diffracted by permanent metal grating ( $I_r$ ) and transient grating ( $I_s$ ), are simultaneously detectable. The permanent grating signal plays the role of the reference beam of the OHD-TG setup and amplifies the transient grating signal. Both diffracted signals pass the color filter and pinhole to be separated from the pump beam and detected onto the photodetector.

Sample solution was nitrobenzene in 2-propanol (5 volume %). The excited energy of nitrobenzene is immediately converted to molecular vibration, translation, and finally heat energy. Such non-radiative relaxation processes of nitrobenzene are completed within a very short time-scale (a few hundred picoseconds) [19]. Therefore, nitrobenzene has been used often as the standard solution of the typical heat source (molecular heater) for photothermal measurement.

### 8.3 Results and discussion

Figure 8.3 shows the semi-log plot of the time-dependent diffraction signals with (a) micron-meter scaled and (b) nano-meter scaled etch width metal grating, respectively. We found the exponential decay component ( $I_s$ ) superimposed on the large non-decayed offset component ( $I_r$ ). The former is due to the transient grating while the latter is due to the permanent grating, respectively. According to the theory, detected total signal intensity ( $I_{total}$ ) can be described by [17, 18]

$$I_{total}(t) = I_r + 2a[\chi^{(3)'}(t)\cos \Delta\phi + \chi^{(3)''}(t)\sin \Delta\phi]I_e I_p + |\chi^{(3)}(t)|^2 I_e^2 I_p \quad (8.1)$$



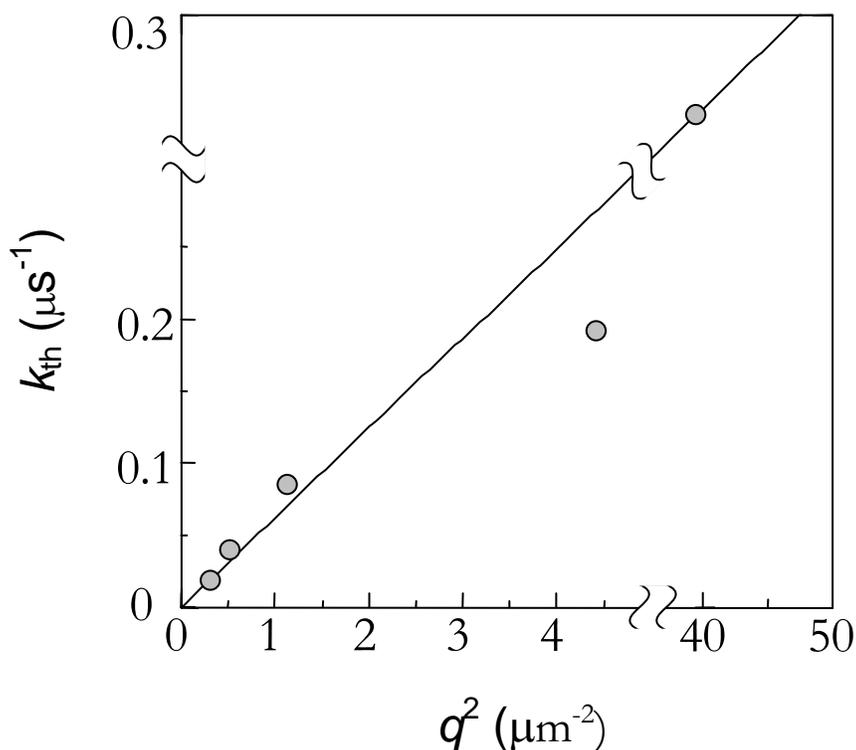
**Figure 8.3** Time profile of the diffracted signals with metal grating of 12, 9, 6, and 3  $\mu\text{m}$  periods (a) and 1  $\mu\text{m}$  period (b). Dashed lines were fitted by the exponential functions.

where  $\chi^{(3)'}(t)$  and  $\chi^{(3)''}(t)$  are the real part and imaginary part, respectively, of the third-order nonlinear electrical susceptibility  $\chi^{(3)}(t)$ , and  $a$  is a real constant. The third term indicates the TG signal with usual homodyne detection and is negligible because involved  $\chi^{(3)}$  in solution should be very small. Thus, only the second term of equation (8.1) indicates  $I_s$ . In this case,  $\chi^{(3)'}(t)$  and  $\chi^{(3)''}(t)$  are equal to the refractive index change  $\delta n(t)$  and the absorbance change  $\delta k(t)=0$  at 633 nm induced by the transient grating, respectively.  $\Delta\phi$  is the phase difference between  $I_r$  and  $I_p$ . In the OHD-TG techniques, unstable  $\Delta\phi$  has been the main difficulty of the experimental setup. However, in our setup,  $\Delta\phi$  is decided only by the structure and thickness of the metal grating. Therefore, the phase stability is excellent without the tuning of beam lines in this setup. Thus,  $\sin\Delta\phi$  in equation (8.1) should be a constant, and  $I_s$  should be proportional to  $\delta n(t)$ .

The spatial modulation of the optical intensity ( $\delta I_e$ ) induced the spatial modulation of the population of the molecular excited states ( $\delta P$ ), temperature ( $\delta T$ ), and density of solvent ( $\delta\rho$ ). Namely,  $\delta n$  should be attributed to  $\delta T$  and  $\delta\rho$  in this time scale. Temperature rising increases  $\delta\rho$ , which decreases  $\delta n$ . Therefore, spatial distribution of temperature (thermal grating) was created, and the signal decay shows the thermal diffusion processes in solution. By solving the Fourier's diffusion equation, the time profile of  $\delta n(t)$  is given by [20]

$$\delta\hat{n}(t) = \left[ \left( \frac{\partial n}{\partial \rho} \right)_T \left( \frac{\partial \rho}{\partial T} \right) + \left( \frac{\partial n}{\partial T} \right)_\rho \right] \frac{Q}{\rho C_p} \delta I_e [C] \exp(-D_{th} q^2 t) \quad (8.2)$$

where,  $Q$ ,  $C_p$ , and  $[C]$  are the heat energy released from unit molecules, specific heat capacity, and solute molecular concentration.  $\delta\hat{n}(t)$  is the spatial Fourier component of



**Figure 8.4 Relationship between the square of the grating constants ( $q^2$ ) and the decay rate ( $k_{\text{th}}$ ) of the TG signals. This slope indicates the thermal diffusion coefficient.**

$\delta n(t)$ .  $q$  is the grating constant described by the grating period ( $\Lambda$ ) as  $q=2\pi/\Lambda$ .  $D_{\text{th}}$  is the thermal diffusion coefficient of solution. Therefore, signal decay rate ( $k_{\text{th}}=1/\tau$ ) obtained by the exponential fitting was described by  $k_{\text{th}}= D_{\text{th}} q^2$ . Figure 8.4 shows the relationship between  $k_{\text{th}}$  and  $q^2$  at each grating period, where a good linear relationship and  $D_{\text{th}}$  value is shown by the slope. The obtained value ( $D_{\text{th}}= 7.0 \pm 0.7 \times 10^8 \text{ m}^2\text{s}^{-1}$ ) is very close to the calculated value ( $D_{\text{th}}= 6.8 \times 10^8 \text{ m}^2\text{s}^{-1}$ ) [18] by the thermal conductivity ( $\kappa$ ) of 2-propanol as  $D_{\text{th}} = \kappa/\rho C_p$ . This agreement demonstrates the validity of this method according to signal analysis above. By the same token, several diffusion processes, such as the molecular

diffusion in solution, energy migration in materials, or the carrier diffusion in semiconductors, should be measurable.

The MPT-TG technique should have many merits for photonic and photochemical application. The experimental setup and the beam alignment of the MPT-TG are simpler and easier than those of the usual OHD-TG technique, while it has very high signal sensitivities and S/N ratios for the optical heterodyne detection. The pump and probe beam should be incident at the same spot on the metal grating film, but the tunings of direction and phase of the beams are not necessary. The lens-free OHD-TG technique [17, 18] has similar merits. But the MPT-TG technique has still more merits compared to the lens-free technique. In the lens-free technique, an optical interference pattern was constructed by the diffraction light with transmission grating on the sample located behind the grating. The phase differential  $\Delta\phi$  can be controlled by the distance ( $\sim 250 \mu\text{m}$  usually) between the grating and the sample. In the MPT-TG technique, metal film grating is suspended into the sample solution and the transient grating structure is created directly behind it. Thus,  $\Delta\phi$  is decided only by the thickness of the metal layer and the incident angle. Therefore,  $\Delta\phi$  stability is controllable by the thickness of the metal layer. Moreover, various patterns can be used flexibly with any metal widths and periods to optimize the sensitivity. The measurement of the grating periods dependence is also very easy to control by sliding the film to change the pattern structure.

#### 8.4 Conclusion

In conclusion, our new technique by using nano or micro metal grating film has many advantages compared to the traditional techniques. This technique should be a powerful

and useful tool for wider applications in physics, chemistry, material, and biological applications.

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