A nanosecond pressure pulse is generated by focusing a nanosecond-pulsed laser onto an aluminum target with plasma confined geometry. A spatially uniform pressure pulse is generated by focusing laser beams with a flat-top spatial energy distribution. High-pressure pulse loading and recovery experiments were performed on yttria-doped (3 mol%) tetragonal zirconia polycrystals at 11 GPa. In the pressure-loaded region, the monoclinic phase was uniformly formed. The transition ratio was approximately 30%. Nanosecond time-resolved Raman spectroscopy was performed on polytetrafluoroethylene under high-pressure pulse loading at 1 GPa, and rapid structural phase transition within 10 ns was revealed.

Materials dynamics is essential for materials science in the mesoscopic domain, as in nanotechnology, because thermal diffusion and mechanical relaxation are comparable in a nanoscale domain, and the behavior and property of materials drastically change in this region. Materials change their phases and crystal structures depending on the surrounding pressure and temperature. Phase diagrams at equilibrium states have been extensively investigated for various materials. However, the kinetics and dynamics of phases with rapid changes of the surrounding conditions are still poorly understood, although the study of molecular motion and rearrangement in materials under phase transition is one of the most important and fundamental issues in physics, chemistry, and materials science. In spite of the importance of materials dynamics, it has been ignored because of the lack of technical methods for dynamic observation under rapid changes of the surrounding conditions. A critical scale of materials, which is named the mesoscopic scale, under high-pressure and temperature states can be defined from the scales of thermal diffusion and mechanical relaxation. The characteristic time of thermalization of inhomogeneous temperature distribution \( \tau_\text{t} \) can be estimated from thermal diffusion equations as follows:

\[
\tau_\text{t} = \frac{\delta^2}{4D},
\]

where \( \delta \) and \( D \) are temperature distribution width and thermal diffusivity, respectively. On the other hand, the mechanical relaxation time \( \tau_\text{m} \) is simply estimated by

\[
\tau_\text{m} = \frac{\delta}{U_s},
\]

where \( U_s \) is the speed of sound or the shock wave velocity. The critical size \( \delta_c \) can be estimated when \( \tau_\text{t} = \tau_\text{m} \):

\[
\delta_c = \frac{4D}{U_s}.
\]

For example, the critical size and the relaxation time for diamond are 26 nm and 1.7 ps, respectively. These values, in general, are small for most materials and correspond to the values in the mesoscopic domain. The mesoscopic domain is merely a boundary between continuum and discrete
media, both of which are physically related by the speed of sound in the materials as shown in Fig. 1.

Recent laser technologies have great advantages in the field, because pulsed lasers can irradiate a wide range of photon flux from nanojoules to kilojoules at various time domains from femtoseconds to nanoseconds. Furthermore, by using two synchronized or delayed beams, one for triggering transition (pump beam) and the other for diagnosis (probe beam), time-resolved measurements are possible at a time resolution of the laser pulse width: e.g. Raman spectroscopy for measuring transient changes in lattice vibration [1–3]. Moreover, recent ultrafast laser technologies have been able to provide X-ray pulses with an extremely short duration which could be used in time-resolved X-ray diffraction for diagnostics of the dynamic response of material lattices [4,5].

Dynamic pressure pulse loading is a technique that has been used to produce extremely high pressure. Another aspect of this technique is rapid stimulation. On loading the pressure pulse, the material undergoes adiabatic compression because the compression process is much faster than the thermal energy dissipation process. Therefore, high-pressure pulse loading is well suited to investigating materials dynamics. In this paper, we investigated phase transition induced by high-pressure pulse loading, using time-resolved Raman spectroscopy. A nanosecond pressure pulse was generated by pulsed-laser irradiation and the spatial and temporal distributions of the pressure pulse were also investigated.

2. Experimental

2.1. Pressure pulse generation

The pressure pulse is generated as a counterforce of ablation induced by focusing a high-power laser beam onto a metal foil target. Fundamental light of a nanosecond Q-switched Nd:YAG (yttrium aluminum garnet) laser is used in the experiment. The pulse width of the laser beam is 10 ns, and the maximum energy is 3 J/pulse. Spatial and temporal distributions of the laser beam are Gaussian. The laser beam was focused onto a target through a planoconvex lens. By using an additional multilens array, uniform energy distribution was realized at the irradiation spot [6]. The targets used were plasma-confined targets [7], which consisted of a backup glass substrate (3 mm), an aluminum foil (25 µm), a Teflon spacer (130 µm) and a cover glass substrate (3 mm; Fig. 2). By focusing the laser beam onto the aluminum foil, a confined plasma is generated at the interface of aluminum and the backup glass substrate, which drives the pressure pulse in the aluminum.

The free surface velocity of the Al foil has been measured using a velocity interferometer system [9,10]. A continuous YAG laser beam (532 nm) is irradiated perpendicular to the rear surface, and the reflected and scattered light undergoes a Doppler shift in frequency, which is introduced into the interferometer system and detected by a streak camera (Hamamatsu Photonics, C5680).

Fig. 3 shows a schematic of the experimental setup for velocity measurement and time-resolved Raman spectroscopy.

2.2. Time-resolved Raman spectroscopy

The fundamental light of a nanosecond Q-switched Nd:YAG laser was used for shock generation and the second-harmonic light of a picosecond mode-locked Nd:YAG laser was used for the excitation of Raman scattering.

The shock-generating fundamental light was focused on the target through a multilens array coupled with a planoconvex lens to improve the Gaussian laser profile to a flat-top profile. The diameter of the focused light was 1.25 mm. The target assembly was fabricated with a backup float glass substrate (100 £ 100 £ 3 mm³), 50-µm-thick aluminium foil, a 80-µm-thick polytetrafluoroethylene (PTFE) sample, and a cover float glass substrate (100 £ 100 £ 3 mm³). The target assembly was mounted on a motorized X–Z stage. When the laser was pulsing,
the target assembly was moved by the motorized stage. Each laser shot was focused on a fresh sample. By focusing the laser beam into a spot on the aluminum foil, confined plasma was generated near the aluminum–glass interface, which drives a shock wave through the aluminum foil into the sample. The energy of the irradiating pump laser (10 ns) was 495 mJ. The pump and probe lasers were synchronized and delayed using a delay generator (timing jitter of ±1 ns). A delayed Raman probe laser (25 ps) was focused on the rear side of the sample to a spot with a diameter of 500 μm centered opposite the focus of the pump beam. The probe laser energy was 400 μJ. Raman scattered light was collected and focused into a 400 μm core optical fiber through camera lenses and introduced into a spectrometer whose resolution is about 3 cm⁻¹. The dispersed light was detected with an intensified charge-coupled device camera. The Raman spectrum for PTFE was obtained by accumulating data of 400 laser shots [8].

3. Results and discussion

3.1. Spatial and temporal distributions of pressure pulse

Free surface velocities of Al foil irradiated by the pulsed laser at an energy of 500 mJ with the multilens array were measured using an optically recording velocity interferometer system (ORVIS; Fig. 4A). When the laser beam was irradiated, the free surface velocity rapidly increased to 0.8 km/s within 5 ns of the first shock wave. The pressure applied by the first shock wave was estimated to be 6.1 GPa from the known Hugoniot for Al [12]. After 5 ns, the laser-irradiated part of the Al foil was punched out from the foil and was gradually accelerated up to 1.1 km/s. When the space reserved by the Teflon spacer was filled with a sample, the high-pressure pulse was generated in
the sample. The velocity at the interface between the Al foil and the sample was measured using liquid benzene as the sample. Fig. 4B shows the temporal profile of the velocity, which corresponds to particle velocity of liquid benzene. The velocity gradually increased to 0.4 km/s and was stable beyond 60 ns. The peak pressure in the liquid benzene was estimated to be 1 GPa. The duration of the pulse pressure was longer than that of the laser pulse (10 ns). This is due to the plasma confinement effect at the interface between the Al foil and the float glass. The high-pressure pulse can also be generated by impact of an accelerated flyer. The impact of the Al foil, at flyer velocity of 1.1 km/s, onto the Al sample causes a pressure of 8.7 GPa in the sample.

The form of the accelerated Al flyer was characterized on the basis of light emission of highly compressed air between the flyer and the back-up glass, using a streak camera image (Fig. 5). The ordinate and abscissa represent time and space, respectively. Fig. 5a and b show emissions from air layer due to the compression by Al flyer driven by laser beams with Gaussian and flat-top spatial distribution, respectively. The flat-top spatial distribution was generated using the multilens array. The emission profiles represent the flyer form. These results show that the flyer form reflects the spatial profile of the laser beam. Since flyer acceleration is caused by the pressure pulse inside the Al foil, the spatial profile of the pressure pulse generated by the flat-top laser beam is considered to be uniform inside the irradiated spot.

3.2. Pressure pulse loading and recovery experiment

Using the laser-accelerated flyer, high-pressure pulse loading and recovery experiments were performed on yttria-doped (3 mol%) tetragonal zirconia polycrystals (3Y-TZP). The sample used was 3Y-TZP (50 × 50 mm², 50 μm thick) obtained from Tosoh Corporation. The aluminum foil was irradiated by a laser beam at an energy of 500 mJ/pulse using the multilens array. The velocity of the Al flyer was measured to be 0.89 km/s using the ORVIS. Peak pressure induced by impact of the flyer was determined using an impedance-matching method [11] and the measured flyer speed. In calculating the impedance-matching method, the following Hugoniot were used: \( U_s = 5.15 + 1.37u_p \) for Al [12] and \( U_s = 7.02 + 2.20u_p \) for 3Y-TZP [13], where \( U_s \) is the shock-wave velocity and \( u_p \) is the particle velocity. The peak pressure was estimated to be 11.4 GPa and the shock duration was estimated to be 7.8 ns from the thickness of the flyer.

Fig. 6 shows an optical micrograph of the laser shocked 3Y-TZP. The laser-shocked part resembles powder. The crystal structure was examined by X-ray diffraction and micro-Raman measurements. X-ray diffraction of the shocked region shows M[111] and M[111]/C22 lines of a monoclinic phase, while that of the starting material shows only tetragonal-phase lines (Fig. 7). The crystal size of the monoclinic phase was estimated to be 15 nm. Raman spectra of the shocked region also exhibited vibrational lines from the monoclinic and tetragonal phases [14]. Micro-Raman measurements were performed along the diameter of the shocked region but no significant change in Raman spectra was observed. These results indicate uniform
compression within the impacted region. The fraction of the monoclinic phase was estimated to be approximately 30% from the intensity ratio between the 181 cm$^{-1}$ line (monoclinic) to the 148 cm$^{-1}$ line (tetragonal). This phase transition is considered to occur during the pressure-release process from the high-pressure state.

3.3. Time-resolved Raman measurement of PTFE at high pressure state

Fig. 8 shows the time-resolved Raman spectra of the CF$_2$ twisting mode and C–C stretching mode of PTFE under shock compression at about 1 GPa. Time zero denotes the arrival of the pump laser beam at the aluminum surface; thus the arrival of the pressure pulse at PTFE is at a delay time of approximately 20 ns. The C–C stretching mode shows a high-frequency-shifted peak ($\Delta \nu = 8$ cm$^{-1}$) at a delay time of 20 ns, the intensity of which increases with delay time. On the other hand, the CF$_2$ twisting mode shows a low-frequency-shifted peak ($\Delta \nu = -8$ cm$^{-1}$) at a delay time of 30 ns, the intensity of which increases with delay time. The high-frequency and low-frequency shift of C–C stretching and CF$_2$ twisting modes well agree with the high-pressure Raman spectra measurement [15]. The low-frequency shift of the CF$_2$ twisting mode is reported to occur above the phase transition pressure at 0.72 GPa where conformation changes from helical to planar zig–zag. Since there is no delay between the arrival of the pressure pulse and the low-frequency shift, it is suggested that this phase transition occurs within the time step (10 ns) of this experiment.

4. Summary

A nanosecond pressure pulse was generated by focusing a nanosecond-pulsed laser onto an aluminum target with plasma confined geometry. A spatially uniform pressure pulse was generated by focusing laser beams with flat-top spatial energy distribution, which was achieved using the multilens array. By using the plasma-confined geometry, the duration of the pressure pulse was extended to longer than that of the laser pulse. High-pressure pulse loading and recovery experiments were performed on 3Y-TZP at
11 GPa using X-ray diffraction and Raman measurement. In the pressure-loaded region, the monoclinic phase was uniformly formed. The transition ratio was approximately 30%. Nanosecond time-resolved Raman spectroscopy was performed on PTFE subjected to high-pressure pulse loading at 1 GPa. It was found that phase transition occurs within 10 ns of the start of pressure pulse loading. A much higher time resolution such as picoseconds is required for direct measurement of structural dynamics.

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