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Time resolved temperature measurement of polymer surface irradiated by mid-IR free electron laser

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ABSTRACT

We have developed the time-resolved temperature measurement system by using a radiation thermometer FLIR SC620. Temporal temperature profiles of an acrylic resin surface by the irradiation of infrared free electron laser (FEL) pulse were recorded in an 8 ms resolution to measure an instantaneous temperature rise and decay profile. Under the single-shot condition, a peak temperature defined as the temperature jump from the ambient temperature was found to be proportional to the absorbance. Under the multi-shot condition, the temperature accumulation was found to reach a roughly constant value where the supply and release of the heat is balanced.

FEL-TUS (free electron laser at Tokyo University of Science) is a pulsed laser specialized in the mid-infrared region with complete linear polarization. Several works using FEL-TUS as an intense light source have been reported in the field of spectroscopy [1,2] and photochemistry in the gas phase [3,4], surface chemistry [5], nonlinear solid state physics [6], and biosciences in the condensed phase [7–9]. In the gas phase, chemical reactions are, in most cases, initiated by infrared multiphoton absorption (IRMPA) in which a molecule absorbs a number of IR photon in resonance with a specific vibrational mode. A multiphoton ladder climbing scheme generates a highly vibrationally excited "hot" molecule which may dissociate or isomerize when the energy accumulated in the molecule exceeds that of a chemical bond. Under the low pressure regime where energy relaxation by collisions is negligible, the temperature in the reaction zone (near the laser focus with high photon density) is considered to be equal to the ambient temperature. On the other hand, on the surface or in the condensed phase, strong interaction between adjacent molecules may cause rapid relaxation of the excited energy to the surrounding, resulting in the instantaneous temperature rise near the laser irradiation region. Because the rate of chemical reactions is a subtle function of the temperature, it is desirable for discussion of the reaction mechanism in more detail to separate the thermal effect from the photochemical effect. The direct and nondestructive measurement of the topical temperature would provide us with crucial information to reveal a reaction scheme. This is our motivation for developing a time resolved temperature measurement system by visualizing the temperature distribution on the surface. In recent years, combined use of infrared thermal imaging with laser heating has been attracted much attention as a nondestructive diagnostic tool in material sciences [10,11] and medical sciences [12]. The development of third-generation infrared photodetector certainly makes this analytical technique even more sophisticated in the future [13]. In the current experiment, we applied a commercially available radiation thermometer to visualize a temperature rise and fall synchronized with FEL pulses on the polymer surface.

The status of the FEL-TUS facility was reported elsewhere [14,15]. The FEL-TUS delivers macropulses at 5 Hz. Each macropulse is of about 2 μs long and consists of about 6000 micropulses of ~2 ps duration, where the interval of adjacent micropulses is 350 ps. The FEL was tunable over the range of 4.5–12 μm, where the spectral width (full width at half-maximum) is ~0.08 μm at 6.1 μm [15]. The infrared FEL beam was focused on a sample surface by using a ZnSe lens with a focal length of $f = 1000$ mm. The typical focal sizes of 0.4, 0.8, and 1.9 mm in diameter were used. To obtain a relation of the temperature to the absorbance of the sample, the sizes of 0.8 and 1.9 mm were employed to prevent sample damage. The typical pulse energies of a macropulse at the sample surface were set to 2–3 mJ/macropulse, corresponding to the order of nJ for a micropulse.

In our newly developed time-resolved temperature measurement system, we adopted the radiation thermometer SC620, thermography camera made by FLIR Systems, Inc., having a sensitivity range of 7.5–13 μm for black body radiation [16]. The frame speed

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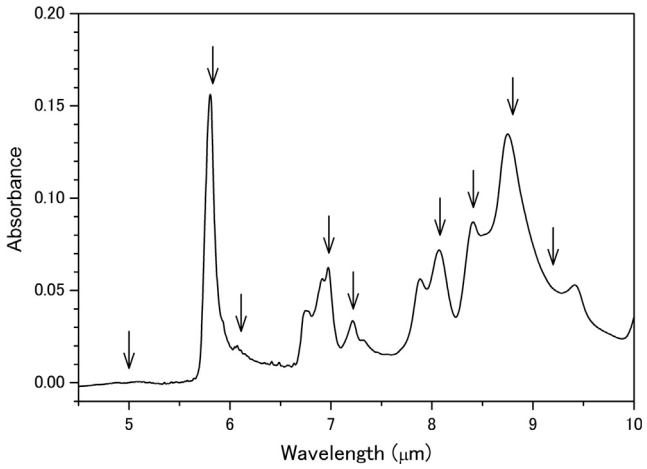

Fig. 1. Infrared absorption spectrum of the acrylic-resin surface recorded by attenuated total reflection mode. The arrows show irradiation wavelengths of FEL.

was set at 120 Hz, corresponding to the 8-ms time resolution. To spatially resolve the irradiated small area on the surface, a ZnSe lens of $f = 400$ mm was put in front of the front lens of SC620, leading to the spatial resolution of 0.13 mm as one pixel in the detector array. Since the focal sizes were larger than the spatial resolution, the temperature we refer hereafter in the current paper represents the averaged temperature over the irradiated area except for the brim. Under our spatial resolution, no hot spot was observed inside the irradiated region. TTL trigger signals from the FEL controller were fed into a personal computer via the RS-232C port in order to synchronize SC620 to the macropulse. An electric shutter and its controller (Lambda SC SmartShutter and Controller, Sutter Instrument Company) were employed to extract the desired number of FEL pulses. The calibration of temperature was carried out by using a reference material made by a polyimide resin film and a precise liquid thermometer. The resolution and the absolute accuracy of the temperature is estimated to be 0.03 K and 1.0 K, respectively.

To determine irradiation wavelengths, Fourier-Transform Infrared (FT-IR) spectrum of a sample was recorded on the FT-IR 6100 spectrophotometer (Jasco International Co., Ltd.) by Attenuated Total Reflection (ATR) mode with a resolution of 4 cm^{-1}. Absorbance of vibrational bands was calculated by using the software Spectra Manager Ver. 2 (Jasco International Co., Ltd.).

Acrylic resin (Polymethyl methacrylate: PMMA) was selected as a sample in the present measurement, because this polymer has distinct absorption bands at 5.83, 6.11, 6.98, 7.22, 8.08, 8.41, and 8.80 μm which are all covered by the output range of FEL, as shown in Fig. 1. Since the polymer shows no absorption peak below 5.7 μm, we employed 5.0 μm as a non-absorption wavelength. The acrylic resin used was a small disc having a diameter of 10 mm and a thickness of 0.5 mm. The small disc was fixed at a position of ~10 cm over a laboratory table by three screws, and the transmitted FEL beam was terminated by an absorber on the table.

Temporal temperature profiles by single shot irradiation of FEL at 5.83 and 7.22 μm are shown in Fig. 2a and b, respectively. Here, the absolute temperature rise cannot be compared directly. One can notice that at 7.22 μm the temperature rise and decay between 0 and 0.05 s are much faster than that at 5.83 μm. Considering the sensitivity of SC620 above 7 μm, it is likely that the sharp peak in the region of <0.05 s in Fig. 2b is the artifact by a reflection of FEL from the surface. This estimation is supported by the fact that the temperature rise time of the sharp peak in Fig. 2b is <8 ms, which is limited by the time resolution of the detector array. While, because 5.83 μm is out of the sensitivity, the absolute value on the vertical axis in Fig. 2a, ~15 K, representing the correct temperature rise, stays almost constant for 16 ms (three data points).

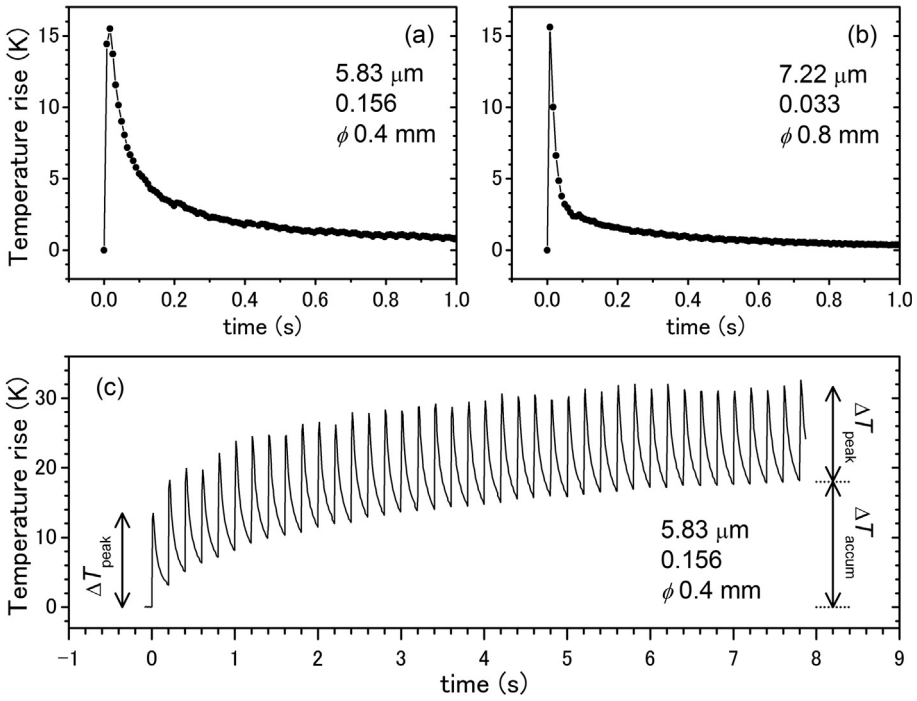

Fig. 2. Temporal temperature profiles of the acrylic-resin surface by irradiation of FEL. The values in each graph show the irradiation wavelength, the absorbance, and the focal size in diameter. (a) Single-shot condition: the irradiation wavelength is 5.83 μm which is out of the detection range of the thermometer SC620. (b) Single-shot condition: the irradiation wavelength is 7.22 μm. The sharp peak in the region of <0.05 s is the artifact by a reflection of FEL due to the sensitivity of the detector at this wavelength. (c) Multi-shot condition: ΔT_{peak} and ΔT_{accum} represent the peak temperature and the temperature accumulation, respectively.