Spatiotemporal Control of Crystal Growth of Organic Compounds by Femtosecond Laser Ablation II ~ Laser Energy Dependence~

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1. Introduction

Crystallization is crucial for various experimental processes such as purification, crystalline devices, and determination of molecular structures by X-ray/Neutron diffraction. The preparation of crystals with appropriate size and shape is one of the important factors for the success of the above-mentioned processes. In general, researchers try to make such crystals by optimizing the environmental parameters such as temperature, solvents, and additives. On the other hand, our group has recently succeeded in the control of protein crystal growth by directly modifying the local crystal structures via femtosecond laser ablation [1]. Here the key is to induce the spiral growth mode, which is energetically advantageous compared to the spontaneous 2D nucleation growth mode. In the previous account, we reported that this technique can also be applied to crystals of a low-weight organic compound, glycine [2]. In this work, we systematically investigated the dependence of laser energy on the organic crystal growth to explore the optimized condition for the preparation of crystals with desired size and shape.

2. Experimental procedure

Glycine powder (300 mg) was completely dissolved in 1 g of water at 55 °C by using a rotary shaker (240 rpm). Then the supersaturated solution (300 mg/g) was prepared in a custom-made glass/PDMS chamber at 20 °C. After crystals spontaneously appeared in the solution, a supersaturated solution (230 mg/g) was added into the chamber. Then the chamber was completely sealed and incubated for approximately 12 hours until the solution became almost saturated. After that, a single pulse from a regeneratively amplified Ti:Sapphire laser (λ = 800 nm, Δt = 120 fs) was shot to the (010) face of the crystal through an 20× objective lens (NA = 0.5). The dynamics of glycine crystal growth before and after the laser irradiation was monitored by laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM), which allows in-situ observation of crystal growth steps with the height of nanometers.

3. Results and Discussion

Fig. 1 shows LCM-DIM images of the (010) face of glycine crystals before and after the laser shot. The laser irradiation with the laser energy below the ablated threshold of the (010) glycine crystal face (~0.3 μJ/pulse) did not change the crystal growth behavior at all (Fig. 1a). On the other hand, crystal growth steps were newly generated from the ablated area with the laser energy above the ablated threshold (Fig.1b and 1c). Interestingly, the etching on the crystal surface was completely covered with a single spiral hillock at the ablation threshold energy (0.58 μJ/pulse), while multiple spiral hillocks were generated from cracks at higher laser energy (1.2 μJ/pulse). These results clearly indicate that the laser irradiation with the energy around the ablation threshold can enhance the single crystalline growth with the reduced damage. In the presentation, we will show the detailed dynamics of the crystal growth induced by femtosecond laser ablation and discuss the mechanism behind it.

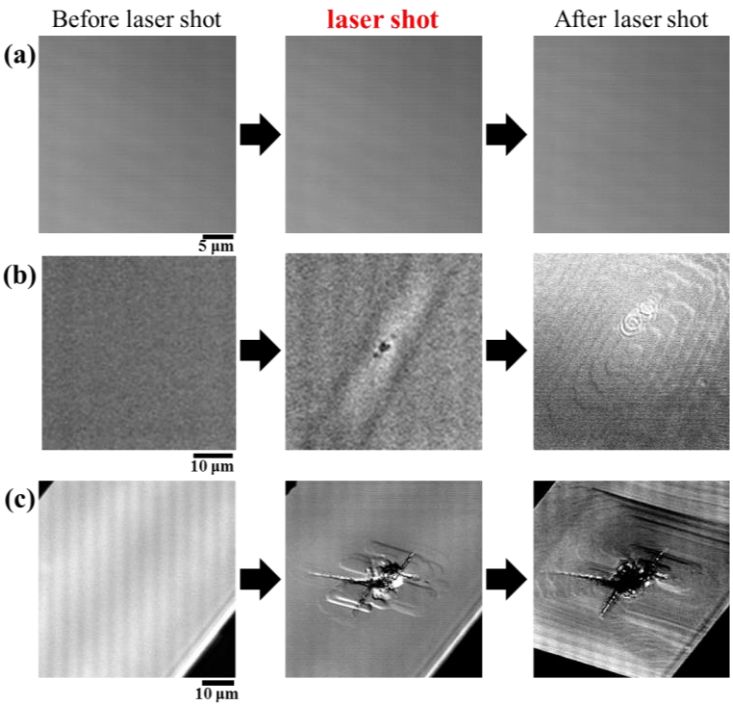

Fig.1 LCM-DIM images of (010) glycine crystal faces before and after the laser shot at (a) 0.23 μJ/pulse, (b) 0.58 μJ/pulse and (c) 1.2 μJ/pulse.

4. References

[1] T. Tominaga, M. Maruyama, H. Y. Yoshikawa et al., *Nature Photonics*, **10** (2016) 723.

[2] D. Suzuki et al., *the 64th Japan Society of Applied Physics Spring Meeting*, 14p-512-5 (2017).