Dynamics and mechanism of discrete etching of organic materials by femtosecond laser excitation

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ABSTRACT

Laser ablation and etching of microcrystalline Cu-phthalocyanine thin films were examined by changing pulse duration (170 fs, 250 ps, 100 ns) of a 780 nm Ti:Sapphire laser. Above fs (40 mJ/cm²) and ps (50 mJ/cm²) ablation thresholds, the etch depth becomes constant and is almost independent of laser fluence, and further increase in the fs fluence results in complete removal of the film. We name the unique ablation phenomenon discrete etching. On the other hand, the depth etched by ns laser excitation increases gradually with the fluence above its ablation threshold (80 mJ/cm²). In order to reveal the difference between the etching behaviors in fs laser ablation, we measured directly excitation energy relaxation and surface morphology change with time-resolved absorption spectroscopy and time-resolved surface scattering imaging, respectively. The fs discrete etching phenomenon and its mechanism were considered in view of time evolutions from highly intense fs laser excitation to the step-wise etching. On the basis of the results, we propose a fs laser ablation model that ultrafast stress increase brings about mechanical disruption leading to the discrete etching behavior.

Keywords; femtosecond laser ablation, discrete etching, time-resolved spectroscopy, time-resolved imaging, phthalocyanine film

1.INTRODUCTION

Femtosecond laser ablation and etching of organic materials have attracted much attention as interesting light-matter interactions and for their high potentials in applications to laser microprocessing. Organic molecular solids are expected to show morphological changes characteristic of ultrafast excitation as the molecules associate with each other by weak cohesion due to Van der Waals’ force. This will be quite different from laser-induced dynamics of polymer films where long chain molecules interpenetrate with each other. Recently, we have studied fs laser ablation of amorphous films of a substituted Cu-phthalocyanine (CuPc) and a substituted triphenylamine, and found a unique etching behavior that has never been reported as far as we know. Above the ablation threshold, a constant etch depth is observed in some fluence range, and the further increase in the fluence results in multistep etching. Nanosecond 351 nm excimer laser ablation of the same CuPc film shows the normal etching behavior, namely, the depth increases gradually with the fluence.

It is important and indispensable to confirm whether the discrete etching behavior is general or not and to reveal the dynamics and the underlying mechanism. The fs UV-visible absorption spectra of the amorphous CuPc film were measured at different excitation fluence and compared with each other. At early delay time, excited state absorption and ground state bleaching of CuPc molecules were detected and their spectral shape changes dramatically in 100 ps. At ns after excitation, the absorption spectra are similar to the temperature difference spectra of the ground state obtained by subtracting the high-temperature spectrum from that at room temperature. Thus the spectral change was interpreted in terms of efficient photothermal conversion due to mutual interactions between excited states. In the ns time domains, the film surface becomes rough, which evolves to fragmentation of the film and its etching.

In the present work, microcrystalline thin film of CuPc is systematically studied and considered. Effects of excitation pulse width on etching pattern and depth were examined in detail for the first time. Furthermore, how electronic excitation energy evolves to etching was directly followed by fs absorption spectroscopy and time-resolved surface light scattering imaging.

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on which we propose a new fs ablation model.

2. EXPERIMENTAL

2.1 MATERIAL

Microcrystalline CuPc film was deposited on a quartz or a glass substrate at 10^{-4} Torr at an ambient temperature. Deposition rate was 100 nm/min, and, by controlling deposition time, films with thickness of 100-to-300 nm were prepared. Each microcrystal has a size around about 50 nm and takes \( \alpha \)-form, whose molecular orientation with chemical structure is shown in Figure 1.

2.2 EXCITATION LASER PULSE AND ETCH PROFILE

Femtosecond laser pulses (780 nm, 120 fs, 76 MHz) from an Ar-ion-laser-pumped Ti:sapphire laser (Coherent, Mira Basic) were amplified by a Ti:sapphire chirped-pulse amplification system (Continuum, TR70-10). The typical output from the amplifier has 3mJ pulse energy and 170 fs fwhm after the pulse compression, and it was used as a fs excitation light. The ps laser pulse (fwhm 250 ps) is provided when the amplified pulse did not pass the compressor in the amplification system. The ns laser pulse (fwhm 100 ns) was obtained when the regenerative amplifier is not seeded by the oscillation. The temporal and spatial profiles of the excitation pulses are shown in Figure 2. The temporal profile of the fs pulse is given as an auto-correlation trace measured by second harmonic generation. The profile of the chirped ps and ns pulse were directly measured by a streak camera (Hamamatsu, C4334) and by a pin photodiode (Thorlabs, 201/579-7227), respectively. The spatial profiles were confirmed to have Gaussian distribution by a CCD camera (Sony, XC-7500). The femtosecond spot dimmer was typically 500 µm, estimated from etched diameter formed after multi-shot excitation at 5 times larger fluence than the ablation threshold. One pulse was picked up as an excitation light from the pulse train with the frequency of 10 Hz by a mechanical shutter and focused on the film surface through a lens \( f = 300 \) mm. The etched pattern was observed by an optical microscope (Olympus, BX 50) and the etch depth was measured by a stylus profiler (Sloan, Dektak \( \text{XT} \)).
2.3 TIME-RESOLVED SURFACE LIGHT SCATTERING IMAGING

The schematic diagram of the surface light scattering imaging is given in Figure 3, whose principle is the same as reported before \(^1, 14\). The fundamental beam of a regenerated amplified fs Ti:Sapphire laser (780 nm, 3-4 mJ/pulse, fwhm 170 fs) was divided into two; one was used as an excitation light and the other for generation of a fs white continuum extending from 400 to 1000 nm. The scattered light of the probe pulse was detected at an angle of 50±18°, and the image was recorded with a CCD camera. The observation wavelength was set to be 535±17 nm using an optical band path filter. The origin of the time axis was determined by measuring transient absorption spectra of amorphous CuPc films. The continuum light pulse probes transient scattering from film surface. The excitation and probe pulse are normally incident on the film. All the measurements were done for the original surface of the film by changing the sample position from shot to shot.

2.4 TIME-RESOLVED UV-VISIBLE ABSORPTION SPECTROSCOPY

The above continuum light pulse was also used to probe transient UV-visible absorption spectra \(^15, 16\). The white continuum was detected by a pair of polychromators
coupled with multichannel photodiode arrays (Otsuka electronics, MCPD HH4-0913). Each transient absorption spectrum was obtained by one shot excitation. For fs spectral measurement, the chirping (dispersion) of the white continuum should be considered for correct and reliable analysis. The temporal dispersion of the white continuum was estimated by measuring the time correlation profile between the white continuum and the excitation light, and transient absorption spectra were corrected by using this time dispersion profile.

3. ETCHING BEHAVIOR

Laser ablation of CuPc microcrystalline thin films were investigated by tuning the laser width of the Ti:sapphire laser (780 nm) to 150 fs, 250 ps, or 100 ns. The film with thickness of about 230 nm was optically clear, and the absorption coefficient at 780 nm is 7 μm⁻¹. Femtosecond laser excitation (780 nm, 170 fs) gives etching whose behavior is given in Figure 5 (a). The estimated ablation threshold was 40 mJ/cm², as an etching by one shot excitation was observed above this value. The etched area increased with the fluence, which is ascribed to the Gaussian-like excitation beam profile. Dark spots are assigned to some particles, which was confirmed by the depth profiler. In figure 6 (a), the depth of the central area is plotted against the fluence. It is worth noting that the depth becomes suddenly 150 nm above the threshold and further increases up to 250 mJ/cm². In the higher fluence range, the film with the thickness of 230 nm was completely removed. Picosecond laser excitation (780 nm, 250 ps) induces similar etching behavior whose etched patterns are summarized in Figure 5 (b). The ablation threshold was estimated to be 50 mJ/cm², and the etch depth is almost constant and width

Figure 5: Microphotographs of CuPc microcrystalline film surface exposed to (a) fs, (b) ps, and (c) ns laser pulses.

Figure 6: Plots of etch depth against fluence for (a) fs, (b) ps, and (c) ns laser pulses.
increases with the fluence. Above 80 mJ/cm², central part became deep but the surrounding area still remains constant value of 80 nm.

Nanosecond laser excitation (780 nm, 100 ns) gave microphotographs shown in Figure 5 (c). Ablation threshold was determined to be 80 ml/cm², and the etched area increased with the laser fluence. Each etched spot becomes gradually deep from its edge to the central part. Etch profile of the central part is gradual and no clear step was observed. A relation between the etch depth of the central part and laser fluence is plotted in Figure 6 (c). A smooth increase with the fluence was observed, which was also observed by 351 nm excimer laser excitation.

Thus, a novel etching phenomenon was confirmed typically in fs and ps ablation, which we name here “discrete etching”. On the other hand, the depth etched by ns laser ablation increases gradually with the laser fluence above the ablation threshold. The “gradual etching” behavior is well known in general and has been reported for laser ablation of various materials. How such a novel discrete etching is brought about in fs and ps ablation is studied in the following by interrogating dynamics from the electronic excitation to the morphological change.

4. SURFACE ROUGHNESS FORMATION

Nanometer surface morphological change are considered to be initial steps of laser ablation. Melting, expansion, gas bubbling, microparticles formation, and so on may result in surface roughening, and then ejection of μm-sized debris induces the shock wave propagation. The ejection and propagation were confirmed directly by time-resolved shadowgraphy. To observe surface dynamics of nm morphological changes, time-resolved interferometry was developed and applied for measuring 10 nm laser-induced displacement of flat surface. Another method that we have recently proposed is time-resolved surface light scattering imaging. Its advantage was demonstrated for liquid benzene and amorphous CuPc film, namely, as initial phenomenon before material ejection was observed.

As typical example, time-resolved surface scattering images at 62 and 223 mJ/cm² are shown in Figure 7. At the former fluence, which is 1.5 times larger than the ablation threshold (40 mJ/cm²), the surface scattering from the central part of excited area was observed. This is consistent with the Gaussian-like intensity distribution. The similar images were obtained at the fluence of 120 mJ/cm². As shown in Figure 8, scattering images from the central part increased in ns time range.

It is noticeable that no change in appreciable scattering intensity was observed in ps time range. The surface scattering increases in ns time range even for higher laser fluence, while the intensity at the center region of excitation area is lower than that of the surrounding region. Namely, a doughnut-like pattern was observed at the fluence higher than 140 mJ/cm², indicating that surface scattering intensity from the central part decreases with increasing fluence.

In general, there are two possible origins giving the scattering light. One is Rayleigh scattering due to generated vaporized CuPc molecules and/or CuPc nanoclusters, and the other is specular reflection from roughened surface. The latter surface scattering is considered to contribute enough strongly compared to the Rayleigh
scattering. It is expected that decomposition proceeds more efficiently and CuPc nano-clusters were generated more at higher fluence. Consequently, with the fluence, the scattering intensity increases at first, then shows saturation, and decreases. This can explain the doughnut structure in the surface light scattering images at 223 mJ/cm².

Thus, we consider that the light scattering intensity is correlated to surface roughness of the original material. Back scattering light intensity as a function of delay time \( t \), \( I(t) \), is assumed to be proportional to angle-integrated light scattering probability, \( \text{Rdiff} \), and the probe light intensity, \( I_0 \). It is well known that \( \text{Rdiff} \) and root mean-square surface roughness, \( R_{\text{rms}} \), are related to each other as in the following equation 19, 20.

\[
\text{Rdiff} I_0 = R_0 (4\pi R_{\text{rms}} / \lambda)^2 I_0.
\]

Here \( R_0 \) is the specular reflectance of a perfectly smooth surface of a sample and \( \lambda \) is wavelength of the probe light. Light scattering intensity of the probe white light continuum for some CuPc samples was measured without fs excitation, while their surface roughness were observed by the surface profiler. The former corresponds to the output signal of CCD camera, and the latter is obtained by averaging the surface profile \( f(x) \) from \( x = 0 \) to \( x = L \) in following way,

\[
R_{\text{rms}} = \left\{ \frac{1}{L} \int_0^L f(x)^2 dx \right\}^{1/2},
\]

where \( f(x) \) is the height at the position \( x \) and normalized as

\[
\int_0^L f(x) dx = 0.
\]

When \( R_{\text{rms}} \) is small compared to \( \lambda \) and when the correlation length in the lateral direction is larger than \( \lambda \), specular reflectance of a rough surface is proportional to the square of \( R_{\text{rms}} \).

The time profile of total scattering intensity of the probe pulse at the fluence of 62 and 124 mJ/cm² are shown in Figure 8. No appreciable intensity change was observed before 1 ns, while intensity rise was observed and it was steeper for 124 mJ/cm². Using the correction curve we prepared, the surface roughness was obtained from the scattering light intensity. This is very interesting and important observation for understanding the ablation phenomena. From 1 ns to 10 ns, the surface roughness increased up to a few tens nm at a few tens ns after excitation.

5. ELECTRONIC EXCITATION ENERGY RELAXATION AND HEATING

Femtosecond transient absorption spectroscopy has been applied to the microcrystalline CuPc film for elucidating photoprimary processes causing the surface roughning. Typical spectra below and above the ablation threshold are shown in Figures 9. A broad positive band around 520 nm can be assigned to the electronically excited state of CuPc 14, and negative peaks correspond to breaching of the ground state absorption. The temporal profiles at 520 nm, shown in Figure 10, gives a rapid decay curves depending on the excitation fluence. Since the sample film has a high absorption coefficient at the excitation wavelength (\( \alpha \approx 2 \times 10^4 \text{ cm}^{-1} \)), high excitation density is attained with the present condition. Excited state density can be estimated approximately to be \( 0.8 \times 10^{21} \text{ cm}^{-3} \) at the fluence of 10 mJ/cm². The value is almost half of the density of molecule in the CuPc microcrystal (~1.8 x 10^{21} molecules/cm³). Above a fluence of several mJ/cm², the majority of excited
molecules will have excited molecules as nearest neighbors. Therefore, the observed rapid decay is ascribed by exciton-exciton annihilation\(^1, 15, 21-23\).

After the decay at the excited state absorption, a new positive absorption peaking around 660 nm appears and the shape of bleach spectra changes. The new absorption doe not decay up to 5 ns. The temporal profile at 660 nm is shown in Figure 10 (b). At a high fluence, the rise corresponds well to the decay of the excited state. The absorption spectra at late delay times can be assigned to a photothermal phenomenon. Figure 11 shows the difference spectra obtained by subtracting the ground state spectra at high temperatures from that at 25 °C. This similarity means that thermal energy, corresponding with intra- and inter-molecular vibrational energy, increases with relaxation of the electronically excited states in the time region within 20 ps.

The femtosecond transient absorption measurements clearly demonstrate that laser excitation energy rapidly changes vibrational energy of lattice and molecular through exciton-exciton annihilation. Comparing the transient absorption at late delays to the temperature difference spectra, we can estimate a temperature jump with fs laser (see Figure. 12). At a fluence of 100 mJ/cm\(^2\), temperature jump is estimated to be 250 K. When all CuPc molecules in the crystal is excited by 780 nm laser pulse, a temperature jump is calculated to be 300 K, using molecular specific heat of 500 J K\(^{-1}\)mol\(^{-1}\)\(^\text{21}\) and is in a good agreement to that of transient spectral measurement. It is notable before that temperature jump is only 100 K at the fs ablation threshold, but the rate of temperature elevation is very fast due to the rapid photo-thermal conversion. The rate \(dT/dt\) is roughly to be \(10^{13}\) K/sec.

It is noticeable that the rapid decay of about 10 ps corresponds well to a rise at 660 nm. This means that the exciton-exciton annihilation results in heating, and the temperature is estimated by comparing transient absorption spectra with temperature difference one. Fluence dependence of this obtained temperature at 500 ps after excitation is shown Figure 12. Absolute elevation temperature is not so large but temperature elevation rate is estimated to be \(10^{13}\) K/sec, which is one of

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**Figure 9:** Transient absorption spectra at the fluence of 108 mJ/cm\(^2\) (solid line) and 9.2 mJ/cm\(^2\) (broken line).

**Figure 10:** Time evolution of transient absorption at 520 nm (a) and 660 nm (b). Femtosecond excitation intensity is 108 mJ/cm\(^2\) (●) and 9.2 mJ/cm\(^2\) (○).
characteristic of fs laser ablation.

6. DYNAMICS AND MECHANISM

Electronic excitation energy is converted to thermal energy in about 20 ps, while attained temperature seems not enough to eject CuPc molecules. Nanometer surface morphological change was not observed until ns after excitation by the scattering imaging. Namely, there is a time lag between the heating and the morphological change, which we consider the key to understand the discrete etching. During the lag time, a mechanical stress should be accumulated in the film. Then the deeper layer is similarly heated and ejected, successively. Thus no mechanical shock is left. On the other hands, in the ns laser ablation, injection of excitation energy, conversion to thermal energy, and morphological change takes place simultaneously in the same ns time region. Surface layer receives excitation energy, becomes hot, and undergo vigorous molecular motion and fragmentation. The key evolution process is schematically summarized in Figure 13. The present work demonstrated experimentally for the first time the importance of time evolution from fs electronic excitation energy to morphological change in laser ablation.

It is known that such a stress in fs excitation triggers mechanical disruption due to brittle fracture in the low-weight molecular solids. As the pressure due to the internal stress is in principle isotropic, the film ruptures into almost halves and the upper half is ejected and the lower half is remained on the substrate. The disruption is induced when the fluence exceeds the threshold, which is schematically in Figure 14 (A).

On the basis of direct spectroscopic and morphological measurements of the fs, ps, and ns laser ablation, we consider at the
present stage of investigation that novel etching phenomena of fs and ps ablation is due to time lag leading to the increase in stress.

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