Nonlinear ionization control by temporally shaped fs+ps double-pulse sequence on ZnO

We designed a femtosecond (fs) + picosecond (ps) double-pulse sequence by using a Mach–Zehnder-like apparatus to split a single 120 fs pulse into two sub-pulses, and one of them was stretched to a width of 2 ps by a four-pass grating system. Through observing the ripples induced on the ZnO surface, we found the ionization rate appeared to be higher for the sequence in which the fs pulse arrived first. The electron rate equation was used to calculate changes of electron density distribution for the sequences with different delay times. We suggest that using a temporally shaped fs+ps pulse sequence can achieve nonlinear ionization control and influence the induced ripples.

Keywords: ZnO; ultrafast double-pulse sequence; ripple; temporal shaping; nonlinear ionization.

DOI: 10.3788/COL202321.021602

1. Introduction

ZnO is one of the well-known near ultraviolet luminescence semiconductors owing to its wide band gap of 3.4 eV and large exciton binding energy of 60 mV, and its surface nanostructures have been reported to improve the photoelectron conversion efficiency[1,2]. Therefore, nanostructured ZnO is a promising material for high-power emitting devices and photodetector applications[3]. Among the methods of nanostructure preparation on ZnO, femtosecond (fs) laser irradiation has been regarded as an efficient technique for high-speed precision processing by virtue of flexible non-contact one-step direct writing capability[4,5].

In recent years, improving the fs laser processing efficiency has attracted more and more attention[6–8]. Previous studies usually focused on adjusting laser parameters such as pulse energy, pulse number, and pulse width. Nowadays, the use of the double-pulse sequence has become an emerging strategy to improve processing efficiency[9] and quality[10]; because it can precisely control the material ionization process by adjusting delay time, energy ratio, and polarization state[11]. For example, Barberoglou et al. reported the capability of double-fs pulses to switch the induced structures from low to high spatial frequency ripples on ZnO[12]. Our group has also used double-fs pulse sequence irradiation to study the mechanism of nanograting formation by adjusting two sub-pulses’ delay time [from sub-picoseconds (ps) to hundreds of ps] in SiO2[13,14]. In addition, there are some extended schemes for the double-pulse sequence. Höhm et al. compared the experimental results of 800 nm + 400 nm double-fs pulses on different materials and proposed a wavelength-dependent plasma generation mechanism[15]. Miyamoto et al. used a coaxial combination of fs laser and continuous-wave laser to explore more efficient ways to enhance the ionization process in glass. Because the characteristics of both types of lasers can be fully taken into account for material ionization, the processing speed was about 500 times higher than that of ordinal methods[16]. These studies have provided a range of evidence for double-pulse sequence irradiation improving the processing efficiency. However, for the ordinal double-fs pulse sequence, the pulse width is so short that the interaction between two sub-pulses is only indirect through the induced excitons or defects in the materials. As far as for the sequence of two short–long sub-pulses [e.g., fs + microseconds (μs)], their widths differ greatly, so the long pulse far exceeds the lifetime of the electrons excited by the short pulse, leading to the inefficiency of energy deposition. In addition, the long pulse easily causes thermal effects and melts the nanostructures[17]. Based on an idea of taking advantage of direct interaction between two sub-pulses for nonlinear ionization control, we propose using the fs+ps double-pulse sequence (FPDPS) to improve the processing efficiency.

In this Letter, we generated a 120 fs + 2 ps double-pulse sequence by a Mach–Zehnder-like apparatus, which included a four-path grating system. The induced ZnO surface ripples showed obvious structural difference through changing the delay times between the two sub-pulses. This is because the electron density excited by different FPDPSs made a strong effect on formation of surface structure. The experimental result agrees
with the assumption based on the calculation by using the electron rate equation. This research contributes to a deep understanding of the role of the temporal shaping double-pulse sequence in laser material processing.

2. Experiment

A commercial chirped pulse Ti:sapphire regenerative laser amplifier system (Spitfire Pro, Spectra-Physics Co.) was employed to obtain a linearly polarized fs pulse train with a wavelength of 780 nm, a pulse width of 120 fs, and a repetition rate of 1 kHz. The output laser was split into two arms by a Mach–Zehnder-like apparatus, as shown in Fig. 1(a). A grating (600 lines/mm) was inserted in the ps arm to build a four-pass system to separate the spectra of this sub-pulse for temporal broadening. In the four-pass design, the optical path is always incident to the grating by precisely adjusting two retroreflectors mounted on guide rails, and the spatial intensity distribution of the temporally stretched ps pulse basically remained a Gaussian profile, as shown in Fig. 1(c). The intensity distributions were measured by a laser beam profile (SP503U, Ophir-Spiricon). The major axes of the spot in Figs. 1(b) and 1(c) are 3.9 mm and 4.2 mm, respectively. The two spots will be limited to the same size by a shutter with an aperture of 3 mm. In this apparatus, the double-pulse sequence was set to 120 fs + 2 ps, which was measured by an autocorrelator (Pulse Scout, Spectra-Physics). The delay time \( \tau \) between these two sub-pulses was motor controlled from \(-80\) to \(80\) ps by a delay line (in the fs arm) with a resolution of 16.7 fs. Figure 1(d) shows three delay times of this FPDPSs. Specifically, the fs pulse arriving prior to the ps pulse is defined as a negative delay. Neutral density filters and a half-wave plate were set to adjust the pulse energy and polarization in two arms, respectively. The generated FPDPSs with the same polarization were focused onto the surface of ZnO through a 5x objective (NA = 0.15, Nikon ECLIPSE 80i). The sample was placed on a computer-controlled XYZ stage. The laser-irradiated surface regions were inspected by scanning electron microscopy (SEM) (Hitachi, SU5000).

3. Result and Discussion

A constant number \((N = 25)\) of FPDPSs were used to irradiate the ZnO surface with each sub-pulse energy of 0.72 \(\mu\)J (the spot diameter is about 14 \(\mu\)m, corresponding to the fluence of 0.45 J/cm\(^2\)), and then we found the laser-induced periodic surface structure (LIPSS, ripples) appeared accordingly. Generally, these ripples can be divided into two types: near-wavelength LIPSS with low-spatial-frequency (LSFL) and sub-wavelength LIPSS with high-spatial frequency (HSFL). In our experiment, both of these ripples have been observed. In Fig. 2, we plot the trend of the ripple area over the delay time. With an increase of the delay time, the ripple area gradually decreases until no structure appears in the irradiated region. A series of SEM pictures of nanostructures corresponding to different delay times are shown as the insets in Fig. 2.

In the irradiation with a negative delay of \(\tau = -0.32\) ps, both types of ripples can be observed, and they covered an area of about 127 \(\mu\)m\(^2\). The LSFL with a period of 620 – 650 nm formed in the area center, and the HSFL with a period of 220 – 250 nm appeared at the outer region. The orientations of both LSFL and HSFL were perpendicular to the laser polarization. On the other side with a positive delay of \(\tau = +0.32\) ps, the ripple area was only about 53 \(\mu\)m\(^2\), much smaller than the negative delay case. Next, we continued increasing the delay time to \(\tau = \pm 1\) ps. The area difference between these two cases was more obvious. When \(\tau = -1\) ps, the induced ripple area increased fourfold over the one for \(\tau = +1\) ps. In addition, both HSFL and LSFL could be observed at \(\tau = -1\) ps, while the positive delay irradiation only

![Fig. 1](image1.png)  
**Fig. 1.** (a) Schematic diagram of experimental setup based on a Mach-Zehnder-like apparatus. M, mirror; BS, beam splitter; HRF, horizontal retroreflector; VRF, vertical retroreflector. (b) Spatial light intensity distributions of fs pulse. (c) Spatial light intensity distributions of temporally shaped ps pulse. The scale bar is 3 mm. (d) Schematic diagram of temporal delays between two sub-pulses.

![Fig. 2](image2.png)  
**Fig. 2.** Induced ripple areas over the delay times. The markers in two curves correspond to different color blocks for the SEM insets.
produced HSFL. Previous studies claimed that the transition between HSFL and LSFL strongly depends on pulse fluence\cite{12,20}. For example, Barberoglou et al.\cite{12} found that the LSFL could not form on ZnO when the fluence was below 0.55 J/cm², however, the HSFL could be observed. That indicates that the generation of LSFL needs a higher fluence compared to the HSFL. As the delay time continued increasing, the ripple area gradually contracted until it cannot be observed anymore at $\tau = +1.33$ ps. However, on the other side of negative delay time, the ripples still could form even at $\tau = -80$ ps (not displayed in Fig. 2). Therefore, either the ripple area or the induced structure type reflects that a relative high processing efficiency can be achieved when using a negative delay FPDPS. Moreover, we also clearly realized that the formation of the nanostructure was closely related to the excited electron density\cite{13,14}. These phenomena possibly imply that the arrival order of sub-pulses in single FPDPS could make a significant effect on the electron density control.

We used the electron rate equation to calculate the maximum density ($\rho$) induced by an FPDPS\cite{21,22}:

$$\frac{\partial \rho}{\partial t} = \frac{1}{n_0^2 E_g} \sigma |E|^2 + \frac{\beta E |E|^2 K}{\hbar \omega} - \gamma \rho^3 - \rho / \tau_R \quad (1)$$

where avalanche ionization, multiphoton absorption, Auger recombination, and electron lifetime are involved, respectively. In addition, inverse bremsstrahlung cross-section $\sigma$ and laser light intensity $E$ are expressed as

$$\sigma = \frac{e^2 \tau_e}{c n_0 e_0 m_{\text{eff}} (\omega^2 \tau_e^2 + 1)} \quad (2)$$

$$E = \sqrt{\frac{F}{\tau_1 \sqrt{\pi} / 2} \cdot e^{\frac{t^2}{\tau_1^2}} + \sqrt{\frac{F}{\tau_2 \sqrt{\pi} / 2} \cdot e^{\frac{t^2}{\tau_2^2}}}} \quad (3)$$

In Eq. (1), $K$ is the number of instantaneous absorbed photons required for the band transition, and three-photon absorption is considered here. Other parameters are described in Table 1.

Figure 3(a) summarizes the maximum electron density over radial position $r$ and delay time $\tau$. On the side of negative delay, a large area of high concentration electrons can be excited. As an example, Fig. 3(b) shows two curves of electron density distributions corresponding to the two cases of $\tau = \pm 1$ ps. In the case of $\tau = +1$ ps, following the incident Gaussian intensity distribution, the electron density decreases quickly along the radial position. But, different from the front, the case of negative delay shows a higher flat top, indicating higher energy absorption efficiency. The difference between these two electron density distributions might result from different avalanche ionization rates, because the first arrival pulse could affect the generation number of seed electrons. As for the reason for different structural types, it is generally accepted that LSFL arises from the interference of incident radiation with a surface electromagnetic wave, which might include the excitation of surface plasmon polaritons (SPPs)\cite{28}. To induce the LSFL according to the SPP-based model, two conditions need to be satisfied\cite{15}: the electron density is high enough to instantly turn the transparent ZnO surface into a metallic state, and the incident light interferes with...

### Table 1. Parameters for ZnO in Electron Density Rate Equation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_0$</td>
<td>Original material index</td>
<td>2</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Band gap</td>
<td>3.46 eV</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Multiphoton absorption coefficient</td>
<td>0.016 cm³/GW\cite{23}</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Light frequency for 780 nm c/780 nm</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Auger recombination coefficient</td>
<td>0.96 x 10⁻³⁹ cm⁶/s\cite{24}</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>Electron hole recombination time</td>
<td>2.8 ns\cite{25}</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of light</td>
<td>299,792,458 m/s</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of vacuum</td>
<td>8.85 x 10⁻¹² F/m\cite{26}</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>Electron collision time</td>
<td>46 fs\cite{27}</td>
</tr>
<tr>
<td>$m_{\text{eff}}$</td>
<td>Effective electron mass</td>
<td>0.28m₀\cite{26}</td>
</tr>
<tr>
<td>$F$</td>
<td>Incident fluence</td>
<td>0.451/cm²</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>Spot radius</td>
<td>5.5 μm</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>Parameters related to ps pulse</td>
<td>$\tau_{ps}/\sqrt{2 \ln 2}$</td>
</tr>
<tr>
<td>$\tau_{fs}$, $\tau_{ps}$</td>
<td>Parameters related to fs pulse</td>
<td>$\tau_{fs}/\sqrt{2 \ln 2}$</td>
</tr>
<tr>
<td>$\tau_{fs}$, $\tau_{ps}$</td>
<td>Pulse width</td>
<td>120 fs, 2 ps</td>
</tr>
<tr>
<td>$r$</td>
<td>Radial position</td>
<td>–10 to 10 μm</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Maximum electron density at different radial positions and delay times. (b) The electron density distributions corresponding to $\tau = \pm 1$ ps, respectively. (c) The center area electron density over delay times. (d) Dependence of LSFL area on delay time. The insert shows an SEM picture of the LSFL covered area. The scale bar is 5 μm.
the electromagnetic field of SPP. Dufft et al. reported that the ZnO surface would turn into a metallic state if the generated electron density exceeds $\sim 5 \times 10^{21} \text{cm}^{-3}$\cite{29}. In our case, the negative delay FPDPS may produce $\rho \gg 5 \times 10^{21} \text{cm}^{-3}$, which is conducive to the excitation of SPP and the formation of LSFL. The formation mechanism of HSFL is controversially discussed. One point of view is that the interference between the generated second harmonic and the surface electromagnetic wave gives rise to HSFL \cite{29,30}. As a result, the areas of HSFL can be larger than those covered by LSFL.

Figure 3(c) shows the maximum electron density at the area center ($r = 0$) with various delay times. The decreasing trend of electron density over delay time is basically consistent with the decreasing trend of the induced LSFL area in Fig. 3(d), although some HSFLs formed around the center. It is known that the total ripple area consisting of HSFL and LSFL depended closely on the electron density distribution\cite{31}. Both theoretical and experimental results clearly prove that the FPDPS can affect the excited electron density distribution, and the first arriving fs pulse may cause a higher ionization rate.

As for the mechanism of the controlling ionization rate on the ZnO surface by temporally shaped FPDPSs, we proposed the following physical scenario: when an ultrashort pulse is focused on the ZnO surface, in the irradiated area, the valence band electron instantaneously absorbs three photons to transit to the conduction band. When the sub-pulse energy is constant, the multiphoton absorption is more intensive in the case of fs pulses first arriving due to the relatively higher peak power, resulting in more free electrons being excited in a larger area, as shown in Fig. 4(a). Very shortly, some of the excited electrons may behave as seeds to efficiently absorb the ps pulse energy via the inverse bremsstrahgen effect. This electron acceleration process will lead to seed avalanche ionization and further increase the electron density\cite{32}. After a number of FPDPSs accumulation, a ripple area consisting of LSFL and HSFL forms. However, it is important to point out that an increasing delay time will greatly weaken the seed avalanche ionization between two sub-pulses in an FPDPS. Therefore, the ripple area decreased with the delay time increasing, as shown in Fig. 2. Figure 4(b) shows a diagram with the ps pulse arriving first. As the original fs pulse was temporally stretched to lower its peak power, the excited electron density possibly becomes too small to support the growth of LSFL or HSFL in the whole irradiated area. The above assumption presents a dynamic nonlinear ionization control in material processing.

4. Conclusion

In this study, we used a home-built Mach–Zehnder-like apparatus, which included a temporally shaped system to obtain a 120 fs + 2 ps double-pulse sequence. These sequences with two sub-pulses energy ratio of 1:1 were irradiated on the ZnO surface to induce ripples. We found that the arrival order of sub-pulses in single FPDPS could make a difference on the formation of LSFL or HSFL. This selection possibly associates with the excited electron density. With the calculation using an electron rate equation, the FPDPS in which the fs pulse first arrives could excite the higher electron density because strong seed avalanche ionization is easier to trigger shortly in irradiation of the second ps pulse. That nonlinear ionization process elongates the photon–electron interaction time and promotes the energy absorption efficiency. We suggest that this temporally shaped FPDPS provides a new method to enhance pulse energy deposition in material processing.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (Nos. 12274280, 11774220 and 11974147).

References


