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Theoretical analysis of ultra-short pulsed laser ablation of SiO_2 material based on a Coulomb explosion model

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Abstract: Based on the kinetic theoretical Vlasov-Poisson equation, a surface Coulomb explosion model of SiO_2 material induced by ultra-short pulsed laser radiation is established. The non-equilibrium free electron distribution resulting from the two mechanisms of multi-photon ionization and avalanche ionization is computed. A quantitative analysis is given to describe the Coulomb explosion induced by the self-consistent electric field, and the impact of the parameters of laser pulses on the surface ablation is also discussed. The results show that the electron relaxation time is not constant, but it is related to the microscopic state of the electrons, so the relaxation time approximation is not available on the femtosecond time scale. The ablation depths computed by the theoretical model are in good agreement with the experimental results in the range of pulse durations from 0 to 1 ps.

Key words: ultra-short pulsed laser; Coulomb explosion; non-equilibrium distribution; material ablation

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The laser processing is based on the rapid thermal process induced by the laser radiation of material. The focusing power density is about 102 W/mm^2 when the laser pulse duration is about 10 ns. The laser pulse can produce very high temperatures, which can make the material melt, and when the laser pulse duration is very short (on a picosecond or a femtosecond time scale), metal gasification phenomena may occur. In the past few decades, femtosecond laser processing has attracted wide attention, and it has been widely used in micro-nanoelectromechanical device machining processing, so the mechanism of femtosecond laser ablation has become an international research focus.

The mechanism of femtosecond laser ablation is a physical mechanism which contains a variety of complex physical processes. And there are some explanations for the physical mechanism, such as surface stress induced by laser, phase explosion, Coulomb explosion, the critical electron number density and surface stripping[1-17]. The experiments [9-11] and the silicon surface ablation simulation by molecular dynamics[7-8] have proved that, when using nanometer level wavelength and femtosecond level pulse duration laser to irradiate semiconductor materials, the Coulomb explosion occurs on the material surface.

Bulgakova et al. [3, 6, 18-20] separately proposed the Cluster model and the drift-diffusion model to quantitatively describe the Coulomb explosion ablation mechanism of femtosecond laser radiation of materials. These two theoretical models separately use macro-hydrodynamic continuity equations, motion equations and two-temperature equations to describe the dynamic state of electronics. In these two models, the electron microstate is assumed to be the equilibrium, but the assumption is reasonable only on the condition that the laser pulse duration, such as nanosecond laser pulse, is much longer than the electronic relaxation time. However, the pulse duration of the femtosecond timescale pulsed laser is on the femtosecond timescale and is on the same order with the relaxation time $\tau_{e\text{-}e}$ or even smaller. And the experiments[21-22] show that electrons are in a non-equilibrium state on the femtosecond and picosecond scale, and the electron temperature concept is meaningless[23]. So two-temperature equations will not be applied [24].

In order to describe the dynamic process of electrons on the femtosecond time scale, we use the Vlasov equation with two source terms of multi-photon absorption and avalanche ionization mechanisms to describe the evolution of the electronic non-equilibrium process. The self-consistent electric field distribution is described by the Poisson equation, and the SiO_2 surface Coulomb explosion ablation model during femtosecond laser radiation is described by the Vlasov-Poisson equations. The SiO_2 surface ablation mechanism induced by the Coulomb explosion is analyzed on the microscopic level during femtosecond pulsed laser processing, and the impact of femtosecond laser parameters on the SiO_2 surface ablation is discussed.

1 Theoretical Model of Coulomb Explosion Under Ultra-Short Pulsed Laser Ablation

Atoms under ultra-short pulsed laser radiation will produce free electrons and form plasma due to two main mechanisms of multi-photon ionization and avalanche ionization. The two mechanisms will strip electrons which are under the bound state from atoms, and not only one electron will be ionized from an atom, accordingly, high charged maternal ions are formed. But the maternal ions are unstable because of the internal Coulomb repulsive force. The maternal ions composed by atomic ions will decompose quickly due to the Coulomb repulsive force, and this process is called the Coulomb explosion. The Coulomb explosion is an energy transfer process. After femtosecond laser radiation of the material, free electrons are ionized from the atoms. Because the pulse duration of the femtosecond laser is extremely short, free electrons are in a non-equilibrium state. Assuming that the velocity of free electron is isotropic, for nano-thin film devices, it is considered that the distribution function changes only along the film thickness direction, so the distribution function is only a function of z, v, t, and the Vlasov equation is

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$$\frac{\partial f(t,z,v)}{\partial t}+v\frac{\partial f(t,z,v)}{\partial z}+\frac{qv^2E}{m_e}\frac{\partial}{\partial v}\left(\frac{f(t,z,v)}{v^2}\right)=v^2\frac{C}{n_0}S \quad (1)$$

where m_e is the electron mass; q is the electronic charge; E is the electric field intensity; t, z, v represent time, location, and speed, respectively; C is the speed of light; and S is the source term.

In order to simplify the Gaussian pulse expression, $t=-\infty$ is used as the initial time. So the initial condition is

$$f(-\infty,z,v)=0 \quad (2)$$

The physical meaning of Eq. (2) is that the number density of free electrons is zero in the conduction band before the laser radiation.

The velocity boundary conditions are

$$f(t,z,-C)=0 \quad (3)$$
$$f(t,z,C)=0 \quad (4)$$

The negative sign indicates that the speed is inverted.

The spatial boundary condition is

$$f(t,L,v)=0 \quad (5)$$

The physical meaning of Eq. (5) is that in the film whose thickness is L, the free electrons will escape when they reach the top surface of the film.

$$f(t,0,v)=\alpha f(t,0,-v)+(1-\alpha)\left(\frac{m_e}{2\pi K_B T}\right)^{3/2}C\cdot \exp\left(\frac{m_e v^2}{2\pi K_B T}\right)v^2 \quad (6)$$

Eq. (6) is the Maxwell boundary condition, which means that the free electrons that reach the bottom surface of the film will be partly reflected back to the film with the same speed, while the other part will reach a thermal equilibrium with the surface and transiently return to the film with the Maxwell distribution. $S=R_{pi}+R_{imp}$, where R_{pi} and R_{imp} represent multi-photon ionization and avalanche ionization items, respectively.

For the multi-photon ionization item, the Keldysh formula[25] is adopted,

$$R_{pi}=\frac{2\omega}{9\pi}\left(\frac{m_e\omega}{\sqrt{\gamma_1}\hbar}\right)^{3/2}Q(\gamma,x)\cdot \exp\left\{-\pi\langle x+1\rangle\frac{\kappa(\gamma_1)-E(\gamma_1)}{E(\gamma_2)}\right\}\frac{F(v)}{v^2C} \quad (7)$$

where ω is the laser frequency; γ is the Keldysh parameter in solids, $\gamma=\omega\sqrt{mU_p}/(eE)$; $\gamma_1=\gamma^2/(1+\gamma^2)$; $\gamma_2=1-\gamma_1$; and $\hbar$ is the reduced Planck constant.

$$Q(\gamma,x)=\sqrt{\frac{\pi}{2\kappa(\gamma_2)}}\sum_{n=0}^{\infty}\exp\left\{-n\pi\frac{\kappa(\gamma_2)-E(\gamma_2)}{E(\gamma_1)}\right\}\cdot \Phi\left\{\frac{\pi}{2}\sqrt{\frac{[2(x+1)(2+n)]}{\kappa(\gamma_2)E(\gamma_2)}}\right\}$$

where Φ is the Dawson integral; $x=\frac{\pi}{2}\frac{U_p}{\hbar\omega}\frac{\sqrt{1+\gamma^2}}{\gamma}E\left(\frac{1}{1+\gamma^2}\right)$; $\Phi(z)=\int_0^z\exp(y^2-z^2)\,dy$; κ and E are the first and the second complete elliptic integral; $F(v)$ is an arbitrary normalized function, and arbitrary $\int_0^v F(v)\,dv=1$.

The avalanche ionization item is expressed by[14]

$$R_{imp}=\alpha I(t)n(t,z,v)=\alpha I(t)\frac{f(t,z,v)n_0}{v^2C} \quad (8)$$

where α is the avalanche ionization coefficient, $\alpha=9.7\times10^{-4}$ m^2/J[26].

In this paper, the laser pulse intensity $I(t)$ is the Gaussian distribution, $I(t)=I_{max}(1-R)\exp[-4\ln2\times(t/t_p)^2]$, where R is the reflectivity, and I_{max} is the laser peak intensity.

With the increase in free electrons, the surface of the material forms an electric field, and as the free electrons continue to absorb the laser energy, the kinetic energy of the free electrons will increase gradually. When the energy of the free electrons is large enough, these free electrons will free themselves from the constraints of the lattice and escape, while the surface of the material will generate a positive charged plasma area. Then this area will form a self-consistent electric field[27], and this electric field can be described by the Poisson equation (9). Because of the impact of the electric field, ions in the plasma area will be affected by their own Coulomb repulsive forces. With the laser continuing irradiating, the electric field intensity grows larger and larger. When it exceeds the critical threshold of the lattice interaction potential, the repulsive force is greater than the lattice binding force and the ions become free particles and escape from the lattice, and the Coulomb explosion occurs.

$$\frac{\partial E}{\partial z}=\frac{q\rho}{\varepsilon\varepsilon_0} \quad (9)$$

where ρ is the number density of free electrons; ε and ε_0 represent the dielectric constants in vacuum and material, respectively.

$$\rho=n_0\int_0^{\infty}f(t,z,v)\,dv \quad (10)$$

2 Results and Analysis

SiO_2 material is simulated by the above coupled model. The parameters used in calculation are listed in Tab. 1.

Tab. 1 Physical constants in calculation

Parameter	Value
Free electron number density of SiO_2[28] n_0/m^{-3}	8.22×10^{28}
Band gap energy of SiO_2[29] U_L/eV	9
Electron mass[28] m_e/kg	9.11×10^{-31}
Electron charge[28] e/C	1.60×10^{-19}
Vacuum permittivity[28] ε_0/(C^2·(N·m)$^{-2}$)	8.9×10^{-12}
Relative permittivity of SiO_2[28] ε	1.56
Latent heat of SiO_2[30] Λ_{at}/(kJ·mol^{-1})	2.65
Reduced Planck constant[28] $\hbar$/(J·s)	1.055×10^{-34}
Reflectivity[28] R	0.945
Avalanche ionization coefficient[14] α/(m^2·J^{-1})	9.7×10^{-4}
Boltzmann coefficient[28] K_B/(J·K^{-1})	1.38×10^{-23}
Speed of light[28] C/(m·s^{-1})	3×10^8

Fig. 1 is the nondimensional free electron distribution variation process of SiO_2 with nondimensional velocity. The wavelength of the laser is $\lambda = 800$ nm, the pulse duration $t_p = 800$ fs, frequency $\omega = 4.45 \times 10^{14}$ Hz, and the peak intensity $I_{max} = 8.5 \times 10^{13}$ W/cm^2. It is shown in Fig. 1 that the free electron distribution deviates from the Maxwell distribution under femtosecond laser radiation. The free electron distribution under the non-equilibrium state suggests that femtosecond laser radiation is a non-equilibrium thermal process, and it is meaningless to define the electron temperature on the femtosecond time scale. The distribution tends to be an equilibrium state as time goes by. It can be seen from Fig. 1 that, at the beginning of the radiation, the number of high energy free electrons is small and it increases with time. However, during the later period, the number of high energy free electrons decreases and the number of low energy free electrons increases. The reason of such a phenomenon is that at the beginning of the radiation, the valence band electrons absorb photon energy and jump in the conduction band, and then become free electrons and keep absorbing photon energy because of multi-photon ionization. So the number of high energy free electrons becomes greater. However, because of the collision relaxation process of the electrons, the high energy free electrons stimulate numbers of valence band electrons in the conduction band, and then become low energy free electrons themselves. As a result, the number of high energy free electrons becomes smaller with time and the number of low energy free electrons becomes greater in the conduction band. This suggests that the multi-photon ionization absorption plays a leading role at the beginning, and the avalanche ionization plays a leading role during the later period.

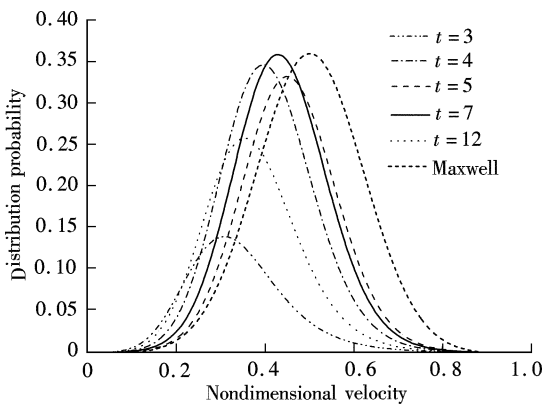

Fig. 1 Nondimensional free electron distribution variation process of SiO_2 with nondimensional velocity

Fig. 2 shows the variations of self-consistent electric fields of SiO_2 with the location condition under the radiation of laser pulses with a peak intensity of $I_{max} = 8.5 \times 10^{13}$ W/cm^2 and a pulse width of 800 fs. The latent heat of sublimation and the critical value of the electric field for the Coulomb explosion can be calculated by $E_{th} = \sqrt{\frac{2\Lambda_{at}}{\varepsilon\varepsilon_0 V_{at}}} = \sqrt{\frac{2\Lambda_{at} n_0}{\varepsilon\varepsilon_0}}$. It can be found that materials will be ablated under the laser radiation.

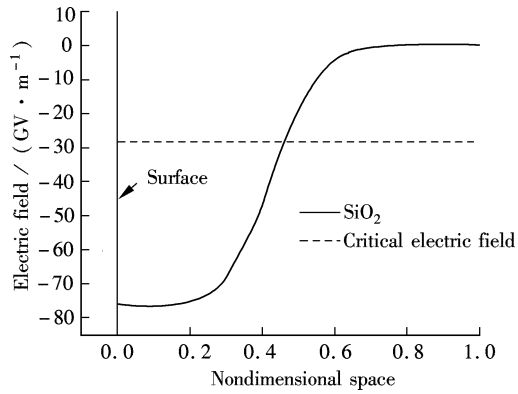

Fig. 2 Variation of self-consistent electric fields of SiO_2 with location

It can be seen from Fig. 3 that the self-consistent electric field is obviously affected by the laser peak intensity under the same wavelength, frequency and pulse duration, where wavelength $\lambda = 800$ nm, pulse duration $t_p = 800$ fs, frequency $\omega = 4.45 \times 10^{14}$ Hz. As the intensity increases, the number of free electrons becomes greater, and as a result, the maximum value of the self-consistent electric field becomes greater.

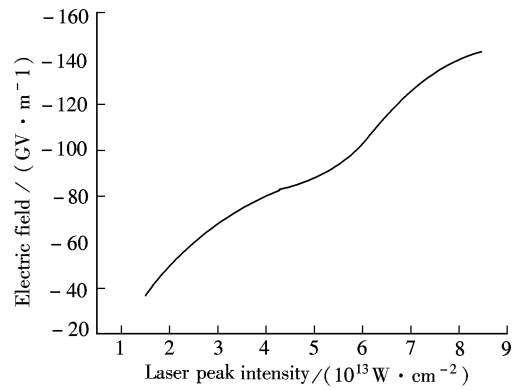

Fig. 3 The maximum value of electric field induced by laser with laser peak intensity at the same wavelength, frequency and pulse duration

The laser parameters are as follows: peak intensity $I_{max} = 8.5 \times 10^{13}$ W/cm^2, pulse duration $t_p = 800$ fs, and wavelength $\lambda = 800$ nm. Results show that the free electron number density in the conduction band reaches a stable value (see Fig. 4).

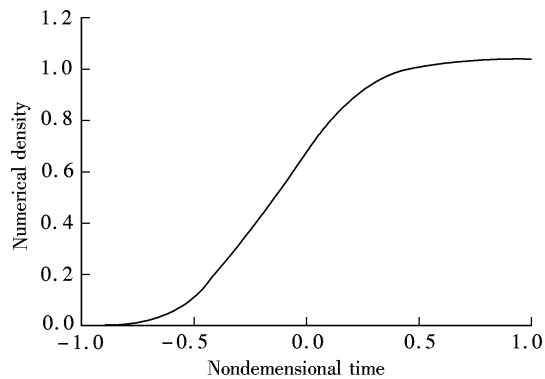

Fig. 4 Nondimensional free electron number density with time

Fig. 5 is the curve of free electron relaxation times with conditions of non-dimensional free electron energy density, where $I_{max} = 8.5 \times 1.0^{13}$ W/cm^2, $\lambda = 800$ nm, $t_p = 800$ fs. It can be seen that the relaxation time is not constant, and it drops off with the increase in the average electron energy density. The electron relaxation time decreases with the increase in the free electron energy density in the low energy density area ($0 \leqslant$ nondimensional electron energy density $\leqslant 0.4$), and then it becomes an approximate constant in the high energy density area ($0.4 \leqslant$ nondimensional electron energy density).

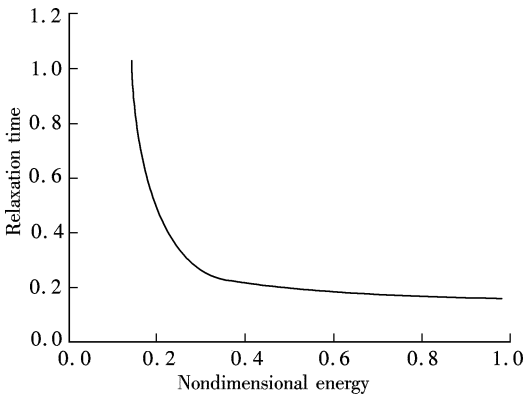

Fig. 5 Relaxation time with nondimensional free electron energy density

The ablation depth with the condition of the laser fluence is depicted in Fig. 6, where $t_p = 70$ fs, $\lambda = 700$ nm. It can be seen that when the laser fluence is less than 3 J/cm^2, the error is relatively big between the theoretical results computed via the coupled model and the experimental results of Ref. [31]. But with the increase in the laser fluence, the error decreases gradually, and the theoretical results are in good agreement with the experimental results. When the laser fluence is greater than 7.8 J/cm^2, the ablation depth approaches a constant, which is in good agreement with the results of Ref. [32]. That is because the free electron number density reaches the saturated state when the laser fluence reaches a certain value, and the energy transfer will decrease between the photons and the electrons.

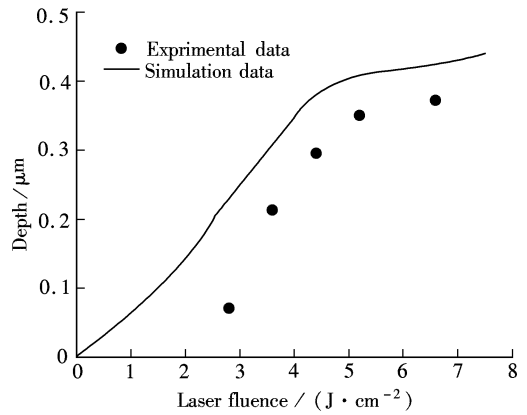

Fig. 6 Ablation depth vs. laser fluence

3 Conclusion

In this paper, a surface Coulomb explosion model of SiO_2 material induced by ultra-short pulsed laser radiation based on the kinetic theoretical Vlasov-Poisson equation is established, and multi-photon absorption and avalanche ionization mechanisms are two source terms. Compared with the macro model in Refs. [3, 6], the model established in this paper abandons the concepts of electron temperature and relaxation time approximation on the femtosecond time scale. The free electron relaxation time is not a constant but it relates to the microscopic state of electrons. The self-consistent electric field intensity induced by free electrons increases with the increase in laser fluence. The ablation depths computed by this theoretical model are in good agreement with the experimental results in the range of pulse durations from 0 to 1 ps.

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超短脉冲激光烧蚀 SiO_2 材料的库仑爆炸模型理论分析

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摘要:基于动理论 Vlasov-Poisson 方程,建立了超短脉冲激光引起的 SiO_2 材料表面库仑爆炸烧蚀机理的理论模型,计算了在多光子吸收与雪崩 2 种电离机制下材料中自由电子的非平衡态分布,并在此基础上定量分析了自洽电场导致的材料表面库仑爆炸的机理及激光参数对材料表面烧蚀的影响. 结果表明,在飞秒激光作用下自由电子弛豫时间不是常数,而是与自由电子微观状态有关,表明弛豫时间近似模型在飞秒时间尺度下是不适用的. 理论模型的烧蚀深度数值计算结果在 0 ~ 1 ps 脉宽范围均与实验吻合得较好.

关键词:超短脉冲激光;库仑爆炸;非平衡态分布;材料烧蚀
中图分类号:O434; TH161