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Microscopic energy transport through photon-electron-phonon interactions during ultrashort laser ablation of wide bandgap materials Part Ⅱ: phase change

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Abstract Energy transport in femtosecond laser ablation can be divided into two stages: 1) laser energy absorption by electrons during the pulse irradiation, and 2) phase change stage that absorbed energy redistributes in bulk materials leading to material removals. We review challenges in understanding the phase change process mainly for the femtosecond ablation of wide bandgap materials at the intensities on the order of $10^{13} \sim 10^{14}$ W/cm^2. Thermal vaporization and Coulomb explosion are two major mechanisms considered for material removals. Based on the discussions of energy transport, the estimation equations and unsolved problems for threshold fluence and ablation depth are presented.

Key words thermal vaporization; coulomb explosion; threshold fluence; ablation depth
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1 Introduction

During the process of femtosecond laser ablation of wide bandgap materials, the material removals mostly occur after the pulse duration. We focus on the arguments on mechanisms of material removals. The mechanisms of material removals are reviewed, especially for thermal vaporization and Coulomb explosion. Subsequently, based on the discussions of energy transport, we summarize the estimation methods and some unsolved problems for threshold fluence and ablation depth.

2 Material removal mechanisms

The dissipation of the absorbed energy in bulk material and the corresponding material removals take place mostly after pulse duration. The phase change mechanism during the material removal process of femtosecond laser ablation depends on the fluence, pulse duration, wavelength, repetition rate, pulse number, and material properties. The major phase change mechanisms include thermal processes (non-equilibrium thermal vaporization and melting) and non-thermal processes (the Coulomb explosion and electrostatic ablation)[1]. In melting, the electron-phonon collisions increase the local temperature above the melting point and generate significant liquid phase. In non-equilibrium thermal vaporization[2~4], the electron-phonon collisions increase the local temperature above the vaporization point so fast that the liquid phase can be neglected. In Coulomb explosion[5~7], excited electrons escape from the bulk material, generating high positive changes and a strong Coulomb repulsion that repulses ions out of the bulk material. In electrostatic ablation[8], a strong electric field formed by escaped electrons pulls out the ions within the impact area. The four competing mechanisms may coexist and/or transit to each other in material removals. The role of each mechanism remains

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poorly understood and there are many different views[3,4,9,10].

The Coulomb explosion and electrostatic ablation are closely related. It is very often mixed up with these two mechanisms. The difference is that the electrostatic ablation takes place at the surface when ejected electrons pull ions out, but the Coulomb explosion takes place as a result of the repulsive forces between the ions in the bulk. The relative role of two mechanisms has been intensively debated[1,5~8,11]. So far, no widely accepted agreement has been achieved. Some researchers claimed that the Coulomb explosion dominates during femtosecond laser ablation of dielectrics at fluences slightly higher than the threshold fluences[1,5~7,11], while in the similar conditions, others believe that electrostatic ablation is the key mechanism[4].

Another widely discussed debate regarding phase change mechanisms during femtosecond laser ablation is the relationship between the Coulomb explosion and thermal vaporization. It is very challenging yet critical to clarify the augments and identify the roles of the competing phase change mechanisms[1~7,9,12~16]. In the following sections, the mechanisms of material removals are reviewed especially for thermal vaporization[2-4,16] and Coulomb explosion[1,5~7,14,15].

2.1 Coulomb explosion

Compared with thermal vaporization, characteristics of the Coulomb explosion include [2,3,13,14,17~19]: 1) ions of different materials have similar momenta; 2) majority of ions is much faster than those in thermal vaporization; 3) volume of removal materials is on the order of tens of nanometers; 4) the ablated surface tends to be smooth and material removal is accurately controllable on the nanometer scale, thus it is called gentle ablation; and 5) there are two distinct velocity regimes of electrons: prompt electrons with energy order of eV and slow electrons with energy order of meV. Slow electrons actually are trapped by positive ions[11].

Figure 1 (a) shows the time-of-flight mass spectrometer of emitted materials from Al_2O_3 at 4 J/cm^2 by a 200-fs, 800-nm laser[11]. There are two contributions to the signal: prompt electrons with energies on the order of eV and slower (meV) plume electrons. Figure 1 (b) is an expanded scale showing prompt electrons. The characteristics of the Coulomb explosion are very obvious: slow electrons and ions in Fig.1 (a), and prompt electrons in Fig.1 (b). Please note the different time scales in two sub figures. The slow electrons can be considered as plasma electrons. Using time-of-flight and emission spectroscopy measurement, Ye *et al.*[20] found the kinetic energy of titanium ions could reach up to 3～10 keV ablated by a 80-fs, 800-nm laser at 1.25×10^{13} W/cm^2, which demonstrated that the Coulomb explosion was the mechanism of the material removal.

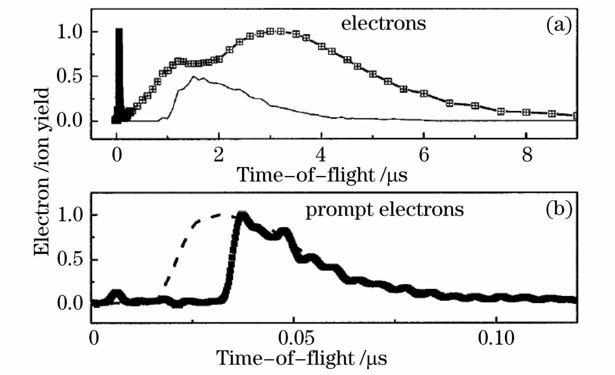

Fig. 1 Electron and ion time-of-flight (TOF) data of Al_2O_3 by a 200-fs, 800-nm laser at 4 J/cm^2. (a) Full range. Squares: both prompt electrons and slow, plasma electrons. Solid line depicts the TOF of the corresponding positive ions (O^+ + Al^+); (b) expanded scale showing prompt electrons. Squares (thick line): from Al_2O_3; dashed line: from Al[11]

The magnitude of the electric field formed in the Coulomb explosion depends on the electron kinetic energy and the gradient of electron density along the normal to the target materials[21] as

$$E_a = -\frac{\varepsilon(t)}{e}\frac{\partial \ln n_e}{\partial z}. \tag{1}$$

This electric field consequently pulls ions out of the bulk materials if its magnitude is high enough. The electrostatic force of this field on the ions, F_{st}, can be calculated by $F_{st}=eE_a$. Another force on the ions by the electric field is the ponderomotive force due to the gradient of the electric field that is estimated by[22]

$$F_{pf} = -\frac{2\pi e^2}{m_e c\omega^2}\nabla I \approx \frac{I}{2n_e c l_s}\frac{\omega_{pe}^2}{\omega^2}, \tag{2}$$

where I is the laser intensity, c is optical velocity, l_s is the field penetration length (skin depth), n_e is free electron number density, ω is the laser frequency, ω_{pe} is the electron plasma frequency, and m_e is the mass of electron. However, ponderomotive force is much smaller than the electronic force and can be ignored[23].

Bulgakova *et al*. theoretically demonstrated that Coulomb explosion occurred in dielectrics for 800-nm femtosecond laser irradiation, while it was strongly inhibited for metals and semiconductors[24,25]. The threshold for Coulomb explosion is assumed that under specific conditions, the electric field generated in the irradiated target can reach a threshold value so that the atomic bonds are broken and a surface layer of the material is disintegrated. Thus, the threshold electric field can be approximated as[25]

$$E_{\mathrm{th}}\big|_{x=0}=\sqrt{\frac{2\Lambda_{\mathrm{at}}}{\varepsilon\varepsilon_0 V_{\mathrm{at}}}}=\sqrt{\frac{2\Lambda_{\mathrm{at}}n_0}{\varepsilon\varepsilon_0}}. \quad (3)$$

where ε_0 and ε are the dielectric constant of vacuum and the relative dielectric constant respectively, Λ_{at} is the latent heat of sublimation for a single atom and n_0 is the valence band electron density. For femtosecond laser pulses, where the lattice is cold, the threshold electric field E_{th} is $\sim 5\times10^{10}$ V/m sapphire whereas for gold and silicon, the threshold electric fields are smaller, 2.76×10^{10} and 2.65×10^{10} V/m, respectively.

2.2 Thermal vaporization

High electron mobility enhances electron screening. Electron screening reduces the accumulation of positive charge during a femtosecond laser pulse, and thus reduces the electric field, which decreases the effectiveness of the Coulomb explosion. If electron screening is sufficiently high, the Coulomb explosion becomes insignificant. In these cases, excited electrons inside bulk material are trapped by ions and cooled down by transferring energy to photons. The materials are emitted when temperature is above the vaporization point, i. e., thermal vaporization happening. However, this explanation based on electron screening mechanism for ablation dominated thermal vaporization rather than Coulomb explosion is just a qualitative assumption, which needs further investigation.

Compared with the Coulomb explosion, characteristics of thermal vaporization include[1,11,14,17-19]: 1) emitted species are likely to have the similar kinetic energy; 2) temperatures of emitted species are near the vaporization point; 3) the temperature of the interface in bulk material side is near the vaporization point during the ablation process; 4) volume of removal material per pulse is on the order of submicrometer that is about one order of magnitude higher than that by Coulomb explosion, thus it is called strong ablation; and 5) ablated surface is rough.

Ladieu *et al*. measured heating and estimated the local temperature of the crater on a quartz sample at miliseconds after the sample was ablated by a 50-fs, 790-nm laser at 1～6 times of threshold fluence[26]. They found temperatures above 3000 ℃ even at the fluence close to threshold after a virtually infinite time (several milliseconds) with respect to pulsewidth of 50-fs. Hence, they concluded that thermal vaporization dominated the material removals in the whole fluence regime of 1～6 times of threshold fluence. Schmidt *et al*. observed that desorption of metals (Al, Ag, Fe, and Ni) by a 30-fs, 800-nm laser at 10～50 mJ/cm^2 using interferometric time-resolved pump-probe measurements[27]. They concluded that thermal vaporization was mainly responsible for the ablation, while Coulomb explosion was insignificant due to effective electron screening in metals. This conclusion was supported by the experiments on the ablation of metals (Au) and semiconductors (Si) by a 200-fs, 800-nm laser at 4 J/cm^2[11]. Stoian *et al*. believed that the Coulomb explosion was not a major mechanism in the ablation of Au and Si [11]. Recently Axente *et al*. investigated experimentally the ultrafast ablation of fused silica under 100-fs laser pulses at 800 nm in vacuum with incident laser fluences of 5 J/cm^2, which was higher than the threshold value (1.4 J/cm^2)[28]. They concluded that the ablation mechanism was dominated by thermal material removal processes in their case, which was contrary to the results of Bulgakova *et al*.[24].

2.3 Transitions between Coulomb explosion and thermal vaporization

Actually, the two competing mechanisms may coexist in material removals. The particular mechanism depends on material properties, pulse duration, fleunce, wavelength, number of pulses, and so on[29]. As shown in Fig. 2, Stoian *et al*. identified from the momentum as shown in Fig. 2(a) and energy of O^+ and Al^+ species as shown in Fig. 2(b) that in the initial several pulses, the Coulomb explosion dominated material removals of crystalline Al_2O_3 by a 100-fs, 800-nm laser at fluence slightly above the threshold, where different ions had similar momenta and the kinetic energy was high[1]. After a certain incubation period, the material removals gradually switch to thermal vaporization. At a large number of pulses (>100), thermal vaporization dominates the material removals, where different ions have similar kinetic energy and the kinetic energy of ion is relatively low. Although the characteristics of thermal vaporization and Coulomb explosion seem obvious, it remains a challenge to convincingly explain the transition from Coulomb explosion and thermal vaporization and theoretically predict the relative roles of two competing mechanisms in material removals.

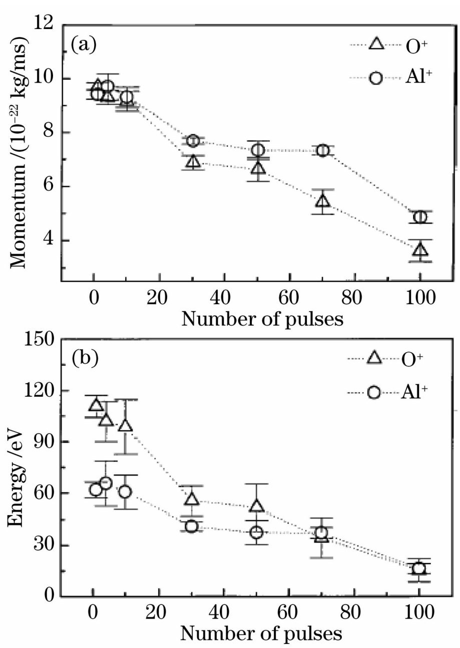

Fig. 2 (a) Momentum and (b) energy of O^+ and Al^+ species within the plume as a function of number of laser shots. The values were calculated from the measured maxima in the velocity distributions[1]

3 Threshold fluence and ablation depth

On the basis of the previous discussion of the fundamental mechanisms in the femtosecond ablation, this section will discusse the methodologies to estimate the threshold fluence and ablation depth.

3.1 Threshold fluence

Jeschke *et al*. defined the ablation threshold fluence as "the laser fluence for which lattice instabilities of such magnitude are induced that the system is irreversibly damaged and at least a mono-layer of material is removed"[30]. In experiments, threshold fluence is actually determined by visual acquisition, ablation depth measurement[31], or plasma radiation monitoring[32].

In femtosecond laser ablation, the electron temperature dominates the electron-phonon temperature. Thus, photon absorption depth instead of the thermal diffusion depth governs the heated volume. Thermal diffusion depth is linearly proportional to the square of pulsewidth, while photon absorption depth is not. Hence, threshold fluence of femtosecond lasers deviates from the law of the square root of the pulsewidth that is valid for long pulses[31,33].

It is widely assumed that ablation starts when the free electron density reaches the critical density[33]. According to this assumption, threshold fluence can be considered as the minimal fluence to create the critical density. Based on this assumption, the theoretical threshold logarithmically depends on the value of critical density described as[34]

$$F_{th} = \frac{2}{\alpha_i}\ln\left(\frac{n_{cr}}{n_0}\right), \tag{4}$$

where n_{cr} is the critical electron density and n_0 is the seed electrons generated by multiphoton ionization; α_i is the avalanche coefficient as flollowing

$$n_0 = \int_0^\infty P(I)\mathrm{d}t. \tag{5}$$

The threshold predictions based on the model of Perry's group are in good agreement with their experiments[34,35].

From the viewpoint of material removal mechanisms, for the Coulomb explosion, it is assumed that threshold fluence is the minimal fluence to create an electric field high enough for electrons to overcome the sum of the binding energy of ions in the lattice, ε_b, and ionization potential, U_{PI}. Under this assumption, the threshold fluence of wide bandgap materials can be expressed as[23]

$$F_{th} = \frac{3}{4}(\varepsilon_b + U_{PI})\,\frac{l_s n_e}{\alpha}. \tag{6}$$

Equations (35) and (37) present only rough estimation methodologies that are by no means mature.

Most recently Gruzdev[37~40] *et al*. propose a model of laser-induced breakdown in wide band-gap solids based on the modification of the Keldysh photo-ionization theory[36] by introducing a rigorous energy dependence of the reduced effective electron-holemass. The threshold intensity evaluated is[40]

$$I_1\,\frac{\lambda^2 d^2}{n_0(d,\lambda)} = \frac{c_0\varepsilon_0}{20000}\left(\frac{h\xi_1 c_0}{\mathrm{e}}\right)^2, \tag{7}$$

where h is the Planck constant, n_0 is refractive index depending on crystal constant d and laser wavelength λ, and is assumed to be intensity-independent in the first approximation, c_0 is the speed of light in vacuum, ε_0 is the electric constant. The unit of intensity I_1 is W/cm^2. Numerical evaluations show that for most wide band-gap cubic crystals the threshold of the first singularity I_1 is close to 10^{13} W/cm^2 at the laser wavelength of 800 nm frequently utilized in experiments[41~45]. Numerical values of Eq.(6) also agree well with the estimations obtained from the experimental results[41, 46~48].

Jia *et al*. studied the wavelength dependences of the threshold fluences in fused silica and CaF_2 crystals[49]. The experimental (square) and theoretical (solid curve) results are presented in Fig.3. It is about 0.9 J/cm^2 in fused silica as the laser wavelengths λ = 267 nm, and increases rapidly to 2.3 J/cm^2 as λ = 800 nm. The theoretical threshold fluences for the visible lasers correspond well to the results reported previously[34,35,50]. The threshold fluence is observed to increase rapidly with laser wavelength λ in the region of 250~800 nm, while it is nearly a constant for λ = 800~2000 nm.

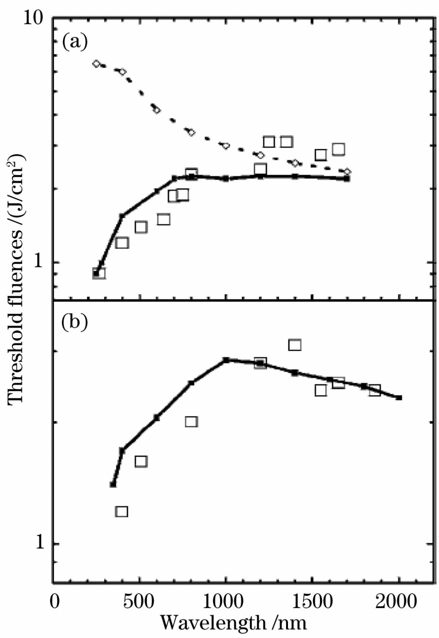

Fig.3 Wavelength dependences of the threshold fluences in (a) fused silica and (b) CaF_2 crystals[49]

Oh *et al*. also investigated the characteristics of ultra-short pulse laser-induced breakdowns of fused silica at different wavelengths of 526, 780, and 1053 nm[51]. The Fokker-Planck (F-P) equation is applied to describe the transient behaviors of electron densities and to predict the damage threshold fluences for laser pulse widths of 10 fs to 10 ps. They concluded that the damage threshold fluences increased with laser pulse durations and laser wavelengths, while decreased considerably as the electric field intensities increased, especially for longer pulse durations.

The ablation thresholds fluences of femtosecond laser ablation of dielectrics also strongly depends on the number of pulses[52~54]. It was found that the surface ablation thresholds decreased significantly with the increase of the radiation pulse number until the saturation level was reached due to the incubation effect, as demonstrated in Fig.4[53].

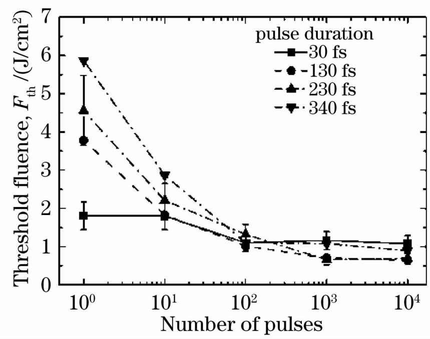

Fig.4 Ablation threshold fluence F_{th} versus the number of pulses N for the ablation of Schott BG36[53]

3.2 Ablation depth

Ablation depth is governed by photon absorption depth that is typically longer than thermal diffusion depth during a femtosecond pulse. It is assumed that the actual fluence at the ablation depth, d, equals to absorbed threshold fluence, $F(z=d) = (1-r)F_{th}$[55]. Based on this assumption, under the limit of linear absorption and constant optical properties, the ablation depth can be estimated by[55]

$$d = \frac{1}{\alpha}\ln\left(\frac{F}{F_{th}}\right), \tag{8}$$

where F is the laser fluence. The assumption of that reflectivity is constant seems unacceptable during the femtosecond laser ablation process[56]. The ablation depth of a femtosecond pulse can be approximated by the skin-effect model as following[23]

$$d = \frac{l_s}{2}\ln\left(\frac{F}{F_{th}}\right). \tag{9}$$

This estimation is very rough, which is also based on constant optic properties. Jiang *et al*.[57] improved the prediction precision of ablation depth and for the first time theoretically predicted the crater shape in femtosecond ablation of wide band materials by considering time and space dependent optical properties and quantum effects of the plasma. Their predicted threshold fluence and ablation depth for fused silica and barium aluminum borosilicate are in agreement with published experimental data. Figure 5 shows the flat-bottom crater shape for wide bandgap materials ablated by a 50-fs laser pulse[57]. The ablation of dielectrics by femtosecond pulse train that consists of one or multiple pulses was still analyzed by using the plasma model[58]. The results show that repeatable structures at the desired smaller nanoscales can be achieved in dielectrics by using the femtosecond pulse train technology, even when the laser fluence is subject to fluctuations.

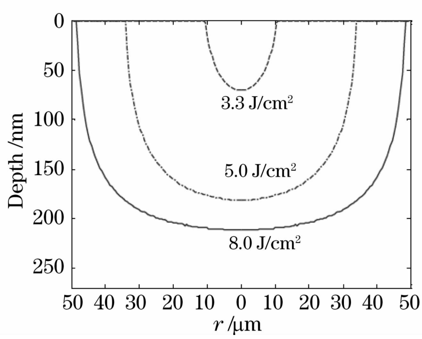

Fig. 5 Ablation crater shape at different fluences by a 50-fs, 780-nm laser pulse[57]

Another assumption for the ablation depth is that the free electron density at the ablation depth equals to critical density. Based on this assumption, the model of Stuart *et al*.[34] can be used to discuss the ablation-depth dependence on pulsewidth. If avalanche ionization dominates photon absorption, electron density (thus, ablation depth) is independent of pulsewidth at a fixed fluence. By contrast, if multiphoton ionization dominates photon absorption, electron density (thus, ablation depth) is expected to rapidly decrease with decrease of pulsewidth at a fixed fluence[31]. Burakov *et al*. concluded that the observed difference in the crater shapes generated in fused silica and sapphire was conditioned by the difference in dynamics of electron excitation and recombination channels characteristic of these two materials[59]. This presents an approach to determine the ionization mechanism of free electron generations during femtosecond laser ablation.

4 Summaries and conclusions

Irradiated under a femtosecond pulse, the impact area of a wide bandgap material is firstly transformed into absorbing plasma with metallic properties and the subsequent laser-plasma interaction causes the phase changes of bulk materials. The major conclusions and unsolved problems regarding energy transport during the phase change stages of femtosecond laser ablation are summarized as follows:

1) Mechanisms of material removals by femtosecond laser remain controversial. The particular mechanism strongly depends on material properties, laser fluence, pulse duration, wavelength, and number of pulses. Incubation and electron screening can significantly reduce the probability of Coulomb explosion. However, it remains a challenge to clearly explain the transition from one phase change mechanism to another and predict the roles of the ablation mechanisms.

2) The ablation depth of the femtosecond laser is governed by photon absorption depth and phase change mechanisms. The calculations of femtoseconds laser ablation shape of dielectrics by Jiang *et al*. have been based on free electron density distribution without the actual consideration of the phase changes. The models are based on the following two assumptions: ⅰ) threshold fluence can be considered as the minimal fluence that just creates the critical density and ⅱ) ablation depth can be considered to be the maximum depth at which the maximum free electron density is equal to the critical density in a given processing window. In the limit of negligible recast and phase change dominated by non-thermal ablation, the plasma model is applicable. However, at this time, the energy loss due to electron escape and the electron-lattice coupling factor cannot be precisely determined in a general form for the dense plasma (with metallic properties), which limits the application of the two-temperature equation in femtosecond ablation. Also, if recast occurs and multiple phase change mechanisms coexist, the material removals mechanism must be taken into consideration, which is still a challenge.

References

1 R. Stoian, D. Ashkenasi, A. Rosenfeld *et al*.. Coulomb explosion in ultrashort pulsed laser ablation of Al_2O_3[J]. *Phys. Rev. B*, 2000, **62**(19): 13167～13173

2 E. N. Glezer, Y. Siegal, L. Huang *et al*.. Behavior of $\chi^{(2)}$ during a laser-induced phase transition in GaAs[J]. *Phys. Rev. B*, 1995, **51**(15): 9589～9596

3 A. Miotello, R. Kelly. Laser-induced phase explosion: new physical problems when a condensed phase approaches the thermodynamic critical temperature[J]. *Appl. Phys. A Suppl.*, 1999, **69**(7): S67～S73

4 M. Toulemonde, C. Dufour, A. Meftah *et al*.. Transient thermal

processes in heavy ion irradiation of crystalline inorganic insulators[J]. *Nucl. Instrum. Methods Phys. Res. B*, 2000, **166**: 903～912

5 R. Stoian, H. Varel, A. Rosenfeld *et al*.. Ion time-of-flight analysis of ultrashort pulsed laser-induced processing of Al_2O_3[J]. *Appl. Surf. Sci.*, 2000, **165**(1): 44～55

6 T. Brabec, F. Krausz. Intense few-cycle laser fields: Frontiers of nonlinear optics[J]. *Rev. Mod. Phys.*, 2000, **72**(2): 545～591

7 V. P. Krainov, A. S. Roshchupkin. Dynamics of the Coulomb explosion of large hydrogen iodide clusters irradiated by superintense ultrashort laser pulses[J]. *Phys. Rev. A*, 2001, **64**(6): 063204

8 E. G. Gamaly, V. T. Tikhonchuk, A. V. Rode. COLA03, October 5-10, Hersonissos, Crete, Greece, 2003

9 P. L. Silvestrelli, A. Alavi, M. Parrinello *et al*.. Ab initio molecular dynamics simulation laser melting of silicon[J]. *Phys. Rev. Lett.*, 1996, **77**(15): 3149～3152

10 L. Jiang, H. L. Tsai. Femtosecond Laser Ablation: Challenges and Opportunities, NSF Workshop on "Unsolved Problems and Research Needs in Thermal Aspects of Material Removal Processes, June 10-12, Stillwater, OK, 2003

11 R. Stoian, A. Rosenfeld, D. Ashkenasi *et al*.. Surface charging and impulsive ion ejection during ultrashort pulsed laser ablation [J]. *Phys. Rev. Lett.*, 2002, **88**(9): 097603

12 P. Stampfli, K. H. Bennemann. Dynamical theory of the laser-induced lattice instability of silicon[J]. *Phys. Rev. B*, 1992, **46**(17): 10686～10692

13 K. Sokolowski-Tinten, J. Bialkowski, M. Boing *et al*.. Thermal and nonthermal melting of gallium arsenide after femtosecond laser excitation[J]. *Phys. Rev. B*, 1998, **58**(18): R11805～R11808

14 C. Cornaggia. in Molecules and Clusters in Intense Laser Fields, edited by J. Posthumus Cambridge University Press, Cambridge, U. K., 2001

15 H. P. Cheng, J. D. Gillaspy. Nanoscale modification of silicon surfaces via Coulomb explosion[J]. *Phys. Rev. B*, 1997, **55**(4): 2628～2636

16 P. Simon, J. Ihlemann. Machining of submicron structures on metals and semiconductors by ultrashort UV-laser pulses[J]. *Appl. Phys. A*, 1996, **63**(5): 505～508

17 A. C. Tam, H. K. Park, C. P. Grigoropoulos. Laser cleaning of surface contaminants[J]. *Appl. Surf. Sci.*, 1998, **127～129**: 721～725

18 J. L. Brand, A. C. Tam. Mechanism of picosecond ultraviolet laser sputtering of sapphire at 266 nm[J]. *Appl. Phys. Lett.*, 1990, **56**(10): 883～885

19 D. Ashkenasi, A. Rosenfeld, H. Varel *et al*.. Laser processing of sapphire with picosecond and sub-picosecond pulses[J]. *Appl. Surf. Sci.*, 1997, **120**: 65～80

20 M. Ye, C. P. Grigoropoulos. Time-of-flight and emission spectroscopy study of femtosecond laser ablation of titanium[J]. *J. Appl. Phys.*, 2001, **89**(9): 5183～5190

21 E. M. Lifshitz, L. P. Pitaevskii. Physical Kinetics[M]. Pergamon, Oxford, 1981

22 V. Y. Bychenkov, V. T. Tikhonchuk, S. V. Tolokonnikov. Nuclear reactions triggered by laser-accelerated high-energy ions [J]. *J. Exp. Theor. Phys.*, 1999, **88**(6): 1137～1142

23 E. G. Gamaly, A. V. Rode, B. Luther-Davies *et al*.. Ablation of solids by femtosecond lasers: ablation mechanism and ablation thresholds for metals and dielectrics[J]. *Phys. Plas.*, 2002, **9**(3): 949～957

24 N. M. Bulgakova, R. Stoian, A. Rosenfeld *et al*.. Electronic transport and consequences for material removal in ultrafast pulsed laser ablation of materials[J]. *Phys. Rev. B*, 2004, **69**(5): 054102

25 N. M. Bulgakova, R. Stoian, A. Rosenfeld *et al*.. A general continuum approach to describe fast electronic transport in pulsed laser irradiated materials: The problem of Coulomb explosion[J]. *Appl. Phys. A*, 2005, **81**(2): 345～356

26 F. Ladieu, P. Martin, S. Guizard. Measuring thermal effects in femtosecond laser-induced breakdown of dielectrics[J]. *Appl. Phys. Lett.*, 2002, **81**(6): 957～959

27 V. Schmidt, W. Husinsky, G. Betz. Dynamics of laser desorption and ablation of metals at the threshold on the femtosecond time scale[J]. *Phys. Rev. Lett.*, 2000, **85**(16): 3516～3519

28 E. Axente, S. Noel, J. Hermann *et al*.. Correlation between plasma expansion and damage threshold by femtosecond laser ablation of fused silica[J]. *J. Phys. D: Appl. Phys.*, 2008, **41**(10): 105216

29 K. Sokolowski-Tinten, J. Bialkowski, A. Cavalleri *et al*.. Transient states of matter during short pulse laser ablation[J]. *Phys. Rev. Lett.*, 1998, **81**(1): 224～227

30 H. O. Jeschke, M. E. Garcia, K. H. Bennemann. Theory for the ultrafast ablation of graphite films[J]. *Phys. Rev. Lett.*, 2001, **87**(1): 015003

31 M. Lenzner, J. Krüger, S. Sartania *et al*.. Femtosecond optical breakdown in dielectrics[J]. *Phys. Rev. Lett.*, 1998, **80**(18): 4076～4079

32 M. Li, S. Menon, J. P. Nibarger *et al*.. Ultrafast electron dynamics in femtosecond optical breakdown of dielectrics[J]. *Phys. Rev. Lett.*, 1999, **82**(12): 2394～2397

33 D. Du, X. Liu, G. Korn *et al*.. Laser-induced breakdown by impact ionization in SiO_2 with pulse widths from 7 ns to 150 fs[J]. *Appl. Phys. Lett.*, 1994, **64**(23): 3071～3073

34 B. C. Stuart, M. D. Feit, S. Herman *et al*.. Nanosecond-to-femtosecond laser-induced breakdown in dielectrics[J]. *Phys. Rev. B*, 1996, **53**(4): 1749～1761

35 M. D. Perry, B. C. Stuart, P. S. Banks *et al*.. Ultrashort-pulse laser machining of dielectric materials[J]. *J. Appl. Phys.*, 1999, **85**(9): 6803～6810

36 L. V. Keldysh. Ionization in the field of a strong electromagnetic wave[J]. *Sov. Phys. JETP*, 1965, **20**: 1307～1314

37 V. E. Gruzdev. Photoionization rate in wide band-gap crystals [J]. *Phys. Rev. B*, 2007, **75**(20): 205106

38 V. E. Gruzdev. in Laser Ablation and its Applications[M]. ed. by C. R. Phipps, Springer, Berlin Heidelberg New York, 2006, 99～121

39 V. E. Gruzdev. Features of the laser ionization of crystalline broad-band insulators[J]. *J. Opt. Technol.*, 2006, **73**(6): 385～390

40 V. E. Gruzdev, J. K. Chen. Laser-induced ionization and intrinsic breakdown of wide band-gap solids[J]. *Appl. Phys. A*, 2008, **90**(2): 255～261

41 O. Efimov, S. Juodkazis, H. Misawa. Intrinsic single- and multiple-pulse laser-induced damage in silicate glasses in the femtosecond-to-nanosecond region[J]. *Phys. Rev. A*, 2004, **69**(4): 042903

42 S. Juodkazis, T. Kondo, A. Rode *et al*.. Three-dimensional recording and structuring of chalcogenide glasses by femtosecond pulses[C]. *SPIE*, 2004, **5662**: 179～184

43 I. H. Chowdhury, A. Q. Wu, X. Xu *et al*.. Ultra-fast laser absorption and ablation dynamics in wide-band-gap dielectrics[J]. *Appl. Phys. A*, 2005, **81**(8): 1627～1632

44 A. Q. Wu, I. H. Chowdhury, X. Xu. Femtosecond laser

absorption in fused silica: Numerical and experimental investigation[J]. *Phys. Rev. B*, 2005, **72**(8): 085128

45 J. B. Ashcom, R. R. Gattass, C. B. Schaffer *et al.*. Numerical aperture dependence of damage and supercontinuum generation from femtosecond laser pulses in bulk fused silica[J]. *J. Opt. Soc. Am. B*, 2006, **23**(11): 2317～2322

46 L. B. Glebov. Intrinsic laser-induced breakdown of silicate glasses [C]. *SPIE*, 2002, **4679**: 321～331

47 L. B. Glebov, O. M. Efimov. Study of the characteristics of and mechanism of optical breakdown[J]. *Bull. Acad. Sci. USSR Phys. Ser.*, 1985, **49**: 94

48 O. M. Efimov, L. B. Glebov, V. S. Popikov *et al.*. Laser-induced damage of glasses by pulsed radiation in nano-picosecond region[C]. *SPIE*, 1996, **2770**: 162～167

49 T. Q. Jia, H. X. Chen, M. Huang *et al.*. Ultraviolet-infrared femtosecond laser-induced damage in fused silica and CaF_2 crystals [J]. *Phys. Rev. B*, 2006, **73**(5): 054105

50 T. Q. Jia, Z. Z. Xu, X. X. Li *et al.*. Microscopic mechanisms of ablation and micromachining of dielectrics by using femtosecond lasers[J]. *Appl. Phys. Lett.*, 2003, **82**(24): 4382～4384

51 Y. M. Oh, S. H. Lee, S. Park *et al.*. A numerical study on ultra-short pulse laser-induced damage on dielectrics using the Fokker-Planck equation[J]. *Int. J. Heat Mass Transfer*, 2006, **49**(7～8): 1493～1500

52 D. Ashkenasi, M. Lorenz, R. Stoian *et al.*. Surface damage threshold and structuring of dielectrics using femtosecond laser pulses: the role of incubation[J]. *Appl. Surf. Sci.*, 1999, **150**(1～4): 101～106

53 J. Krüger, M. Lenzner, S. Martin *et al.*. Single- and multi-pulse femtosecond laser ablation of optical filter materials[J]. *Appl. Surf. Sci.*, 2003, **208～209**: 233～237

54 X. C. Wang, G. C. Lim, H. Y. Zheng *et al.*. Femtosecond pulse laser ablation of sapphire in ambient air[J]. *Appl. Surf. Sci.*, 2004, **228**(1～4): 221～226

55 J. Krüger, W. Kautek. The femtosecond pulse laser: a new tool for micromachining[J]. *Laser Phys.*, 1999, **9**(1): 30～40

56 M. D. Shirk, P. A. Molian. A review of ultrashort pulsed laser ablation of materials[J]. *J. Laser Appl.*, 1998, **10**(1): 18～28

57 L. Jiang, H. L. Tsai. Energy transport and material removal in wide bandgap materials by a femtosecond laser pulse[J]. *Int. J. Heat Mass Transfer*, 2005, **48**(3～4): 487～499

58 L. Jiang, H. L. Tsai. Energy transport and nanostructuring of dielectrics by femtosecond laser pulse trains[J]. *J. Heat Transfer*, 2006, **128**(9): 926～933

59 I. M. Burakov, N. M. Bulgakova, R. Stoian *et al.*. Theoretical investigations of material modification using temporally shaped femtosecond laser pulses[J]. *Appl. Phys. A*, 2005, **81**(8): 1639～1645