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LASER-SOLID INTERACTION AND DYNAMICS OF THE LASER-ABLATED MATERIALS

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ABSTRACT

Rapid transformations through the liquid and vapor phases induced by laser-solid interactions are described by our thermal model with the Clausius-Clapeyron equation to determine the vaporization temperature under different surface pressure condition. Hydrodynamic behavior of the vapor during and after ablation is described by gas dynamic equations. These two models are coupled. Modeling results show that lower background pressure results lower laser energy density threshold for vaporization. The ablation rate and the amount of materials removed are proportional to the laser energy density above its threshold. We also demonstrate a dynamic source effect that accelerates the unsteady expansion of laser-ablated material in the direction perpendicular to the solid. A dynamic partial ionization effect is studied as well. A self-similar theory shows that the maximum expansion velocity is proportional to c_s/α, where $1-\alpha$ is the slope of the velocity profile. Numerical hydrodynamic modeling is in good agreement with the theory. With these effects, α is reduced. Therefore, the expansion front velocity is significantly higher than that from conventional models. The results are consistent with experiments. We further study the plume propagates in high background gas condition. Under appropriate conditions, the plume is slowed down, seperates with the backgrund, is backward moving, and hits the solid surface. Then, it splits to be two parts when it rebounds from the surface. The results from the modeling will be compared with experimental observations where possible.

I. INTRODUCTION

Materials processing with lasers is considered to be a technique which will have great impact on materials science and engineering in the 90's and beyond. One of the main techniques for laser materials processing is Pulsed Laser Deposition (PLD) for thin film growth. While experimentalists search for optimal approaches for thin film growth, a systematic effort in theory and modeling of various processes during PLD is needed. In this paper, we will study three physics issues important to PLD: laser-solid interaction, dynamic source effect for an accelerated expansion, and background gas effect on the dynamics of ablated materials.

II. LASER-SOLID INTERACTION

We have extanded a laser-annealing model, "Laser8" [1], to include the vapor production stage. The model employes finite-difference method to solve the heat diffusion equation with enthalpy, temperature, and a state diagram. It can handle phase transitions, which may or may not be in equilibrium, through the state array according to the state diagram. For the phase transition from liquid to vapor, the vaporization temperature is determined by the pressure at the liquid surface, P_s, according to the Clausius-Clapeyron equation:

$$T_v = [\frac{1}{T_o} - \frac{ln(P_s/P_o)}{\Delta H}]^{-1}, \qquad (1)$$

where T_o is a known reference vaporization temperature at a reference pressure, (P_o), and ΔH is the latent heat for vaporization. Here, we have assumed that the materials emitted from the surface before vaporiation due to other mechanisms such as ionic emission maintain an equilibrium pressure with the background. In this model, the surface pressure is given as a constant for boiling cases or by the surface pressure from the gas dynamic model.

When the surface pressure is at one atmosphere, the corresponding boiling temperature is 3267 C for silicon. We calculate the interaction of the silicon solid with a 40 ns (FWHM) KrF (248 nm wavelength) laser. The modeling results give the time history of the surface temperature for the cases of the laser energy density, E, being 3.8 and 3.9 J/cm^2, respectively. With 3.8 J/cm^2, the silicon surface never reaches the boiling temperature and no material is vaporized while it reaches the boiling temperature and about 4.4×10^{-8}cm thin layer of silicon becomes vapor with 3.9 J/cm^2. So, the laser energy density threshold for boiling of silicon in air with KrF laser is about 3.9J/cm^2. This is consistent with experimental measurementd, which show that the silicon surface remains liquid with 1.9 J/cm^2[2] and that visible surface damage by vaporization was found not to occur until $E \sim 4.5$J/cm^2 of XeCl (308 nm wavelength) laser[3].

For the surface pressure being at 1 mTorr, the corresponding boiling temperature is 1615 C. From the modeling, we know that the laser energy density threshold is about 1.4J/cm^2. The experimental data of D. B. Geohegan show that his ion probe receives signal at 1.5J/cm^2 or higher and no signal is detected at lower laser energy density. Again, the modeling result agrees with experimental measurement.

Fig. 1 shows the laser energy density threshold and the boiling temperature versus the surface pressure for silicon. For the surface pressure below 3.1×10^{-5}Torr, the boiling temperature is equal to the melting temperature; that is, there is no liquid phase to exist and the solid can become vapor directly. The laser energy density required to reach this temperature is about 0.7J/cm^2. For the surface pressure higher than that, the higher is the pressure, the higher is vaporization temperature. The modeling results show that the laser energy density threshold is linearly proportional to $\log P_s$. We also know the amount of material removed under different laser energy density. Fig. 2 show that both the maximum speed of surface recession due to vaporization and the depth of vaporization are linearly proportional to the laser energy density above its threshold at different background pressures.

III. DYNAMIC SOURCE EFFECT FOR ACCELERATED EXPANSION

For laser ablation in materials research, the quality of film deposited critically depends on the range and profile of the kinetic energy and density of the ablated plume[7, 8, 9]. When it is the advantage of pulsed laser deposition to have high kinetic energy, plume being too energetic have been observed to cause film damage. It has long been an important conclusion[4]-[5],[12, 13] that the maximum escape velocity of an original stationary gas has a limit, which for an ideal gas is $c_s\sqrt{2/(\gamma - 1)}$ for a steady expansion and $2c_s/(\gamma - 1)$ for an unsteady expansion, where c_s is the initial sound speed and γ is the ratio of specific heats. However, experimental measurements always show that, at low laser fluence in which the laser energy absorbed by the plume is negligible, the expansion front is a factor of 2-3 faster than predicted from unsteady adiabatic expansion with typical vaporization temperature[7, 10, 11, 12]. The effect of a Knudsen layer[15] was studied in order to explain the higher expansion velocity. It gives a velocity of $4u_k$[12, 13], where $u_k < c_s$ is the Knudsen layer velocity. This front expansion velocity is still too low. The inability to explain the experimental observation through gas dynamics has prompted a suggestion[14] of increased vapor temperature due to violent interactions inside the target such as phase explosion[17, 18].

We will demonstrate a dynamic source effect that accelerates the unsteady expansion significantly faster than predicted from conventional models in the direction perpendicular to the target surface. An effect of dynamic partial ionization that increases the expansion in all directions is also studied. This may explain the historical puzzle observed in laser ablation experiments. As in previous work[10]-[14], we are interested here in a laser fluence range high enough for hydrodynamic theory to be applicable but low enough for the absorption of the laser energy by the plume to be weak so that we can compare with free expansion models that do not include absorption.

In free expansion model the plume is given in a reservoir at $t = 0$. When the gate of the reservoir is removed, the gas adiabatically expands forward and a rarefection wave moves with the sound speed from the gate to the back wall in a period of time (t_r) during which the wall pressure remains constant. Then the wall pressure drops quickly. The average velocity gained per particle after the wall pressure drop is $c_s/\sqrt{\gamma}$. The maximum expansion velocity is $2c_s/(\gamma - 1)$ [4]-[5],[12, 13].

In our model the same material is treated as a source dynamically into the system after $t = 0$. For the plume pressure, P, below its thermodynamic critical pressure and with low plume viscosity, we may assume that the plume behaves as an ideal gas such that $P = n(1+\eta)k_BT$, where n (T) is the density (temperature) of the plume, η is the ionization fraction, and k_B is the Boltzmann constant. We use Euler's equations to model the plume dynamics and the Saha equation to determine the ionization fraction[16]:

$$\frac{\partial}{\partial t}(n) = -\frac{\partial}{\partial x}(nv) + S_n\delta(x - x_s)\,, \tag{2}$$

$$m\frac{\partial}{\partial t}(nv) = -\frac{\partial}{\partial x}(P + mnv^2)\,, \tag{3}$$

$$\frac{\partial}{\partial t}(E) = -\frac{\partial}{\partial x}[v(E + P)] + S_E\delta(x - x_s)\,, \tag{4}$$

$$\frac{\eta^2}{1-\eta} = \frac{2}{n}\frac{u_+}{u_o}\left(\frac{2\pi m_e k_B T}{h^2}\right)^{3/2} e^{-\frac{U_i}{k_BT}}\,, \tag{5}$$

where v is the plume velocity, $E = mne + mnv^2/2$ is the plume energy density, $e = (1 + \eta)(k_BT/m)/(\gamma - 1) + \eta U_i$ is the plume enthalpy, U_i is the ionization potential, u_+ and u_o are the electronic partition functions, m is the mass of the plume atom, m_e is the electron mass, h is Plank's constant, $S_n = n_{liq}v_{rs}$ is the density source, $S_E = n_{liq}v_{rs}k_BT_v/(\gamma - 1)$ is the energy source, n_{liq} is the liquid density, v_{rs} is the recession speed of the target surface due to ablation, and T_v is the vapor temperature. Here we take the small Knudsen layer limit, use $v = 0$ at the surface, and let S_n and S_E be constant. Because $c_s >> v_{rs}$, the surface recession on the plume expansion can be neglected[21]; i.e., $x_s = 0$.

A self-similar theory for the dynamic source effect. For simplicity and comparision with the free expansion results, our analysis considers the gas to be neutral, which is a good approximation for $T_v \ll U_i$. With an energy source, the system is not adiabatic near the surface. We expect self-similar expansion, except for early times and a transition region near the surface (δx). The self-similar variable is $\xi \equiv x/v_m t$, where v_m is the maximum expansion velocity. The source boundary conditions at $\xi = \delta \equiv \delta x/v_m t \ll 1$ are given by the constants $n = n_\delta$, $T = T_\delta$, and $v = v_\delta$. The downstream boundary conditions are $n = 0$, $v = v_m$, and $T = 0$ at $\xi = 1$ for expansion in vacuum. We assume a velocity profile of $v = v_m[\alpha+(1-\alpha)\xi]$, where α is determined by the flow properties ($1 \geq \alpha \geq 0$). We transform the independent variables from (x, t) to ξ. From Eqs.(2) and (3) we obtain the density profile $n = n_\delta(1-\xi)^{(1-\alpha)/\alpha}$ and the pressure profile $P = n_\delta v_m^2 m\alpha^2(1-\alpha)/(1+\alpha)\,(1-\xi)^{(1+1/\alpha)}$. So the temperature profile is $k_BT/m = v_m^2\alpha^2(1-\alpha)/(1+\alpha)\,(1-\xi)^2$. From mass, momentum, and energy conservations, we know the relations of v_m, α, n_δ, and T_δ. We note that if $\alpha = (\gamma - 1)/(\gamma + 1)$ is used, as for adiabatic cases, the analytical theory can recover the previous results[12, 13] of free expansion with a Knudsen layer. Figure 3 shows the normalized maximum expansion velocity as a function of α for a monatomic gas, $\gamma = 5/3$. The rapid rise of the maximum expansion velocity at $\alpha \leq 0.1$ is due to the $1/\alpha$ dependence. The value $v_m/c_\delta = 4$ for $\alpha = 1/4$ corresponds to the case of adiabatic expansion with a Knudsen layer[12, 13]. The flow at δ is sonic for the case of adiabatic expansion with the Knudsen layer. Figure 3 also shows that the flow at $\xi = \delta$ is subsonic (supersonic) for $\alpha < 1/4$ ($\alpha > 1/4$). The local temperature in terms of T_v is not sensitive to α.

Numerical hydrodynamic modeling. The Rusanov scheme[22] is used to solve Euler's equations, Eqs.(2)-(4); the nonlinear calculation of T and η is done with the Newton-Raphson method[23]. We use the logarithm of Eq.(5) for numerical stability. The system size is 1,000 spatial grids, Δx. The initial adaptive size is 10^{-5}cm, which is required for numerical convergence. New vapor is added into the first cell near the surface perturbatively. This limits the size of time step according to $n_{liq} v_{rs} T_v \Delta t \ll n_1 T_1 \Delta x$, where the subscript 1 represents the first cell.

The typical physical parameters are as follows. The system is initiated with a uniform background gas with its density $n_{bg} = 1 \times 10^{10}\,\mathrm{cm}^{-3}$ and its temperature $T_{bg} = 293\,^\circ\mathrm{K}$, which give a pressure $P_{bg} \sim 0.3\mu$Torr. A constant source of vapor is specified for 6 ns with a temperature $T_v = 7000\,^\circ\mathrm{K}$, given by the Clausius-Clapeyron equation, and the target recession speed is $v_{rs} = 1 \times 10^3\,\mathrm{cm/s}$, which are typical for the ablation of silicon with laser fluence of a few $\mathrm{J/cm}^2$ [1]. We choose the mass of both source and background gas to be 28 a.m.u., a solid density of $5.01 \times 10^{22}\,\mathrm{cm}^{-3}$, an ionization potential of 1.3×10^{11} erg (8.1 eV), $u_+ = 6$, and $u_0 = 15$. These parameters correspond to silicon. The normalized results should also be applicable to different materials. We use $\gamma = 5/3$ appropriate for monatomic gas. Thus, $c_s = 1.85 \times 10^5\,\mathrm{cm/s}$. We note that the conventional free expansion model for no background gas (vacuum) gives a maximum expansion velocity of $5.55 \times 10^5\,\mathrm{cm/s}$.

We first study the case without the Saha equation (no ionization; i.e., $\eta = 0$). Figure 4 shows the profiles of density and velocity at $t = 5\,\mathrm{ns}$, at which time the expansion is almost steady state. From the simulations, we observe that the expansion develops self-similarly after 0.1 ns. The front position is at $x = 0.0069\,\mathrm{cm}$ at $t = 5\,\mathrm{ns}$. The maximum expansion velocity at this time is defined to be the ratio of the front position and the time; i.e., $v_m = 1.38 \times 10^6\,\mathrm{cm/s}$ or $7.46\,c_s$. From the slope of the velocity profile, we estimate $\alpha = 1/14 = 0.07143$, which gives $v_\delta = 9.85 \times 10^4\,\mathrm{cm/s}$. Thus, $\delta x = 6.4 \times 10^{-5}\,\mathrm{cm}$. The simulation also shows that $n_\delta = 4.7 \times 10^{20}\,\mathrm{cm}^{-3}$ and $T_\delta = 3693\,^\circ\mathrm{K}$. The analytical maximum expansion velocity is $7.42\,c_s$. Also, $n_\delta = 5.07 \times 10^{20}\,\mathrm{cm}^{-3}$ and $T_\delta = 2836\,^\circ\mathrm{K}$. The analytical profiles in the figure are given by $n = n_\delta (1 - x/0.0069\,\mathrm{cm})^{13}$ and $v = v_m/14 + (13/14)(x/5\,\mathrm{ns})$ from the self-similar theory. Although the profiles at the shock front are flattened due to the finite background pressure (not included in this analytical theory), the overall profiles and scalings are in good agreement with the analytical theory. Figure 5 shows how the dynamic source causes the surface pressure to rise quickly and approach a saturation level of about 6×10^8 dyne/cm^2, or 600 atmospheres. Then the surface pressure exponentially drops after the source is terminated at $t = 6$ ns. Meanwhile, the maximum velocity from the velocity profile rises and saturates due to the surface pressure and the nonadiabatic unsteady expansion. The maximum velocity at $t = 10$ ns is about 1.22×10^6 cm/s. When we use the Saha equation (the more physical case), we find that the surface pressure remains unchanged and the maximum velocity is about 40% higher. It reaches 1.70×10^6 cm/s or $9.2\, c_s$ at $t = 10$ ns. As discussed earlier, the higher maximum velocity is an effect due to dynamic partial ionization as a result of increased energy channeled into directed motion. This effect is reduced when the vapor temperature is lower; it gives only about a 6% increase when $T_v = 3500\,°$K, for example.

IV. PLUME DYNAMICS IN BACKGROUND GAS

Laser ablation experiments have shown that the plume paopagation in background gas can lead to the stopping of the ablated materials. In some cases, the materials can even move backward and several reflected shocks within the plume are evidenced.

With the hydrodynamic modeling, we have simulate the plume dynamics in following parameters: the recession speed of solid silicon surface is 100 cm/s lasting for 6 ns with a vapor temperature 7000 K and the background gas density is 6.6×10^{15}cm^{-3} with room temperature (i.e., the background pressure is 200 mTorr). Fig. 6 shows the plume dynamics at different times. At t=10ns as shown in Fig. 6(a), the background gas has been snowplowed. Also, the temperature and ionization fraction rise at the shock front. Fig. 6(b) show that the relative higher pressure at shock front has split the plume and background. This couples with the rarefaction of the plume to begin pushing the main body of the plume (2nd peak) backward and, thus, to slow it down. As a result, the velocity of the second peak is decreased toward zero. By t=100 μs, the velocity has become negative: that is, the second peak moves backward as inidcated in Fig. 6(c). The backward moving plume eventially hits the target surface, rebounds, and moves forward again. The resultant plume splits as shown on Fig. 6(d).

We have also checked the scaling law of the turnover position of ablated plume. The numerical modeling results show that the turnover position of ablated plume is inversely proportional to the gas pressure and is proportional to the amount of ablated materials.

V. SUMMARY

Both a thermal model for studying laser-solid interaction and a hydrodynamic model for the dynamics of laser-ablated materials have been developed. It is shown that lower background pressure results lower laser energy density threshold for boiling, which is consistent with experimental measurements. Both the recession speed of the surface due to vaporization and the vaporization depth are proportional to the laser energy density above its threshold. We have treated the laser-ablated materials as a dynamic source, which is closer to experimental condition, instead of an initial constant source as in free expansion models.

It is demonstrated that the dynamic source and partial ionization effects can dramatically increase the front expansion velocity, which becomes significantly higher than predicted from conventional free expansion models, while the average momentum in the direction perpendicular to the solid surface is moderately increased. Since the expansion is accelerated mainly in the perpendicular direction, it should become more nonsymmetric and forward-peaked. Two dimensional model would be required to study the resultant plume profile and dynamics away from the target surface. The profiles and scalings from numerical hydrodynamic modeling are in good agreement with our self-similar theory. The results are consistent with experimental observations. For plume propagation in a background gas, our results show that the background gas acts on the main body of the rarefying plume, tends to slow it down, and in some cases even results in backward going materials.

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