Dynamics of Plume Propagation and Splitting during Pulsed-Laser Ablation

R. F. Wood, K. R. Chen,* J. N. Leboeuf, A. A. Puretzky, and D. B. Geohegan
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032
(Received 28 April 1997)

An innovative new approach has been developed for modeling the expansion of laser-generated plumes into low-pressure gases where initially the mean free path may be long enough for interpenetration of the plume and background. The model is based on a combination of multiple elastic scattering and hydrodynamic formulations. Although relatively simple in structure, it gives excellent fits to new experimental data for Si in He and Ar, and provides for the first time a detailed, coherent explanation of the observed splitting of the plume into a fast and slow component. [S0031-9007(97)03820-9]

PACS numbers: 79.20.Ds, 52.50.Jm

Pulsed laser deposition (PLD) has become an important technique for depositing a variety of materials [1,2], most notably thin films [3] and superlattices [4] of high-T_c superconductors. As a consequence, a very active field of research into laser ablation phenomena underlying PLD has developed [5]. But this is not a new field since it dates back to the earliest days of the laser era when many materials were irradiated with high-powered laser pulses [6–8]. Thus, the work reported here has applications far beyond the PLD process itself. More recent work has provided a wealth of new diagnostics with which to study the laser ablation process [9]. It is of crucial importance to know the constitution and dynamical behavior of the plume of ablated material in order to understand how film growth can be optimized by varying the laser parameters, the target-substrate distance, and ambient gases introduced into the deposition chamber. In particular, the often observed but little understood phenomenon of "plume splitting" [10] into fast ($\sim$ vacuum speed) and background-slowed components is of great interest because the fast component may damage the growing film or otherwise affect its microstructure. Also, clustering of film constituents in the gas phase or on the surface may cause problems, but may also provide a technologically important method of producing nanostructures [5,11,12].

In this paper, a new modeling approach, combining multiple scattering and hydrodynamical elements, is described and applied to recently obtained experimental data on Si ablated into He and Ar gases. The resulting model is remarkably successful in describing quantitatively the data and resolves long-standing uncertainties about the interpretation of many previous experimental observations.

Silicon was selected for the target in the experiments because it is well characterized, is readily obtained as single crystals, and has been thoroughly studied in the laser-annealing regime [13]. Background gases of He and Ar were chosen because their ionization energies are high (25 and 16 eV, respectively), hence avoiding ionization, and because one is lighter and one heavier than Si. KrF laser pulses of 3.0 J/cm^2 provided a good supply of singly ionized Si for the ion-probe detector while avoiding higher ionization states. Measurements revealed only neutral and singly ionized Si in the plume and only neutral atoms in the background. A description of the experimental setup has been given by Geohegan [14] and a more extensive report on the new experiments will be given in a later paper. Figures 1(a) and 1(b) show measured ion currents at 5 cm from the target as a function of time. Splitting of the plume into two components is apparent, but the behavior in Ar and He is clearly different.

The experiments suggest that plume splitting may occur because the mean free path in the expanding plume is initially comparable to the target-detector distance. This is a difficult regime for hydrodynamics because characteristics of both continuous fluid and discrete particle formulations must be included. Of the many attempts to model the behavior of the plume of ejected material, virtually all have employed some form of hydrodynamical formulation [15,16]. We explored a number of them ourselves [16,17], but were unable to obtain splitting of the plume. Monte Carlo calculations have also been pursued [18,19]. A scattering model adapted from Ref. [8] does yield splitting but relies on a preionized background gas to do so. It is precluded here by the fact that the background gas is not ionized.

We turn now to our modeling. A number of assumptions must be made, all of which cannot be discussed here. We feel that the remarkable agreement with the experimental data that is obtained is the strongest justification of our approach. In the quasi-two dimensional (2D) formulation [20], we consider only elastic collisions, albeit both head-on and non-head-on, so that the transfer of translational energy into internal energy is minimal under the experimental conditions used.

The plume is broken into orders corresponding to the number of collisions with the background gas. The first order reaches the detector without any scattering, the second order undergoes one scattering event, and so fourth. We let $\rho_p(t,x,k)$ be the density of the kth order plume at time t and distance x, $\rho_p^s(t,x,k)$ the density scattered from $\rho_p(t,x,k)$, and $\rho_b(t,x,k)$ the density of background gas. The total plume density $\rho_p(t,x)$ is

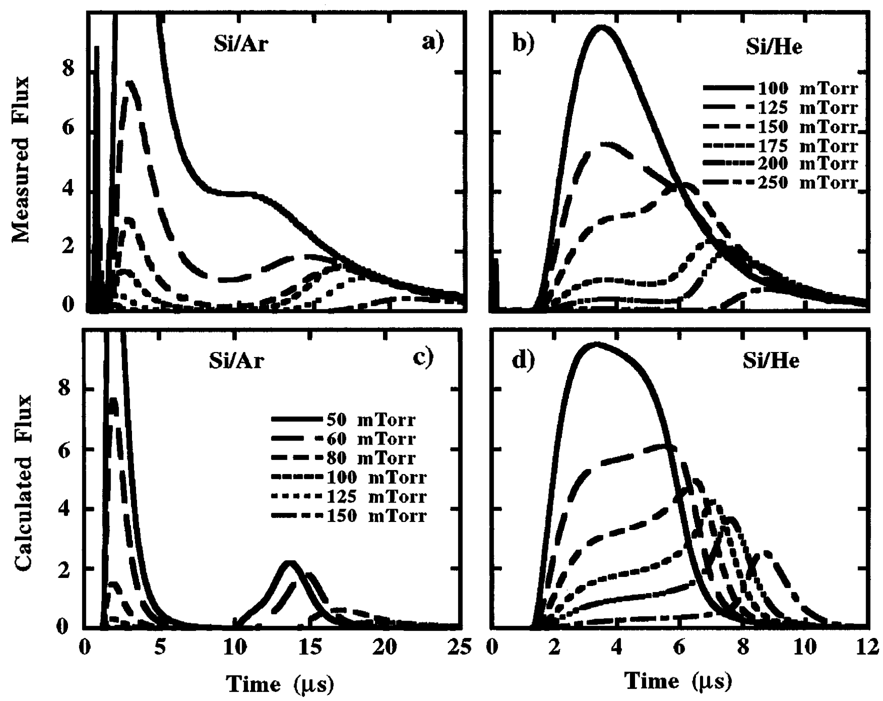

FIG. 1. Calculated and experimental flux results. Only the value of σ_{pb} was allowed to vary freely in going from He to Ar background gases. The fluxes have been normalized to a convenient scale for graphical presentation. One unit of flux on the experimental graphs corresponds to 0.0125 A/cm^2 for Si/Ar and 0.125 A/cm^2 for Si/He.

a sum of $\rho_p(t, x, k)$ over k. At any time and in any spatial cell, collisions may occur which scatter particles from the $k - 1$ order into the kth order and from the kth order into the $k + 1$ order. While particles can be transferred between the various orders only by collisions, the densities in the individual orders propagate to give the overall expansion. The propagation is determined by the usual equations for conservation of mass and momentum. We write the differential equations for the ablated plume, including the scattering terms (with $\partial_t \equiv \partial/\partial_t$ and $\partial_x \equiv \partial/\partial_x$), as

$$\partial_t \rho_p = -\partial_x(\rho_p v_p) + \partial_t \rho_p^s, \quad (1)$$

$$\partial_t(\rho_p v_p) = -\partial_x(\rho_p v_p^2 + P_p) + \partial_t(\rho_p^s v_p^s). \quad (2)$$

Here, terms with the superscript s represent the rate of change of the scattered density and momentum, while v and P are the velocity and pressure, respectively. Similar equations hold for the background, but we have generally found it unnecessary to resolve it into components in order to describe the plume data. The scattering terms provide the transfer of momentum from plume to background.

The simplest finite different discretization scheme was used, and care was taken to ensure mass and momentum conservation. For the plume scattering term, with plume-background scattering cross section σ_{pb}, and i and j the time and space indices, respectively, we have

$$\rho_p^s(i, j, k) = \rho_p(i, j, k)\rho_b(i - 1, j) \times [v_p(i, j, k) - \bar{v}_b(i - 1, j)]\sigma_{pb}\Delta t. \quad (3)$$

The bar over $\bar{v}_b$ implies that we have not generally resolved the background into scattered orders. Since this may seem inconsistent with the plume treatment, calculations were made with the background resolved into a few orders before averaging. They showed that only small variations in σ_{pb} and N_K of Eq. (4) were required to fit the data as the number of orders was changed.

The plasma formed in the experiments consists of Si and Si$^+$; the background gas is always entirely neutral. Hence, only neutral-neutral, ion-neutral, and Si$^+$-Si$^+$ collisions occur. The last of these can be neglected for the following reasons. The Si plume is collisionless in vacuum beyond the "Knudsen layer" [21] and Si-Si collisions may occur only after one of the ions has been scattered by the background gas. Also, the collision of two Si ions will have little effect on the mass and momentum transport of the plume itself (none at all for truly head-on collisions) and no direct effect on the transfer of momentum from plume to background. Consequently, all Si-Si collisions are of secondary importance. The important collisions are those between the plume and the neutral background. In this case, the only difference between σ_{pb} for Si and Si$^+$ is a weak polarization contribution which is negligible compared to the dominant hard-core nuclear-nuclear repulsion. Therefore, for all plume orders we take $\rho_p(i, j, k) = \rho_p^0(i, j, k) + \rho_p^+(i, j, k)$ and $\sigma_{pb}^0 = \sigma_{pb}^+ = \sigma_{pb}$. In other words, the kinetics of the propagation and scattering processes are virtually the same for ions and neutrals. Introduction of a velocity dependence into σ_{pb} destroyed the excellent agreement obtained with a constant value.

Calculations without the pressure term in Eq. (2) showed that the background is quickly "snowplowed" into a peak that is much greater than that of the plume [Fig. 3(b)]. Consequently, we assumed that the plume is in thermal equilibrium with the background in this region while the latter is adiabatically compressed during plume expansion. Including the pressure in this way resulted in broader background peaks and improved agreement with the widths of the plume peaks. Moreover, the adiabatic temperature in the shock region was found to be only $\sim$1000 K (for Si in 175 mTorr of He), consistent with the measurements of the ionization states of the gases involved.

Plume propagation in vacuum was investigated first using various assumptions for ρ^0, the starting pulse at $t = t_0$. Kelly and Dreyfus [21] discuss the half-range Maxwellian and Knudsen forms, both of which were studied. The latter given by

$$\rho_K^0(v_x, v_y, v_z) = n_K \exp\{-m[(v_x - u_K)^2 + v_y^2 + v_z^2]/2kT_K\} \qquad (4)$$

provided better fits to the experimental data. Here m is the mass, and u_K is the "Knudsen center of mass velocity." T_K is $\sim$25 eV for the laser pulses used. Minor variations in the form of ρ^0 made little difference in the calculated plume properties in the presence of a background gas, and we emphasize that plume splitting occurs regardless of the details of ρ^0.

Figure 1 gives an overall comparison of the results for Si/Ar and Si/He when only head-on collisions are considered. Only σ_{pb} was allowed to vary freely in going from Ar to He while N_K in Eq. (4) was taken somewhat less for He than for Ar, consistent with the experimental data. For Ar, σ_{pb} and N_K were fixed by obtaining a reasonably good fit at 80 mTorr, after which only the Ar pressure was varied. The same procedure was followed for He with the 200 mTorr data. N_K is $\sim 10^{15}$ cm^{-3} in both gases and $\sigma_{pb} = 5.1 \times 10^{-16}$ cm^2 in Ar and 3.0×10^{-16} cm^2 in He, consistent with the "atomic cross section" ($=\pi a_0^2$, with a_0 the Bohr radius) of 0.88×10^{-16} cm^2. Also, $\sigma_{pb}(\mathrm{Si/Ar})/\sigma_{pb}(\mathrm{Si/He}) = 1.69$ is very close to $[r(\mathrm{Si}) + r(\mathrm{Ar})]^2/[r(\mathrm{Si}) + r(\mathrm{He})]^2 = 1.66$, where $r(\mathrm{Si}) = 1.17$ Å is the covalent radius of Si and $r(\mathrm{Ar}) = 1.91$ Å and $r(\mathrm{He}) = 1.22$ Å are van der Waals radii.

The calculated results are in excellent general agreement with the great quantity of experimental data on Fig. 1 with plume splitting apparent in both background gases. In He, the slight dip between the shallow peak and the delayed sharp peak is not resolved in the calculations. We believe this is due to the neglect of recombination. In Ar, the flux drops nearly to zero between the two peaks in all the calculated curves, whereas it does not in some of the experimental results. This is at least partially due to the assumption of only head-on collisions, as was substantiated in calculations not discussed here.

A detailed comparison of the calculated and measured ion-probe signals from Fig. 1 for Si/He is shown in Fig. 2. The vacuum results are given in Fig. 2(a). Slight improvements in this fit would have little effect on the other results, except perhaps at 125 mTorr. The remarkable fits for the other pressures could be refined by minor variations in N_K and σ_{pb}, as illustrated in Fig. 2(b) where a better fit for 125 mTorr is obtained by varying σ_{pb} by $\sim$10%. On Fig. 2(e), the dotted curve shows the result of dividing the flux by the time to simulate the effects of three-body recombination. This does indeed give the observed minimum between the peaks. We stress again that only the 200 mTorr data were used for fitting. The peak positions and structures on the other curves then follow.

The resolution of the plume into orders is shown in Fig. 3(a) for 175 mTorr He; only the first (no collisions)

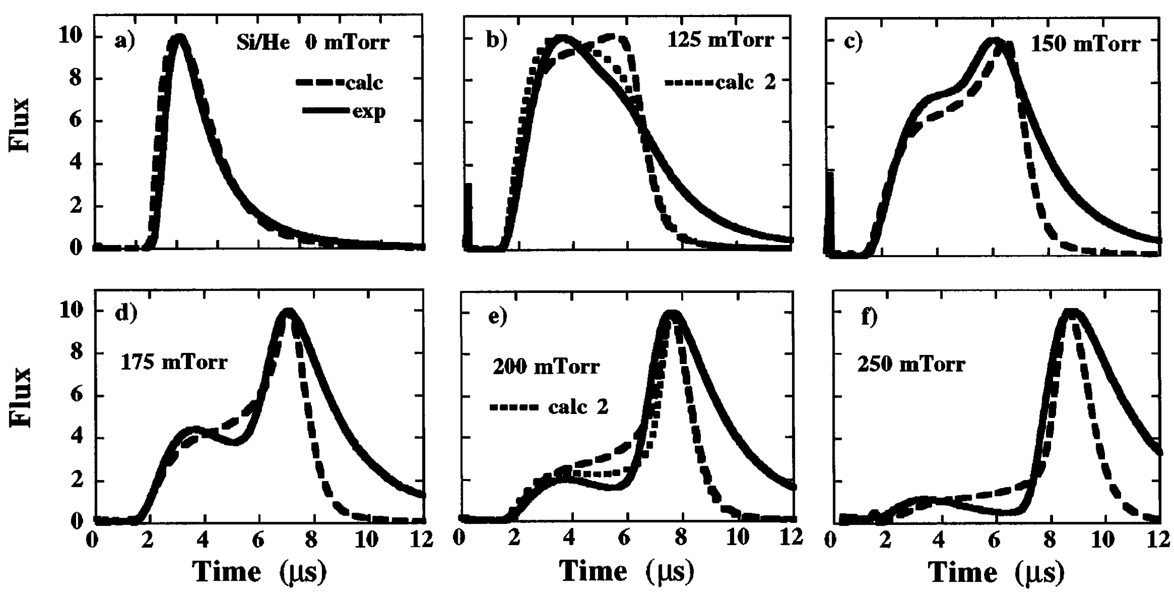

FIG. 2. Detailed comparison of the experimental and calculated results for Si/He. N_K and σ_{pb} were varied to obtain a satisfactory fit at 200 mTorr after which only the pressure was assigned the other experimental values. The various panels are discussed in the text.

and subsequent even orders are given. For convergence, $\sim$11 orders are required for Si/He but only $\sim$4 for Si/Ar, because each collision in He transfers only a small amount of momentum to the background. The second order plume in Si/He is barely split off from the first order, whereas in Si/Ar it is already well resolved. This is a direct result of the greater slowing down of the Si ions by the massive Ar atoms compared to the He atoms. It also explains why the fast peak is shifted away from the vacuum peak in He and not in Ar.

On Fig. 3(b), ρ_p and ρ_b are shown for Si/He. The He density, roughly an order of magnitude greater than the Si density, is snowplowed into a sharp peak, while the Si also piles up. However, considerable interpenetration of the peaks occurs so that snowplowing is not an entirely apt description. The velocities of the Si and He peaks can be calculated from Fig. 3(b). At 5 cm the plume velocity is $\sim\frac{1}{5}$ its value in vacuum; in 60 mTorr of Ar, it is only $\frac{1}{10}$ the vacuum value of 2.5×10^6 cm/sec.

To summarize, we have developed a multiple scattering/hydrodynamical model for expansion for a laser-ablated plume into background gases that gives excellent agreement with numerous new experimental results. It explains plume splitting quantitatively and makes clear the observed differences between He and Ar background gases. Measured peak heights, splittings, and attenuations are reproduced with physically meaningful cross sections.

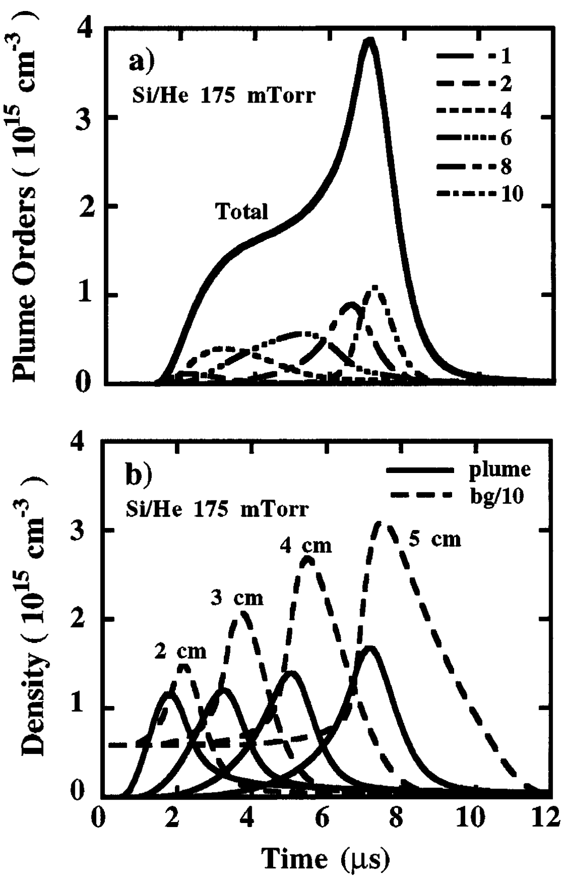

FIG. 3. (a) Resolution of the plume flux into scattering orders in 175 mTorr of He. The number of orders required for convergence is $\sim$11 so that only the first (unscattered) and subsequent even ones are shown. (b) Si and He densities for different target-detector distances. Note that the background (bg) density is divided by 10.

This work was supported in part by Laboratory Directed Research and Development Funds and by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-96OR22464, with Lockheed Martin Energy Research Corporation.

*Present address: Physics Department, National Changhua University of Education, Changhua, Taiwan 50058, Republic of China.

[1] H. M. Smith and A. F. Turner, Appl. Optics **4**, 147 (1965). These authors appear to have been the first to demonstrate thin-film deposition by PLD.
[2] For recent reviews, see the various chapters in *Pulsed Laser Deposition of Thin Films*, edited by D. B. Chrisey and G. K. Hubler, (Wiley, New York, 1994).
[3] D. Dijkkamp *et al.*, Appl. Phys. Lett. **51**, 619 (1987); X. D. Wu *et al.*, *ibid.* **51**, 861 (1987).
[4] J.-M. Triscone *et al.*, Phys. Rev. Lett. **64**, 804 (1990); Q. Li *et al.*, *ibid.* **64**, 3086 (1990); D. H. Lowndes *et al.*, *ibid.* **65**, 1160 (1990).
[5] See, e.g., D. H. Lowndes *et al.*, Science **273**, 898 (1996).
[6] For an extended discussion of the early work, see J. F. Ready in *Effects of High-Power Laser Radiation* (Academic Press, New York, 1971).
[7] D. W. Koopman, Phys. Fluids **15**, 1959 (1972).
[8] D. W. Koopman and R. R. Goforth, Phys. Fluids **17**, 1560 (1974).
[9] A review of many of these is given by D. B. Geohegan in Ref. [2], Chap. 5.
[10] D. B. Geohegan and A. A. Puretzky, Appl. Phys. Lett. **67**, 197 (1995); Appl. Surf. Sci. **96–98**, 131 (1996).
[11] I. A. Movtchan *et al.*, Appl. Surf. Sci. **96–98**, 251 (1996).
[12] T. Yoshida *et al.*, Appl. Phys. Lett. **68**, 1772 (1996).
[13] R. F. Wood and G. A. Geist, Phys. Rev. Lett. **57**, 873 (1986); R. F. Wood and G. A. Geist, Phys. Rev. B **34**, 2606 (1986).
[14] D. B. Geohegan, Thin Solid Films **220**, 138 (1992).
[15] See e.g., J. N. Leboeuf *et al.*, Phys. Plasmas **3**, 2203 (1996), and references therein.
[16] P. W. Rambo and J. Denavit, J. Comput. Phys. **98**, 317 (1992).
[17] K. R. Chen *et al.*, J. Vac. Sci. Technol. A **14**, 1111 (1996).
[18] J. C. S. Kools, J. Appl. Phys. **74**, 6401 (1993).
[19] D. L. Capewell and D. G. Goodwin, in *Laser Induced Thin Film Processing,* edited by Jan J. Dubowski, SPIE Proceedings Vol. 2403 (SPIE–International Society for Optical Engineering, San Jose, California, 1995), p. 49.
[20] We refer to the approach as quasi-2D because of the frequent averaging over scattering angles for non-head-on collisions that have not been emphasized in this paper.
[21] R. Kelly and R. W. Dreyfus, Surf. Sci. **198**, 263 (1988).