Nanoparticle formation in the expansion process of a laser ablated plume

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Abstract. In the present article, we describe the process of nanoparticle formation during pulsed laser ablation in an inert gas atmosphere. We investigated the interaction between laser ablated plumes and shock waves using one dimensional Eulerian fluid dynamics equations combined with a rate equation relating to a classical nucleation model of supersaturated vapors. The initial values for the plume immediately after laser irradiation onto a silicon target were calculated based on stochastic thermodynamics, which was first used by Houle et al. We found a certain case wherein the rate of nanoparticle formation becomes higher when a reflected shock wave passes through the plume. In that particular case, mono-dispersed nanoparticles can be generated by carrying out nucleation and nanoparticle growth as separate processes.

1. Introduction
Pulsed laser ablation is a promising technique that has been applied to the growth of high quality thin films, such as high temperature superconductors. This technique has been recently used for the preparation of thin films made from nanoparticles [1]. Since the properties of the thin films are highly dependent on the size dispersion of the nanoparticles, it is important to find a way to prepare mono-dispersed nanoparticles [2].

Iwata et al proposed a new method to form mono-dispersed nanoparticles by controlling the expansion of a laser ablated plume in a closed space filled with an inert gas [3]. In order to shed light on the plume expansion process, a number of experimental studies have been conducted, for example, using infrared spectroscopy of nanoparticles produced by reactive pulsed laser ablation [4]. In addition to experimental approaches, numerical analyses have been performed, such as numerical studies to investigate the interaction between plumes and shock waves in ambient gas atmosphere using the Monte Carlo method [5] or using the Navier-Stokes equations [6]. However, there has been no attempt to simulate plume dynamics in ambient gas atmosphere that include a model for nanoparticle formation. Simulations based on one dimensional fluid dynamics equations that include a classical nucleation model for supersaturated vapors can give us vital information for understanding the formation processes of mono-dispersed nanoparticles. We performed such a numerical investigation, in order to further clarify factors that are relevant to nanoparticle formation during the expansion of a laser ablated plume in a closed space filled with a buffer gas.

2. Basic equations and initial conditions
The basic conservation equations of mass, momentum and energy for the one-dimensional unsteady flow of a vapor and an inert gas in Eulerian coordinates may be expressed as

$$\frac{\partial \mathbf{Q}}{\partial t} + \frac{\partial \mathbf{E}}{\partial x} = \mathbf{W}$$

(1)

$$\mathbf{Q} = \begin{bmatrix} \rho_v & \rho_g & \rho_m \end{bmatrix}^T, \ \mathbf{E} = \begin{bmatrix} \rho_vu & \rho_gu & p + \rho_mu^2 \end{bmatrix}^T, \ \mathbf{W} = \begin{bmatrix} 0 & 0 & \lambda(1+\omega) \rho \omega \end{bmatrix}^T$$

Here, $x$ and $t$ are independent space and time coordinates and $\rho$, $u$, $p$ and $e$ express the density, flow velocity, pressure and total energy per unit volume, respectively. The values of the vapor, inert gas and their mixture are denoted by the subscripts $v$, $g$ and $m$, respectively. The variables $\omega$ and $\lambda$ are the mass density ratio of generated nanoparticles and the latent heat of nanoparticle specie.

The rate equation for the mass of nanoparticles is written along the particle trajectory as

$$\dot{\omega} = 4\pi \rho_i \left\{ \frac{I(1+\omega)}{(1+\omega)\rho_v} \frac{r^3}{3} + \frac{dr}{dt} \int \frac{I(1+\omega)}{(1+\omega)\rho_v} \left( r_v^2 + \int \frac{dr}{dt} d\theta \right)^2 d\tau \right\}$$

(2)

Here, $\rho_i$ is the internal density of nanoparticle, and $r$ the radius of nanoparticle. We used the equation proposed by Volmer and Weber as a nucleation rate $I$ [7]. The critical radius, $r_\star$, and the growth rate of a nanoparticle, $dr/dt$, can be written as follows:

$$r_\star = \frac{2\sigma v_c}{kT \ln S}$$

(3)

$$\frac{dr}{dt} = \xi v_c \sqrt{\frac{kT}{2\pi m}} (n-n_m)$$

(4)

Here, $\sigma$ is the surface free energy, $v_c$ is the volume per atom, $m$ is the mass of atom, $\xi$ is the accommodation factor, $k$ is Boltzman constant, $T$ is temperature, $S$ is supersaturation and $n$ is the number density of vapor. The variable $n_m$ represents the number density at equilibrium condition.

The initial conditions are given at $t=0$, based on stochastical thermodynamic calculation [8] and Knudsen analysis as indicated in Table 1. The surface temperature reached maximum during laser pulse irradiation and the values after Knudsen Layer (KL) was obtained from the surface temperature through the Knudsen analysis. The total number of vapor atoms was counted within a definite period in which the surface temperature is higher than the boiling point. A shock tube problem is solved in the calculation space in which both boundary at $x=0$ and $x=x_{\text{max}}$ is a solid wall.

| case | Laser pulse duration (ns) | Laser fluence (J/cm$^2$) | Surface temperature of target (K) | Vapor temperature after KL (K) | Vapor density after KL (kg m$^{-3}$) | Flux velocity after KL (ms$^{-1}$) | Total number of vapor atoms | Ambient gas pressure (Pa) |
|------|--------------------------|---------------------------|----------------------------------|-------------------------------|--------------------------------------|-------------------------------|-----------------------------|---------------------------|
| 1    | 10                       | 2.55                      | 6100                             | 4080                          | 1.54                                 | 1420                          | $1.61 \times 10^{14}$     | 100                       |
| 2    | 10                       | 7.65                      | 12500                            | 8350                          | 15.0                                 | 2030                          | $2.25 \times 10^{15}$     | 1000                      |

3. Results and Discussion

3.1. Typical flow field

The calculated profiles for the density of the silicon plume, helium gas and nanoparticle mass with the distance between two solid walls are shown in figure 1. The density distributions in an early stage of ablation are shown in figure 1(a). Although the vapor plume expanded and pushed the buffer gas away, the expansion did not continue. Since the ejection of the ablated plume from the target surface is limited to a very short time, the plume was pushed back from the buffer gas and was compressed. In the compressed region, the supersaturation becomes so high resulting to a clustering or nanoparticles formation. It was clearly observed that a shock wave was generated in front of the plume and
propagates into the buffer gas. It was also seen in figures 1(b)-(d) that the shock wave transmitted was faster than the plume. The peak in the plume density gradually decreased with time, while the nanoparticle density increased. In figure 1(e), the shock wave is shown colliding with the right side wall. Furthermore, the peak in the nanoparticle density deviated from that of the vapor plume. The reflected shock wave intensified and collided with the plume as shown in figure 1(g). Figure 1(h) shows the wave patterns immediately after the collision. The shock wave penetrated into the plume raising its density and the plume was forced back and slightly moved to the left direction as in figure 1(i). When the shock wave completely passed through the plume, the nanoparticle density effectively increased as in figure 1(j).

3.2. Nucleation and nanoparticle growth

Figure 2(a) shows the time variation of total mass of nanoparticles in the closed space. The abscissa is the time in logarithmic scale, which is convenient for expressing several different phenomena that occur with various time scales. The mass of nanoparticles increased up to 0.1 $\mu$s in both cases 1 and 2. In case 1, the mass became stable after 0.1 $\mu$s and increased again at 10 $\mu$s. The time of the second increase in the mass corresponds with the time when the reflected shock wave was transmitted to the plume.

The time dependency of nucleus number integrated in the space is shown in figure 2(b). Since the numbers are saturated at $t=0.01 \mu s$ for both cases 1 and 2, it is clearly seen that the nucleation has been completed in the early stage of expansion. Unlike the mass of nanoparticles, the nanoparticle number was not affected by the reflected shock wave.

The averaged radius of nanoparticles in the closed space is shown in figure 2(c). The value of radius reached around 1.5 nm, which is consistent with the value obtained by Muto et al [9], where silicon clusters of 2-3nm in diameter were formed by pulsed laser ablation in a closed space filled with a helium buffer gas. Since the nanoparticles are concentrated in the narrow region near the interface between the plume and the buffer gas, then the averaged value is considered to be a typical value at the region [9]. The radius began to increase at $t=0.001 \mu s$ in both cases 1 and 2, and continued to increase until $t=0.1 \mu s$ and $t=10 \mu s$ in case 1 and case 2, respectively. A second increase in radius was observed for case1 at $t=10 \mu s$ when the reflected shock wave passes through. In case 1, the increase was so large as to actually determine the nanoparticle radius. On the other hand, in case 2, the period between 0.001 $\mu s$ to 0.01 $\mu s$ shows a corresponding increase between the nanoparticle number and the radius. In case 1, a substantial increase in the radius was observed after $t=10 \mu s$, which was
greatly attributed to the effect of the reflected shock wave, and the radius increase was completely separated from the nuclear increase. Such separation may prove to be preferable for generating mono-dispersed nanoparticles.

4. Conclusions
In the present calculations the problem of nanoparticle formation during pulsed laser ablation was analysed numerically by solving the fluid dynamic equations with nucleation terms. Based on the results we may conclude as follows:

(1) It is possible to form nanoparticles using pulsed laser ablation in a closed space filled with a buffer gas.
(2) Certain conditions for nanoparticle formation in the narrow region between the plume and the buffer gas were obtained.
(3) The calculated value for nanoparticle radius coincides with that found by Muto et al.
(4) Reflected shock waves can cause a burst of nanoparticle growth, which may prove to be an important factor in making mono-dispersed nanoparticles.

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