Perturbation of the substrate temperature by the impingement of laser ablated particles

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During the process of pulsed laser deposition of thin film materials, the impingement of the laser ablated particles onto the substrate increases the substrate temperature. In this work, the energy exchange between the ablated particles and the substrate is analyzed. The substrate temperature rise is studied via a transient two dimensional heat transfer model. In particular, the temperature evolution of silicon and quartz substrates induced by the deposition of carbon and copper films are examined. The effects of experimental conditions on the maximum substrate temperature rise are discussed. © *1995 American Institute of Physics.*

Pulsed laser deposition (PLD) is emerging as one of the leading technology for fabricating thin film materials, including high T_c superconducting films, diamond-like films, dielectric, ferroelectric, piezoelectric films, and semiconductor super lattice layers.[1] In order to understand the mechanism of the PLD process and produce high quality thin films, various diagnostic techniques have been developed such as mass spectroscopy, emission spectroscopy, and high speed photography. Information obtained from these measurements helped to quantify the behavior of the laser ejected particles and laser induced plasma plume. However, due to the difficulty of direct monitoring *in situ* thin film growth, the study on the particle-substrate interaction is only at a preliminary stage.[2]

In the PLD process, the substrate temperature is one of the most crucial parameters for the growth of thin films from the laser ablated vapor. By controlling the substrate temperature, thin films with different microstructure and crystal orientation have been obtained.[3,4] This is because that, in the process of nucleation of vapor on the substrate, the desorption time of the vapor atoms on the substrate, the diffusion distance of the vapor atoms, and the nucleation rate are strong functions of temperature.[5] The substrate temperature dominates the crystal growth process. In practice, the temperature of the substrate is controlled by an electric heating unit and monitored by a pyrometer or an embedded thermocouple in the substrate. However, when the laser ablated particles strike the substrate, the temperature at the substrate surface is altered due to the energy transfer between the particles and the substrate. In the case of a deposition process involving a nanosecond (or shorter) pulsed laser, only the temperature within the top several microns of substrate is increased for a period of a few microseconds. The temperature variation within such a short period of time and depth cannot easily be probed by conventional temperature measurement techniques.

The energy transferred from the laser ablated particles can be viewed as an energy flux incident onto the substrate. Although this energy transfer process is complex, the amount of the energy transferred to the substrate is the instantaneous release of the kinetic energy and latent heat of the arriving particles. The latter, which is the difference between the Gibb's free energy between the vapor and the solid, is essentially the energy consumed to break the atomic bonds when the atoms were evaporated from the solid phase.[5] The total energy per unit area, Q_{tot}, released by the incoming particles during one laser pulse is:

$$Q_{\text{tot}}=\rho_s R\frac{A}{M}E_m+\rho_s L_{\text{sv}}R, \tag{1}$$

where ρ_s is the density of the thin film material, R is the deposition rate per pulse (Å/pulse), A is the Avogadro's number, M is the molecular weight of the particles. E_m is the mean kinetic energy of the particles, which typically ranges from 2 to 100 eV.[1] A much higher value of 500 eV has also been reported.[6] L_{sv} is the latent heat of solid-vapor phase change. Therefore, the first and the second term on the right hand side (RHS) of Eq. (1) are the kinetic energy and the latent heat released from the particles, respectively.

The total energy of the particles is released in a time period during which the particles arrive at the substrate surface. Time-of-flight experiments[7,8] have shown that the number intensity, $N(t)$ of the laser ablated particles can be well represented by a Maxwellian distribution, which is expressed as:

$$N(t)=\frac{C}{t^4}\exp\left(-\frac{Md^2}{t^2E_m}\right), \tag{2}$$

where d is the distance between the target and the substrate. C is the normalization constant, which is found from: $\int_0^\infty N(t)dt=R$. The above equation is used to obtain the time period t_t [or the full width half maximum (FWHM), $t_t/2$] during which the energy of the particles is transferred to the substrate. Since the kinetic energy of the particle is proportional to $1/t^2$, the energy flux is:

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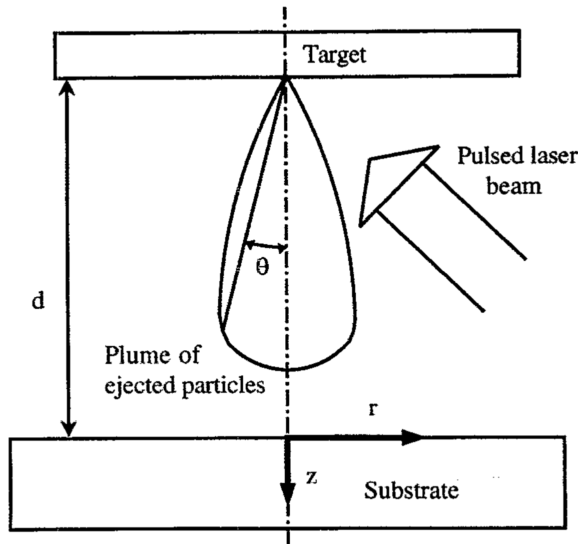

FIG. 1. Schematic of the pulsed laser deposition process.

$$Q(t)=\frac{C'}{t^2}N(t)+\rho_s L_{sv}N(t), \quad (3)$$

where the normalization constant C' is calculated from $\int_0^\infty (C'/t^2)N(t)dt=\rho_s R(A/M)E_m$.

The diffusion of the above energy flux into the substrate is governed by a two-dimensional transient heat conduction equation:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right)=\rho C_p\frac{\partial T}{\partial t}. \quad (4)$$

A two dimensional analysis is used, since the ejected particles peaks strongly towards the normal direction with a $\cos^n\theta$ distribution (Fig. 1), where n varies between 8 and 16.[7,8] The boundary condition at the substrate surface is the energy flux of the ejected particles Eq. (3). In calculation, $Q(t)$ is approximated by the following triangular temporal distribution:

$$I(t,r,z=0)=\frac{2Q_{\text{tot}}\cdot t\cdot\cos^n(\theta)}{t_t\cdot t_p} \quad 0<t<t_p,$$

$$I(t,r,z=0)=\frac{2Q_{\text{tot}}\cdot(t_t-t)\cdot\cos^n(\theta)}{t_t\cdot(t_t-t_p)} \quad t_p<t<t_t,$$

$$I(t,r,z=0) \quad t_t<t. \quad (5)$$

Where $\theta=\tan^{-1}(r/d)$, t_p is the time when the flux reaches the maximum value. Initially, the temperature of the target is at a designated temperature T_i. At the boundaries, $r\to\infty$ and $z\to\infty$, the temperature of the substrate remains at its initial temperature T_i:

$$T(t=0,r,z)=T_i, \quad (6a)$$

$$T(t,r\to\infty,z)=T_i, \quad (6b)$$

$$T(t,r,z\to\infty)=T_i. \quad (6c)$$

Equation (4) combined with the initial condition (6a), and the boundary equations (5), (6b), and (6c), are solved numerically by the finite-difference scheme to obtain the transient temperature evolution in the substrate. The ADI method and the Thomas algorithm are applied to solve the discretized equations.[9] Calculations are performed for atomic carbon and copper particles deposited on crystalline silicon and quartz substrates. It is assumed that the deposition conditions are: $d=5$ cm, $R=1$ Å/pulse, and $T_i=300$ K. E_m is varied between 10 and 100 eV. The temperature dependent thermal properties[10] and the solid-vapor latent heat[11] are used in the calculation.

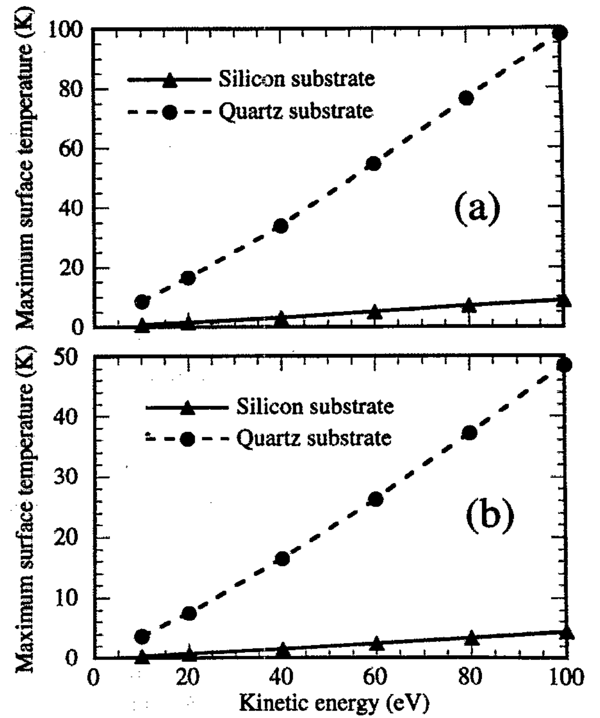

FIG. 2. Maximum temperature rise at the silicon and carbon substrate surface due to the impingement of (a) carbon particles and (b) copper particles. $R=1$ Å/pulse, $d=5$ cm.

Given the above conditions, the transient temperature field in the substrate is calculated. Figure 2(a) shows the maximum surface temperature rise on the silicon and quartz substrate due to the impingement of the carbon particles. Figure 2(b) shows the maximum temperature rises due to the impingement of copper particles. In case of the carbon particles with mean kinetic energy of 100 eV deposited onto the quartz substrate, the total incident energy, Q_{tot} is 19.1 mJ/cm^2 (1 mJ/cm^2 of energy is the vapor-solid latent heat). The time duration of this energy flux, t_t is approximately 2.4 μs. Such an energy flux causes the surface temperature rise on the quartz substrate to be as high as 100 K. A comparison between Figs. 2(a) and 2(b) illustrates the influences of various experimental conditions on the substrate temperature:

Effect of the kinetic energy of the incident particles: The maximum temperature rise increases almost linearly with the mean kinetic energy of the incident particles. Evidently, an increase of the particle energy increases the total incident energy, Q_{tot} [Eq. (1)]. Further, increasing the particle kinetic energy compresses the time t_t during which the particles

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strike the substrate. A reduction of t_t increases the energy flux $Q(t)$.

Effect of the diffusivity of the substrate material: Among the common substrate materials for PLD, silicon has the highest thermal diffusivity while quartz has the lowest thermal diffusivity. The temperature rise at the substrate surface is approximately inversely proportional to the square root of the thermal diffusivity of the substrate material. Thermal diffusivity of quartz is nearly two orders of magnitude smaller than that of silicon. Therefore, the temperature rise at the quartz surface is about one order of magnitude larger.

Effect of the molecular weight of the incident particles: Comparing Figs. 2(a) and 2(b), it can be seen that deposition of carbon causes a higher surface temperature rise than deposition of copper. This is because lighter molecules (carbon) condense on the substrate in a shorter period of time t_t [Eq. (2)], which causes a higher energy flux.

Effect of the single pulse deposition rate: Due to the linear dependence of the energy flux on the deposition rate [Eqs. (1)–(3)], the maximum temperature rise at the substrate surface increases linearly with the deposition rate.

Effect of the vapor-solid latent heat: Materials with higher vapor-solid latent heat releases more energy when they are condensed. However, the latent heat is about one order of magnitude smaller compared with the kinetic energy of the particles. Kinetic energy of the ablated particles is the major factor for the substrate temperature increase.

Effect of the target-substrate spacing: The target-substrate spacing (taken as 5 cm in the above calculation) affects the total time period during which the particles strike the sample surface [t_t, Eq. (2)]. In a deposition process using a closer target-substrate spacing, the value of t_t is reduced so that the temperature rise of the substrate is higher. Numerical calculation shows that the maximum surface temperature rise is *approximately* proportional to $1/d^2$.

To illustrate the transient temperature profile in the substrate, Fig. 3(a) shows the transient surface temperature of a quartz substrate induced by deposition of the carbon particles with the mean kinetic energy of 100 eV. The surface temperature reaches its maximum in 1.5 μs and drops to half of its maximum in about 2 μs. In a common PLD process, the pulsed laser repitition rate varies between 5 and 100 Hz. Calculation also shows that, within the time duration between two pulses (10 ms) at the highest practical repetition rate (100 Hz), the surface temperature of the target is reduced to about 0.7 K above its initial temperature. The accumulative effect of this temperature increases due to the sustained laser pulses can be offset by a feedback temperature control unit. Shown in Fig. 3(b) is the temperature profile within the quartz substrate under the same experimental conditions. It can be seen that the depth of the regime whose temperature is affected is less than 10 μm.

In summary, a temperature increase at the substrate surface during the pulsed laser deposition of thin films is predicted. For the deposition processes involving highly energetic particles at high deposition rates and utilizing substrates with low thermal diffusivities, the steady-state temperature condition at the substrate surface could be largely disturbed.

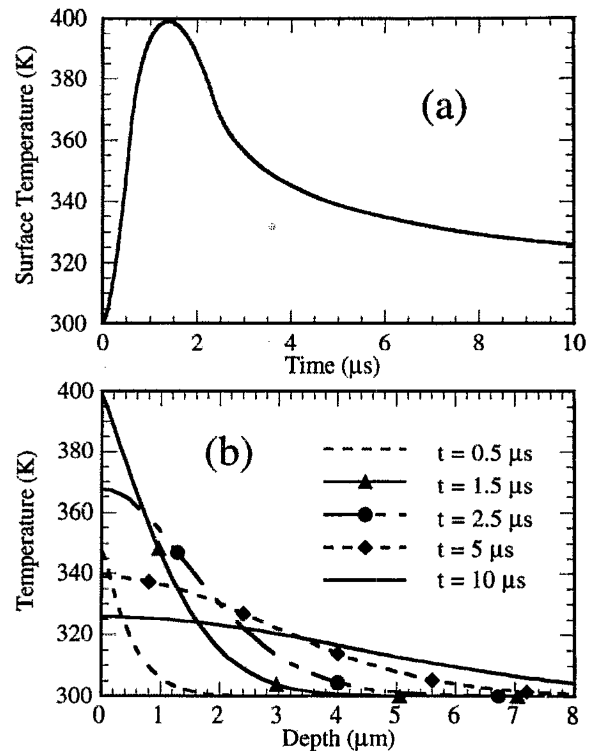

FIG. 3. (a) Transient temperature at the quartz substrate surface and (b) transient temperature profile in the quartz substrate due to the impingement of carbon particles with E_m=100 eV.

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