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# Transient Temperature During the Vaporization of Liquid on a Pulsed Laser-Heated Solid Surface

The thermodynamics of the rapid vaporization of a liquid on a solid surface heated by an excimer laser pulse is studied experimentally. The transient temperature field is measured by monitoring the photothermal reflectance of an embedded thin film in nanosecond time resolution. The transient reflectivity is calibrated by considering a temperature gradient across the sample based on the static measurements of the thin film optical properties at elevated temperatures. The dynamics of bubble nucleation, growth, and collapse is detected by probing the optical specular reflectance. The metastability behavior of the liquid and the criterion for the onset of liquid-vapor phase transition in nanosecond time scale are obtained quantitatively for the first time.

# 1 Introduction

The accurate measurement of temperature of the short-pulsed laser irradiated target is essential for understanding laser beam interaction with materials and assessing the optimal operating parameters in many technical laser applications such as pulsed laser micromachining. There have been a significant number of endeavors to quantify the temperature development during laser irradiation processes. Earlier attempts include the temperature estimate by thermocouples (Dyer and Sindhu, 1985), pyroelectric crystals (Gorodetsky et al., 1985), probing the absorptance change of dye (Lee et al., 1992), and NiSi thermistors (Brunco et al., 1992). These studies aimed at resolving fundamental questions on the physical mechanism of the ultraviolet excimer laser ablation of polymers. The NiSi thermistor was successful in obtaining the time-resolved temperature profile in the polyimide film. The thermistors utilizing the temperature-dependent electrical resistance, however, have a significant drawback, which is the inapplicability to a metallic sample. It is necessary to deposit a layer of electrical insulator between the sample film and the thermistor, which in turn significantly lowers the temperature sensitivity.

The laser beam interaction with materials in a liquid environment exhibits unique characteristics in a variety of technical applications. The explosive vaporization of liquids induced by short-pulsed laser irradiation is utilized in laser cleaning of microcontaminants (Park et al., 1994) and medical laser surgery. The physical understanding of superheated liquids and phase transitions has been sought in order to achieve better control of such applications. The transient development of the bubble nucleation process and the onset of phase change in nanosecond time scale were monitored by simultaneous application of optical reflectance and scattering probes (Yavas et al., 1993). The numerical heat conduction calculation also shows that the solid surface achieves temperatures of tens of degrees of superheat (Yavas et al., 1994). However, no real-time measurement of the surface temperature development in the course parameters in heterogeneous nucleation. Furthermore, thermodynamic considerations such as the degree of superheat in a liquid-vapor transition at the nanosecond time scale have never been addressed. Disturbances by bubbles near the solid surface and the relatively low temperature change have prohibited a precise detection of surface temperature. Recently, it has been demonstrated that probing the transient optical transmission or reflectivity is a fast and reliable method with nanosecond resolution to monitor the temperature field development (Jellison et al., 1986; Lowndes, 1982; Park et al., 1993; Xu et al., 1995). The photothermal reflectance technique is based on the detection of a change of surface reflectivity, i.e., the change of material optical properties, induced by temperature change. It works best for thin film semiconductors due to their large sensitivity of optical properties on temperature (Jellison and Burke, 1986). In this work, the metallic film that provides the laser-induced bubble nucleation sites is combined with a semiconductor film (a temperature sensor) to form a single sample. To this end, a thin semiconductor film is embedded between the metallic top layer and the substrate. The photothermal reflectance probe is thus applied from the backside to the semiconductor film. The backside reflectance probe is not affected by events occurring near the laser-irradiated surface. In addition, the temperature sensitivity can be greatly maximized so that it is successfully implemented for the first time to measure nonintrusively the temperature field development during the rapid vaporization.

of the laser-induced vaporization process has been made, al-

though the surface temperature is one of the most important

## 2 Sample Structure and Fabrication

The solid sample has three layers as shown in Fig. 1(*a*). The top layer is an absorbing film (chromium). The intermediate layer is a thin film optical temperature sensor whose optical properties vary with temperature. The bottom layer is a transparent quartz substrate. Polycrystalline silicon (p-Si) is selected as the optical sensor. The heating source is an ultraviolet (UV) KrF excimer laser ( $\lambda = 248$  nm, pulse width = 16 ns FWHM). Water and methanol are test liquids, which are both transparent to the KrF excimer laser beam. The thickness of the chromium layer is chosen to be greater than the optical penetration depth, 0.01  $\mu$ m, for the excimer laser operating conditions to prevent direct heating of the p-Si layer by the excimer laser. The thickness of the temperature sensor layer has to be carefully designed

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Fig. 1 Schematic of the experimental setup: (a) optical detection scheme and (b) overall view

for optimal temperature sensitivity. It is noted that the change of reflectivity due to the change of refractive index is maximum when the optical thickness *nh* is close to the wavelength (Born and Wolf, 1980). Thus, the sample is composed of a 0.15- $\mu$ m-thick Cr film and 0.35- $\mu$ m-thick p-Si film deposited on a 500- $\mu$ m-thick fused quartz substrate. Figure 2 shows the calculated temperature profile in the sample that is irradiated with the excimer laser at a fluence of 42.2 mJ/cm<sup>2</sup>.

The sample was prepared at the Microfabrication Laboratory of the University of California at Berkeley. The p-Si film was deposited on a fused quartz wafer at 878 K and 300 mTorr in a chemical vapor deposition furnace. Postdeposition annealing of the p-Si film was performed in a nitrogen environment at 1323 K for 30 minutes so as to make the film thermally and optically stable in transient heating experiments. A Nanospec interferometer was used to measure the thickness of the p-Si film. The metallization of chromium on the p-Si film was carried out by argon RF plasma sputtering at 300 W.

The optical properties of the top chromium layer were determined by ellipsometric measurements. It was found that the complex refractive index at  $\lambda = 248$  nm is  $\hat{n} = 1.026 - i \ 1.754$ , which is different from the bulk value,  $\hat{n} = 0.85 - i \ 2.01$  (Palik, 1991). Such a difference is consistent with previous results (Henderson and Weaver, 1966).

# **3** Static Temperature Calibration

The photothermal reflectivity from the backside of the sample is calibrated in a static experiment. In this paper, the backside refers to the quartz side. The front side refers to the chromium film side on which nucleation takes place. The sample is mounted on an aluminum block whose temperature is controlled within  $\pm 0.1$  K. Figure 3 shows the results of the static reflectivity measurement from the backside of the sample. The backside reflectivity is the superposition of contributions from the change of the optical properties of both the p-Si film and the

#### - Nomenclature -

- a = fitting parameter for the conversion of reflectivity to temperature
- b = fitting parameter for the conversion of reflectivity to temperature
- C = constant
- $C_p$  = specific heat at constant pressure
- E = energy
- f = vaporized mass fraction
- F = excimer laser fluence
- h =thickness
- $i = \text{imaginary unit} = \sqrt{-1}$
- k =imaginary part of material refractive index
- K = thermal conductivity
- L = latent heat of vaporization

# **Journal of Heat Transfer**



- n = real part of material refractive in-
- uex
- $\hat{n} = \text{complex refractive index} = n ik$
- N = bubble number density
- p = pressure
- $Q_{ab} =$  laser energy absorption
- $r_c = critical$  bubble radius
- R = bubble radius
- $\Re = reflectivity$
- t = time
- T = temperature
- x = coordinate in the direction normal to the sample surface

- $\alpha_{th}$  = linear thermal expansion coeffi
  - cient
  - $\lambda = \text{laser light wavelength}$
  - $\rho = density$
  - $\sigma$  = surface tension

#### Subscripts

- fs = fringe spacing
- l =liquid
- p-Si = polycrystalline silicon
- qtz = quartz
- sat = saturation property
  - t =liquid-vapor phase transition
- v = vapor
- $\infty = ambient$

480 at 8 ns at 16 ns at 24 ns TEMPERATURE (K) 440 at 40 ns at 100 ns 400 360 320 280 water Cr S quartz 0.4 0 0.8 0.4 1.2 DEPTH (µm)

Fig. 2 Calculated spatial temperature profile at the nucleation threshold of water.  $F = 42.2 \text{ mJ/cm}^2$ 

quartz substrate. The static reflectivity goes through a series of maxima and minima as temperature changes. Such fringe behavior is caused by changes in both the fused quartz refractive index and the p-Si refractive index. The reflectivity goes through a complete (one maximum and one minimum) cycle when the change of optical path length imparted by the temperature change  $\Delta T$  is equal to half of the light wavelength:

$$n(T + \Delta T)h(T + \Delta T) - n(T)h(T) = \lambda/2$$
(1)

The change of the optical path length can be approximated as:

$$a(T + \Delta T)h(T + \Delta T) - n(T)h(T)$$
  
 $\simeq \left(\frac{dn}{dT}\Delta T\right)h + n(\alpha_{th}h\Delta T)$  (2)

The temperature coefficient of refractive index dn/dT for the HeNe probing laser wavelength,  $\lambda = 632.8$  nm, is found from literature to be approximately  $10^{-5}$  for fused quartz (Matlison, 1965) and  $3 \times 10^{-4}$  for p-Si (Xu and Grigoropoulos, 1993). The thermal expansion coefficient  $\alpha_{th}$  is  $5 \times 10^{-7}$  and  $3 \times 10^{-6}$  for fused quartz and silicon, respectively (Touloukian et al., 1975). It is noted that the contribution from the change of path length due to thermal expansion is negligible, i.e.,  $n\alpha_{th} \leq dn/dT$ . Therefore, the temperature increment corresponding to one fringe spacing becomes:



Fig. 3 Measured static reflectivity as a function of temperature; the probe is an unpolarized HeNe laser beam ( $\lambda$  = 632.8 nm) at an incident angle of 15 deg in air

$$(\Delta T)_{fs} = \frac{\lambda}{2(dn/dT)h}$$
(3)

The fringe spacings due to the quartz substrate and the p-Si layer are calculated to be approximately 60 K and 3000 K, respectively. The experimental data in Fig. 3 show good agreement. The heat-affected zone in the substrate during the transient process is confined within a depth of about 1  $\mu$ m. The bulk of the substrate remains at ambient temperature due to low thermal conductivity of quartz. The ensuing change in the optical path length is negligible. Hence, the reflectivity response during transient heating exhibits a monotonic dependence on the temperature of the p-Si layer over a few hundred degree range.

A multiparameter fitting of the static calibration data coupled with thin-film optics (Born and Wolf, 1980; Heavens, 1965) has been utilized to determine the optical properties of the p-Si film and the fused quartz substrate. The following expressions are obtained from fitting measured static reflectivity changes with temperature for the quartz substrate and p-Si film:

$$n_{\text{qtz}} = 1.457 + 9.64 \times 10^{-6} \times (T - 293)$$
  
+  $6.1 \times 10^{-9} \times (T - 293)^2$  (4a)

$$n_{\rm p-Si} = 4.01 + 3.31 \times 10^{-4} \times (T - 293)$$
 (4b)

$$k_{\rm p-Si} = 0.0355 \times \exp\left(\frac{T - 273}{590}\right)$$
 (4c)

where the temperature T is in degrees Kelvin. It is noted that the determined optical properties are close to the literature values (Xu and Grigoropoulos, 1993). The accuracy of the fit is better than 1 percent.

# 4 Modeling of Temperature and Transient Reflectivity Response

The temperature profile penetration is of the order of 1  $\mu$ m, whereas the laser beam spot area on the sample surface is about 1 cm<sup>2</sup>. Accordingly, it may be assumed that the heat transfer at the center of the irradiated area is essentially one-dimensional. Hence, the temperature profile can be calculated using the onedimensional heat diffusion equation:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial T}{\partial x} \right) + Q_{ab}(x, t)$$
(5)

The phase change in the liquid is not considered. The temperature-dependent thermal properties of bulk material are utilized. The error induced by the assumed bulk thermal properties is estimated to be of the order of 10 K. For instance, the peak surface temperature increases from 476 K to 488 K at F = 42.2mJ/cm<sup>2</sup> when the thermal conductivities of both chromium film and silicon film are reduced to 50 percent of bulk values in the calculation. Further details of temperature modeling appear elsewhere (Park et al., 1993; Park, 1994).

At early times when a temperature gradient is present across the sample (see Fig. 2), the static calibration data cannot be used directly to convert reflectivity to temperature. This has been considered by Lompré et al. (1983) in the picosecond laser irradiation of thin c-Si films by assuming an average temperature for the fitting of the measured reflectivity. It can be dealt with more accurately by treating the sample as a stratified multilayer structure of varying complex refractive index (Jacobsson, 1965). Utilizing the formalism of the characteristic transmission matrix, the lumped structure reflectivity and transmissivity can be obtained (Born and Wolf, 1980; Heavens, 1965). The calculated temperature profile is utilized to compute the theoretical reflectivity response. This procedure is also applied in the inverse way to extract the experimental temperature profile T(x, t) from the measured reflectivity, i.e., T(x, t) = $f(x, \Re(t))$ . Figure 4 shows the relation between the surface temperature and normalized reflectivity at various times. Here, the reflectivity is normalized with its initial value, i.e., unity reflectivity at  $t = 0^{-}$  (at room temperature). The use of normalized reflectivity eliminates the procedures for correcting losses at the cuvette windows and the interference filters. It is clearly seen in Fig. 4 that the dependence of the surface temperature on reflectivity differs with time due to the presence of a temperature gradient. The temperature is nearly a linear function of normalized reflectivity,  $\Re(t)/\Re(0)$ :

$$T(x,t) = a(x,t)\frac{\Re(t)}{\Re(0)} + b(x,t)$$
(6)

The fitting parameters a and b are dependent upon the time and the location where the temperature is to be determined.

# 5 Transient Temperature Measurement

The experimental setup is shown in Fig. 1(b). The liquid is contained in a pressure cell (maximum pressure  $\sim 100$  atm). The pressure  $p_l$  of the liquid is varied by applying compressed nitrogen. The KrF excimer laser pulse is directed at normal



Fig. 4 Calculated relation of normalized reflectivity with surface temperature at various times; the sample is immersed in water

704 / Vol. 118, AUGUST 1996

Transactions of the ASME

incidence onto the sample. The spatial uniformity of the excimer laser beam is achieved by the fly's eye-type beam homogenizer and found to be within  $\pm 5$  percent. The laser energy is monitored by a calibrated pyroelectric energy meter. Since the UV-grade quartz window and the liquid (spectroscopic grade) are highly transparent to the excimer laser beam, the absorption and fluorescence losses are ignored.

The behavior of the front side of the sample, i.e., the liquidchromium interface, is also monitored by specular reflectance from its surface. Since the Cr film has no intrinsic thermoreflectance effect within the temperature range used in this work (≤600 K), any change in the optical specular reflectance from the chromium surface is ascribed to the formation of bubbles on the probe beam path. On the other hand, due to the absence of bubbles in the backside, any change on the reflectance from the p-Si layer is caused by only the temperature change. Hence, the temperature and the bubble nucleation behavior can be obtained independently. Previous work utilizing the optical transmission probe (Leung et al., 1992) failed to resolve the temperature and the bubble growth in their optical transmission signal from the liquid film on the amorphous silicon surface. This is because the transient transmission signal carries information from the combined effects of bubble growth and the temperature-induced optical property change in the amorphous silicon film. The specular reflectance from a metallic surface, whose thermoreflectance effect is negligible, can distinguish the bubble growth behavior but does not produce temperature data (Yavas et al., 1993). In this work, a HeNe laser ( $\lambda = 632.8$  nm, unpolarized, incident angle = 15 deg in air) and an Ar<sup>+</sup> laser ( $\lambda$  = 488.0 nm, s-polarized, incident angle = 10-32 deg in liquid) are used as the back-side and front-side reflectance probe, respectively.

Figure 5 shows the results from measurements of the transient temperature and bubble growth at atmospheric pressure for the water/chromium interface for two excimer laser fluences. The bubble growth behavior can be observed from the front-side reflectance signal. As bubbles form and grow on the surface, the specular reflectance shows distinct transient behavior, as seen in the top panels. The signal shown in the figure is an average of five shots of laser pulses. The reflectance increase following the excimer laser pulse is caused by the formation of a thin layer of small embryonic bubbles (Yavas et al., 1993).



Fig. 5 Experimental reflectance curves (solid lines) for water are shown in both top panels for the front-side reflectance and both second panels for the back-side photothermal reflectance. The dotted lines in the second and third panels are calculated transient reflectivity response and surface temperature, respectively. Shown in solid lines in the third panels are resultant surface temperature traces from the measured reflectances. The bottom panels show the excimer laser pulses,  $F = 42.2 \text{ mJ/cm}^2$ (left) and 46.4 mJ/cm<sup>2</sup> (right).

The trailing decrease is due to scattering losses caused by enlarged bubbles. Finally, the slow recovery is due to unconcerted bubble collapse. At the lower excimer laser fluence, the initial increase in the front-side reflectance (top left panel) is rather moderate, indicating the water/chromium interface is barely above the nucleation threshold. The second row panels show the experimental photothermal reflectance curve (solid line) and the theoretical response (dotted line). It is seen that the modeling result closely follows the experimental curve. The measured and calculated evolutions of surface temperature are compared in the third row panels. The measured temperature traces are obtained by deconvoluting the measured reflectance signals following the steps described above. The precision of the temperature measurement can be demonstrated as follows. At the fluence  $F = 42.2 \text{ mJ/cm}^2$ , the measured and calculated peak surface temperatures are 466 K and 476 K, respectively. The difference is within the experimental error. At this condition the measured degree of superheat is 93 K. The delay of the experimental trace as compared with the calculated trace is due in part to the time constants of the electronic data acquisition system. A similar measurement for methanol yields the peak temperature of 430 K at the threshold and hence the degree of superheat of 92 K (boiling point = 337.9 K). It is noted that the nucleation starts instantaneously as the surface temperature exceeds the boiling temperature. The onset of nucleation is manifested as an increase in the front-side reflectance. For instance, the first noticeable change in the front-side reflectance at  $F = 46.4 \text{ mJ/cm}^2$  is detected at t = 13 ns. At this moment, the measured surface temperature is 389 K, only 16 K above the boiling point. For all the conditions tested, this trend remains true. It is therefore concluded that the degree of superheat required for the nucleation of embryos is significantly lower than that for the formation of bubbles. This effect is observed only by simultaneously monitoring time-resolved bubble growth and surface temperature. On the basis of this observation, the dynamics of bubble growth can be understood as follows: Microscopic embryos are nucleated as soon as the surface reaches the boiling condition ("nucleation threshold"). Bubbles can grow in size if sufficient heat is supplied from the surface. When their radii exceed the limit  $R \ge \lambda/2\pi n$ , i.e., about 0.06  $\mu$ m ( $\lambda$ = 488 nm and n = 1.34), scattering losses become much more appreciable and specular reflectance decreases. From the temperature measurements, bubble growth takes place only if the surface temperature is about 100 K above the boiling temperature for water and methanol at atmospheric pressure ("threshold for the onset of bubble growth").

The measured peak surface temperature at atmospheric pressure is plotted as a function of the excimer laser fluence in Fig. 6 for water. The temperature is approximately linear with fluence. The discrepancy between the measurement and calculation arises from the possible departure of thermal properties of thin films from bulk values and the existence of contact resistance between layers. Nevertheless, it can be stated that the technique used in this work can measure the surface temperature with accuracy of 30 K in nanosecond resolution. The different slope of the temperature rise versus fluence between experiment and calculation is in part due to the assumption in the computation that no phase change is taken into account. This is a reasonable assumption, however, because the amount of heat transferred to the solid is predominantly greater than that to the liquid. Therefore, the temperature field is not strongly affected by the occurrence of vaporization and the interface temperature can be well estimated by the simple conduction equation. It is, however, noted that the trend of lower measured temperature compared with the calculated values at higher laser fluence suggests an increasing amount of vaporization at higher temperatures.

## 6 Effect on the Ambient Liquid Pressure

Bubble growth monitoring and transient temperature measurement are also performed at various ambient liquid pressures.

# Journal of Heat Transfer



Fig. 6 The measured peak surface temperature is compared with the calculated surface temperature as a function of laser fluence for water. The nucleation threshold is indicated by arrow. Solid line is a linear fit of experimental data.

The dependences of the front-side reflectance signal and surface temperature on pressure at two fixed excimer laser fluences are shown in Fig. 7 for water. The initial rise of front-side reflectance, occurring during the nucleation of embryos and when the embryo radius  $\ll \lambda/2\pi n$ , i.e., when Rayleigh scattering is predominant, is nearly insensitive to the liquid pressure. This effect shows that surface tension force would dominate at this stage of nucleation. The surface tension  $\sigma$  of water is 0.059 N/ m at boiling point and zero, by definition, at critical temperature (Carey, 1992). However, at pressures exceeding 3.3 MPa, the magnitude of the initial rise decreases, as can be seen from the case of water at  $F = 48.2 \text{ mJ/cm}^2$ . As bubbles grow in size, scattering in the Mie regime becomes dominant and causes a subsequent drop in the front-side specular reflectance. The amplitude of the specular reflectance drop is proportional to the total scattering cross section of bubbles, which is a function of bubble radius and number density (Yavas et al., 1994). It is observed that the amplitude of the reflectance drop decreases with pressure increase, which indicates a smaller total volume of bubbles at a higher pressure. It is also noted that bubble growth and collapse rates are nearly independent of ambient pressure in the pressure range studied.

The fact that a smaller total volume of bubbles is produced at higher pressures is explained by the lower degrees of super-

heat. The measurements show that the maximum surface temperature is independent of pressure at a constant excimer laser fluence. For the case of water at  $F = 54.1 \text{ mJ/cm}^2$  (Fig. 7, right column), the peak surface temperatures are measured to be around 496 K while the boiling point increases from 373 K at 0.101 MPa to 492 K at 2.2 MPa. Hence the degrees of superheat reduce from 123 K at 0.101 MPa to 4 K at 2.2 MPa. There is, therefore, less superheat to drive bubble growth at higher pressures. Consequently, a smaller volume of bubbles is produced. This fact can be well illustrated by comparing the amplitude of reflectance drop with the maximum bubble radius, estimated on the basis of measured surface temperature, i.e., degree of superheat. The bubble growth speed at the liquid inertiacontrolled limit can be estimated by equating the kinetic energy of the flow to the work performed by pressure forces, dR/dt = $((2/3)(p_{\nu} - p_{\infty})/\rho)^{1/2}$ , where  $p_{\nu}$  is the vapor pressure inside the bubble,  $p_{\infty}$  the ambient pressure, and  $\rho$  the liquid density (Carey, 1992). It is noted that this estimate provides an upper bound for the growth velocity (Prosperetti and Plesset, 1978). The vapor pressure  $p_{\nu}$  is approximated by the saturation vapor pressure at the measured peak surface temperature so that the bubble growth speed can be calculated. The front-side reflectance curve provides the duration of bubble growth (excimer laser pulse to the reflectance minimum  $\sim 100 \text{ ns}$ ), which in turn yields the maximum bubble radius from the growth speed. A comparison between the amplitude of reflectance drop and the estimated maximum bubble radius is made in Fig. 8. It is seen that the reflectance drop can be correlated with the maximum bubble radius estimated from the measurements of surface temperature and ambient pressure. The scatter of the data is mainly attributed to the different number density of bubbles.

The pressure dependence of the "bubble-growth threshold" was also examined. This threshold is defined as the minimum fluence for the occurrence of the front-side reflectance signal to become smaller than its pre-laser pulse value, namely, the first appearance of bubbles causing Mie scattering. The peak surface temperature for water at the bubble-growth threshold for each ambient pressure is measured and plotted in Fig. 9. The solid line indicates the saturation curve and the dashed line the limit of superheat (Avedisian, 1985). The area between the saturation curve and the limit of superheat curve is the region of metastable states. The actual superheat in the experiment is the area between the saturation curve and the bubble growth threshold. The measured bubble-growth thresholds (p, T) are represented by symbols and connecting dotted lines. It is observed that the threshold temperature increases with pressure until it merges with the saturation curve at 2.2 MPa. Hence the



Fig. 7 Specular reflectance signals and measured surface temperature transients at various pressure at fixed excimer laser fluences; the probe beam is Ar<sup>+</sup> laser ( $\lambda$  = 488 nm, angle of incidence = 10.5 deg)

706 / Vol. 118, AUGUST 1996



Fig. 8 Relationship between the amplitude of specular reflectance drop and the estimated maximum bubble radius

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Transactions of the ASME



Fig. 9 The bubble-growth threshold temperatures and liquid pressures are identified as symbols  $\bigcirc$  and connecting dotted lines in p-T diagram

degree of superheat required for the bubble growth in nanosecond time scale decreases with pressure and becomes zero near 2.2 MPa. In the case of methanol, the decrease of degree of superheat with pressure is also observed. The spontaneous growth of bubbles is known to depend on the radius of embryonic nuclei ("critical bubble") and cavity centers on the solid surface. The critical bubble radii can be calculated (Carey, 1992) as a function of liquid temperature at various pressures, as shown in Fig. 10. The maximum thickness of superheated liquids (thermal boundary layer) determined from the heat transfer calculation is also shown as a function of peak surface temperature. The comparison between the critical radius and the thickness of superheated liquid indicates that the growth of bubble occurs when the thickness of superheated liquids exceeds the size of critical bubbles. Therefore, the condition for laser-induced vaporization of superheated liquid would be:  $d_{sat}$  $\gtrsim r_c$ , where  $d_{sat}$  is the thickness of superheated liquid layer. This condition implies that the heat transfer from the solid to liquid is a limiting factor for the onset of phase change. It is now clear that the degree of superheat for vaporization, i.e., the quantity  $(T_t - T_{sat})$  in Fig. 10, decreases and approaches zero at high liquid pressures. By assuming that the formation of critical nuclei causes the transition from Rayleigh scattering to



Fig. 10 The critical radius of bubble is plotted as a function of temperature at various liquid pressures (symbols with line) for water. The calculated maximum thickness of superheated water layer on a solid surface is also plotted. The boiling point  $T_{\rm sat}$  and the phase transition temperature  $T_{\rm r}$  are located by arrows.

#### **Journal of Heat Transfer**



Fig. 11 Measured peak surface temperature as a function of liquid pressure at a fixed laser fluence; dotted lines are linear fits of experimental data

Mie scattering, the radius of nucleus can also be estimated by the scattering transition size,  $R \equiv \lambda/2\pi n = 0.06 \ \mu\text{m}$ . This estimate is comparable to the calculated radius at the bubblegrowth threshold (see Fig. 10). It is noted that the critical radius concept is derived on the basis of the assumptions of chemical or mechanical equilibrium (Carey, 1992; Kagan, 1960) and may not be valid in the nanosecond time scale.

The temporal signatures of the photothermal reflectance show little difference upon the change of pressure as shown in the bottom of Fig. 7. The peak temperature, however, increases slightly with pressure as plotted in Fig. 11. The arrows in the figure indicate the bubble growth threshold, i.e., bubble growth does not takes place when  $p > p_t$ . The dotted line is a linear curve fit of experimental data illustrating the trend of a slight increase of peak surface temperature. This can be explained by the lower conversion of the absorbed energy to the latent heat of vaporization as bubble growth is suppressed at higher pressure. The total content of (thermal) energy in the system is:

$$E = \int_{-\infty}^{\infty} \int_{T_{\infty}}^{T_n(x)} (\rho C_p)_n dT dx$$
<sup>(7)</sup>

where the subscript n denotes liquid, chromium, p-Si, and quartz. The integral has to be evaluated for each material. When a mass of m kg of liquid is transformed to vapor, the total content of energy in the system is:

$$E' = \int_{-\infty}^{\infty} \int_{T_{\infty}}^{T'_{n}(x)} (\rho C_{\rho})_{n} dT dx + mL + \sum_{n=1}^{N} 4\pi \sigma R^{2}$$
(8)

where the first term gives the sensible heat, the second the latent heat of vaporization, and the third the energy of bubble surface formation. At the same excimer laser fluence, the contents of energy for two cases, with and without bubble formation, have to be the same as predicted by the energy conservation, i.e., E = E', neglecting kinetic energy. It is assumed that the work for bubble surface formation is negligible since the radius of bubbles is very small. Then by knowing the temperature difference T(x) - T'(x), the total mass of vapor can be obtained by:

$$m = \frac{1}{L} \int_{-\infty}^{\infty} (\rho C_{\rho})_{n} \{ T_{n}(x) - T'_{n}(x) \} dx$$
(9)

It is assumed that the temperature field is not grossly disturbed by the bubble formation. Thus, the spatial shape of the temperature is the same, i.e.,  $T'(x) - T_{\infty} = C(T(x) - T_{\infty})$ , where the constant C is a function of time and pressure. The experimen-

AUGUST 1996, Vol. 118 / 707

tally determined C values are used to estimate the vaporized mass m:

$$m = \frac{1-C}{L}E\tag{10}$$

The accuracy of the temperature measurement (~30 K) does not allow the exact evaluation of *m*. However, a typical value of temperature difference between the peak temperature at atmospheric pressure and that at elevated pressure where no vaporization is detected can be extracted from the fitting curves in Fig. 11. Thus  $\Delta T = T - T'$  is estimated at 10 K for the case of water and consequently the vaporized mass is calculated to be 0.006 g/m<sup>2</sup>. The total mass of superheated liquid per unit area is  $\rho d_{sat} = 0.089$  g/m<sup>2</sup>. The vaporized mass fraction is therefore f = 0.067; only 6.7 percent of superheated liquid undergoes phase transition. It is noted that improvement in the accuracy of the temperature measurement is necessary for more precise estimate of vaporized mass.

# 7 Conclusion

The experiments described in this work investigate the thermodynamics of phase transformations of liquids on a solid surface heated by a short laser pulse at the nanosecond time scale. A novel photothermal reflectance probe is developed with specially fabricated samples. Static measurements of temperaturedependent reflectivity from the embedded optical sensor film have been performed. Transient conversion of reflectivity to temperature is achieved by accounting for the temperature gradient inside the sample on the basis of the calculated spatial temperature profiles. The time-dependent calibration of reflectivity enables measurement of temperature in nanosecond time resolution with 30 K accuracy. It has been found that embryonic nucleation begins as the surface reaches the boiling temperature ("nucleation threshold") but bubble growth is not initiated until higher surface temperature is attained ("bubble growth threshold"). The bubble growth threshold requires surface temperatures up to 100 K higher than the boiling temperature. The total scattering cross section of bubbles, obtained optically from the front-side reflectance drop, correlates well with the maximum bubble radius, which is estimated using thermodynamic considerations and transient surface temperature measurement data. An investigation on the threshold temperature as a function of pressure reveals a criterion for the onset of bubble growth. The radius of the embryonic bubbles for the onset of bubble growth is found to scale with the thermal boundary layer thickness in the liquid. The comparison of surface temperature with and without bubble formation, i.e., at low and at high pressures, at the same laser energy results in an estimate of the vaporized mass, which is of the order of 1 percent.

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