9-2006

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Scholarly Commons Citation

Kudryashov, S. I., Lyon, K., Shukla, S. D., Murry, D., & Allen, S. D. (2006). Laser Ablation of Optically Thin Absorbing Liquid Layer Predeposited onto a Transparent Solid Substrate. *Journal of Applied Physics, 100*(5). https://doi.org/10.1063/1.2338827

Laser ablation of optically thin absorbing liquid layer predeposited onto a transparent solid substrate

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(Received 6 April 2006; accepted 6 June 2006; published online 13 September 2006)

Ablation of optically thin liquid 2-propanol layers of variable thickness on IR-transparent solid Si substrate by a nanosecond CO_2 laser has been experimentally studied using time-resolved optical interferometric and microscopy techniques. Basic ablation parameters—threshold fluences for surface vaporization and explosive homogeneous boiling of the superheated liquid, ablation depths, vaporization (ablation) rates, and characteristic ablation times versus laser fluence—were measured as a function of alcohol layer thickness. The underlying ablation mechanisms, their thermodynamics, and microscopic details are discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338827]

Laser ablation of bulk weakly absorbing materials and, in particular, liquids has been intensively studied during the past several years because of fundamental physical character (see the related theoretical problems of subsurface temperature distribution,[1,2] kinetics and thermodynamics of near-spinodal explosive boiling,[3,4] and hydrodynamics of ablation products in the form of vapor-droplet mixture[4,5]) and various, mostly biomedical applications in surgical laser ablation of tissues.[6] Optical imaging studies have revealed the sudden onset of explosive boiling and subsequent dynamics of vapor bubbles,[4,5] visualized on a microscopic level in molecular dynamics simulations,[7,8] while photoacoustic measurements provided fluence dependences of thermoacoustic and vapor pressure amplitudes.[9] However, the most important characteristics of laser ablation of bulk absorbing liquids—ablated volume (mass), vaporization rate or ablated (crater) depth per laser shot—were experimentally measured only *indirectly* as *average* values by studying transport of ablation products during multishot exposures.[10] The corresponding experimental techniques are complicated by condensation of vaporized matter and/or redeposition of removed liquid droplets or fragments. As a result, fundamental relationships between amount of ablated material and laser fluence have not yet been established experimentally and, thus, mass transport has not been related to well-known ablation mechanisms such as surface vaporization and fast (explosive) homogeneous boiling.[1–9] In this work we report use of a time-resolved optical interferometric technique to measure with a subwavelength precision crater depths produced after each laser shot in micron-thick absorbing liquid 2-propanol layers predeposited onto IR-transparent solid Si substrates and ablated by radiation of nanosecond transversely excited atmospheric (TEA) CO_2 laser. These and auxiliary time-resolved optical microscopy experiments allowed to obtain basic laser ablation parameters—surface vaporization and explosive boiling thresholds, and ablation depths—as functions of laser fluence and thickness of liquid layers and provide detailed and consistent phenomenological interpretation of the underlying basic ablation mechanisms.

A 10.6 μm TEA CO_2 laser beam (Lumonics 100-2, TEM_{00}, 0.1 J/pulse, with an initial 70 ns [full width at half maximum (FWHM)] spike storing about $\gamma_1 \approx 50\%$ of the total energy, accompanied by a 0.6 μs long tail, repetition rate of 1 Hz, vertical polarization) was focused by a ZnSe spherical lens (focal distance $L=10$ cm, Gaussian focal spot radius $\sigma_{1/e} \approx 0.2$ mm) at an angle of 67° onto a free surface of thin liquid layers of 2-propanol (isopropyl alcohol, IPA, research grade, Fisher) predeposited onto 0.25 mm thick, IR-transparent commercial atomically smooth Si wafers (Motorola). Laser energy was varied using a number of clear polyethylene plastic sheets (20% attenuation per piece) and was measured in each pulse by splitting off a part of the beam to a pyroelectric detector with digital readout (Gentec ED-500).

A dosing system described elsewhere[11] consisted of a source of pressurized nitrogen gas with a triggered valve, connected to a bubbler immersed in a glass flask filled with heated IPA and directed onto the Si surface through a heated output nozzle. The dosing system (gas pressure of 0.7 bar, flask and nozzle temperatures of 50 °C, and dosing pulse of 0.1–0.5 s) was employed to deposit a homogeneous liquid layer of a variable thickness $L=0.2-3.5$ μm onto the Si wafer placed at a distance of 5 cm from the nozzle. The heating laser was fired 0.1 s after the end of each deposition step. The gas valve and laser were triggered manually in a single-shot mode with the corresponding delays using a pulse generator (Stanford Research Systems DG 535). Deposition and ablation of the IPA liquid layer were measured in real time by recording the transient interference fringes of optical reflectance, $R_S(\lambda \approx 633\ \text{nm}, 48°)$, of an *s*-polarized HeNe laser beam focused on the center of the irradiated area at an angle of incidence $\varphi \approx 48°$ and detected by a fast photodiode and LeCroy storage oscilloscope (Wavepro 940). While the same number of fringes was observed during dosing (S) and drying (S^*) stages in the absence of laser ablation ($S=S^*$), $S > S^*$ when the heating laser was fired after the end of the dosing stage [Fig. 1(a)]. Thickness of the initial and final

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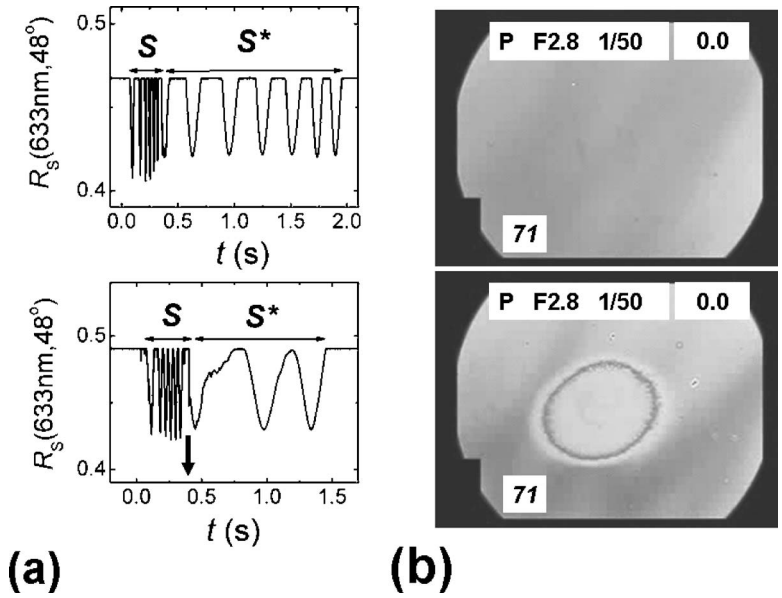

FIG. 1. (a) Transient interference fringes of reflectivity R_S (633 nm, 48°) in a liquid IPA layer onto a Si wafer for the dosing time of 0.5 s with (bottom) and without (top) the heating laser fired (the arrow shows the laser firing moment); (b) transient images of IPA layers onto a Si wafer before (top) and right after (bottom) the heating laser pulse at $F \approx 2.3$ J/cm^2 and $L \approx 1.5$ μm (frame size 310×240 μm^2).

(after ablation) IPA layers L and L^*, respectively, was calculated using the inverted interference maxima condition $L^{(*)} = (\lambda \cos \varphi / 2n_{\mathrm{IPA}})S^{(*)}$ and refractive indices of IPA and solid Si, $n_{\mathrm{IPA}}(10.6\ \mu\mathrm{m}) \approx 1.37$ (Refs. 12 and 13) and $n_{\mathrm{Si}}(10.6\ \mu\mathrm{m}) \approx 3.42$,[14] respectively. Ablation of the IPA layers was visualized using time-resolved optical microscopy. Movies of evolution of the IPA layers on the Si substrate placed on a two-dimensional (2D) stage of a Mitutoyo Wide Field-high eyepoint (WH) microscope equipped with a digital camera (Olympus 3030) were taken at a rate of 30 frames/s and magnification of 400× and analyzed using WINDOWS MOVIE MAKER graphics software frame by frame [Fig. 1(b)]. Due to the limited (33 ms/frame) time resolution, these movies do not show dynamics of ablative removal, but demonstrate transient ablation craters in the liquid layers [see the bright and sharp spot in the center of the bottom image in Fig. 1(b) as an example of a transient crater in the IPA liquid layer] persisting during several subsequent 33 ms capture intervals after each laser shot for the relatively slow liquid IPA transport on the Si surface.

In the interferometric measurements, the ablated depth, $\Delta L = L - L^*$, demonstrates for $L \approx 0.2-3.5$ μm no observable ablation for laser fluences $F \leqslant F_{B0} = 0.6 \pm 0.1$ J/cm^2 [Fig. 2(a)], and then a sharp increase of ΔL at $F \geqslant F_{B0}$ terminated by the abrupt saturation of all $\Delta L(F)$ curves at a plateau level, $\Delta L_{\mathrm{pl}} < L$, for $F \geqslant F_{B1(\mathrm{inter})} \approx 1.3 \pm 0.1$ J/cm$^2 \approx 2F_{B0}$.

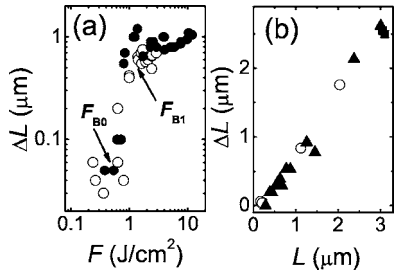

FIG. 2. (a) Ablated depth ΔL vs F for $L \approx 0.9$ (open circles) and 1.2 (dark circles) μm; (b) ΔL vs L for $F \approx 1.2$ (dark squares), 2.2 (open circles), and 5.5 (dark triangles) J/cm^2.

Similar ablation threshold, $F_{B1(\mathrm{imag})} = 1.1 \pm 0.2$ J/cm^2, was independently and directly measured for transient craters in the IPA liquid layers of variable thickness from time-resolved optical microscopy experiments [Fig. 1(b)]. Moreover, studies of ΔL_{pl} as a function of L at various $F \approx 1.2$, 2.2 and 5.5 J/cm$^2 \geqslant F_{B1(\mathrm{imag,inter})}$ showed its linear increase with the slope $K = 0.9 \pm 0.1$ and positive offset $L_0 \approx 0.2$ μm [Fig. 2(b)].

From an energy balance analysis, laser irradiation of an optically thin weakly absorbing IPA layer with the fluence F_{B0} provides at the end of the laser pulse a volume energy density within the layer $\varepsilon_0 \approx A(L)F_{B0}/L \approx 1.2 \times 10^2$ J/cm^3 calculated using the IPA/Si thin-film absorptivity $A(L) \approx 0.02$ (Ref. 15 for $L \approx 0.9-1.2$ μm [Fig. 2(a)] at the 10.6 μm wavelength, the angle of incidence 67°, IPA and Si optical constants from the literature,[12–14] and $C_p \approx 2$ J/K cm^3 for the IPA isobaric heat capacity.[13] The ε_0 value corresponds to an IPA surface temperature $T_S = T_0 \approx 2.9 \times 10^2$ K$+\varepsilon_0/C_p \approx 3.6 \times 10^2$ K, which is very close to its normal boiling temperature $T_{\mathrm{boil}} \approx 355$ K,[13] indicating onset of IPA surface vaporization at $F \geqslant F_{B0}$. If we assume that the IPA surface temperature increases nearly linearly versus F at $F \geqslant F_{B0}$ (neglecting surface evaporative cooling), then the plot of ΔL versus F may replicate in the range $F_{B0} \leqslant F \leqslant F_{B1(\mathrm{imag,inter})}$, the corresponding fragment of the IPA binode curve, as surface vaporization rate and the related integral value ΔL increase proportionally to the saturated IPA vapor pressure $P_{\mathrm{sat}}(T_S)$.

As a result, in the fluence range $F_{B0} \leqslant F \leqslant F_{B1(\mathrm{imag,inter})}$ surface vaporization should eventually merge with explosive boiling under thermal confinement conditions,[7] providing laser ablation via expulsion of vapor/droplet mixture.[4,5,7] The explosive boiling process may start at F close to $F_{B1(\mathrm{imag,inter})} = 1.1-1.3$ J/cm^2 corresponding to estimates for the volume energy density $\varepsilon_1 \approx (2.7 \pm 0.2) \times 10^2$ J/cm^3 [for the same value of $A(L)$] and surface temperature $T_1 \approx 2.9 \times 10^2$ K$+\varepsilon_1/C_p \approx (4.3 \pm 0.1) \times 10^2$ K, where T_1 approaches liquid/vapor spinode temperatures $(0.9-1)T_{\mathrm{cr}} \approx (4.5-5)$

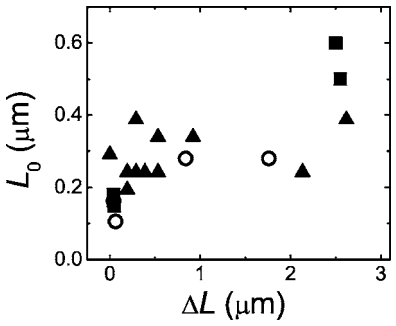

FIG. 3. Offset L_0 vs ΔL for $F \approx 1.2$ (dark squares), 2.2 (open circles), and 5.5 J/cm^2 (dark triangles).

$\times 10^2$ K at positive external pressures[16] for the critical temperature of IPA $T_{cr} \approx 508$ K.[13] Since IPA is weakly absorbing at 10.6 μm [the IPA skin depth $\delta(10.6\ \mu\text{m}) \approx 50\ \mu$m (Ref. 12)], it should explosively boil at $F \geqslant F_{B1}$ over the depth on an order of $\delta \gg L > \Delta L_{pl}$, exhibiting complete removal of the predeposited optically thin IPA layers at the *single* threshold F_{B1} [see coinciding curves in Fig. 2(a) and the linear unity slope of $\Delta L_{pl}(L)$ curve in Fig. 2(b)] and the maximum ablation depth ΔL approaching δ. Note that complete surface vaporization of the IPA layers during the laser pulse could be realized only for much higher, *L-dependent* laser fluences $F_{vap}(L) \approx (\varepsilon_0 + \lambda_{vap})L/A(L) > F_{B1}$ for $\varepsilon_0 + \lambda_{vap} > \varepsilon_1$, where the value $\varepsilon_0 + \lambda_{vap} \approx 6.5 \times 10^2$ J/cm^3 is the minimum volume energy density of IPA vaporization at the normal boiling temperature and the latent vaporization enthalpy of IPA $\lambda_{vap} \approx 5.3 \times 10^2$ J/cm^3.[13]

Surprisingly, there is a dependence of the parameter L_0 on ΔL (or L) at different laser fluences (Fig. 3). The presence of the corresponding residual thin IPA sublayer ($L_0 \ll L$) is yet to be understood requiring its studies by other experimental means; one potential explanation could be cooling of the IPA sublayer below T_1 via heat conduction to the cooler transparent Si substrate over the ablation time of the superheated IPA layers.

In conclusion, we have measured basic laser ablation parameters-threshold fluences for surface vaporization and explosive homogeneous boiling and characteristic ablation depths—for optically thin liquid 2-propanol layers of variable thickness on IR-transparent solid Si substrate irradiated by a TEA CO_2 laser and interpreted them in terms of the underlying ablation (surface vaporization and explosive boiling) mechanisms.

The authors are grateful to Dr. Alexander Samokhin (General Physics Institute, Moscow) for useful discussions and National Science Foundation for financial support (Grant No. 0218024).

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