Optical and Acoustic Study of Nucleation and Growth of Bubbles at a Liquid-Solid Interface Induced by Nanosecond-Pulsed-Laser Heating

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Abstract. The dynamics of liquid-vapor phase-change in the nanosecond time-scale induced by pulsed-laser heating of a liquid on a solid sample is studied by means of optical reflectance and scattering measurements, and the piezoelectric detection technique. The liquids studied include water, ethanol, methanol, IsoproPropyl Alcohol (IPA), and mixtures of water and IPA. The threshold fluence for nucleation is determined with high accuracy using the optical and acoustic signals. Heat diffusion calculations performed for the threshold fluences indicate that the liquids are sufficiently superheated before nucleation sets on. The transient optical reflectance signal is analyzed by an effective-medium theory to provide bubble-growth kinetics, so that the bubble-growth velocity for the test liquids could be estimated. In addition, it is observed that, following the thermally induced nucleation, repetitive acoustic cavitation at the surface of the solid sample occurs, with a time interval related to the speed of sound in the liquid.

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The science of the metastability behavior of superheated pure or mixed liquids is well established only in the near-steady-state regime with a time scale of microseconds or longer [1–4]. In the much faster regime with a time-scale of nanoseconds, superheated liquids may have different behavior, including the limit of the superheat, bubble nucleation and growth kinetics, and heterogeneous nucleation process at a surface. Such behaviors in the fast regime have not been investigated, because the traditional experimental techniques, such as short-pulsed electrical-current heating [1] and bubble column apparatus [5], lack speed and sensitivity. Recently, we have used pulsed-laser heating to produce faster superheating of liquids in the nanosecond-time-scale. In pulsed-laser heating the liquid can be heated directly if it is absorptive at the laser wavelength, as has been the approach in the heating of a liquid with the free surface in a container [6], or in the studies of explosive vaporization of aerosol droplets by CO₂ lasers [7, 8]. Alternatively, the

liquid can be heated indirectly if it is transparent to the laser wavelength but is in contact with an opaque solid sample which absorbs the laser light. Recently, it was observed that this kind of liquid evaporation can be efficiently used to remove submicron-sized particles from solid surfaces [9, 10]. Due to the practical significance of this “steam laser cleaning”, many physical aspects such as nucleation dynamics, explosion thresholds for different liquids and substrates, and the pressures generated by the evaporation process need detailed investigation. Various methods including piezoelectric detection [11], optical transmission probe [12, 13], and probe-beam deflection [14] have been applied previously to the studies of these phenomena with some experimental restrictions.

A more general method for the study of nucleation and growth of bubbles at a liquid-solid interface is the optical reflectance probe, which can be applied to opaque solid samples of any thickness. Recently, we have reported for the first time that the threshold fluence for nucleation could accurately be determined from the optical reflectance transients, which could also be analyzed by an effective-medium theory to provide bubble-growth dynamics [15]. Here, we present, in addition to the optical reflectance and scattering monitoring, the simultaneous application of the piezoelectric transducer measurements to the study of nucleation dynamics and explosive vaporization of various liquids on an opaque solid sample that is flash heated by a short laser pulse. In an analogy to the reflectance signal, it is also observed that the transient acoustic signal exhibits a threshold behavior which confirms bubble nucleation. Furthermore it is observed that the pressure wave generated by the liquid explosion causes repetitive cavitations at the surface of the solid sample.

1 Experimental Arrangement and Procedure

The experimental setup is shown in Fig. 1. The liquid is filled in a cuvette made of fused quartz. The dimensions of the cuvette are chosen so as to minimize possible lensing effects and free surface effects of the liquid. The solid sample is mounted on a massive aluminum block immersed

Fig. 1. Experimental setup for the measurement of optical reflectance and scattering, and acoustic resonance signal to probe the nucleation and growth of bubbles at a liquid-solid interface induced by pulsed 248 nm KrF-excimer-laser heating

entirely into the liquid. The 248 nm KrF-excimer laser pulse (FWHM ~ 16 ns) is directed at normal incidence onto the sample and irradiates a relatively large area ($1 \text{ cm} \times 1 \text{ cm}$). The probe beam is directed to the center of this area at an angle of incidence adjustable from 7° to 46° . The specularly reflected and the scattered light, and the acoustic signal can be detected simultaneously by fast photodetectors (rise time < 1 ns) and by a piezoelectric transducer (bandwidth 20 MHz). A thin liquid film (~ 0.5 mm thick) couples the transducer acoustically to the sample. All the signals are monitored on a digital storage oscilloscope (Tektronix TDS540) triggered by the excimer-laser pulse. Several liquids including water, IPA, ethanol, methanol, and mixtures of water and IPA have been studied. The absorbing solid sample was at first a $0.2 \mu\text{m}$ thick amorphous silicon film on a quartz substrate; the optical properties of amorphous silicon are temperature-dependent making the analysis of the data quite cumbersome. Therefore $0.2 \mu\text{m}$ thick chromium films on a sapphire substrate ($250 \mu\text{m}$ thick) have been used for the present studies, because the optical properties of chromium are expected to be insensitive to the induced temperature changes. Sapphire was chosen as a substrate due to its high thermal conductivity causing a rapid cooling of the chromium film and limiting the time for superheating the liquid to tens of nanoseconds. By performing a careful position-sensing experiment using a photodetector of a large area ($5 \text{ mm} \times 5 \text{ mm}$), a bicell, and a knife edge, we have verified that there is no measurable contribution to the reflectance signal due to any probe-beam deflection. Accordingly, any change on the reflectance signal can be ascribed to nucleation and growth of bubbles at the liquid-solid interface.

2 Experimental Results and Discussion

2.1 Optical Reflectance Measurements

The experiment is first conducted by irradiating the chromium sample in air using excimer-laser fluences up to 100 mJ/cm^2 . No change in the reflectance signal is observed, indicating that the optical properties of the chromium

film are temperature-independent in the present temperature range. The computations based on the heat diffusion equation result in a peak temperature of 711 K for this highest applied fluence of 100 mJ/cm^2 (see Sect. 3). When the experiment is conducted with liquid in the cuvette, the reflectance signal shows distinct transients above a certain liquid-dependent threshold fluence. Figure 2 shows one set of the transient reflectance signals with increasing excimer-laser fluence for IPA and water, where the probe beam of a 752 nm diode laser is s-polarized and incident at an angle of 7° . Similar transients with minor differences are obtained for all the investigated liquids. The shape of the reflectance signal depends on the angle of incidence and the polarization of the probe beam. When the angle of incidence is small ($< 40^\circ$) the same shape for the transient reflectance signal is observed both for s- and p-polarized probe beam: an abrupt reflectance increase followed by a more gradual dip. When the angle of incidence exceeds 40° , however, the leading positive part of

Fig. 2a, b. Transient reflectance signal with increasing excimer laser fluence for $0.2 \mu\text{m}$ chromium film, $\lambda_{\text{probe}} = 752 \text{ nm}$, s-polarized, $\theta = 7^\circ$. a IPA, b water

Fig. 3. Transient reflectance signal with increasing excimer-laser fluence for IPA in contact with a $0.2 \mu\text{m}$ chromium film, $\lambda_{\text{probe}} = 752 \text{ nm}$, p -polarized, $\theta = 46^\circ$

Fig. 4. Transient reflectance (top curve) and scattering (middle curve) signals for IPA measured simultaneously. $\lambda_{\text{probe}} = 633 \text{ nm}$, unpolarized, $\theta = 20^\circ$. Lower curve represents the KrF-excimer pulse ($F = 32 \text{ mJ/cm}^2$)

the signal is only observable for the s -polarized probe beam. The result for the p -polarized probe beam incident at an angle of 46° is shown in Fig. 3, for IPA as a test liquid. Note that the time for the signal to return to the initial reflectance level before heating is comparable to that in Fig. 2, with the only difference that the initial peak is not observed. Previous studies using the optical transmission probe have already indicated that above a certain threshold fluence bubble nucleation at the liquid-solid interface occurs causing light scattering and a subsequent decrease of the transient transmission signal [12]. The same argument holds also for

the reflectance signal decrease. This is well confirmed by the results of the simultaneous measurements of the specular reflectance and scattered light as shown in Fig. 4. The probe beam is unpolarized and the angle of incidence is 20° . The scattered light is collected with the help of two short focal length lenses with a collection angle of about 50° from the forward direction (see Fig. 1). The increase of the scattering signal is in coincidence with the decrease of the specular reflectance signal. The initial increasing peak of the reflectance signal, on the other hand, seems at first sight to be inconsistent with the above argument. It could, however, be explained by means of the effective-medium theory by Maxwell-Garnett [16] which will be discussed in detail in the Sect. 2.4.

2.2 Piezoelectric Transducer Measurements

The change in the reflectance signal is accompanied by a sudden increase of the amplitude of the acoustic signal detected by the piezoelectric transducer simultaneously. Figure 5a shows a set of transient acoustic signals for a $0.2 \mu\text{m}$ thick chromium film immersed in IPA. The corresponding optical reflectance signals obtained simultaneously are shown in Fig. 5b. Since the transducer is placed at the non-irradiated side of the sample, the acoustic wave generated at the liquid/Cr interface has to penetrate the chromium film, the sapphire substrate, and the liquid film in order to be detected. Due to the large acoustic impedance mismatch at the Cr/liquid and sapphire/liquid interface (the acoustic impedance, which is given by $Z = \rho c$, with ρ the density of the medium, and c the speed of sound in it, is calculated to be $\sim 10^7$, $\sim 10^7$, and $\sim 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ for chromium, sapphire, and the liquid, respectively) the acoustic wave is strongly reflected at these interfaces [17]. This causes a resonance in the sapphire substrate, which predominantly determines the shape of the transient acoustic signal since resonances in other media are considerably weaker. Thus, the observed frequency of the acoustic signal ($\sim 11 \text{ MHz}$) corresponds to the first fundamental natural frequency of the sapphire substrate [18]. This is calculated to be 11.2 MHz according to the relation

$$\nu_{\text{acou}} = \frac{c_{\text{sapp}}}{4d_{\text{sapp}}},$$

where $c_{\text{sapp}} = 11.2 \times 10^3 \text{ m/s}$, is the velocity of sound in sapphire [19] and $d_{\text{sapp}} = 250 \mu\text{m}$, is the thickness of the sapphire substrate in the present studies. At low laser fluences the acoustic wave is generated thermo-elastically [11, 14] and its amplitude increases in direct relation to the induced temperature at the sample surface. When the laser fluence exceeds the nucleation threshold, however, the amplitude of the acoustic wave is increased by an additional amount due to the explosive bubble growth and collapse. The generation of strong pressure due to bubble collapse, often causing undesired cavitation damage on technical equipment, such as propeller blades, pumps, and hydraulic machines, is known for many years [20] and can also be used to remove particulate contaminants from solid surfaces (ultrasonic and megasonic cleaning) [21].

Fig. 5. a Transient acoustic signals for a 0.2 μm thick chromium film immersed in IPA induced by 248 nm KrF-excimer-laser irradiation (FWHM ~16 ns) for various laser fluences. b The simultaneously observed optical reflectance signals, $\lambda_{\text{probe}} = 633$ nm, p -polarized, $\theta = 45^\circ$

2.3 Correlation between the Optical Reflectance Transients and Bubble Growth

The experimental results can be explained by the following physical picture: a uniform layer of bubbles is created at the surface of the chromium film when it is suddenly heated above the saturation temperature of the liquid. Due to the fast heating process, superheating above the boiling point is expected, until nucleation of bubbles sets in at a “cloud point”, which marks the limit of supersaturation, as it is similarly observed during phase separation in a supersaturated fluid [22]. Initially, the radius of the bubbles scales with the surface roughness of the chromium film and is much smaller than the probe beam wavelength. At this stage, the bubble growth is inertia-controlled [1, 23] and the bubbles start to grow almost instantaneously without any significant time delay. An estimate of the time delay for the bubble growth by considering simple momentum balance between pressure force and inertia force [23], and by assuming that the liquid is superheated 20 degrees above its boiling point, results in a waiting time < 1 ns, which is below the experimental resolution. In this initial stage of bubble growth, as long as the average bubble radius $R \ll \lambda_{\text{probe}}/2\pi n_{\text{liq}}$, where n_{liq} is the refractive index of the test liquid, Rayleigh scattering dominates [24, 25], and depending on the angle of incidence and polarization of the probe beam an increase or decrease of the reflectance can be observed. At later time when bubbles grow in size, $R \gg \lambda_{\text{probe}}/2\pi n_{\text{liq}}$, Mie scattering becomes important, resulting in a decrease of the specular reflectance. When the bubbles detach from the chromium surface or collapse, the reflectance signal returns to the initial level before heating.

2.4 Modeling of Bubble Growth by an Effective-Medium Theory

The initial stage of bubble growth can be modeled by Maxwell-Garnett’s effective-medium theory [16], where three basic assumptions are needed: the bubbles are spherical, their average size is much smaller than the probe-beam wavelength in liquid, and macroscopically they are distributed uniformly at the interface. With these assump-

tions, the ensemble of small bubbles in a liquid is considered as a medium with an effective dielectric constant:

$$\epsilon_{\text{eff}} = \epsilon_l \left(1 - \frac{3f(\epsilon_l - \epsilon_v)}{2\epsilon_l + \epsilon_v + f(\epsilon_l - \epsilon_v)} \right)$$

where f is the fractional volume of bubbles, and ϵ_l and ϵ_v are the dielectric constants for liquid and vapor, respectively. The effective dielectric constant simply equals to that of the liquid when $f = 0$, i.e. when no bubble is present at the liquid/solid interface. It equals to that of the vapor, when $f = 1$, i.e. when a vapor film is created at the liquid/solid interface. The system is considered as multilayered consisting of a bulk liquid (5 mm thick), a “foamy” liquid film with an effective dielectric constant (0.05–5 μm thick), a chromium

Fig. 6a, b. Computed reflectance based on the effective-medium theory (Maxwell-Garnett) for the system: foamy water film/Cr film/sapphire (0.1 μm/0.2 μm/250 μm). t : thickness of the foamy film. f : fractional volume of the bubbles, $\lambda_{\text{probe}} = 632.8$ nm, a p -polarized, b s -polarized

film (0.2 μm thick), and a sapphire substrate (250 μm thick). Using thin-film optics we have calculated the reflectance for such a system for different angles of incidence, polarizations of the probe beam, and different thickness and bubble content of the foamy film. The optical constants for the bulk-Cr from the literature (at 632.8 nm, $n = 3.57$ and $k = 4.36$) [39] have been used for the calculations. An example of the results for a 0.1 μm thick foamy IPA film and for a probe beam of wavelength 632.8 nm is shown in Fig. 6. The results are in qualitative agreement with the experimental observation: if the angle of incidence of the probe beam is small, i.e. $< 40^\circ$, the reflectance signal increases with increasing fractional volume or initial bubble growth for both s and p -polarization. If the angle of incidence exceeds 40° , however, the reflectance increases for s -polarization, whereas it decreases for p -polarization.

2.5 Estimate of the Bubble-Growth Velocity

It is well known that the transition from Rayleigh to Mie scattering occurs when the bubble radius is roughly in the order of $R_{tr} \equiv \lambda_{\text{probe}}/2\pi n_{\text{liq}}$ [24, 25]. Accordingly, the average bubble-growth velocity can be estimated by assuming that the time of the initial peak in the reflectance signal (considering an s -polarized probe beam) corresponds to the time, t_{tr} , needed for a bubble to grow up to this specific transition radius, R_{tr} . In addition, it is recalled that the bubble radius increases linearly with time during the initial inertia-controlled stage of bubble growth, and increases with the square root of time in the later heat-transfer-controlled stage [23]. We observe $t_{tr} \sim 45$ ns for IPA and ~ 25 ns for water using a 752 nm probe laser (see Fig. 2). For this probe-beam wavelength, R_{tr} corresponds to 87 nm for IPA ($n_{\text{liq}} = 1.38$) [26] and 90 nm for water ($n_{\text{liq}} = 1.33$) [26]. This results in an average bubble-growth velocity of ~ 1.9 m/s for IPA and ~ 3.6 m/s for water. The growth velocities estimated in the same way for the other investigated liquids are also found to be in this range, showing a trend in qualitative agreement with the predictions for the inertia-controlled bubble growth, which is theoretically described by the Rayleigh formulation [23]. The upper limit for it is given by [27]

$$\left(\frac{dR}{dt}\right)_{\text{inertial}} = \left(\frac{2}{3} \frac{p_v(T_\infty) - p_\infty}{\rho}\right)^{1/2},$$

where R is the bubble radius, ρ is the liquid density, $p_v(T_\infty)$ is the vapor pressure at the superheated liquid temperature, and p_∞ is the ambient liquid pressure. The peak temperature at the water/chromium interface induced by an excimer-laser pulse of $F = 27.4$ mJ/cm² (experimentally determined threshold fluence for nucleation of water), for instance, is calculated to be 426 K (see Sect. 3). However, there is a high temperature gradient in the water layer adjacent to the chromium surface and therefore its average temperature could be assumed to be 400 K. The vapor pressure for water at this temperature is 247×10^3 Pa [23], resulting in an inertia-controlled bubble-growth velocity of 10 m/s. It is noted that the Rayleigh formulation for the inertia-controlled bubble growth, which is based on some idealizations [28], had been explored at longer, microsecond time scales [1]. The estimated growth velocities are, however, much smaller

Fig. 7. Temperature profile in the system of water/chromium/sapphire (1 $\mu\text{m}/0.2$ $\mu\text{m}/5$ μm thick) calculated for a 248 nm KrF-excimer-laser of fluence 27.4 mJ/cm² using the numerical solution of the one-dimensional heat diffusion equation. Thermophysical material properties given in Table 1 are used in the computation. The water/chromium interface is at depth = 0 μm

than the velocities observed in experiments for the inertia-controlled stage of homogeneous bubble nucleation. For the homogeneous nucleation of butane, for example, a growth velocity of 14.3 m/s was observed experimentally [29]. In the experiments presented here, bubbles form on the surface of the solid sample and are described by the heterogeneous nucleation theory, which predicts much less superheat for the onset of nucleation compared with the homogeneous nucleation theory [23]. In addition, the bubbles cannot grow beyond a certain radius which is limited by the thickness of the superheated liquid layer at the Cr surface. Thus, except for the very initial phase of growth, bubbles grow as the heat diffuses into the liquid, i.e. the speed of heat diffusion into the liquid limits the bubble-growth velocity. This is confirmed by the results of the numerical computations of the heat diffusion equation as shown in Fig. 7, where the temperature profile in the system of water/Cr/sapphire (1 $\mu\text{m}/0.2$ $\mu\text{m}/5$ μm) is plotted at 16 ns after the onset of the excimer-laser irradiation of $F = 27.4$ mJ/cm², the nucleation threshold fluence for water. It is seen that only a thin layer of about one hundred nanometers of water is superheated at that moment, while the temperature at the water/chromium interface amounts to 426 K.

2.6 Wavelength Dependence of the Transient Reflectance Signal

The above presented interpretation of the reflectance signal is confirmed by probing the same location of the chromium-IPA interface with three lasers of different wavelengths ($\lambda = 488, 632.8$, and 752 nm) under similar conditions, i.e. polarization and angle of incidence. The result shown in Fig. 8 is acquired with s -polarized probe beams incident at an angle of 10° , and for an excimer-laser fluence of 27 mJ/cm². A widening of the initial peak and a shift of its maximum to later times is observed with increasing probe beam wavelength as expected, since the bubble radius $R_{tr} \equiv \lambda_{\text{probe}}/2\pi n_{\text{liq}}$, at which the transition from Rayleigh to Mie scattering occurs, depends linearly on the probe beam wavelength. With the average growth velocity of bubbles

Fig. 8. Comparison of the reflectance transient for IPA at three different probe beam wavelengths. $\lambda_{\text{probe}} = 488$ nm (top), 632.8 nm (middle), and 752 nm (bottom), $\theta = 10^\circ$, s-polarized

for IPA being 1.9 m/s, and the transition radii of 73 nm and 87 nm for the probe beam wavelengths of 632.8 nm and 752 nm, a time delay of 7 ns is expected for the peak position of the two corresponding reflectance signals. The observed value ~ 8 ns is in good agreement with this prediction and supports the proposed interpretation that the optical reflectance transient represents the bubble-growth dynamics.

2.7 Determination of the Threshold Fluence for Nucleation

The threshold fluence for the nucleation can be determined accurately when the amplitude of the reflectance drop is plotted versus the excimer laser fluence. The results for the test liquids are shown in Fig. 9. There is a liquid-dependent threshold fluence above which the reflectance signal suddenly starts to drop. The threshold fluences for the test liquids determined from this plot are listed in Table 1, together with boiling points and the calculated maximum temperatures at the liquid/chromium interface for the corresponding threshold fluences. The procedure of

Fig. 9. Optical reflectance drop vs 248 nm KrF-excimer-laser fluence (FWHM ~ 16 ns) for different liquids in contact with a 0.2 μm thick chromium film. The onset of reflectance drop provides the threshold fluence for nucleation. $\lambda_{\text{probe}} = 632.8$ nm, p-polarized, $\theta = 46^\circ$

Table 1. The experimentally determined 248 nm excimer-laser threshold fluences, F_{th} , for the onset of nucleation for different liquids, the boiling points, bp [23, 26, 30], and the peak temperatures at the liquid/chromium interface, T_{pk} , calculated for the corresponding threshold fluences by the numerical solution of the heat diffusion equation

Liquid	F_{th} [mJ/cm ²]	bp [K]	T_{pk} [K]
Ethanol	14.9	351.5	375
Methanol	15.4	337.9	377
IPA	15.7	355.6	379
50:50 (Water: IPA)	19.1	369.8	390
75:25 (Water: IPA)	23.1	371.9	408
85:15 (Water: IPA)	25.9	372.5	420
Water	27.4	373.2	426

the computation will be discussed in detail in Sect. 3. The nucleation threshold fluences for the test alcohols are found to be in a very narrow range around 15 mJ/cm². On the other hand, the threshold fluence for water (27.4 mJ/cm²) is almost twice as high as those for alcohols, consistent with the higher boiling point of water. The sharp increase of the amplitude of the reflectance drop is followed by a much slower rate of change at about 10 mJ/cm² above the threshold fluence. This observation could be explained by a hypothesis that the bubbles can grow largely enough to agglomerate and build a continuous vapor layer at the solid surface when the superheat is sufficient. It is also possible that the bubble growth beyond a certain point impedes the activation of new nucleation sites. It is further observed that the threshold fluences for water/IPA mixtures do not depend linearly on the alcohol content (volume percent), which is consistent with the fact that the properties of liquid mixtures do not depend linearly on the volume or mole fraction of their constituents [30].

The threshold fluence for nucleation could also be determined from a plot of the acoustic resonance amplitude versus excimer laser fluence. Such a plot for water on the surface of a 0.2 μm thick Cr film irradiated by 248 nm KrF-excimer laser is shown in Fig. 10. Below the threshold fluence for nucleation indicated by an arrow, the acoustic resonance amplitude increases linearly with the excimer-laser fluence since the laser energy is coupled thermo-elastically into the solid sample, i.e. the fast temperature rise at the surface of

Fig. 10. Acoustic resonance amplitude versus 248 nm excimer-laser fluence (FWHM ~ 16 ns) for water in contact with a 0.2 μm thick chromium film. The line is a guide to the eye. The onset of the step indicated by the arrow marks the threshold fluence for nucleation

the solid sample causes a sudden expansion of the irradiated area, resulting in acoustic wave generation [11, 14, 31]. In the case of a bare solid surface this linear dependence remains unchanged for excimer-laser fluences well above the threshold fluence for the onset of phase change in liquids. When liquid is present on the chromium surface, however, and the excimer-laser fluence exceeds the threshold for nucleation, the amplitude of the acoustic wave is additionally increased due to bubble growth and collapse, resulting in a sudden change of the slope of the curve, as seen in Fig. 10, which marks the threshold fluence for nucleation.

2.8 Long-Time Scale Measurements and Repetitive Cavitation

In a longer time scale, it is observed that the reflectance signal drops repeatedly in a certain time interval with decreasing amplitude, as shown in Fig. 11. The time interval between these "echo" signals depends on the distance between the chromium sample and the quartz window of the cuvette and on the speed of sound of the studied liquid. Thus, it corresponds to the time for the round-trip of the acoustic wave from the sample surface to the quartz/liquid interface and back. This kind of "echo" phenomena has been also observed earlier in the pulsed-laser-induced transient phase transformations at the Si-H₂O interface [32]. It is assumed that the first dip is due to bubble formation by superheating of the liquid, while the following echo signals are only due to acoustic cavitation. This assumption is justified by the results of the heat-diffusion calculations, which indicate that the temperature at the liquid/chromium interface is already decreased to room temperature at about 1 μ s after the excimer-laser irradiation, as shown in Fig. 12. The optical properties of water are nearly insensitive to pressure, for

Fig. 11. Optical reflectance signal for ethanol in contact with a 0.2 μ m thick chromium film irradiated by 248 nm KrF-excimer laser (FWHM $\sim$ 16 ns) shows that cavitation takes place at the ethanol/chromium interface after each round-trip of the acoustic pulse in methanol between the chromium sample and the quartz window (distance sample-quartz window $\approx$ 7 mm). The decay in the signal amplitude is caused by attenuation due to diffraction, absorption and reflection losses

Fig. 12. The evolution of temperature at the water/chromium interface calculated for a 248 nm KrF-excimer-laser irradiation of 27.4 mJ/cm² using the numerical solution of the heat diffusion equation by the finite difference method. Thermophysical material properties given in Table 1 are used in the computation

instance, the refractive index of water at $\lambda = 589$ nm increases by only 0.12% as the pressure increases to 100 times the atmospheric pressure [33, 34]. It is therefore concluded that the piezooptical effect or the lensing effect is negligible and the repetitive reflectance drops can be explained only by bubble formation. In addition, for all the echo signals, the acoustic signal is detected sooner by the piezoelectric transducer than the optical reflectance drop, confirming that the echoes of optical signals are caused by bubble formation due to acoustic cavitation. The bubbles giving rise to the initial reflectance drop could also be due partly to superheating and partly to cavitation. In this respect, acoustic cavitation needs to be studied in more detail using specially designed experiments. No reflectance echo is observed when the quartz window is probed. This result can be explained by the possible existence of residual ultramicroscopic bubbles at the irradiated Cr surface [35], which provide themselves as seeds for cavitation, consequently resulting in a lower cavitation threshold. The decrease of the reflectance drop in the successive echo signals is ascribed to the attenuation of the acoustic wave due to diffraction, absorption, and reflection losses. It should be possible to determine the cavitation thresholds for different liquids and solid samples by calibrating the amplitude of the transducer signal for absolute pressure measurements.

3 Temperature Modeling

The temperature at the liquid/chromium interface induced by the excimer-laser pulse is of fundamental interest for a better understanding of the nucleation process. It is expected that the liquid is superheated above the boiling point before nucleation sets on. The temperature profile penetration is of the order of 1 μ m, whereas the laser beam spot area on the sample surface is measured to be about 1 cm². Accordingly, it may be assumed that the heat transfer at the center of the irradiated area is essentially one-dimensional. Hence, we have calculated the temperature profile in the multilayered structures (liquid/chromium/sapphire) using the one-dimensional heat diffusion equation:

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

Table 2. Thermophysical properties of chromium and water [26, 37, 40, 41] used for the heat-diffusion calculations

Material	Property
Chromium	$\rho = 7190 \text{ [kg/m}^3\text{]}$
	$K(T) = 139.79 - 0.16475T \text{ [W/mK]} \quad (273 \text{ K} \leq T < 311 \text{ K})$ $= 77.584 + 8.5188 \times 10^{-2}T - 1.8816 \times 10^{-4}T^2 + 9.0307 \times 10^{-8}T^3 \text{ [W/mK]} \quad (311 \text{ K} \leq T \leq 1100 \text{ K})$
	$C_p(t) = 201.01 + 1.2517T - 1.6586 \times 10^{-3}T^2 + 8.0767 \times 10^{-7}T^3 \text{ [J/kgK]}$
Water	$\rho(T) = 1000 - 7.792 \times 10^{-3}(T - 273.2)^{1.8478} \text{ [kg/m}^3\text{]}$
	$K(T) = -0.33 + 4.92 \times 10^{-3}T - 5.97 \times 10^{-6} \text{ [W/mK]}$
	$C_p(T) = 4169.53 + 1.203 \left(\frac{T - 173.2}{100} \right)^{5.26} + 467.1T^{-0.036(T-273)} \text{ [J/kgK]}$

where z is the coordinate normal to the sample surface into the solid, ρ is the density, T is the temperature, C_p is the specific heat for constant pressure, and K is the thermal conductivity. The temperature dependence of the material thermal properties are considered. The energy absorption, $Q_{ab}(z, t)$, follows an exponential decay in the material:

$$Q_{ab}(z, t) = (1 - \mathcal{R}_{exc})I(t)\alpha e^{-\alpha z},$$

where $\mathcal{R}_{exc}$ is the reflectivity of the quartz window/liquid/chromium sample for the excimer-laser light, I is the incident laser-beam intensity, and α is the absorption coefficient. The heat diffusion equation is solved numerically by the finite-difference method [13, 36]. The optical constants for the thin Cr film used for the computations were determined by ellipsometry measurements (at $\lambda = 248 \text{ nm}$, $n = 1.2$ and $k = 1.55$), which were found to be distinctly different from those for bulk-Cr ($n = 0.85$ and $k = 2.01$) [39]. This is in agreement with the observation that the optical properties of evaporated thin Cr films are, in general, different from those of bulk-Cr [38, 39]. The temperature dependence of the thermophysical properties for bulk-chromium and water are listed in Table 2. It is noted that the thermophysical properties of thin Cr films may be different from those of bulk-Cr. In addition, a simple assumption is made that no phase change in the liquid occurs in the computation. The results of the computations indicate that the liquids are superheated tens of degrees above boiling points before the nucleation sets in. This can be seen in Fig. 12, showing the transient temperature profile at the water/chromium interface calculated for an excimer-laser fluence of $F = 27.4 \text{ mJ/cm}^2$, which corresponds to the nucleation threshold fluence for water; the peak temperature is achieved at 16 ns after the onset of the excimer-laser irradiation and amounts to 426 K. The peak temperatures for the test liquids obtained from the computation results are listed in Table 1, together with the boiling points of the liquids from the literature and the experimentally observed threshold fluences for nucleation, for which the computations were performed. Another important result of the calculations, as already discussed in Sect. 2.3, is that the thickness of the superheated liquid layer is limited to a few hundred nanometers, as expected because of the low thermal conductivity of water.

4 Conclusion

In conclusion, we have demonstrated that the relatively simple optical reflectance probe is a powerful method for the study of nucleation dynamics at a liquid/solid interface in the nanosecond time scale, where the liquid film is superheated via pulsed-laser heating of the contacting solid surface. The excimer-laser threshold fluences for the nucleation of different liquids and liquid mixtures at the surface of a chromium film are determined. In addition the bubble-growth velocity for various test liquids is estimated to be of the order of m/s. Compared to other probe methods it is shown that the optical reflectance technique has a higher sensitivity in detecting the nucleation threshold and has further advantages of the applicability to opaque solid samples of any thickness. The threshold fluence for nucleation could also be determined by piezoelectric transducer measurements in a similar way.

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