Behavior of thin metallic films upon melting with a ns-laser pulse

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ABSTRACT

Thin metal films (Cu, Au, Ni) and thin Si films with different thicknesses on fused silica were irradiated with a ns-pulse from a Nd:YAG-laser ($\lambda=532$ nm, FWHM 7 ns). In this paper we want to focus on the optical properties of an undercooled metallic liquid and the observed dewetting of the thin films. The ongoing processes were monitored *in situ* with ns-time-resolved reflectivity measurements. We determined the thresholds for partial and complete melting of these films. Due to the high cooling rates (up to 10^{11} K/s) different „frozen“ stages of the dewetting phenomenon can be studied in detail with *ex situ* microscopic investigations, e.g. optical microscopy and scanning near field acoustic microscopy. We present measurements which show that we have observed spinodal dewetting of these thin films.

Keywords: thin films, optical properties, undercooled metallic liquid, dewetting, spinodal dewetting, laser annealing.

1. INTRODUCTION

Research on the temperature dependence of the optical properties of metals is a long standing topic. Already from the sixties on detailed studies of the temperature dependence of the optical properties in the solid state were made, whereas for the liquid only data at the melting temperature T_m have been obtained [1,2]. Only since a few years the properties of the liquid have been studied as a function of temperature [3,4], but the data are still sparse. Especially in the range of the undercooled liquid, due to the experimental limitations of the methods used, only a small temperature interval could be investigated. One of the best-studied metallic liquids is liquid silicon due to the industrial interest. Here our group has already contributed to the investigations in the high temperature range with the method of heating with nanosecond laser pulses [5].

In this paper we show that our method of ns-pulse heating of thin metallic films allows to study the molten phase in the high-temperature range above T_m as well as in the highly undercooled regime. In addition we have observed the phenomenon of dewetting which occurs upon long enough melt duration. This is a currently studied topic also in polymer physics [6-9]. We present measurements of dewetting in different stages, which can be well understood within the framework of the theory of spinodal dewetting of thin liquid films [10].

2. EXPERIMENTAL SETUP

The samples used were thin metal films (Cu, Ni, Au) thermally evaporated onto fused silica substrates. The thickness of the investigated films varied between 25 nm and 50 nm. In order to enhance the adhesion we evaporated additionally an intermediate layer of chromium with a thickness of less than 2 nm.

The heating laser was a frequency doubled Q-switched Nd:YAG laser with a pulse length of 7 ns full width at half-maximum and a beam profile close to TEM₀₀. The Nd:YAG pulse, incident nearly perpendicular to the surface, was only mildly focused to a spot diameter of about 1 mm. The laser pulse heats the thin film, and due to the heat flux into the substrate the metal film subsequently cools down on a time scale of some 100 nanoseconds.

Fig. 1: Schematic setup of the experiment. The cw-laser was used to measure *in situ* the changes in the reflectance of the sample upon the action of the laser pulse. L: lens; I: interference filter; PD: PIN photodiode.

To investigate *in situ* the temporal development of the processes initiated by the laser pulse we measured the reflectivity of the sample with a cw HeNe laser ($\lambda = 633 \text{ nm}$, 8 mW) (Fig. 1). This s-polarized laser beam was reflected from the surface at an angle of incidence of 45 degrees. Since it was focused to a $1/e$ -diameter smaller than $25 \mu\text{m}$ variations of the pulse laser intensity across the probed area could be neglected. The reflected intensities of the probe laser were detected by a PIN diode with rise time less than 1 ns and registered by a fast digital storage oscilloscope (HP 54111D). Interference filters in front of the PIN diodes were used to suppress contributions of the annealing pulse to the measured signals. *Ex situ* characterization was carried out by optical microscopy and scanning near field acoustic microscopy [19,20].

3. TIME-RESOLVED MEASUREMENTS

In Fig. 2 typical time-resolved measurements of the reflectivity $R(t)$ of the probe laser are presented for a sample consisting of 40 nm Cu on 1 nm Cr on fused silica. The applied energy density of the pulsed laser increases from Fig 2a to Fig. 2d.

Different scenarios can be distinguished. The top curve 2a corresponds to heating of the metallic film to a temperature of about 1000 K, well below the melting temperature $T_m = 1356 \text{ K}$ of copper. In graph 2b the energy density of 115 mJ/cm^2 leads to partial melting of the Cu film. This means that only a fraction of the film, starting at the free surface, is transformed into the liquid phase. The lower two curves 2c and 2d show $R(t)$ for the case of complete melting of the film. In graph 2d the energy density is significantly higher than in 2c. This leads to a higher maximum temperature and thus to a longer melt duration τ_m , which is also labeled in these two plots. The reflectivity returns to the starting value for all four curves on a longer time scale (not shown here), indicating that the film was not damaged by the laser intensities used in this run.

3.1 Comparison with known optical properties and theory

The data of Figs. 2c and d are again plotted in Fig. 3 for a more detailed consideration, together with horizontal lines which correspond to reflectivity values at the labeled temperature calculated on the basis of optical constants from the literature [1]. Since the absolute values given by different authors for the optical constants vary to some extent [1,11-14] we have taken only the relative changes upon temperature variation for comparison.

At room temperature the reflectivity is about 90.5 %. The laser pulse leads to a heating of the metallic film which causes a decrease in the reflectivity. This can be well understood by the known temperature dependence of the optical constants of the solid. For the liquid, however, only data at the melting temperature are available. Yet the qualitative behavior at the wavelength of the probe laser (632.8 nm) is in agreement with the Drude model [15], which predicts a decrease upon increasing temperature. Thus it is obvious that for the higher energy density in curve 3b compared to 3a a higher temperature, related to a lower minimal reflectivity, is reached. The increase in the reflectivity for $t \geq 10 \text{ ns}$ marks the cooling of the Cu film taking place due to the heat flux into the substrate.

The quench rates reached here are in the range of some 10^{10} K/s . It is obvious that such high quench rates lead to an extreme non-equilibrium condition in the melt and high undercooling can be obtained. From theoretical and experimental investigations [16] one knows that the undercooling can be in the range of several hundred Kelvin. Although liquid metals have been studied already for some time by optical means, to our knowledge the resolution achieved so far had not been sufficient to observe a temperature dependence of the optical properties of an undercooled melt.

Fig. 2: Time-resolved reflectivity of the free surface at $\lambda = 633$ nm under the influence of a laser pulse incident on a sample of 40 nm Cu on 1 nm Cr on fused silica. The qualitative temporal shape of the laser pulse is plotted schematically in each graph and the respective energy density is given in the lower right corner of the graphs. The arrows in the last two plots mark the onset of solidification.

Fig. 3: Comparison of the reflectivity with calculated values for optical constants taken from the literature. The last two curves of Fig. 2 are plotted, which correspond to complete melting of the thin Cu film. Horizontal lines indicate the calculated reflectivity at the labelled temperature, where $T_m = 1356$ K is the melting temperature of Cu. The unidirectional arrows mark the onset of solidification.

The maximum undercooling is reached at that time when resolidification sets in. This point can be clearly identified by the kink in the reflectivity which is marked with an unidirectional arrow at both curves in Fig. 3.

The obvious difference at the point of resolidification of the two curves is the following: curve 3b corresponding to the higher incident pulse energy density shows resolidification at a value of the reflectivity close to the one expected for the liquid at the melting temperature. By contrast, curve 3a shows resolidification at a distinctively higher value of the reflectivity. This difference is indicated by the bi-directional vertical arrow in Fig. 3. Calculations with a one-dimensional heat flow model reveal that for the lower density a higher undercooling is reached¹.

Thus we can conclude that after the crossing of $R(t)$ in curve 3a with the lowest horizontal line - corresponding to the liquid at the melting temperature - at $t = 20$ ns the metallic liquid is in the undercooled state. The undercooling increases with time, and finally at a reflectivity which is 2.3 % higher than the one for the liquid at the melting temperature resolidification sets in.

We have also measured at energy densities in between the ones given in Fig. 3. For those the expected behavior is observed at the onset of resolidification: the higher the energy density the closer the reflectivity is to the value of the liquid at T_m .

These results show that we have observed a clear variation of the optical properties of an undercooled liquid with temperature. Since a direct measurement of the temperature on the short timescale of this experiment was not yet possible, we have carried out a calculation using a one-dimensional heat flow model. As can be seen from table 1 this theoretical approach accounts quite well for the experimental values of the thresholds in energy density for the onset of melting and for complete melting.

Thresholds in energy density	measured [mJ/cm ²]	calculated [mJ/cm ²]
onset of melting	100 ± 10	80 - 90
complete melting	120 ± 10	110 - 120

Tab. 1: Comparison of measured and calculated thresholds in energy density of the Nd:YAG laser pulse ($\lambda = 532$ nm, FWHM 7 ns) for different scenarios of a 40 nm thick Cu film on fused silica. The uncertainty in the calculated values arises from the variation of the absorptivity of the Cu-film upon the action of the laser pulse.

In the framework of the model we can also calculate a lower bound for the achieved undercooling. For the curve 3a an undercooling ≥ 400 K is obtained.

Fig. 4 shows that the temperature dependence of the optical properties can be studied with other thin metal films as well. In this case the sample consisted of 35 nm Ni on 1.5 nm Cr on fused silica. The data exhibit the same qualitative behavior as those of the copper film. Again the curve for the lowest energy density corresponds to heating below the melting temperature $T_m = 1728$ K of Ni. For an energy density of 185 mJ/cm² partial melting of the film is observed, and for 240 mJ/cm² and 270 mJ/cm² complete melting takes place. Although the absolute changes in the reflectivity of Ni are smaller than 3 %, one can resolve a difference in the value of the reflectivity at the onset of resolidification, again indicating the temperature dependence of the optical constants of the liquid in the undercooled state.

¹ This can be seen by the following argument: the driving force for the cooling is the temperature gradient between metal film and substrate. Higher energy densities lead also to a significant heating of the substrate. Thus higher energy densities are associated with a lower temperature gradient which causes lower quench rates and consequently a lower undercooling.

Fig. 4: Time-resolved reflectivity at $\lambda = 633 \text{ nm}$ of the free surface under the influence of a laser pulse incident on a sample of 35 nm Ni on 1.5 nm Cr on fused silica. The respective energy densities are given in the lower right corner of the graph. The higher the energy density the lower is the reached minimum reflectivity. The laser energy densities correspond from the top to the bottom curve to 95 mJ/cm², 185 mJ/cm², 240 mJ/cm² and 270 mJ/cm² respectively.

4. DEWETTING

Melt durations longer than those in Figs. 3 and 4 are achieved by still higher laser energy densities. Under these conditions dewetting of the liquid metal films is observed as irreversible change in the reflectivity occurring after incubation times of some 100 nanoseconds. Since this is long compared to the laser pulse duration we can safely exclude rupture due to plasma formation or interactions with the radiation pattern of the laser beam as the origin for the dewetting.

A close examination of the dewetting structures finally frozen in on resolidification of the metal reveals that dewetting occurs via two distinctly different modes. On one hand, there is *nucleation* of dry patches which grow during the melting period due to the high surface tension of the metals. On the other hand, the negative Hamaker constant of the metal/silica system gives rise to an instability of surface waves of the liquid metal film which grow exponentially in time resulting in a characteristic „*spinodal*“ dewetting structure.

4.1 Nucleation of holes

Concerning the dewetting of the metallic liquid films the setup used here possesses two advantages. First we have a nearly gaussian lateral variation of the pulse laser energy across the laser spot. Thus one can observe upon one shot the whole qualitative development of the structures by investigating various portions of the spot. Secondly, due to the high quench rates the liquid freezes very rapidly, thus preserving the developed structures at the different stages. In the outer most molten region no nucleation of holes takes place. There the energy density is in the range where the measurements given in chapter 3 were made. The nucleation of holes only takes place above a certain melt duration. Upon increasing the energy density, the holes grow in diameter. Fig. 5a shows the central part of a molten area of a Cu film observed with optical transmission microscopy. One can see single holes and holes which have merged during the growth process. The latter develop distinct ridges between them which finally become unstable via the Rayleigh instability in equivalence to the behavior observed in polymer films [18]. That the holes really develop via the mechanism of dewetting becomes obvious by the topographic line scan across a typical hole given in Fig. 5b. The outer rim of the hole is elevated. The excess volume in this rim with respect to the film thickness corresponds to the material removed from the „dry“ patch. This indicates that the material is conserved and that evaporation of the material upon the laser heating is negligible. From Fig. 5b one can also determine a contact angle of copper on glass of about 20°. The nucleation of holes was not only observed with Cu films but also with Au and Ni films. They appear randomly distributed over the area treated with the laser and the diameter of the holes in a certain distance away from the center is monodisperse. Furthermore, examination with a scanning electron microscope revealed that in the center of many holes, there are small particles which may have provided the centers of nucleation for the holes. This observations are indicating that a heterogeneous mechanism is leading to the nucleation of the holes.

Fig. 5: a) Nucleation of holes: picture taken with an optical transmission microscope after laser treatment of a 40 nm thick Cu film on fused silica. b) Topographic line scan across a typical hole taken with an scanning near field acoustic microscope.

4.2 Spinodal dewetting

In addition to the nucleation of holes we observed the growth of quasiperiodic surface modulations. Fig 6a (on the next page) shows a picture taken with an optical microscope in reflection of the central part of the completely molten area. The sample was a 47 nm thick Au film on 1.7 nm Cr on fused silica. It is obvious that two different sizes and types of holes dominate the picture. The energy density increases from the bottom to the top of the picture. The bigger circular holes with typical diameters of 5 μm correspond to the nucleation as described in the previous chapter. Apart from those also irregularly shaped holes with typical sizes near 2 μm are visible. The latter break through via a height modulation of the surface with a characteristic length scale. This can be seen from Fig. 6b which shows the same area as Fig. 6a but with the microscope slightly defocused in order to make the surface modulations more prominent. The characteristic length scale can be extracted to be $2.4 \pm 0.4 \mu\text{m}$. This length was found to depend on the Au film thickness as shown in Fig. 7. The dashed line corresponds to a quadratic dependence of the characteristic wavelength λ_m on the film thickness, as predicted by the theory of spinodal dewetting [10]

Fig. 7: Dependence of the characteristic wavelength of the surface modulations on Au film thickness. The fit is based on the theory of spinodal dewetting.

structures are expected to develop according to the dewetting theory. The calculated values of τ_m range from 150 ns for the thinnest up to a 4500 ns for the thickest investigated film. The measured melt durations are in fairly good agreement with these calculated values. We take this self-consistency, together with the observed evolution of the structures, as a clear indication that we have, for the first time unambiguously, observed spinodal dewetting of thin liquid films.

$$\lambda_m = \frac{d^2}{\alpha}$$

with the parameter α being characteristic of the material combination substrate/film. For this characteristic wavelength the rise time τ_m is

$$\tau_m = \frac{d^5}{\alpha^4 v}$$

where the velocity v is approximately given by the ratio of surface energy to viscosity. Data from the literature [17] for liquid gold at the melting temperature yield a value of $v = 240 \text{ m/s}$.

From the fit in Fig. 7 we can extract the constant α to be 4.1 nm. Thus we can derive the timescale on which these

6a focused

6b defocused

Fig. 6: Pictures taken with an optical reflection microscope of the central part of a molten area. The sample consisted of a 47 nm Au film on 1.7 nm Cr on fused silica. Pictures 6a and 6b display the same area. The only difference is that in picture 6b the film surface is slightly out of focus, thus enhancing modulations of the film surface in the regions without holes.

5. CONCLUSIONS

We have presented ns-time-resolved measurements of the reflectivity upon the treatment of thin metal films with a ns-laser pulse. We have shown that we can thereby distinguish between heating, partial melting and complete melting of the film. For the case of complete melting we have presented evidence that we reach undercoolings of the liquid of more than 400 K. We have achieved a resolution which enabled us to resolve a temperature dependence of the optical properties of the undercooled liquid. Finally, upon long enough melt duration, dewetting of the thin liquid films was observed. There are two different modes of the dewetting process - nucleation of holes and spinodal dewetting - which we have described. We have observed the theoretically predicted behavior upon spinodal dewetting in the scaling of the characteristic surface modulation as function of film thickness as well as an agreement in the time scales needed for these modulations to develop. Thus we conclude that we have unambiguously identified the process of spinodal dewetting.

6. ACKNOWLEDGMENTS

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