Photoacoustic and Photothermal Phenomena III


With 501 Figures
Photoacoustic and Photothermal Investigations of Thin Films

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Abstract. Three different techniques - mirage effect, photothermal displacement, and thermoreflectance - have been installed for investigating ablation thresholds and thermal properties of thin films. By monitoring the shock wave signal the mirage effect was used to measure ablation thresholds of optical coatings. For multilayer systems of type polymer-metal SiO 2 changes in the shock wave signal allowed to distinguish between the ablation of different layers. The photothermal displacement method was applied to measure periodicity and decay of transient thermal gratings on surfaces of thin films. This technique yields information about lateral and vertical heat diffusion and is, therefore, sensitive to anisotropic heat transport in thin films. The potential of this technique for precise measurements of thermal diffusivities is illustrated for thin films of gold and amorphous diamond.

1. Introduction

During the past decade thermal properties of thin films have received increased attention [1,2]. They are inherently connected with the quality of thin films and are, therefore, most appropriate for their characterisation. Precise measurements of thermal diffusivities provide information about finite size effects, structural anisotropies, interface absorption, defect and impurity absorption, and incubation effects. Also, it has been suggested by several workers in the field [3,4] that optical damage thresholds are strongly correlated to thermal properties of thin films, which means that these also play an important role for laser processing of thin films. Hence, the interest in thermal data ranges from optical, protective, and polymer coatings to semiconducting and metallic films as well as to high- T c superconducting films.

These prospects led us to start an activity where several techniques like mirage effect, photothermal displacement and thermoreflectance are employed to yield complementary information about the same or similar films material. We also find it important to work both in the time and frequency domain in order to have the possibility for cross-checking the results. One ultimate goal of this project is to quantitatively correlate ablation thresholds to thermal properties of thin films. This contribution summarizes the present status of the work on thin films in our laboratory by presenting informative examples for each technique.

2. Damage thresholds measured by the mirage effect

The mirage effect caused by the transient change of refractive index (5-7) measures both acoustic and thermal waves emerging from a surface when irradiating it with laser pulses of sufficiently large fluence. They can be distinguished by their range as well as by their speed. This technique is particularly well suited for studying ablation thresholds and the development of laser-induced plasma, in which case the thermal wave is substituted by the plasma wave. A typical signal obtained from a Kapton foil with a fluence above the ablation threshold is displayed in the lower part of Fig. 1. It shows a fast signal which we attribute to the refractive index gradient caused by the shock or blast wave. The huge later signal reflects the slowly expanding plasma. Deflection signals from PMMA recorded at 20 times higher fluences are very similar in shape, hence, we consider the one in Fig. 1 as being generically representative for different types of material. In fact, it very closely resembles the pictures taken by an ultrafast imaging technique at above threshold fluences with polyimide [8] and PMMA [9]. Notice however, that the "clean" signal in Fig. 1 can, for certain materials, be badly distorted by probe laser scattering from large size fragments leaving the surface.

When applying the mirage technique to the investigation of ablation thresholds both the shock and plasma signals in Fig. 1 yield identical results, for example for polyimide. Because of its superior reproducibility, however, we prefer to use the fast shock wave signal for measuring optical damage thresholds. An example is shown in Fig. 2, where the deflection signal is plotted as a function of fluence for both pure

Fig. 1: Mirage effect signal from polyimide at a fluence of 0.12 J/cm 2 (lower part). The upper part sketches the origin of the two different refractive index changes.
Fig. 1: Reduction of optical damage threshold by an optical coating on suprasil, measured by the shock wave mirage deflection signal at a pump laser wavelength of 248 nm [10].

Fig. 2: Change of shock wave mirage deflection signal at the transition from a polymeric film to a SiO₂ layer [12]. The lower part of the figure indicates the thickness scale and shows the depth profile of the photoresist layer.

suprasil and suprasil antireflec-coated with MgF₂ and Al₂O₃. Obviously, the coating causes a substantial lowering of the damage threshold. More detailed studies show that the reduction is due to the Al₂O₃-layer, including its interface while the MgF₂-coating alone causes no decrease. The underlying mechanism for this behavior remains to be investigated and calls for a measurement of the thermal diffusivities of these coatings.

For a given laser fluence the amplitudes of both signals in Fig. 1 depend on the absorbance of the material. Consequently the shock wave signal can also be utilized to distinguish between the ablation of layers of different materials [11]. This is illustrated in Fig. 3, where we can see that about 8 laser shots of 0.38 J/cm² at 248 nm are needed to remove a 1.5 μm thick SiO₂ film of photoresist. The deflection signal undergoes a step-like change when the laser light reaches the SiO₂ layer which has a much higher ablation threshold and consequently no shock wave is generated. The small and decreasing signal above 8 shots is due to cleaning of residual photoresist and etching of the Si₃N₄. Measurements of the etch depth profile were carried out to verify this interpretation and are shown in the lower part of Fig. 3.

This technique still works for multilayer systems provided the damage thresholds of the materials involved differ significantly. To demonstrate this point the film sequence polymer-metal-SiO₂ was irradiated with 248 nm light at various fluences [13]. The result for a sample with an Al-layer is shown in Fig. 4. Again, in the fluence range used the ablation of the photoresist starts at the first shot. The fluence of 0.51 J/cm² is too low to damage the Al-film with 30 shots. For 1.05 J/cm² we notice an increase of the deflection signal after about 25 shots, indicating the onset of metal ablation. At 1.38 J/cm² this onset is shifted to 10 shots, and starts still earlier at higher fluences. One can even notice an indication of SiO₂ breakup around 20 shots at 1.6 J/cm².

Clearly, the contrast in the deflection signal between different layers is lost at higher fluences (> 1.7 J/cm²), but within a certain fluence range it is possible to monitor the ablation of individual layers in multilayer systems [14].

3. Thermal diffusivities measured by displacement detection of transient thermal gratings

The pulsed photothermal displacement technique [15] is in principle an ideal tool for measuring the thermal diffusivity $\kappa$ of thin films since the thermal diffusivity length, $l_\text{th} = \frac{2(k\tau)_0}{\kappa}$, is that of the order of micrometer or less for a laser pulse length, $\tau_0$, of nanoseconds or shorter. To our knowledge, however, only few attempts have been made to apply this
The technique to thin films [16]. The reason may be that the
temperatures required for a good signal-to-noise ratio often
come close to the damage thresholds of thin films. In the
following we want to demonstrate that this technique can be
considerably refined by combining it with the excitation of
transient thermal gratings (TGG's) [17] on the film surface.

The use of TGG's instead of a circular beam spot brings
several advantages: (1) It defines a direction in the surface
plane and thereby becomes sensitive to anisotropic lateral
heat diffusion. (2) Under certain conditions [18] theory
predicts the following simple relation between the effective
decay rate $\tau_{\text{eff}}$ and the periodicity $\lambda$ of the grating:

$$\tau_{\text{eff}} = \frac{\tau_0^2 + A_0^2}{\lambda^2} \times \tau_0^2,$$

where $\lambda$ is the extension of the grating perpendicular to its
periodicity, and $\tau_0$ takes into account the vertical heat
diffusion. Hence a measurement of the exponential decay time,
the periodicity, and the width of the grating leads to values
for the thermal diffusivity and the vertical diffusion rate.
(3) As long as the theoretical approximations are valid this
technique leads to a good accuracy for the thermal diffusivity
since $\tau_{\text{eff}}$, $\lambda$, and $\tau_0$ can be measured rather precisely.

However, that strictly speaking the technique determines the
diffusivity constant for heat transport in the plane of the film.

The experimental set-up for probing the surface
self-referencing distribution of the film's by reflecting a HeNe-laser beam is
sketched in Fig. 5. The change in the reflection angle is
recorded by a quadrant diode. The HeNe-laser is always
focused to the same surface spot (beam diameter about 50 μm)
while the interference pattern generated by the two pump beams
(wavelength 543 nm, pulse width 4 ns) is moved across this

spot. Before a grating is measured the interference pattern is
recorded by a CCD-camera to control its general shape and to
measure its width $\lambda$. Scans of the CCD-camera recording of
the corresponding TGG on the surface of a 2.5 μm gold film on
BK7 glass are compared in Fig. 6. The phase shift between both
patterns is $\pi/2$ since the displacement technique measures the
derivative of the grating. We notice the excellent agreement
between the two different sets of data. It also is obvious
that a fit to the grating in the lower part of Fig. 6 will
lead to an accurate value of the periodicity $\lambda$.

The second important quantity needed for Eq. (1) is the
effective decay rate. In Fig. 7 we show typical decays of
TGG's on gold films of different thicknesses on a BK7 glass
substrate [19]. Notice that in each case the decay is well
described by a single exponential function indicated by solid
lines. The striking difference between the decay constants for
films of 100 nm and 2.5 μm reflects the influence of finite
diffusion, the increase of structural defects with
decreasing thickness [20], and an increase of vertical heat
flow with increasing thickness [19]. The latter, however, is
not as important as one might expect, since the straight lines
in Fig. 6, fitted to the data according to Eq. (1), intersect
the ordinate at roughly the same value. The strong thickness
dependence of the slope corresponds to the different decay
times in Fig. 7, and shows the drastic reduction of the
thermal diffusivity with film thickness.

The fact that the straight lines in Fig. 8 fit the data
well gives weight to the theoretical model and the validity of
Eq. (1). However, as discussed in Ref. [19] our results for the
thermal diffusivities are significantly smaller compared to
the values obtained by other techniques. For example,
photothermal reflectance measurements with MHz modulated
Ar"-laser light carried out at our laboratory [21] reproduced for the 2.5 μm film the bulk value of 1.25 cm$^2$s$^{-1}$, in contrast to 0.50 cm$^2$s$^{-1}$ obtained from the fit in Fig. 8. For a 1 μm film the thermorelectance measurement yields 1.9 cm$^2$s$^{-1}$ while the TTG displacement technique gives 0.4 cm$^2$s$^{-1}$. The latter technique does not even replicate the bulk value when applied to 2.5 μm gold plate, instead we obtain the 25 % lower value of 0.94 cm$^2$s$^{-1}$. The deviations are systematically toward lower values and much larger than the experimental uncertainty of about ±8%. We propose that these are caused by surface texture, island structure and other defects [22], and that they reflect the sensitivity of the TTG displacement technique to lateral heat diffusion. Further evidence for this is obtained by studying the influence of surface morphology on the thermal diffusivity. Fig. 9a shows a microscopy picture of the gold plate surface for which the measurement resulted in a 25 % reduced value of $\kappa$. The random texture apparently diminishes the lateral heat conduction. Such is not the case for the polished Ni surface (Fig. 9b) for which we measure $\kappa$ = 0.23±0.01 cm$^2$s$^{-1}$, in perfect agreement with the literature bulk value of 0.22 cm$^2$s$^{-1}$ [18]. The surface of a Ni-foil shown in Fig. 9c provides an example for a strongly anisotropic lateral heat diffusion. If we align the wave vector, $q = 2\pi/\lambda$, of the TTG parallel to the grooves we find $\kappa = 0.19±0.03$ cm$^2$s$^{-1}$, while the thermal diffusivity perpen-

dicular to the grooves is reduced to $\kappa = 0.05±0.02$ cm$^2$s$^{-1}$. These examples confirm that the TTG displacement technique measures predominantly the lateral heat flow in a rather shallow layer defined by the grating amplitude, and that $q$ is the leading term in Eq. (1). Hence this technique is ideally suited for studying the structural quality of thin films.

Due to their small optical absorption depth and the poor thermal conductivity of the substrate, metal films on glass represent a favorable case for the TTG displacement technique. The question is whether Eq. (1) will still be applicable when the optical absorption depth is comparable or even larger than the film thickness. To a first approximation a new case close to the limit of validity are interesting “amorphous diamond” films with a typical optical hydrogen-free absorption length of 0.2 μm [23]. A well developed TTG on a 0.29 μm thick film of this kind is shown in Fig. 10, and a
Fig. 11: Typical decay of the TTR shown in Fig. 10. The solid line is the fit of a single exponential function to the data with $\tau_{\text{eff}} = 1.45 \mu$s.

Fig. 12: Averaged effective decay rates for five different TTR’s on a 0.29 μm amorphous diamond film (24) plotted according to Eq.(1). The solid line represents a fit to the data.

typical decay curve can be seen in Fig. 11. Many of those decay curves were measured and the results averaged to give the effective decay rates plotted in Fig. 12 for five different gratings in the form dictated by Eq.(1). The straight line is a fit to the data with the result $\kappa = (0.45 \pm 0.03) \text{cm}^{-1}$ and $\tau = 6.7 \mu$s. Again the data are perfectly well described by a straight line, which makes us confident that thermal diffusivities of diamond films can be measured by this technique down to thicknesses of about 0.2 μm, depending on their absorption coefficient. This offers the possibility to utilize this type of measurement for a quality control of thin diamond films.

4. Conclusions

It was shown that the mirage deflection signal, caused by the shock wave emerging from the surface, is an ideal tool to measure optical damage thresholds of coatings. It can also be successfully used to monitor the selective ablation of thin films. Whenever the damage thresholds of film and substrate differ within a certain fluence range, determined by the ablation thresholds of the materials involved, this is still true for multilayer systems. Therefore the shock wave detection has great potential for in-situ controlling laser structuring of thin films.

In order to obtain thermal diffusivity with good accuracy the displacement detection of TTR’s was introduced. The power of the technique was demonstrated for gold films on glass and amorphous diamond films on Si. It was shown that the TTR displacement technique is most sensitive for lateral heat diffusion. Therefore the results may be affected by the surface texture. Since the TTR introduces a direction, this technique is well suited for studying anisotropic lateral heat transport.

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References

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Signal Enhancement and Noise Suppression Considerations in Photothermal Spectroscopy

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Abstract. This paper provides physical discussions of factors controlling sensitivity in photothermal spectroscopy, in particular, photothermal spectroscopy and probe-beam deflection spectroscopy. We consider the physical basis for signal generation and enhancement methods for pulsed and continuous-modulated excitations as well as the various sources of noise which become significant when the absorption approaches the part-per-million level or below. Proper signal enhancement and noise suppression are essential to make photothermal spectroscopy a sensitive tool.

1. Introduction

Photothermal (PT) spectroscopy detects certain transient thermal effects in or near a sample irradiated by a modulated excitation beam. It relies on the existence of a "thermal de-excitation" branch (see Fig. 1), which occurs for most materials. As this beam is scanned in wavelength, the PT effect is correspondingly monitored either in magnitude or in shape so that an "excitation spectrum" of the sample is obtained. This technique of PT spectroscopy is in principle "zero-background," which means that if there is no optical absorption, there is no PT signal. This is in contrast to conventional "subtractive" techniques involving the measurement of transmitted or reflected beams from the sample.

Figure 1. Schematics of optical absorption and de-excitation channels that can lead to "prompt" and "delayed" photothermal effects.