

# Nanosecond time-resolved study of pulsed laser ablation in the monolayer regime

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Pulsed laser ablation of few angstroms of organic material is investigated on a nanosecond time scale for the first time. The use of optically excited surface plasmons as a probe provides high sensitivity with respect to the thickness of ablated material. The results show that for the films used in our investigation (isopropanol, acetone, and tetrafluoromethane), ablative photodecomposition is not relevant for the ablation process, although there is evidence for chemical transformations.

The ablation of organic substances with ultraviolet (UV) laser pulses has become a field of great interest. In order to study the underlying mechanisms, real time observation of the ablation process is desirable. Although this has been done successfully at high ablation rates, the methods used so far are not sensitive enough for studying ablation on the order of one monolayer per pulse.<sup>1,2</sup> In this work we demonstrate that optically excited surface plasmons allow us to directly monitor the amount of ablated material with a resolution far better than a monolayer and on a nanosecond time scale.

Optical excitation and detection of surface plasmons (SP) propagating on a metal surface is a well established technique for surface analysis.<sup>3</sup> In our experiment, the sample was prepared by evaporating a silver film with a thickness of about 500 Å onto the base of a glass prism, as shown in the inset in Fig. 1. By illuminating the film from the prism side at a certain angle of incidence, SP propagating on the silver-vacuum interface can be excited resonantly. At this resonance angle, the incoming light is absorbed due to SP excitation, resulting in a sharp dip in the reflected light, with a width of less than a degree (solid curve in Fig. 1). When a transparent film is deposited onto the silver-vacuum interface, the resonance position shifts to larger angles by an amount of typically  $10^{-2}$  deg/Å of deposited material,<sup>4</sup> depending on its refractive index (dashed curve in Fig. 1). Therefore, the reflected light intensity in the vicinity of the resonance angle is very sensitive to deposition of transparent material onto, or ablation from, the silver surface. When the angle of incidence is adjusted to one of the wings of the resonance curve, a change in the adsorbed film thickness of 1 Å will induce a change in the reflected light intensity of several percent.

For the excitation of the SP we used a 5 mW He-Ne laser. The reflected light was detected with a fast *p-i-n* photodiode, amplified with an ac coupled 1 GHz bandwidth amplifier and recorded with an analog storage oscil-

loscope. For the ablation of the adsorbed films we used an excimer laser operating at a wavelength of 248 nm.

While in earlier experiments on UV laser ablation usually polymers were investigated, a recent tendency to employ simpler compounds with better theoretical understanding is apparent.<sup>5-7</sup> In our experiment, isopropanol, acetone, and tetrafluoromethane were used as film materials. Isopropanol and acetone were chosen because both materials are very similar in their thermodynamic properties, while their absorbance at the excimer laser wavelength (248 nm) differs by several orders of magnitude. Tetrafluoromethane was chosen because of its high transparency in the UV and a low evaporation enthalpy; thus, as compared to the other materials employed, it is most likely to undergo thermal evaporation due to substrate heating by the laser pulse.

In order to deposit films of the above materials onto the silver-vacuum interface, the sample was mounted in a high-vacuum chamber and was thermally coupled to a liquid-nitrogen bath, so the organic compounds could be deposited onto the cold ( $\approx 77$  K) silver surface from the vapor phase. Before cooling, the sample cell was filled with the saturated vapor of the deposit and then pumped out

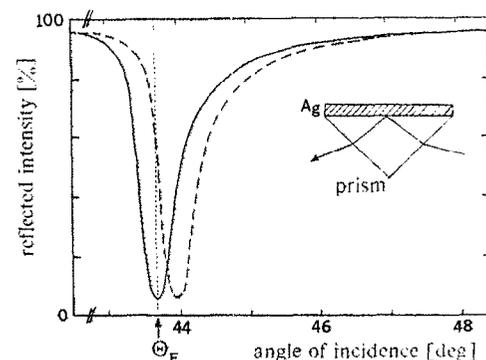


FIG. 1. Schematic plot of the surface plasmon resonance before (solid) and after (dashed) the condensation of a dielectric film onto the silver surface.  $\theta_F$  denotes the fixed angle of incidence relevant for the data presented here. In fact, measurements have been performed at several different angles for confirmation of the data. The inset shows the experimental setup.

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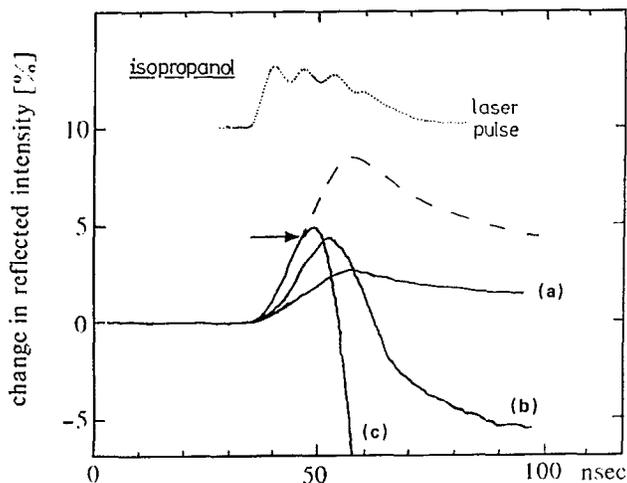


FIG. 2. Intensity transients obtained on ablation of isopropanol from the silver surface for different laser fluences. The fluences and corresponding ablated thicknesses are (a)  $8.0 \text{ mJ/cm}^2$ ,  $<0.1 \text{ \AA}$ ; (b)  $16.5 \text{ mJ/cm}^2$ ,  $2.6 \text{ \AA}$ ; (c)  $24.0 \text{ mJ/cm}^2$ ,  $13.5 \text{ \AA}$ . Data of the ablated thickness were inferred from the saturation value of the signal at longer times. For trace (c) (which cannot be fully displayed at the scale used in the figure), the dashed curve indicates the surface temperature as inferred from trace (a); the arrow denotes the onset of ablation. The dotted curve represents the temporal profile of the laser pulse.

again. After repeating this procedure several times, the residual gas partial pressure, which was measured with a quadrupole mass filter, could be reduced below our limits of detection ( $\leq 10^{-9}$  mbar).

Films were prepared with a thickness of typically  $50 \text{ \AA}$ , corresponding to about ten monolayers (depending on the film material). The reflected intensity was recorded near the inflection point of the left resonance wing (cf. Fig. 1), where a linear relationship between the film thickness and the reflectivity holds to a good approximation. On irradiating the sample with an excimer laser pulse, a fraction of the organic film was ablated. Thus the SP resonance shifted to lower angles, towards the fixed angle of incidence. This resulted in a sudden drop in the reflected intensity, which directly monitored the film thickness as a function of time.

While the aforementioned effects on the SP resonance are due to the adsorbed transparent layer, there occurs in addition a shift of the resonance to larger angles due to laser-induced transient heating of the silver film. This results in a rise of the reflectivity which directly monitors the temperature at the metal surface. This effect has been described in detail elsewhere<sup>8</sup> and is superimposed on the ablation signal. Serving as an *in situ* surface thermometer, it yields further information on the ablation mechanism.

In Fig. 2 we show some intensity transients for different laser fluences near the threshold of ablation (about  $10 \text{ mJ/cm}^2$ ) for isopropanol. The dotted curve represents the temporal profile of the laser pulse. At low fluence [trace (a)], where virtually no material is ablated, only the temperature signal appears. For the subsequent traces the laser fluence is increased, and the onset of ablation is revealed by the sharp downward bending of the trace.

It should be noted at this point that the thermal energy

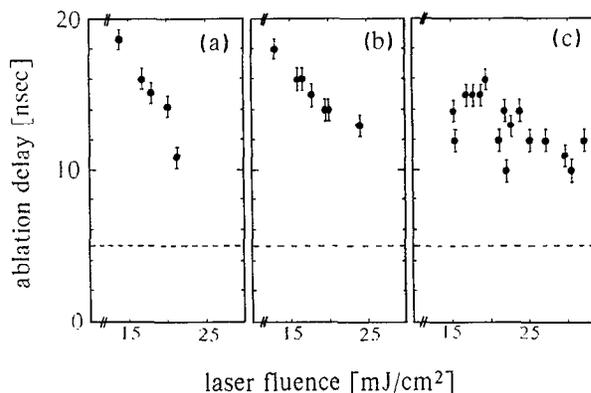


FIG. 3. Delay of the onset of ablation with respect to the beginning of the laser pulse, plotted as a function of laser fluence: (a) tetrafluoromethane, (b) isopropanol, (c) acetone. The dashed line represents the time by which the laser pulse reaches its maximum power. For a power-controlled threshold process, the data would lie below the dashed line.

removed from the sample by the ablation process is expected to be small compared to the thermal energy deposited in the silver film: the energy required to evaporate the whole deposit is on the order of  $1 \mu\text{J/cm}^2$ , whereas the silver film absorbs about 70% of the laser fluence, corresponding to several  $\text{mJ/cm}^2$ . Since the silver film assumes a uniform temperature across its thickness within less than a nanosecond,<sup>9</sup> the temperature signal measured on a nanosecond time scale reveals the overall heat content in the silver film, and thus it will virtually not be affected by the ablation process. Therefore, for all fluences, the temporal evolution of the temperature in the metal film, as well as at its surface, is to a good approximation proportional to the signal obtained below threshold [trace (a)]. For curve (c), the extrapolated surface temperature is shown by the dashed curve, which represents curve (a) multiplied by the ratio of the respective fluences. In the following we will restrict ourselves to consideration of the time and temperature at the onset of ablation, which is indicated by the arrow in Fig. 2.

In Fig. 3, the ablation delay with respect to the onset of the laser pulse is plotted as a function of fluence for all three substances. The dashed horizontal line represents the time by which the laser power reaches its maximum value (cf. Fig. 2). If a power controlled threshold process were responsible for the ablation, it would start within the leading edge of the laser pulse, corresponding to the region below the dashed line. This is obviously not the case in our experiments. While *ablative photodecomposition*, a power controlled threshold process first established for polymer ablation,<sup>1,10</sup> has been shown to dominate the ablation of benzene under certain circumstances,<sup>6</sup> it does not seem to play a role here.

If *thermal desorption* were the relevant ablation mechanism, we would expect the ablation to set on when a definite desorption temperature is reached which depends only on the activation energy for evaporation.<sup>11</sup> In Fig. 4 we plotted the ablation temperature as a function of the laser fluence. The absolute scale of the temperature may not be the same in different plots since the experiments

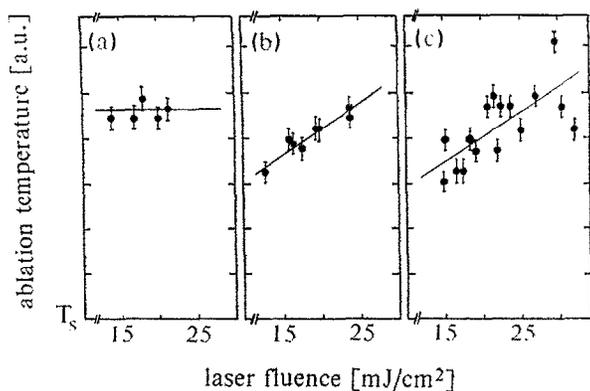


FIG. 4. Ablation temperature, measured relative to the initial (substrate) temperature  $T_s = 77$  K and plotted as a function of laser fluence. Whereas for (a) tetrafluoromethane, the ablation temperature is constant to a good approximation, it depends on the fluence in the case of (b) isopropanol and (c) acetone.

have been performed on different spots of the sample, and the sensitivity of the thermometer effect depends strongly on the thickness of the silver film,<sup>8</sup> which may vary laterally. However, from the thermal properties of the sample we can estimate that one vertical scale division corresponds roughly to 100 K.

In the case of tetrafluoromethane, the data do not show any significant dependence of the ablation temperature on the laser fluence. This is consistent with thermal desorption, which is expected to dominate for this compound, as mentioned above. However, for isopropanol and acetone, a strong dependence on the ablation conditions is observed. Although a quite erratic behavior is found in the case of acetone, the trend of increasing ablation temperature is obvious as well. This indicates that at least for the

latter two compounds, thermal desorption alone cannot account for the observed ablation dynamics.

In fact there is considerable evidence for chemical transformations in the organic layers. We observed that the amount of material ablated with one pulse decreases rapidly as the film becomes very thin. Actually, a saturation thickness on the order of a monolayer is finally reached, as if there were a thin layer of different material which could not be ablated. On increasing the laser fluence, however, further ablation could be achieved. Furthermore, the thickness of this saturation layer could be increased accumulatively by repeated deposition and ablation. Thus, despite the absence of ablative photodecomposition, chemical transformations seem to be present which may account for the demonstrated deviations from thermal desorption behavior.

In conclusion, we introduced a promising tool for real time studies of pulsed laser desorption, at ablation rates on the order of one monolayer per pulse. It yields rather direct insight into the dynamics of the ablation process.

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