

Time resolved study of excimer laser ablation of thin organic films from a metal surface

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ABSTRACT

The dynamics of pulsed excimer laser ablation of thin films of organic material from a metal surface was investigated using optically excited surface plasmons. The metal substrate is formed by a 500 Å thick silver film adjacent to the base of a glass prism, which serves for optical excitation and detection of the surface plasmons propagating at the silver-vacuum interface. The organic films were prepared by cooling the sample to 77 K and depositing the materials (isopropanol, tetrafluoromethane, acetone) from the vapor phase; ablation of the films was accomplished by KrF excimer laser ( $\lambda = 248\text{nm}$ ). Detection of the surface plasmon resonance allows to monitor the ablation process on a nanosecond time scale and with a resolution far better than a monolayer. At the same time, the surface plasmons provide an in-situ probe for time-resolved measurements of the substrate temperature. This allows to determine the temperature at which the ablation sets in. For tetrafluoromethane, the ablation temperature was found to be independent of the laser fluence, suggesting a thermal desorption process. On the other hand, for isopropanol and acetone, a strong dependence of the ablation temperature on the fluence was observed. From the large delay between the leading edge of the laser pulse and the onset of ablation, we conclude that ablative photodecomposition is not present in our experiment. There is, however, evidence for laser-induced chemical transformations in the organic films. Solid films of transformed material, which were stable at room-temperature and under atmospheric conditions, were formed during the isopropanol experiments. We suggest these transformation process to be connected to the observed fluence dependence of the ablation temperature.

1. INTRODUCTION

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 rates on the order of one monolayer per pulse.<sup>1,2</sup> Optically excited surface plasmons, however, allow 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 insert 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.

## 2. EXPERIMENT

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 oscilloscope. For the ablation of the adsorbed films we used a KrF 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 study 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 that the organic compounds could be deposited onto the cold ( $\approx 77$  K) silver

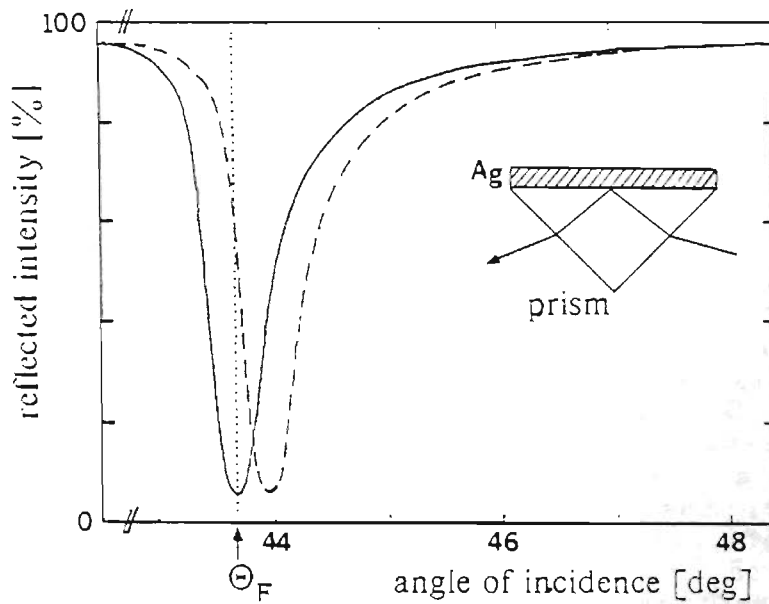


FIG.1. Schematic plot of the surface plasmon resonance before (solid) and after (dashed) the condensation of a dielectric film onto the silver surface.  $\theta_F$  denotes the fixed angle of incidence relevant for the data presented here. In fact, measurements have been performed at several different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

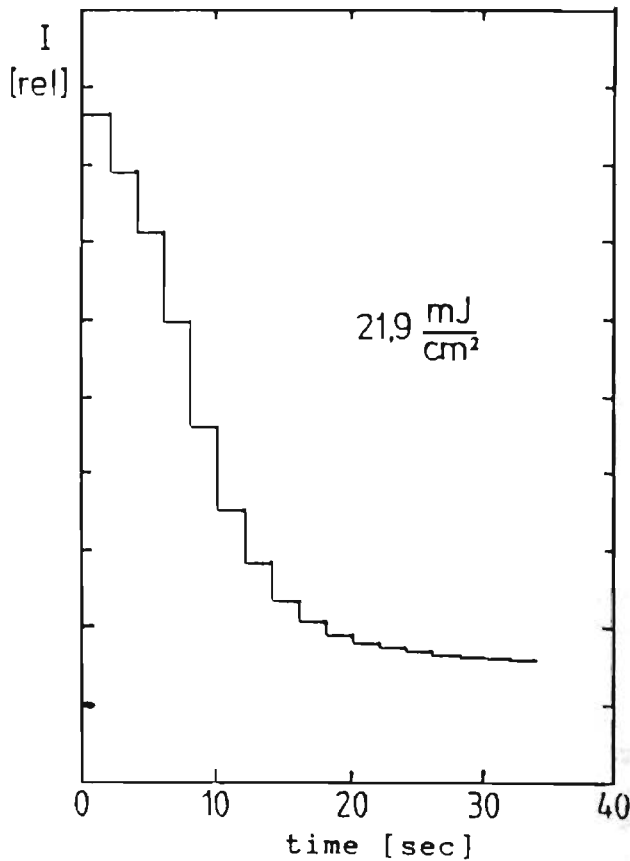


Fig.2. Reflected intensity during stepwise ablation of isopropanol. Each step corresponds to one laserpulse (pulse rate: approximately 0.5 Hz)

surface from the vapor phase. Before cooling, the sample cell was filled with the saturated vapor of the deposit and then pumped out 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 50Å, 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, as shown in fig.2, 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.<sup>8</sup> This results in a rise of the reflectivity which directly monitors the temperature at the metal surface. This effect is superimposed on the ablation signal. Serving as an *in situ* surface thermometer, it yields further information on the ablation mechanism.

### 3. RESULTS AND DISCUSSION

In Fig.3 we show some intensity transients for different laser fluences near to the threshold of ablation (about 10 mJ/cm<sup>2</sup>) 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 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 μJ/cm<sup>2</sup>, whereas the silver film absorbs about 70% of the laser fluence, corresponding to several mJ/cm<sup>2</sup>. 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.3.

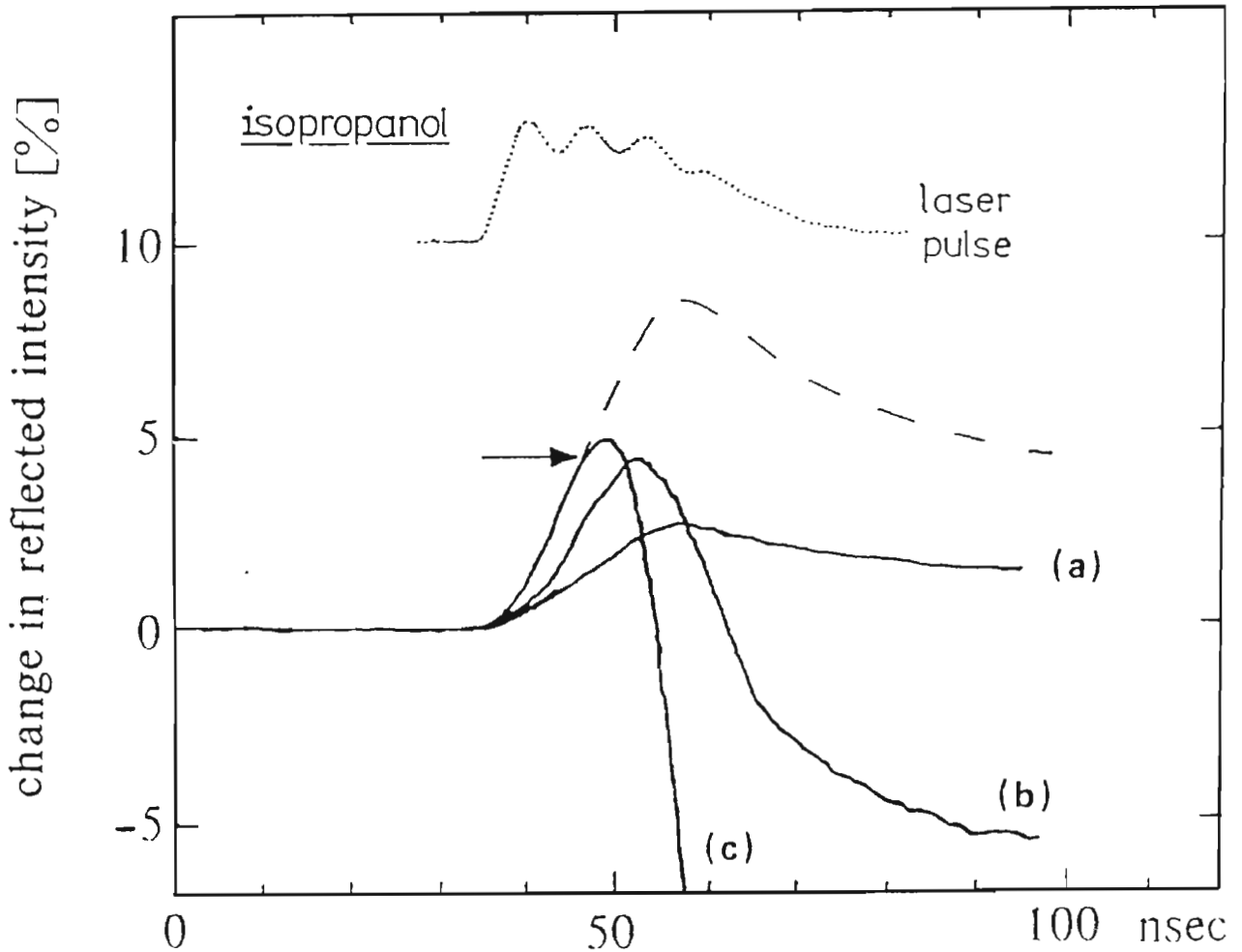


FIG.3. Intensity transients obtained on ablation of isopropanol from the silver surface for different laser fluences. The fluences and corresponding ablated thicknesses are (a)  $8.0 \text{ mJ/cm}^2$ ,  $<0.1 \text{ \AA}$ ; (b)  $16.5 \text{ mJ/cm}^2$ ,  $2.6 \text{ \AA}$ ; (c)  $24.0 \text{ mJ/cm}^2$ ,  $13.5 \text{ \AA}$ . Data of the ablated thickness were obtained from the steps shown in fig.2. 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.

In Fig.4, 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.3). 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

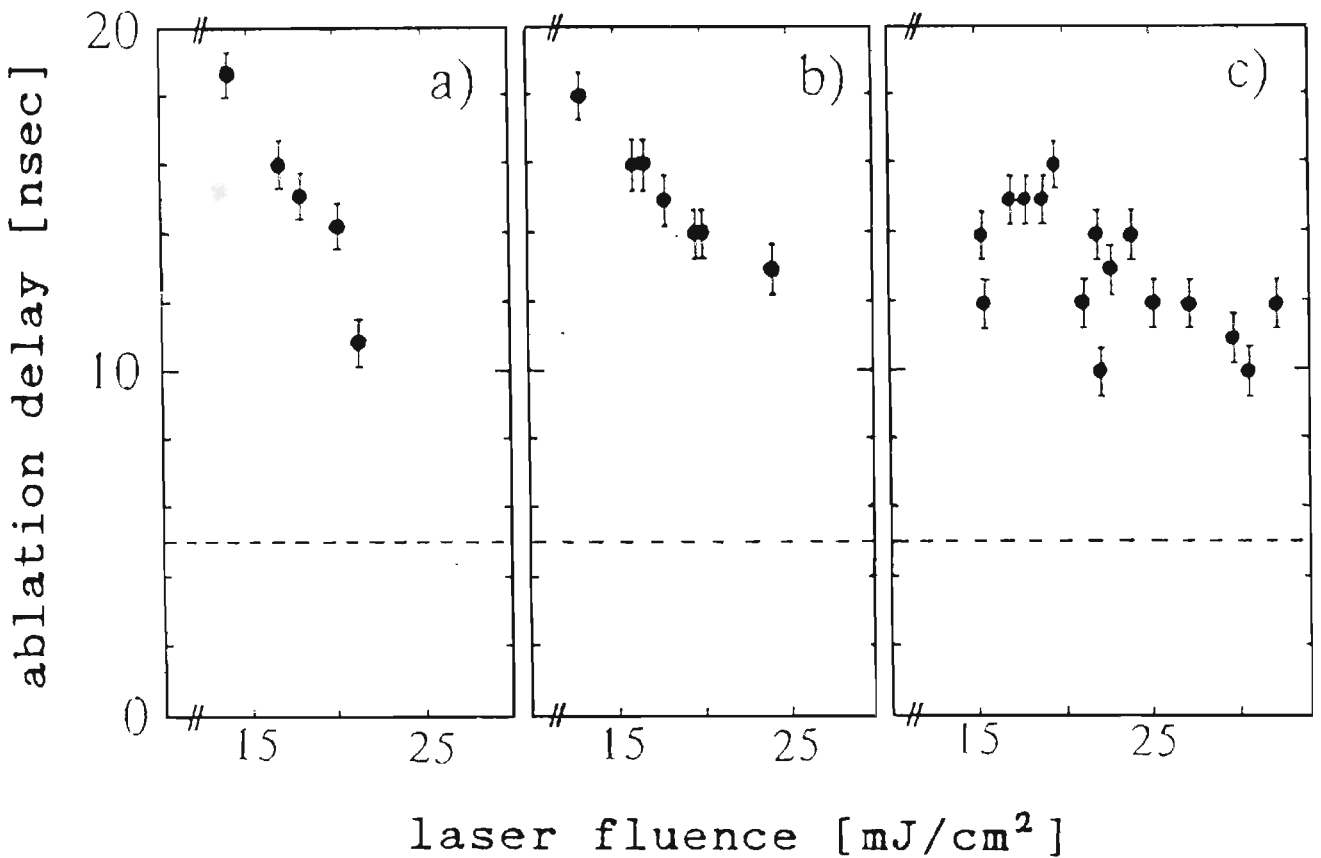


FIG.4. Delay of the onset of ablation with respect to the beginning of the laser pulse, plotted as a function of laser fluence: (a) tetrafluoromethane, (b) isopropanol. (c) acetone. The dashed line represents the time by which the laser pulse reaches its maximum power. For a power-controlled threshold process, the data would lie below the dashed line.

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 in when a definite desorption temperature is reached which depends only on the activation energy for evaporation.<sup>11</sup> In Fig.5 we have 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 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>9</sup> which may vary lat-

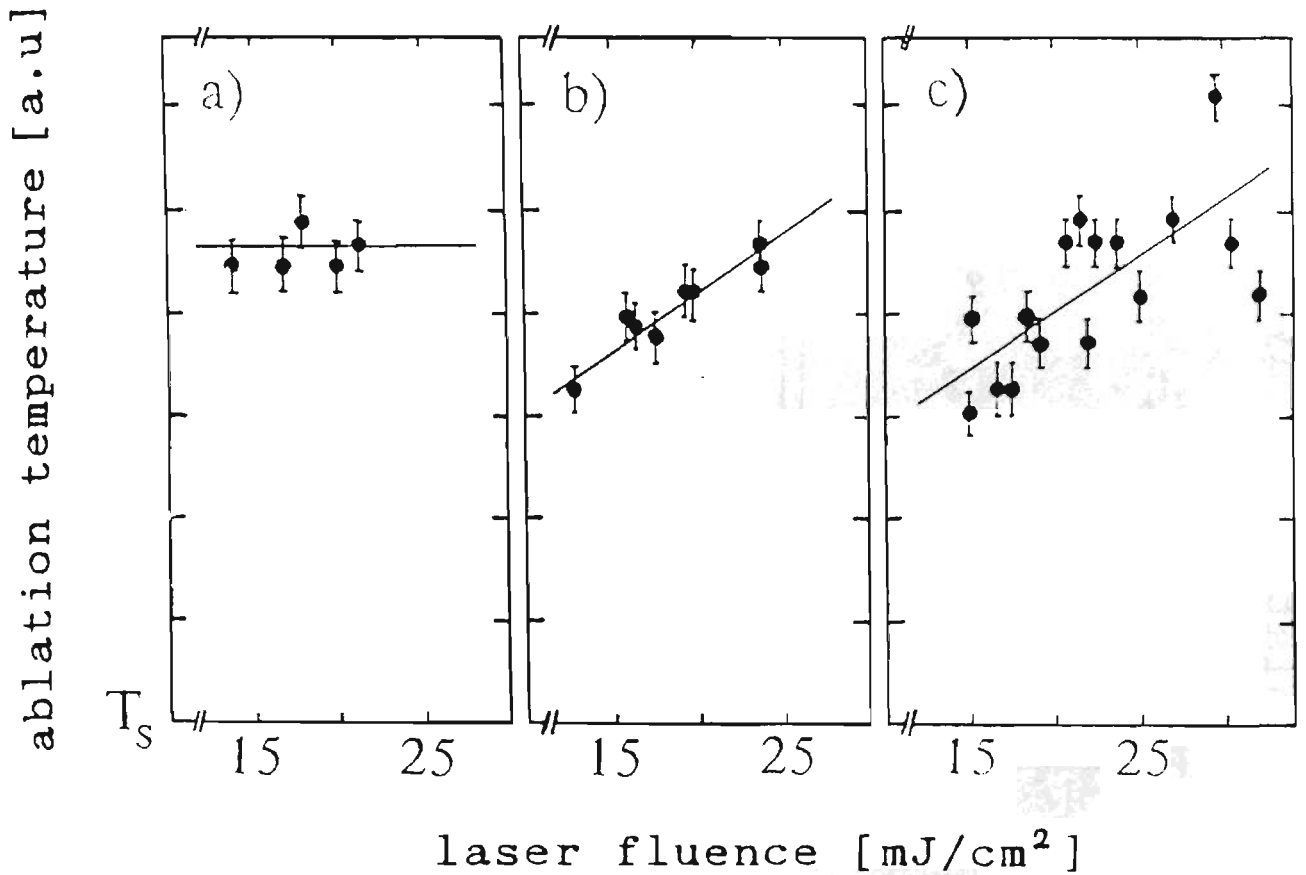


FIG.5. Ablation temperature, measured relative to the initial (substrate) temperature  $T_s = 77$  K and plotted as a function of laser fluence. Whereas for (a) tetrafluoromethane, the ablation temperature is constant to a good approximation, it depends on the fluence in the case of (b) isopropanol and (c) acetone.

erally. Nevertheless, 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. Nevertheless, 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.

In the case of isopropanol, this layer was stable even at room temperature and under atmospheric conditions. This is demonstrated in fig.6 where the surface plasmon resonance is shown at 300K before (a) and after (b) an ablation experiment with isopropanol, which involved several cycles of adsorption and ablation. The resonance shift is clearly visible and corresponds to about 10 angstroms of dielectric adsorbate, assuming a typical optical dielectric constant of  $\epsilon=2$ .

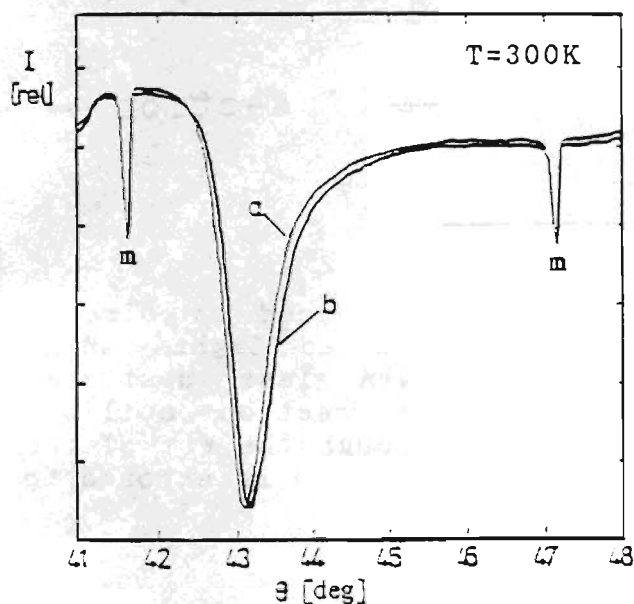


FIG.6. Surface plasmon resonance at room temperature and under atmospheric conditions before (a) and after (b) an ablation experiment with isopropanol. The dips denoted "m" in the figure are artificial marks providing a gauge for the angle of incidence.



It is remarkable that after several weeks of exposure to air, when the remainder of the silver film was corroded and appeared dark brown, the irradiated spot was still as highly reflecting as a freshly evaporated film. Two possible explanations for this phenomenon come to mind. Either the dielectric layer, whose existence is assumed from the above observations, protects the silver from contact with air, thus inhibiting its corrosion; or the silver itself has been morphologically or chemically transformed.

That one is in fact dealing with the former mechanism could be demonstrated by employing the direct-pull-off method, as illustrated in fig.7. The irradiated spot is outlined by region III, whose shiny appearance is visible in fig. 7a. The hole (regions I and II) in the irradiated spot was obtained by touching the sample with a small tip carrying a firmly sticking glue. On removing the tip, part of the layers were pulled off the glass substrate, leaving a clear hole in the silver film (region I). Immediately after the pull-off, region II was not distinguishable from region III, since it had the same shiny

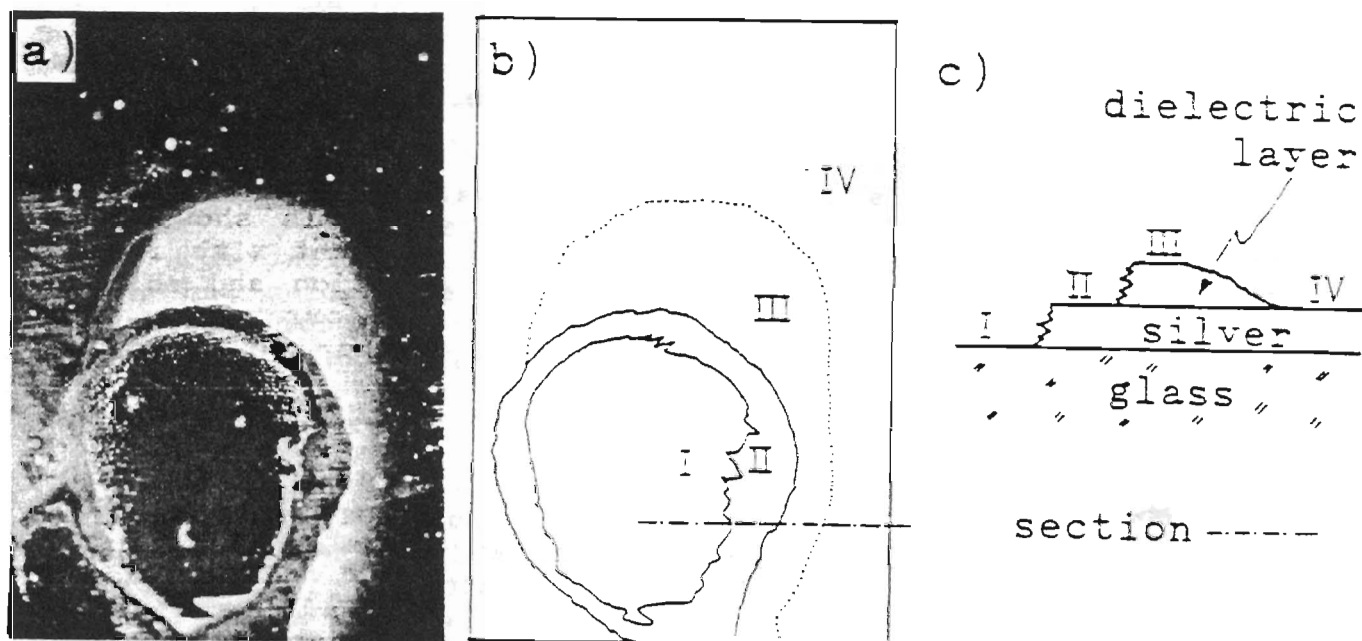


FIG.7. The irradiated spot with the hole obtained by direct-pull-off. a) photograph of specularly reflected light (shiny region: bright; corroded silver: dark; plain glass substrate: dark). b) sketch of a), indicating the section outlined schematically in c) (-.-.-.). c) section through the rim of the hole, schematically. In region II, the silver film is exposed to air by the direct pull-off.

appearance. After another week of exposure to the air, however, region II also was corroded, as shown in fig. 7a. This is easily interpreted in the way indicated in fig. 7c. Due to the different mechanical properties of the silver film and the dielectric adlayer, the rim of the hole is stepped exposing the silver in region II to air. This can explain the corrosion of region II after the pull-off.

#### 4. CONCLUSIONS

Optically excited surface plasmons have been applied for real time observation of pulsed laser ablation of organic thin films in the monolayer regime . Although ablative photodecomposition does not seem to play a role in our experiments, there is evidence for chemical transformations within the films. Dielectric adlayers are formed which are capable of preventing corrosion of the underlying silver, even though their thickness is only few monolayers.

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