

Spatially Resolved Laser Transfer of Organic Surface Films for Infrared Analysis

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The technique of laser transfer sampling is described and applied to obtain IR spectra of organic surface films. Spatially resolved transfer across a vacuum gap is demonstrated at 1064 and 248 nm, occurring by different, highly directional mechanisms. Laser interference in the gap and surface topography of the sample are shown to modulate the transferred film patterns.

INTRODUCTION

Chemical analysis of thin surface films is a task frequently encountered in areas such as the microelectronics industry and environmental monitoring. Intentionally deposited coatings as well as contamination layers need to be characterized. For molecular identification of organic layers the selection of techniques is rather limited. IR spectroscopy is often preferred because it is specific, quantitative, and non-destructive. It can, however, rarely be applied in situ: Difficulties arise when the substrate is highly IR absorbing or has metallic reflection (only absorptions with transition moment perpendicular to the surface are seen, requiring grazing incidence which limits spatial resolution) or if for some other reason an object cannot be directly examined with an IR spectrometer. In all these cases a sampling technique is desirable that separates the organic film from the substrate before analysis. This paper presents such a technique, which we call laser transfer sampling.

We have used laser transfer sampling with some success for analyzing contaminants and lubricants on parts of data storage devices. The principle of the method is shown in Figure 1: A transfer target substrate is mounted close to the surface to be analyzed, separated from it by a vacuum gap. Transfer without a gap at ambient pressure may be feasible, but we have not investigated this possibility. This substrate is transparent for both IR and the laser wavelength used for transfer. A single laser pulse applied through it vaporizes all or part of the surface film and drives it across the gap onto the target. The latter is then dismantled and subjected to transmission IR analysis.

This sampling techniques has the advantage of preserving some or all of the spatial information about the surface deposit, as indicated by the transferred pattern in Figure 1. Thus one can examine the transferred pattern with an IR microscope and recover the spatial distribution present on the original sample. The main purpose of this paper is to characterize the transfer of patterns and its limitations in detail. The results provide a basis for applications and shed some light on the transfer mechanism.

Laser transfer of organic films for other purposes and without spatial imaging has been described in the literature.

UV laser ablation of polymer films (1) and partial vaporization of frozen DNA solutions with 581-nm laser pulses (2) were found to be highly directional processes. Transfer of dust (3) and ice (2) particles driven by laser vaporization of water has also been observed. A theoretical analysis of the strongly forward-peaked expansion plumes encountered in laser sputtering has been given by Kelly (4). The technique described here is suitable for obtaining spatially resolved transfer samples from large or stationary objects by appropriate modification of the basic device shown in Figure 1. It suffices that a vacuum seal can be made against the surface to be examined. Transfer sampling may also be useful with analytical techniques other than IR, where special substrates are required to give optimal results. Examples include secondary ion mass spectrometry (SIMS) (5) (Ag substrate), surface photoionization mass spectrometry (6) (Au substrate), scanning electron microscopy (SEM), and scanning tunneling microscopy.

EXPERIMENTAL SECTION

Coronene was chosen as the test substance for pattern transfer experiments. It has negligible vapor pressure at room temperature ($p < 10^{-12}$ Torr), yet was conveniently vapor-deposited under vacuum (10^{-5} Torr) from a crucible heated to about 225 °C. A mask with a lithography test pattern was pressed against the stainless steel and KBr sample substrates during evaporation, producing a patterned film as shown in Figure 3a. The micrographs of Figures 3 and 4 were obtained by using the fluorescence of coronene under UV illumination. Film thicknesses were measured during evaporation with a quartz crystal balance.

The apparatus used for transfer is shown in Figure 1. Standard 25 mm diameter NaCl windows were used as transfer targets. Some visible coloration due to color centers appeared when using 248-nm laser pulses for transfer, but did not interfere with IR analysis of coronene deposits. A 0.25-mm vacuum gap between the sample and target was maintained by a spacer. Forepump vacuum of about 50 mTorr was sufficient to make the mean free path of vaporized molecules larger than the gap width. The vacuum also served to press and seal the transfer target plate against an O-ring, which made it easy to remove. A complete transfer experiment took no longer than 1 to 2 min including pump-down.

Two different lasers were used to effect the transfers: a Nd:YAG system (1064 nm) with 10-ns pulse duration and maximum fluence of 400 mJ/cm², and a KrF exciplex laser (248 nm) with 25-ns pulse duration and 250 mJ/cm² maximum fluence. Because the beam profile of the Nd:YAG laser is very inhomogeneous at the laser exit, the transfer experiments were set up 10 m away in the far field where the profile is more even. The exciplex laser was operated with the unstable resonator cavity, which produces a beam profile (approximately 0.5 × 2.0 cm) much more uniform than that of the Nd:YAG laser.

Figure 2 compares the Fourier transform infrared (FTIR) spectra of an original coronene film with one that was transferred with a 1064-nm pulse. Obviously no decomposition occurs due to the transfer process. The same observation was made at the 248-nm transfer wavelength. Two strong IR absorption bands

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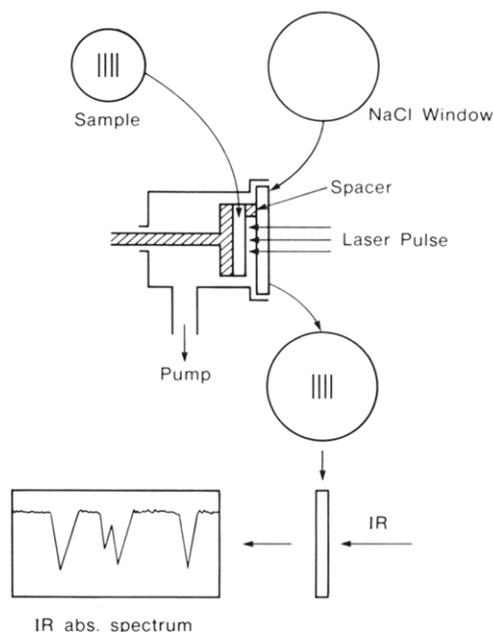


Figure 1. Schematic representation of the laser transfer technique, as applied for obtaining transmission IR spectra of patterned organic films.

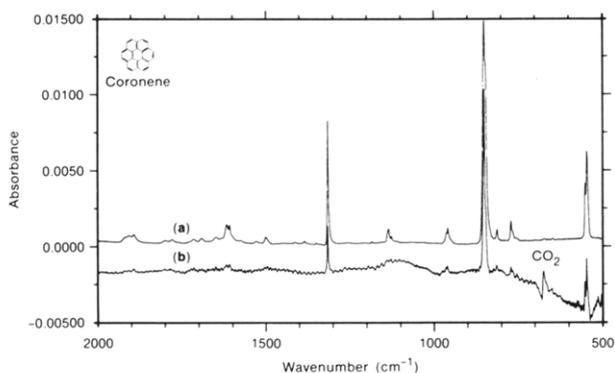


Figure 2. IR spectra of coronene (a) in KBr and (b) 54 nm thick film transferred with one 1064-nm laser pulse from stainless steel substrate to NaCl target; resolution, 2 cm⁻¹.

of coronene at 845 and 1314 cm⁻¹ can readily be observed at 1-nm film thickness, in the 50 × 50 μm² minimum area which can be resolved with the FTIR microscope attachment (Bruker IR/85 or IR/44 with a high gain MCT detector).

RESULTS

(a) 1064-nm Laser, Stainless Steel Substrate. Figure 3a shows the pattern of coronene stripes before transfer. The film was 23 nm thick, the smallest bars measured 160 × 800 μm and were spaced 120 μm apart, about half the vacuum gap distance (250 μm). The substrate was polished stainless steel. Exposure to a single pulse of 1064-nm radiation (200 mJ/cm²) resulted in near-quantitative transfer of the coronene pattern to the NaCl target which is shown in Figure 3b. The transferred pattern is inverted as a result of the geometry of the experiment. Comparison with a film of known thickness evaporated directly on NaCl showed that the transferred pattern contained at least 95% of the original material. Its structure was grainy under higher magnification. The transferred deposit of Figure 3b also shows random, spotlike inhomogeneities which were attributed to imperfections of the transfer target.

Most strikingly the features of the original pattern are reproduced almost exactly in the transferred deposit. Fill-in between the smallest stripes is negligible and amounts to less

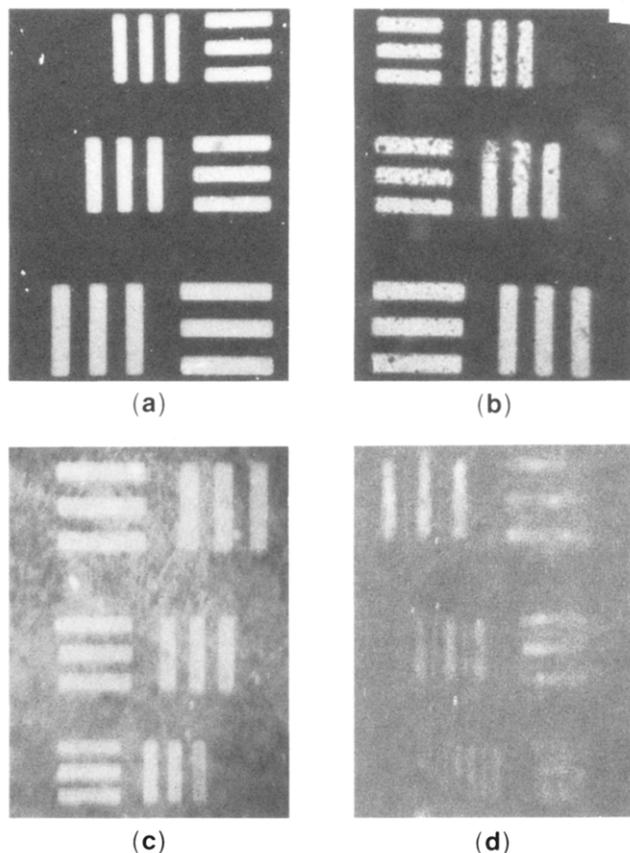


Figure 3. Fluorescence micrographs of patterned coronene films: (a) original pattern on polished stainless steel substrate, (b) same sample after transfer to NaCl target with one 1064-nm pulse, (c) residue on KBr substrate after exposure to one 248-nm pulse, (d) transferred portion of same sample on NaCl target.

than 1 nm of coronene according to IR measurements. Broadening of the stripes is no more than the standard error of the measurement which is about 6 μm.

Figure 4b presents the result of transfer from a rough sample surface shown in Figure 4a, using 400 mJ/cm² fluence. The surface topography is modulated by turning marks. This modulation shows up in the film thickness of the transferred deposit. The transfer process is obviously not just the reverse of the original vapor deposition of coronene.

A quite different modulation effect is exhibited in parts c and d of Figure 4. The latter is an enlargement of the target picture Figure 3b (longest bars, rotated 180°), the former shows its corresponding residue on the steel sample surface after transfer. Both images exhibit a pattern of parallel stripes unrelated to sample topography. This pattern is due to laser intensity variation caused by interference in the vacuum gap. The stripe separation distance of 28 μm can be accounted for with an angle of about 0.5° between sample and target surfaces. Interference patterns generated in this way contain useful information and permit structuring of surface films without using a mask.

(b) 248-nm Laser, KBr Substrate. Figure 3c shows the KBr sample and Figure 3d the NaCl transfer target, both after applying a single, 248-nm laser pulse with about 50 mJ/cm² fluence. The coronene film thickness was 50 nm. Clearly transfer at this fluence was incomplete. At higher fluences, up to 160 mJ/cm², the coronene pattern was completely removed from the sample surface but no transfer image was formed on the target. The transferred stripes in Figure 3d are 20–30% narrower than the original ones, Figure 3c. Surprisingly a thin extra stripe appears in the gap between the bars of the pattern, becoming more pronounced (albeit

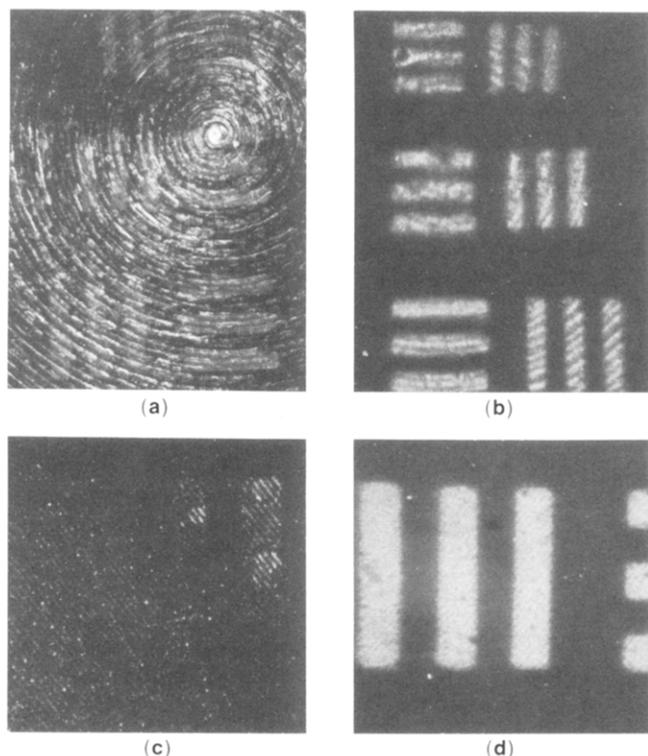


Figure 4. Micrographs in visible light (a) and in fluorescence (b to d) of patterned coronene films: (a) 25 nm thick film pattern before transfer, on stainless steel surface corrugated by turning marks; (b) same pattern after transfer to NaCl target with one 1064-nm pulse; (d) enlargement of the longest bars in Figure 3b, rotated 180°, exhibiting interference fringes; (c) corresponding residue on polished stainless steel sample.

poorly visible in the micrograph) as the bars get narrower.

DISCUSSION

The 1064- and 248-nm experiments are complementary in the sense that the substrate but not the coronene film absorbed the laser radiation in the former, while in the latter the opposite was the case. It is obvious from Figure 3 that in both cases the deposit leaves the surface in a highly directional way with an angular distribution sharply peaked at the surface normal, $\theta = 0$. If the transfer followed a $\cos^2 \theta$ distribution, as is often observed in laser desorption of small surface coverages, the pattern should be obliterated and no image formed. Instead the angular spreading is no more than about 1.4° at 1064 nm. Apart from this directionality the results point to different mechanisms at 1064 and 248 nm.

The grainy deposit formed in 1064-nm transfers indicates that a large fraction of the film is driven across the vacuum gap in the form of solid or liquid particles. Most likely this is due to a blasting mechanism. Rapid heating of the interface between sample and film generates a rapidly expanding vapor layer which breaks up the bulk of the film and drives the fragments vertically from the surface. The process in the latter phase resembles one being used to lift contaminant particles off surfaces (3). Its high directionality, even at film edges, as evident from Figure 3b, is astonishing.

At 248 nm heat is deposited mainly in the top portion of the organic film, generating a dense vapor layer at the vacuum interface. Under these conditions a highly directional, adiabatic expansion of the vapor occurs (4). We speculate that the extra stripes appearing in the transferred pattern, Figure 3d, are due to shock fronts, which are formed when the supersonic expansion plumes coming from adjacent bars of the pattern collide. At high laser fluences, excessive heating of the expanding vapor by light absorption may be responsible for complete disappearance of a transferred pattern.

CONCLUSIONS

Our results demonstrate that pulsed laser heating is a useful method for transferring an organic surface film to a substrate on which it can be analyzed by transmission IR spectroscopy. When a moderate vacuum gap width between sample and transfer target is used, the method preserves spatial information with a precision exceeding the resolution of an IR microscope. This is especially true, and the method works best, when the substrate rather than the film itself is heated by the laser, as was the case in our 1064-nm experiments. Under these conditions particulate matter is transferred by a highly directional blasting mechanism. If the laser light is mainly absorbed by the film, directional transfer again occurs by a strongly forward-peaked expansion of the vapor. Both directional mechanisms depend on formation of a dense vapor layer and will therefore fail eventually when the surface coverage gets very small. Sample surface topography translates into modulation of the transferred film thickness by effects including optical interference.

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