Section 3
ADVANCED TECHNOLOGY DEVELOPMENTS

3.A Measuring Chemically Induced Optical Degradation in Dielectric Thin Films

Plasma-induced etching of dielectric thin films is widely used in integrated-circuit preparation technology. It normally involves the interaction of gas discharge species with a thin-film surface in order to produce volatile reaction products. The ultimate goal is to etch through a film in a spatially selective manner and to thereby generate a desired pattern. This process also occurs unintentionally in the technology related to excimer lasers and fusion reactors. Unintentional etching effects are encountered when dielectric thin films, whose purpose is to establish an optical-interference multilayer stack, are exposed to electrons and ions from the excitation region of excimer gas-lasers. In the same vein, optical coatings that are part of laser-based, nuclear-fuel-reprocessing safeguard monitors and are in direct contact with streams of UF_6 are subject to etching.

While it is not difficult to suspect the performance degradation of a laser or of an optical component following such etching, it is difficult to understand the complexity of physical and chemical surface processes involved in this interaction. In spite of the pioneering efforts by Kay, Winters, Coburn, and Chuang,[1] who systematically ordered etching processes pertinent to plasma-assisted, integrated-circuit etching environments, little is known about the strictly optical consequences of such etching in optical thin films. This report discusses a first attempt to study the optical consequences of dry etching on a simple model system.

This work explores to what extent the absorption (at a certain wavelength) and the thermomechanical properties of a thin film change in response to a corrosive attack. This information is pivotal if one is to predict the optical damage susceptibility of a thin film when that film becomes part of a high-energy excimer laser cavity and is subject to chemical degradation. Damage of a film is understood here as local, permanent lattice disruption caused by rapid heating and local plasma formation by an incident laser pulse within the film. A prediction of damage susceptiblity must therefore be based on observations of local absorbance, i.e., energy deposition from the laser, and local thermal conductance that is responsible for the rate at which this heat is dissipated. Photothermal displacement spectroscopy is a convenient experimental tool for gathering this information. We present here maps of etched and nonetched thin-film samples, taken by the photothermal displacement method.

The general principles of the photothermal displacement (PTD) technique have been outlined elsewhere.[2] The particular experimental setup used in this work has also been described before.[3] Briefly, an amplitude-modulated 514.5-nm beam (modulation frequency 100 kHz) was focused at normal incidence to a 1.2 ($\pm$0.2)-μm-diameter spot on the film surface by a 60 x microscope objective. The same objective also focused a slightly offset, but otherwise collinear, cw He-Ne probe beam next to the green focal spot such that the 632-nm reflection from the film surface was tilted relative to the incident direction whenever the local heating by the green pump beam caused the film surface to expand and form a temporary surface protuberation. This tilt of the reflected red probe beam was monitored by a combination of a position-sensitive detector and two lock-in amplifiers. The tilt-producing slope of the film surface was a product of both the absorbed energy from the pump pulse and the heat conductance of the film. It represented, therefore, an ideal measure for the sought damage susceptibility. Maps of the processed film surface were obtained by stepwise scanning the sample through the pump-probe-foci in x and y directions normal to the beams.

It would clearly be a most definitive experiment that could measure the film changes *in situ* and during the exposure of the film to the chemical agents. However, simple geometrical constraints and other physical limitations make such an endeavor unfeasible. Foremost, the short working distance of a 60 x microscope objective shadows large parts of the film surface so that its uniform exposure to a molecular stream of chemical agents cannot be assured. Furthermore, the dielectric surfaces of the objective's refracting elements would fall victim to similar effects as the sample itself, making control of the experiment exceedingly difficult. The data presented here are therefore records of sample conditions measured after the chemical treatment of each sample was completed.

The sample films studied are 1000-Å-thick ThF_4 films that were thermally evaporated onto Au surfaces. (The choice of an Au film as underlying structure is immaterial within the scope of this work. The gold is required for a more extensive investigation into the stability of optical thin films, for which the gold film serves as an inert electrode for measurements to be reported elsewhere.) The gold film rests on a highly polished quartz single-crystal surface. It also is applied by thermal evaporation.

Exposure of the ThF_4-film samples to the chemical and radiation environment typical of an excimer laser discharge region takes place inside a UHV chamber equipped with separate ports and controls for different stimuli. The mixture of simultaneously applied agents comprises XeF_2 as the bearer of the etchant and an electron beam as an irradiation tool. Facilities for simulating ion-impact phenomena are also available, together with standard control instrumentation for residual gas analysis. No ion-impact related effects are, however, reported here.

The irradiation procedure follows a two-stage regimen. First, electron-impact effects are studied in anticipation of optical absorption changes manifesting themselves in photothermal-displacement maps. In order to fully use the imaging capabilities of the PTD technique, the electron-beam dose is increased across the film (at fixed kinetic energy). Samples of the treatment investigated at this point serve as controls for material which goes through the second phase of exposure.

During the second phase, the film is exposed to a stream of molecular XeF_2 at constant flux, in the presence of constant low-energy electron-bombardment. The reasons for this particular choice of stimuli are not based on any optical considerations. The choice is instead motivated by questions of etching-process kinetics and the hope of unraveling chemical reaction-pathways. Nevertheless, for a sample treated in this manner, interesting observations can be made.

The photothermal-displacement map shown in Fig. 23.33 was obtained from a ThF_4-on-gold sample that had experienced both treatment phases in an uninterrupted sequence. For comparison, a background or control map from an identical sample is shown in Fig. 23.34. Both maps are recorded at the same sensitivity and cover the same dynamic range of about one order of magnitude in photothermal-displacement signal. The gray scale in the legend divides this dynamic range into seven equal parts. It must be mentioned here that the very uniform appearance of the control sample, with the exception of the few noticeable polishing scratches, is somewhat deceptive. When ThF_4 samples are withdrawn from the UHV test chamber after irradiation by the 1-keV, 50-μA electron beam, the irradiated region appears blue to the unaided eye. This presumably is caused by halide-vacancy color centers, whose properties in ThF_4 are up to now undocumented in the literature. By merely letting the samples rest at room temperature in ambient laboratory air for a while the coloration fades, indicating diffusion of gas phase constituents into the structural vacancies. As the photothermal displacement apparatus is operated in a standard laboratory setting at a mapping rate of about 8 hours per 200-μm × 200-μm area, restoration of the sample's initial low optical absorption state is completed before any significant absorption record is assembled.

When electron-damaged ThF_4 is exposed simultaneously to XeF_2 and 1-keV electrons, a different scenario evolves. A restoration of the type shown in Fig. 23.34 does not happen. Even in the absence of added electron bombardment, the incident XeF_2 dissociates at or near the dielectric surface. In this case, the fluorine-depleted surface rapidly

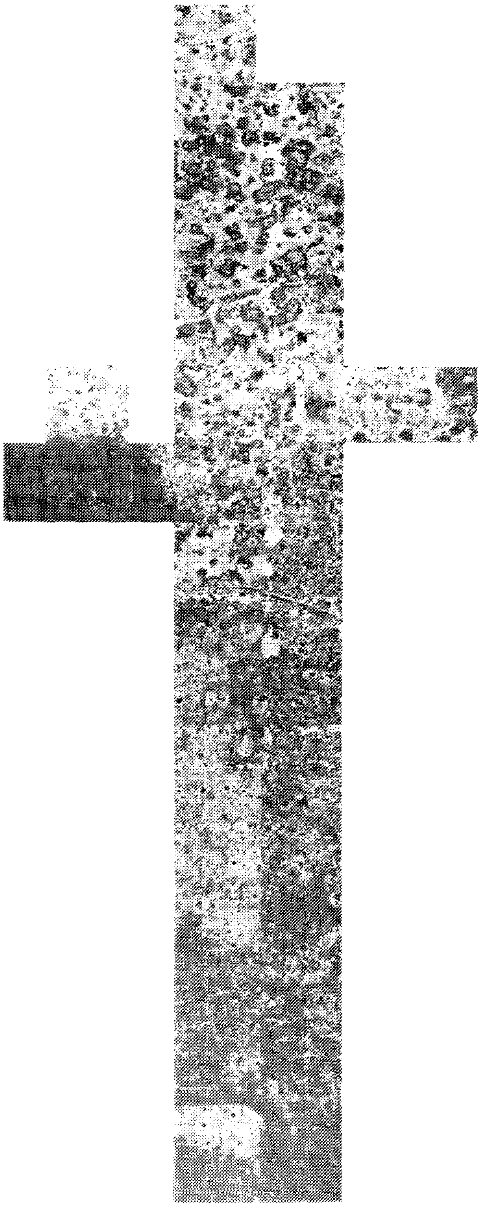

Fig. 23.33
Photothermal-displacement record of 2.5-mm-long strip of 1000-Å ThF_4 thin film displaying chemically enhanced electron-induced damage. Total electron dose varies by a factor of 4 from one end of the strip to the other.

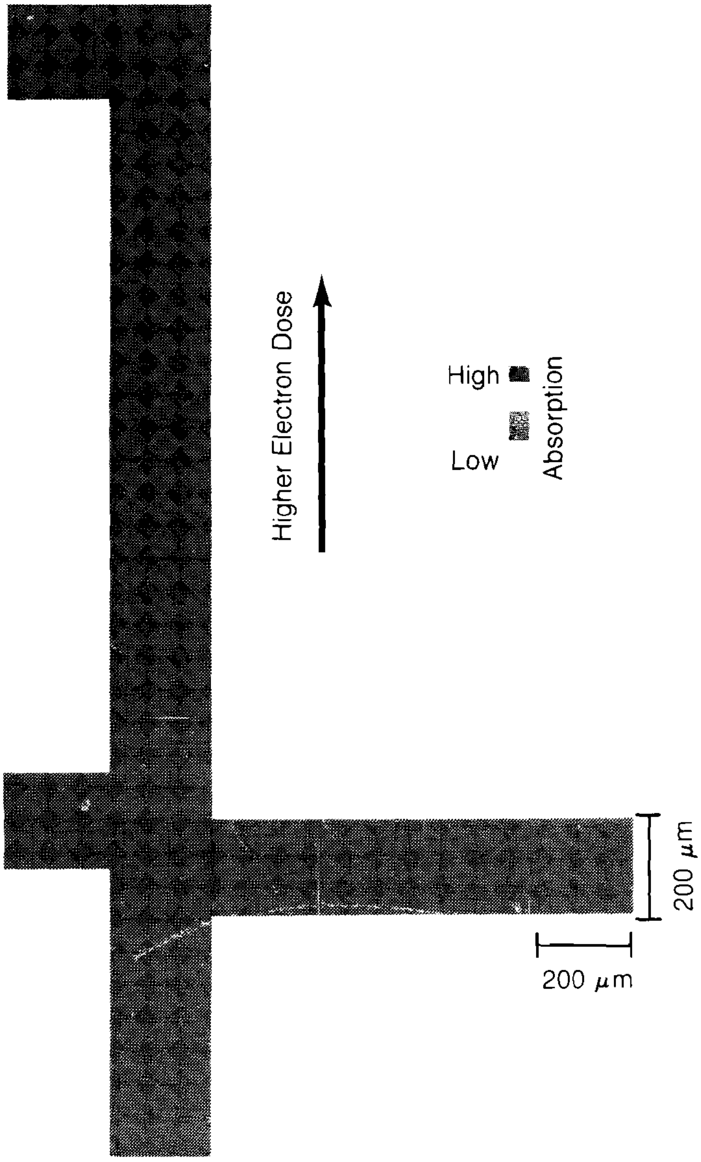

Fig. 23.34
Photothermal-displacement map of ThF_4 control sample that is similar to sample in Fig. 23.33 but was not exposed to chemical agent.

absorbs the equivalent of one monolayer of fluorine; this absorption drops quickly to a rate of one monolayer each seven hours. With the electrons present, two important effects are observed. First, a kinetic-energy-dependent absorption yield is found–i.e., the rate of fluorine uptake per incident electron is energy dependent. This dependence is illustrated in Fig. 23.35, where a resonance-like enhancement near 50 eV becomes apparent. The data in Fig. 23.35 are not deduced optically but by means of microbalance measurements in which the single crystal quartz substrates and the gold electrodes play a key role. Secondly, if uniform co-irradiation by 1-μA, 100-eV electrons is chosen, the fluorine uptake preserves a pattern of the prior, dose-dependent electron-stimulated damage in the film. This is borne out by the photothermal displacement map of Fig. 23.33. There, a sample zone is displayed for which all but one of the experimental parameters are kept constant; the 1-keV irradiation dose increases linearly (within experimental accuracy) by a factor of 4 from top to bottom. A highly structured absorption map results.

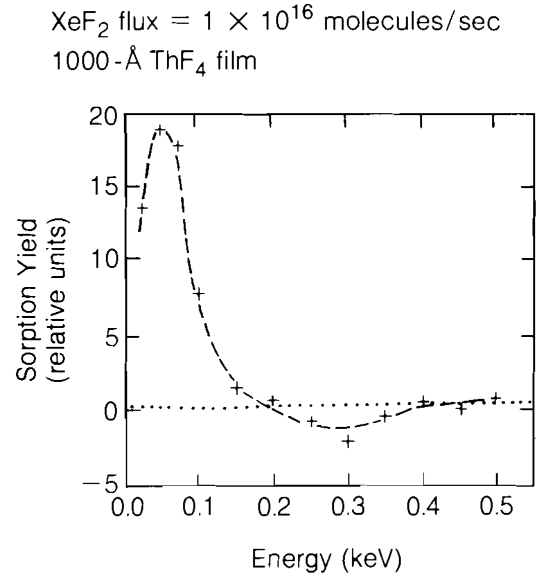

Fig. 23.35
The uptake of fluorine from the XeF_2 stream into the ThF_4 structure is a strong function of the concurrent electron-beam kinetic energy. These data were obtained by Michael Loudiana of Washington State University in samples later analyzed at LLE.

Permission by: Michael Loudiana, Boeing Aerospace Corp.

It is essential that during the long experimental runs required for taking such a map, long-term sample changes are investigated. Contrary to the observed rapid filling of absorbing point defects in the control samples by ambient-air constituents, no significant alterations are observed with time for the macroscopic sample appearance or for the microscopic PTD features. The gradual smoothing of the high spatial frequency of strong absorbers from top to bottom of Fig. 23.33, therefore, cannot be attributed to uncontrolled changes in the sample taking hold during PTD scans. An immediate infiltration upon removal of the treated film from the UHV chamber cannot be ruled out, but it also cannot be accurately measured with existing equipment.

In explaining the clusterlike features of Fig. 23.33, we draw attention to the porous structure of dielectric thin films.[4] Microscopic pores of various throat diameters form during the thin-film growth from the vapor phase, when the component particles arrive at the substrate with thermal kinetic energies. These pores are not unique to the material studied here, nor to the fact that a single layer is being investigated. Pores are known to reach through multilayer thin-film assemblies.[5]

Important effects have been documented for the infiltration of environmental species through these pores.[5] When, for instance, a multilayer, dielectric thin-film stack, which was designed for narrow-band transmission at a certain wavelength, suffered gradual water-vapor invasion through its pores, a frequency shift in the filter's transmission characteristics occurred. By taking advantage of this shift, lateral penetration of water into the stack was imaged in Ref. 5. A pattern of clusters and particles was observed, strikingly similar to the one shown in Fig. 23.33.

Fluid penetration through neutral porous media is controlled by capillary and viscous forces. In the case of dry etching considered here, the etchant does not reach a condensed, fluid state. The driving forces are modified by electrostatic forces arising from charged point defects and defect aggregates in the film lattice. These defects result from the prior electron bombardment of the sample. Their density and absorption cross section at 514 nm are insufficient to cause a significant PTD signal in the control sample (Fig. 23.34). Their formation and aggregation rates in halide crystal lattices are, however, quite dose dependent.[6] It is plausible that an increase in electron dose by a factor of 4 along the strip of Fig. 23.33 produces a significant gradient in the density and spatial frequency of defect clusters. The infiltration pattern of the etchant, and the reaction product formed after infiltration, visually reproduce this condition when monitored by PTD spectroscopy.

These observations have several ramifications for excimer laser systems engineering.

1. The synergism of chemical and physical interaction in fluoride optical thin films is much more deleterious to the film's optical survival strength than each individual effect. This inference can be drawn more forcefully from the microscopic PTD analysis shown here than from traditional thin-film laser-damage experiments.
2. Dose-dependent electron bombardment effects do not "heal" by subsequent, low-energy, continuous irradiation with electrons.
3. The absorption cross section at 514 nm of point defects formed by electron bombardment in ThF_4 is very small.
4. As most fluorides tend to produce stable point defects in the harsh radiation environment typical of excimer laser discharge regions, the findings from ThF_4 can be generalized. Oxides which are less prone to these effects appear to be more favorable thin-film materials for such applications.

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REFERENCES

1. For a review see J. W. Coburn, "Plasma Etching and Reactive Ion Etching," AVS Monographs Series 1982; and the references therein. H. F. Winters, J. W. Coburn, and T. J. Chuang, *J. Vac. Sci. Technol. B* **1**, 469 (1983).
2. M. A. Olmstead, N. M. Amer, S. Kohn, D. Fournier, and A. C. Boccara, *Appl. Phys. A* **32**, 141 (1983).
3. A. Schmid, D. Smith, M. Guardalben, and J. Abate, in *SPIE Vol. 476—Excimer Lasers, Their Applications, and New Frontiers in Lasers*, edited by R. W. Waynant (1984), p. 136.
4. H. V. Leamy, G. H. Gilmer, and A. G. Dirks, "The Microstructure of Vapor-Deposited Thin Films," in *Current Topics in Material Science*, edited by E. Kaldis (North-Holland, 1980), Vol. 6.
5. I. Hodgkinson *et al.*, "Structural Effects in Thin-Film Coatings," Technical Digest of Third Topical Meeting in Optical Interference Coatings, Monterey, CA, April 1984.
6. L. W. Hobbs, A. E. Hughes, and J. Pooley, *Proc. R. Soc. London, Ser. A* **332**, 167 (1973).