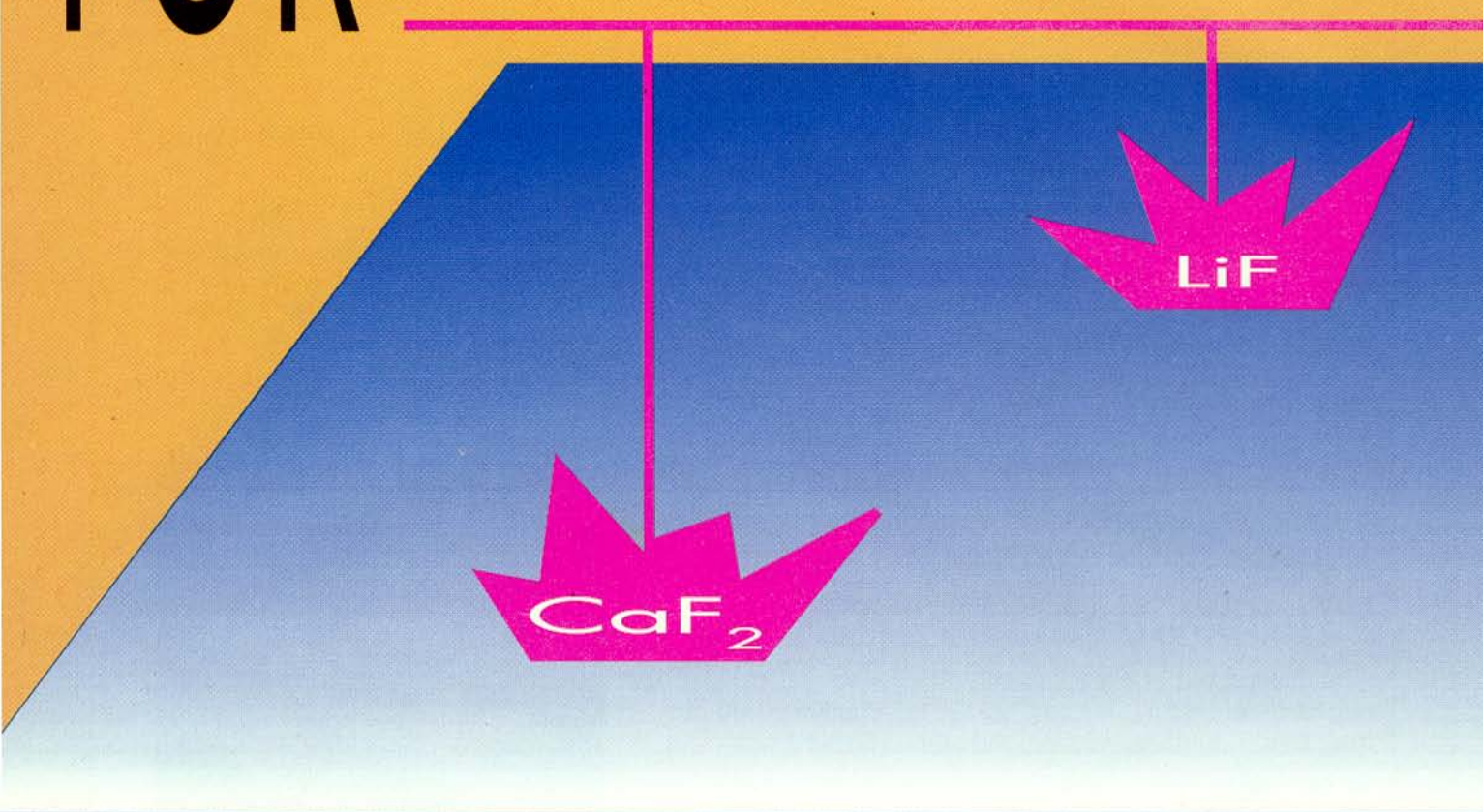
OPTICAL MATERIALS FOR EXCIMER LASER AP



While excimer lasers have been commercially available since the late 1970s, their main use until recently has been as powerful UV photon sources in research and development laboratories. In the R&D environment, large amounts of experimental data can be obtained with few laser pulses (thousands, tens of thousands, and, in rare cases, several millions). The durability of optical components used in these experiments has therefore not been a source of concern. UV-grade lenses, mirrors, and vacuum windows would be incorporated in the experimental setup with the implicit assumption that their optical properties would be invariable over time, as are the properties of visible-grade elements used with, for instance, frequency-doubled pulsed Nd:YAG lasers. Furthermore, not much thought was given to the details of the UV transmission of optical materials. As long as the vendor specified a nominal transmission at the appropriate wavelength (say, 98% excluding surface reflections), the material was frequently deemed adequate for its intended purpose. And indeed it often was.

PLICATIONS

By M. Rothschild

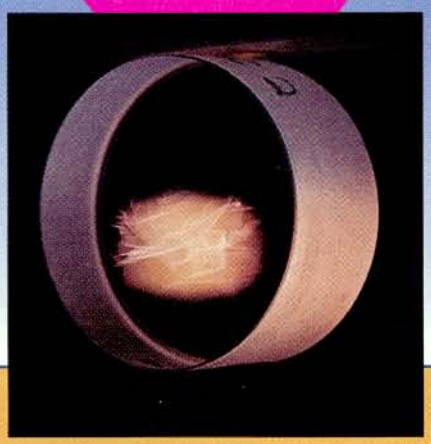


Figure 1. Sample of MgF_2 fluorescing under exposure to 193 nm excimer radiation. The sample has a large number of crystalline grain boundaries. These did not initially fluoresce differently from the rest of the sample, but after ~200,000 pulses at 100 mJ cm^{-2}/pulse they suddenly became much brighter, as seen in the figure. The reason for this behavior is not well understood, although one may conjecture that fluorescing crystalline defects are preferentially formed by the laser at the grain boundaries.

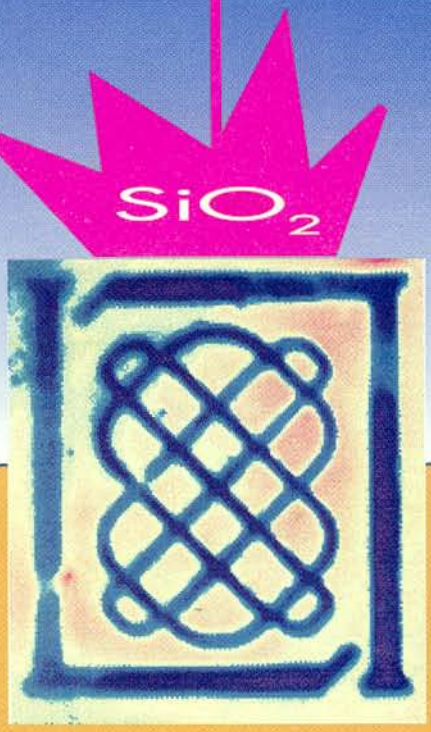


Figure 2. Top view of a sample of fused silica, as seen (in pseudocolors) with a phase measuring interferometer (PMI), following irradiation with a 193 nm excimer laser. The pattern is imprinted in the 1 cm-thick material by laser induced compaction (dark areas) of ~100 nm. The irradiation was performed through a prepatterned Cr-on-quartz mask. The pattern represents Lincoln Laboratory's logo; it is ~4.034.5 mm in size, the thin lines being ~150 μm wide. This sample seems unaltered by the laser radiation, except when viewed through the PMI.

However, from the beginning there were signs that the analogy to visible-wavelength optics was inappropriate. Researchers working with excimer lasers noticed that, during the experiments, optical elements would fluoresce in a variety of intensities and colors, such as blue, pink, milky green, or yellow-brown. This behavior was observed with excimer lasers, but not with pulsed visible sources. Clearly, some interaction did take place between the excimer laser and the optical material, a behavior quite different from that with longer-wavelength lasers.

In the last few years, excimer lasers have come out of the R&D laboratory and have been increasingly incorporated in systems used in industry and medicine. Applications include micromachining of organic and inorganic thin films (ablation, etching, and marking), laser sputtering for the deposition of thin films, photolithography, and surgical procedures. Unlike in the R&D environment, the manufacturers of such systems need to pay close attention to reliability issues, including those of optical components. In addition, some applications require continuous operation at high pulse repetition rates. For instance, excimer-based photolithographic steppers operating in a semiconductor fabrication line are expected to accumulate over one billion pulses a year. Other applications, such as corneal surgery, may require only 100,000 pulses a year, but at fluences 2-3 orders of magnitude higher than those employed in lithography. In all these instances, the optical elements must perform within specifications throughout the system lifetime of several years and maybe decades. This requirement may seem self-evident, but it soon became apparent that it is not always easy to meet. In fact, several excimer-based machines failed in various stages of qualification because the optics were gradually degrading.

As a result of these trends, there has been a growing interest in UV optical materials, with special emphasis on their long-term stability under pulsed excimer irradiation. This paper reviews the key issues in this area, with special emphasis on the 248 and 193 nm wavelengths (KrF and ArF lasers, respectively). It is based on extensive work performed at Lincoln Laboratory over the last few years (including evaluation of new experimental samples), as well as results published by and informal exchanges of information with materials suppliers and other researchers.

General Considerations

The wavelength regime below 300 nm is notable for the small number of available transparent materials. Between 300 and 190 nm, the list is limited to synthetic fused silica (SiO_2), UV-grade sapphire (Al_2O_3), and a few crystalline fluorides: barium fluoride (BaF_2), calcium fluoride (CaF_2), lithium fluoride (LiF), magnesium fluoride (MgF_2), and sodium fluoride (NaF). For special applications at 248 nm, diamond type IIA

is also transparent, as is crystalline sodium chloride (NaCl). Below 190 nm (for instance, at the 157 nm wavelength of the F_2 laser) only the fluorides are transparent, with LiF having the shortest wavelength cutoff at ~105 nm. It should be noted, however, that the meaning of *transparent* is not always unambiguous. More specifically, the transmission T of a slab of material of thickness t is in general given by:

$$T=\frac{(1-R)^2 e^{-\alpha t}}{1-R^2 e^{-2\alpha t}} \quad (1)$$

where α is defined as the absorption coefficient, and R is the reflectivity of each surface, which for normal incidence in air is determined by its index of refraction n:

$$R=\left(\frac{n-1}{n+1}\right)^2 \quad (2)$$

The materials listed above have n in the range 1.3 to 1.8, corresponding to values of R between 1.7 and 8.2%. Thus, even with $\alpha = 0$, losses of several percent per surface are expected. This behavior is, of course, not different from what happens at longer wavelengths. What *is* different below 300 nm is that α may have a finite, non-zero value. Furthermore, its magnitude may vary with specific grade and supplier, from run to run, and even with location within the crystal or boule. For instance, at 193 nm, fused silica was measured to have α as low as 0.005 cm^{-1} and as high as 0.10 cm^{-1}. A particularly large absorption coefficient is measured in most UV-grade sapphire at 193 nm. Although nominally transparent (its bandgap is 8.3 eV, more than the 6.4 eV energy of 193 nm photons), sapphire has a crystalline defect that manifests itself as a broad absorptive band centered at ~205 nm. As a result, sapphire has α ~1 cm^{-1} at 193 nm. For thin samples (2–5 mm) of optical material, even the larger α values may not seem significant. But for longer optical systems, the losses accumulate rapidly. And even small amounts of absorption cause localized heating, which in turn has optical consequences, because the index of refraction is generally temperature dependent (for CaF_2 at 248 nm, it decreases by $\sim 1.1\times10^{-5}$/°C, while for fused silica it increases by $\sim 1.5\times10^{-5}$/°C).

There are other factors besides transmission that limit the usefulness of some of the optical materials listed above. Below are several relevant issues to keep in mind:

- *Birefringence.* Sapphire and magnesium fluoride are both birefringent. For MgF_2 at 193 nm, the difference in index of refraction along the two principal axes is ~0.013. Such materials cannot be used for fabricating high precision lenses.
- *Sensitivity to humidity.* LiF, NaF, and NaCl are hygroscopic to varying degrees. NaCl clouds up in a few hours when exposed to air even at low relative humidity, while LiF lasts much longer. Nevertheless, if used in a practical system, air-exposed LiF components should be monitored closely.
- *Mechanical and thermal properties.* NaF is mechanically soft and therefore must be fixtured (*e.g.*, with O-rings, retainer rings, or clamps) with care. BaF_2 is not easily grown in large sizes (beyond ~100 mm) and is also sensitive to thermal shock.
- *Lapping and polishing techniques.* Processing needs to be optimized for each material. In particular, the hygroscopic and soft crystals are difficult to polish reproducibly to a high degree of surface smoothness.

The considerations outlined above apply to UV materials whether used with cw sources or with pulsed lasers. In addition, irradiation with pulsed excimer lasers can cause gradual changes in optical properties, even at low fluences. These effects are outlined below.

FLUORIDES

Among the fluorides listed above, CaF_2 is the most promising all-purpose material. Its index of refraction at 193 nm is lower than that of fused silica, and therefore the availability of high-quality CaF_2 would enable the design and fabrication of mixed SiO_2/CaF_2 optical systems with a wider performance range than that of systems built of SiO_2 alone. At shorter wavelengths, such as 157 nm, where SiO_2 is opaque, CaF_2 would be the optical material of choice. The index homogeneity of high-quality CaF_2 has been measured to be in the 2-5 ppm range. Unlike in glassy SiO_2, the crystalline nature of CaF_2 dictates that the index homogeneity is inherently three-dimensional. The absorption coefficient of CaF_2 at 193 nm is less than 0.01 cm^{-1}. It has been reported that irradiation at 248 nm does not cause any changes in the transmission of CaF_2.[1] Irradiation at 193 nm can, however, cause formation of absorptive color centers, with peaks in the UV and visible.[2] The laser induced absorbance increases rapidly in the first few hundred thousand pulses, and then it typically exhibits strong saturation. It appears that, in CaF_2, the excimer-induced color centers are formed via pre-existing defects and that impurities may play a critical role in the process. The absorption generated in different grades of CaF_2 can vary by orders of magnitude, indicating that the purity of the raw materials and the details of the crystal growth process are important determinants of susceptibility to laser induced damage.[2,3]

> In the last few years, excimer lasers have come out of the R&D laboratory and have been increasingly incorporated in systems used in industry and medicine.

Crystalline MgF_2 and LiF are two other materials for excimer applications. Historically, MgF_2 has been the most resistant to color center formation, but recently developed commercial grades of CaF_2 approach MgF_2 performance in this respect. MgF_2 is also birefringent. This fact, combined with the availability of high-quality CaF_2, is expected to limit its use for widescale applications. LiF crystals, in our experi-

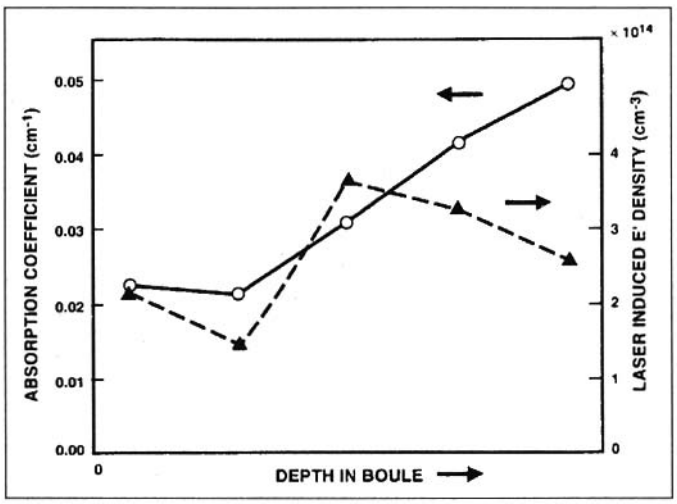


Figure 3. Pre-irradiation absorption coefficient at 193 nm of standard Corning 7940, as a function of the sample's location in the boule (left-hand scale). The broken line represents the density of laser-induced color centers generated by 2×10^6 pulses at 50 mJ cm^{-2}/pulse in the same sample (right-hand scale). While the top of the boule is more transparent and more damage resistant, there does not seem to be a one-to-one correlation between initial absorption and amount of color center formation.

ence, have larger variations in their impurities than CaF_2 or MgF_2. Therefore, the absorption coefficient (α) and excimer induced color centers in LiF exhibit a large range of values. The color centers generated with a 193 nm excimer laser in MgF_2 and LiF exhibit a single peak, centered at ~250 nm for both materials. It should be noted that irradiation with a 248 nm laser has been observed to induce partial bleaching of these bands. All three fluorides listed above have also characteristic visible fluorescence when irradiated with excimer lasers: CaF_2 and LiF in the blue, MgF_2 yellow-brown (see Fig. 1, page 9).

Fused Silica

Synthetic UV-grade fused silica is frequently the material of choice for excimer laser related optical components. Several suppliers offer a variety of grades, which differ in index homogeneity and amount of impurities. The most common impurity is hydroxyl (OH) radicals. In fact, fused silica is sometimes classified as wet or dry, depending on whether the OH concentration is ~100–1000 ppm or ≤10 ppm, respectively. From our experience, wet fused silica is significantly better suited for excimer use than the dry variety, and the remainder of this article will discuss only the wet kind. Other impurities may include Cl ions (up to ~100 ppm if the material is grown in flame hydrolysis of $SiCl_4$) as well as a range of metal ions (typically at ppm levels and below). Index inhomogeneity can be as low 0.5 ppm over a 6 in. (15 cm) slab. It should be noted, however, that in most grades such high degrees of homogeneity are obtained with cylindrical symmetry, and only a few are homogenized in all three dimensions.

Three laser-induced effects have been observed in fused silica, both at 248 and 193 nm. The one alluded to earlier is visible fluorescence. Almost every grade of fused silica fluoresces when exposed to excimer lasers. The spectrum and intensity of the fluorescence change with irradiation conditions such as fluence and total dose. The second effect is formation of absorptive bands in the UV.[4-7] The most prominent of these is centered at ~215 nm. Irradiation at 193 nm, and to a much lesser extent at 248 nm, also causes the formation in many grades of a second, weaker peak at ~260 nm. The 215 nm feature is attributed to the formation of point defects in the glassy SiO_2 network. The same defects have been observed and characterized previously, when fused silica was irradiated with high-energy photons (x-rays, γ-rays) or with particle beams.[8] These are the E' centers, where the -Si-O-Si- atomic chain is broken by an oxygen vacancy and an unpaired electron is left on one of the two adjacent silicon atoms. It now appears that sub-bandgap radiation (*i.e.*, that with excimer lasers) can induce formation of the same defects as those caused by high-energy photons.

The third excimer induced change in fused silica is compaction,[5-7] *i.e.*, an increase in the density of the irradiated volume. The resulting reduction in geometrical thickness of the material is accompanied by an increase in the index of refraction. The two are related by the expression

$$\delta n = -\frac{(n^2+2)(n^2-1)}{6n}\left(1-\frac{\delta r/r}{\delta v/v}\right)\frac{\delta v}{v} \qquad (3)$$

where δn is the change in index and $\delta v/v$ is the fractional change in volume. The quantity $\delta r/r$ is the fractional change in refractivity, which, for fused silica, may be interpreted as the fractional change in the ionic volume of oxygen per unit mass of material. In the simplest case, if the compaction causes only closer packing of the ions, $\delta r/r = 0$. Other values of $\delta r/r$ correspond to the oxygen ions changing their size as well. Eq. 3 is applicable to compaction induced by a variety of processes, such as cooling, external compressive forces, and excimer irradiation. In the latter case we have determined that $(\delta r/r)/(\delta v/v) \approx 0.3$. This result indicates that upon excimer irradiation of fused silica, the oxygen ions are not only brought closer together (the so-called billiard ball model, when $\delta r/r = 0$), but are also compressed in size. The more appropriate imagery would be that of the oxygen ions as soft, spongy balls. The details of the atomic rearrangements leading to the compaction are still unclear. One possibility is that radiation-induced bond-breaking is followed by changes in the intermediate-range structure of fused silica. Such a structure apparently exists[8] in the form of a network of rings, which consists of SiO_4^{-2} tetrahedra. If thermodynamic or steric reasons drive the redistribution of ring sizes to values other than the pre-irradiation ones, then the amount

Synthetic UV-grade fused silica is frequently the material of choice for excimer laser related optical components.

of microcavities is changed, and this process would manifest itself as compaction.

Eq. 3 and our measurements indicate that the net effect of the shrinkage in volume and the increase in index of refraction is a decrease in optical path. The fractional optical path difference (OPD) between exposed and unexposed areas is typically a few parts per million. Such a small amount is difficult to observe directly, except with a phase measuring interferometer (PMI). A striking example is shown in Figure 2 (page 9), where a sample of fused silica was irradiated through a mask, and compaction replicating the pattern on the mask was induced in an otherwise unaltered, transparent material. One has to place the sample in a PMI to view the hidden message imprinted in it.

The compaction has another consequence as well. The area surrounding the irradiated zone experiences deformation, since it has to accommodate the compaction. The deformation causes stress, and the stress causes birefringence. If the sample is placed between two crossed linear polarizers, the transmitted light of a HeNe laser through the stressed areas is readily observed. Indeed, the amount of transmitted light and its spatial distribution can be used as signatures of the birefringence in the unirradiated area, which in turn is related to the compaction in the irradiated parts of the sample.

How does the laser cause these material changes in fused silica? Are they related to each other? Can the material be preprocessed to prevent their formation? It is tempting to answer the first question by pointing to the small amount of absorption present at 193 nm and, to a lesser degree, at 248 nm (α in Eq. 1). This absorption, which may be due to impurities, could be the means by which the excimer energy is coupled into the bulk fused silica. However, there is no one-to-one correlation between 193 nm absorption and excimer induced density of E' centers (Fig. 3). Furthermore, the E' center density varies quadratically with laser fluence rather than linearly, at least at low fluences. Thus, the dominant excimer/fused-silica interaction is not α, but two-photon absorption. The coefficient for two-photon absorption of fused silica at 193 nm has been measured[9] to be $\alpha_1 \approx 2\times10^{-3}$ cm/MW, while at 248 nm it is ~10 times smaller. Thus, for a typical 20 ns long pulse, at a moderate fluence of 100 mJ cm^{-2}/pulse, the equivalent absorption coefficient α is ~0.01 cm^{-1} at 193 nm and 0.001 cm^{-1} at 248 nm. The two-photon absorption model predicts a quadratic dependence of color centers and compaction on laser fluence, and a linear dependence on the number of pulses. Indeed, such behavior has been observed experimentally at low defect densities.[4-7] Saturation-like effects are noted when the laser-induced peak absorption at 215 nm exceeds ~0.15 cm^{-1} and the compaction exceeds ~20 ppm.[5]

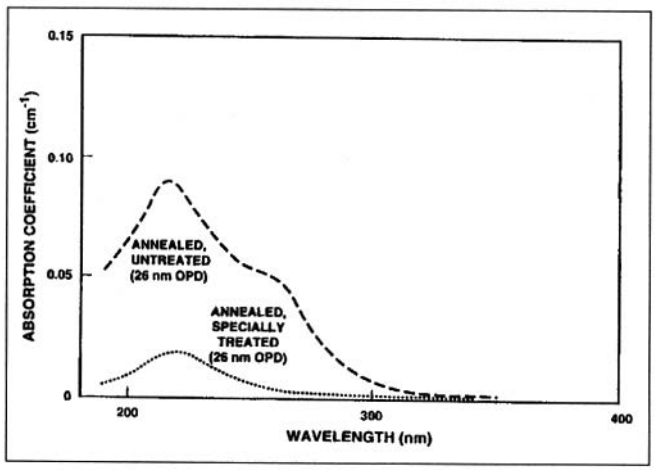


Figure 4. Absorption coefficient of Suprasil 311 irradiated at 193 nm by 2×10^6 pulses of 78 mJ cm^{-2}/pulse. The upper trace shows the response of the standard material, and the lower trace shows the improvement due to a special pre-irradiation treatment. Note that the optical path difference (OPD) is unaffected by the same treatment.

As mentioned above, two-photon absorption is the initiating step for the formation of color centers and compaction. The absorbed energy is converted into excitons and conduction electrons, whose nonradiative decay leads eventually to the observed material changes.[10] However, the E' centers and compaction are not directly related to each other. Rather, they are the outcomes of two different sequences of solid state reactions that start with the same two-photon absorption. One manifestation of this difference is the observed annealing behavior. The E' centers are fully annealed at ~350°C, and partial annealing starts at ~100°C. In contrast, partial annealing of the compaction begins at ~150°C, and full annealing is not achieved even at 600°C. As far as the visible fluorescence is concerned, several recent studies have attempted to correlate it with the other laser induced effects, but the results should at present be considered preliminary.[7,11] As a rule of thumb, the weaker the fluorescence, the lower the magnitude of the other changes.

While the model presented above predicts a functional dependence of laser-induced defects on irradiation parameters, it cannot predict the quantitative values of the laser induced absorption or the compaction. Such values depend on the details of the solid state reactions following the two-photon absorption, and these reactions are strongly affected by subtle differences in the glassy structure and level of impurities. Indeed, the amount of laser induced color center formation varies from grade to grade and may strongly depend on the details of material formation and any other pre-irradiation treatments. For instance, Suprasil 311 can be pretreated to cause a sevenfold reduction in the excimer induced density of E' centers (Fig. 4). Note, however, that the same treatment does not affect the amount of laser induced compaction, in agreement with the discussion above regarding the differences between E' centers and compaction. As shown in Figure 3, even within the same grade of fused silica, the color center formation may vary significantly with a subtle variable such as location in the boule. Therefore, a careful choice of materials used in excimer applications is required, and pre-selection and pre-testing may be desirable.

The excimer induced changes described so far are stable at room temperature, at least for several weeks or months. In addition, some puzzling transient behavior has also been reported recently.[11,12] It seems that the excimer induced absorption at 215 nm tends to recover spontaneously in a matter of seconds or minutes. The permanent (or semi-permanent) E' centers described above are the result of extended irradiation, but at lower doses only short-lived centers are observed. We have also seen transient color centers superimposed on the stable centers previously generated by the same laser.[13] The time scales in these phenomena vary strongly with material properties, such as grade and preprocessing conditions. Currently there is no clear interpretation of the experimentally observed, and sometimes baffling, results.

Dielectric Coatings

Dielectric coatings at excimer laser wavelengths are subject to considerations similar to those of bulk materials. In addition, these coatings need to satisfy other constraints related to stress and adhesion. The distribution of electric field throughout the stack can have an important effect on the durability of a coating, as can the details of the deposition process of the thin films, surface roughness, and the presence of inclusions, among other factors. To date, we have evaluated several coatings at 193 nm, from two different vendors. No degradation has been observed to at least 40 million pulses, at a fluence 100 mJ cm^{-2}/pulse. Except for these preliminary results, little is known about the long term stability of optical coatings for excimer use. Much more work needs to be performed before our knowledge in this area approaches our understanding (limited as it is) of bulk materials.

Conclusions

Optical components in excimer based systems must satisfy a number of requirements. Chief among them are transparency and resistance to radiation induced damage. Synthetic UV-grade fused silica and calcium fluoride, as well as other fluorides, can meet stringent transparency requirements even at the short wavelength of 193 nm. However, extended irradiation with the excimer laser may noticeably change the material properties. Fused silica develops UV color centers and is compacted, and the fluorides develop characteristic color centers. The magnitude of these effects can be reduced by optimized pre-irradiation processes. Therefore, the choice of the most appropriate material for any given application necessitates careful evaluation and pre-testing. A detailed understanding of the relevant solid state processes is beginning to emerge, especially for fused silica. Nevertheless, a self-consistent picture that would explain the available experimental information is still lacking. A significant amount of research, both on the experimental and modeling side, as well as so-

phisticated diagnostic techniques,[14] will have to be applied before the state of the art can be further advanced in this widely interdisciplinary field.

Acknowledgments

The expert technical assistance of J.H.C. Sedlacek and T.J. Pack is gratefully acknowledged. This review would not have been possible without the assistance of all the people who shared their experience and provided experimental samples: D. Cope, B. Flint, D. Gritz, J. Holman, D. Krajnovich, W. McCullom, C. Rowen, M. Saepoff, P. Schermerhorn, R. Sparrow, and R. Takke. This work was sponsored by the Defense Advanced Research Projects Agency.

M. Rothschild *is a group leader at Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Mass.*

References

1. D. Krajnovich *et al.*, "Testing of the durability of single-crystal calcium fluoride with and without antireflection coatings for use with high-power KrF excimer lasers," Appl. Opt. **31**, 1992, 6062-6075.
2. J.H.C. Sedlacek and M. Rothschild, "Optical materials for use with excimer lasers," Proc. SPIE **1835** (in press).
3. I. Toepke and D. Cope, "Improvements in crystal optics for excimer lasers," Proc. SPIE **1835** (in press).
4. K. Arai *et al.*, "Two-photon processes in defect formation by excimer lasers in synthetic silica glass," Appl. Phys. Lett. **53**, 1988, 1891-1893.
5. M. Rothschild *et al.*, "Effects of excimer laser irradiation on the transmission, index of refraction, and density of ultraviolet grade fused silica," Appl. Phys. Lett. **55**, 1989, 1276-1278; M. Rothschild and J. H. C. Sedlacek, "Excimer laser induced degradation in bulk fused silica," Proc. SPIE **1848** (in press).
6. W.P. Leung *et al.*, "Effect of intense and prolonged 248 nm pulsed laser irradiation on the properties of ultraviolet-grade fused silica," Appl. Phys. Lett. **58**, 1991, 551-553.
7. P. Schermerhorn, "Excimer laser damage testing of optical materials," Proc. SPIE **1835** (in press).
8. D.L. Griscom, "Defect structure of glasses," J. Non-Cryst. Solids **73**, 1985, 51-77.
9. R.K. Brimacombe *et al.*, "Dependence of the nonlinear transmission properties of fused silica fibers on excimer laser wavelength," J. Appl. Phys. **66**, 1989, 4035-4040.
10. T.E. Tsai and D. L. Griscom, "Experimental evidence for excitonic mechanism of defect generation in high-purity silica," Phys. Rev. Lett. **67**, 1991, 2517-2520.
11. D.J. Krajnovich *et al.*, "Sudden onset of strong absorption followed by forced recovery in KrF laser irradiated fused silica," Opt. Lett. (in press).
12. N. Leclerc *et al.*, "Transient 210-nm absorption in fused silica induced by high-power UV laser irradiation," Opt. Lett. **16**, 1991, 940-942.
13. M. Rothschild and J. H. C. Sedlacek (unpublished).
14. One such technique may be hydrogen nuclear magnetic resonance. See D.H. Levy *et al.*, "The role of hydrogen in excimer laser induced damage of fused silica," J. Appl. Phys. (in press).