

UCRL- 91737
PREPRINT

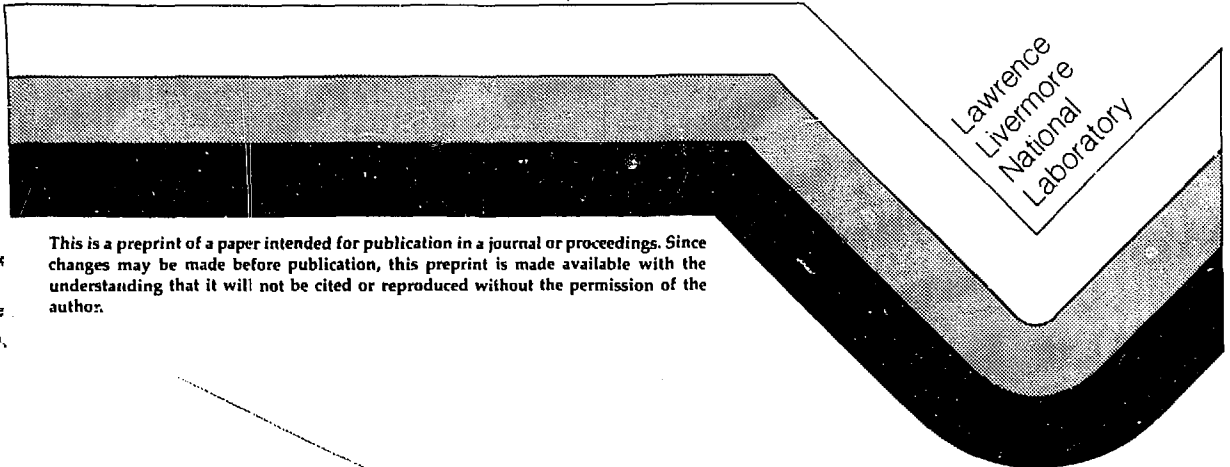
CONF-850345--24

Technical and Historical Overview of the Study
at Livermore of Porous Antireflection Coatings

D. Milam

This paper was prepared for submittal to
Southwest Conference on Optics
Albuquerque, New Mexico
March 4-8, 1985

April 4, 1985



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Technical and Historical Overview of the Study at
Lawrence Livermore National Laboratory
of Porous Antireflection Coatings

D. Milam

Lawrence Livermore National Laboratory

University of California

P.O. Box 5508, L-490

Livermore, California 94550

UCRL--91737

DE85 010925

Abstract

The testing program leading to selection of antireflection coatings for the NOVA laser is reviewed. Limiting problems that prevented use of some coating technologies are described, and estimates are made of the current value of pursuing solutions to those problems.

Introduction

After testing a large number of coatings that were either supplied by industry or fabricated inhouse, we selected two types of porous antireflection coatings for use in the NOVA laser. For lenses and windows made of borosilicate glass and intended for use only at 1064 nm, Schott's Neutral Solution Process^{1,2} was used to convert the bare polished surfaces into porous antireflecting layers. Fused silica components and water soluble crystals of potassium dihydrogen phosphate (KDP) were coated with porous silica films deposited from a metal organic solution.³

MACTED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DB

During the research that led to selection of these coatings, we investigated several other coating techniques. In this paper we review the complete testing program, identify the problems that we encountered with coatings that were not selected, and attempt to comment on whether resolution of the limiting problems might lead to coatings that are superior to those presently in use. Details of the coating processes themselves were given in a recent review.⁴

History of the Testing Program

In the eight year period from 1977 to the fall of 1984, the thresholds for laser-induced damage for 3616 samples were measured at Lawrence Livermore Laboratory.⁵ Table 1 summarizes the wavelengths and durations of the laser pulses used to measure these thresholds and the number of measurements made at each wavelength. More than 80% of these thresholds were measured by either Frank Rainer or James E. Swain. The remainder were measured by Michael E. Staggs, Charmaine Vercimak, Bruce Woods, Carolyn Weinzapfel or myself.

Table 1
Wavelengths and Durations of Laser Pulses Used in Laser-Damage Studies and the Number of Samples Tested at Each Wavelength.

| <u>Wavelength</u> | <u>Pulse Duration</u> | <u>Samples Tested</u> |
|-------------------|-----------------------|-----------------------|
| 1064 nm | 0.1 - 20 ns | 2312 |
| 532 nm | 0.1 - 0.7 ns | 90 |
| 355 nm | 0.1 - 9 ns | 921 |
| 248 nm | 20 ns | 293 |

For the 1064-nm and 355-nm tests that were most directly related to selection of coatings for NOVA, Table 2 gives the number of thresholds

measured for each of several generic types of samples. The samples that received the largest number of tests (1234), were optical coatings deposited in vacuum by electron-beam evaporation. The majority of these were made by the research group at Optical Coating Laboratory, Inc. Samples were also provided by every major industrial supplier of optical coatings and by several research facilities in the United States, and by both industrial research groups in Europe, Japan and China. Deposition techniques that were studied included electron-beam evaporation, thermal evaporation, rf sputtering, ion-beam sputtering, and ion-assisted electron-beam evaporation. Available reviews^{6,7,8} contain the principal results of our study of vacuum-deposited films and cite the initial literature that described various segments of the study.

Table 2

Summary of the damage tests made at LLNL with either 1064-nm or 355-nm pulses during 1977-1984.

| | <u>1064-nm</u> | <u>355-nm</u> |
|-------------------------------|----------------|---------------|
| Vapor Deposited Films | 890 | 344 |
| Porous Surfaces or Films | 219 | 347 |
| KDP Crystals | 274 | 48 |
| Bare Polished Glass or Silica | 141 | 43 |
| Fluorophosphate Glass | 158 | - |
| Index-Matching Fluids | 118 | 3 |
| Plastics | 36 | 6 |
| Miscellaneous | 476 | 130 |
| TOTALS | <u>2312</u> | <u>921</u> |

This paper reviews our study of porous coatings and surfaces. Samples of this type received the second largest number of tests (566). The 1064-nm study of porous surfaces, diagrammed in Fig. 1, began in 1977 with the testing of two, acid-etched samples of Pyrex (Corning Code 7740), a product of Corning Glass Works that is phase separated into

microscopic, silica-poor and silica-rich volumes.⁹ These etched surfaces exhibited broadband antireflectance and their thresholds for damage by 1064-nm, 1-ns pulses were 10 and 14 J/cm², values comparable to the highest thresholds that had been observed in tests of vacuum-deposited coatings.¹⁰ The surfaces of these initial samples were nonuniform and had low resistance to abrasion. Also, Pyrex cannot be produced with adequate homogeneity for large optical components. However, encouraged by the high damage resistance, the four companies identified in Fig. 1A subsequently produced homogeneous phase-separated glasses. One of these, Hoya's ARG-2 was made available as a commercial produce.¹¹ The work at Owens Illinois, Schott and Hoya was funded by LLNL. Corning's work was internally funded. It was found that the phase-separated glasses could be successfully figured by the grinding and polishing procedures used to figure surfaces on homogeneous silicate glasses, and that 1064-nm, 1-ns damage thresholds of etched surfaces were consistently in the range of 10-12 J/cm², about 75% of the threshold for bare polished surfaces on glasses such as fused silica. However, an etching procedure for producing highly uniform antireflectance while preserving surface figure was not found during our study of these glasses.

During 1978 we began testing single-layer films and multilayer antireflection coatings made of oxides, such as TiO₂ and SiO₂, deposited from solutions (see Fig. 1B). The 1064-nm, 1-ns thresholds of these coatings were usually 3-6 J/cm², slightly below the 5 J/cm² median threshold for vacuum-deposited AR coatings. The morphology of laser-induced damage to the liquid-deposited films was similar to that of vacuum-deposited films, and consisted of isolated micropits attributed to damage at defects or particulate inclusions.⁽⁶⁾

The emphasis on homogeneous films decreased when we observed (Jan., 1979) larger thresholds, $8-24 \text{ J/cm}^2$, in tests of liquid-deposited films of borosilicate glasses which were heated to $300-750^\circ\text{C}$ to produce phase separation and then etched to be antireflective.^{12,13,14} The single-surface reflectance of these films was usually less than 2% and sometimes as low as 0.1%. For coatings with low reflectance, the spectral bandwidth was usually large. These films had the mechanical fragility of etched surfaces on bulk, phase-separated glass, but they could be applied to a wide variety of transparent optical materials and had lower scattering loss than the bulk phase-separated material. The difficulty of uniformly etching large phase-separated films was not examined.

Study of all the technologies discussed above largely ceased with the advent of Schott's Neutral Solution Process (NSP) for converting polished surfaces of homogeneous borosilicate glasses to antireflecting surface layers.^{1,2} Thresholds of surfaces made by NSP were equal to those of etched surfaces on phase-separated glass, and the surfaces made by NSP had greater resistance to abrasion.¹⁵ NSP had the additional advantage that it required 40-70 hours and this allowed the formation of the surface to be easily monitored. This process was licensed to LLNL by Schott. Within 15 months after testing the first surface made by NSP, lenses and windows with diameters as large as 1 m were being successfully processed.

Before completion of the 1064-nm experiments diagrammed in Fig. 1, transmittance of several glasses had been measured with intense 355-nm pulses. Fused silica was the only glass found to be free of both transient, nonlinear absorption and coloration when exposed to

irradiation at NOVA design fluences.¹⁷ Because NSP does not form antireflective surfaces on fused silica, we undertook development of a damage resistant 355-nm AR coating for fused silica.

The testing program that led to selection of the 355-nm coating is diagrammed in Fig. 2. Yoldas at Westinghouse demonstrated deposition of porous-silica antireflection coatings from alcoholic solutions containing polymeric siloxane molecules.¹⁸ Since this chemistry had the potential for producing high purity silica, and the coatings made from the siloxane molecules could be etched and converted into graded-index films with broadband antireflectivity, the Westinghouse process was intensively studied. A total of 212 of these films, fabricated at both the Westinghouse Research and Development Center in Pittsburgh and at LLNL, were tested. This effort produced a few broadband antireflective films with damage thresholds of 4-5 J/cm² (measured with 355-nm, 0.6-ns pulses) which were greater than the median threshold that was concurrently established for vacuum-deposited films, 2.5 J/cm². However, the median threshold for the broadband, porous-silica AR coatings was only 2.1 J/cm². By reducing the optical thickness to 89 nm, the quarterwave thickness for 355 nm, we were able to produce high threshold (5-9 J/cm²) homogeneous siloxane coatings.¹⁹ These films had the narrowband transmittance spectrum characteristic of homogeneous quarterwave coatings. However, they were so thin that they could not serve 1064-nm AR films or be converted by etching into graded-index, broadband AR films.

A study by Hoya, under LLNL contract, of porous silica coatings produced results much like those from Westinghouse. Corning independently produced some proprietary coatings with excellent damage resistance, 5-10 J/cm², and evaluation of these films raised questions that were instrumental to the subsequent development by Thomas at LLNL of a highly successful coating.

In early 1984, Thomas devised a coating made from microscopic silica particles formed by the base catalyzed reaction of ethyl silicate with water in either ethanol or methanol.³ The coating was rather fragile and could not be graded to provide broadband antireflectance, but it exhibited excellent resistance to damage at all wavelengths between 248 nm and 1064 nm. The process had several other desirable characteristics. The coating solution was alcoholic and did not contain water, and the dried film did not require heat treatment, so the process could be used to coat water soluble KDP crystals that will not withstand heating beyond about 170°C. The chemicals that were used could be purified by distillation, and the finished solution could be passed through filters with 0.2µm pores, so it was readily possible to produce large batches of highly pure coating solution for use in large scale coaters. The coating solution could be applied by dipping, which was used to coat silica lenses with diameters up to 1 m, or by spinning which was used to coat 27 cm KDP crystals. These characteristics, together with the excellent damage resistance, led to selection of this coating for NOVA.

There was, therefore, a consistent pattern in both the 1064-nm and the 355-nm research programs. In each of these efforts, it was necessary to identify, as quickly as possible, coatings that would be adequate for

the NOVA laser. This forced us to begin a broad search for successful processes, and to rapidly redirect our efforts so that we were always placing greatest emphasis on the coating that seemed to hold the best promise. A program operated under these constraints necessarily leaves a large number of unanswered questions. In the following section we briefly state the advantages and disadvantages that are currently known for coatings made by processes not selected for NOVA, state the difficulty that led to rejection of these processes, and attempt to estimate the progress that could be made through additional research.

Limiting Problems and Potential for Porous Surfaces not Used in NOVA

A. Siloxane porous silica coatings

Of the porous coatings that were not chosen for use in NOVA, the siloxane coating probably holds the greatest promise. We believe that the current process for fabricating these coatings leaves a carbonaceous residue which limits the attainable damage threshold. Carbon is always present in the initial coating solution which is made by an acid catalyzed reaction between ethyl silicate and water in an ethanol carrier.¹⁸ At the water to ethyl silicate ratio used in making porous coatings, typically 2.2 moles of water per mole of ethyl silicate, the reaction product is believed to be a double linear-chain, polysiloxane molecule with either ethyl or hydroxyl groups attached to its periphery. When the solution is spread on a substrate and the alcohol evaporates, the polysiloxane molecules come into contact and bond to each other and to the substrate through reactions between the side groups on molecules and the hydroxyl groups on the substrate. If water is excluded during this initial drying, the dried film is porous.

In the coating technique devised at Westinghouse, dried coatings were baked at 400-500°C, the intent being both to chemically reduce the siloxane to silica through pyrolysis and to reduce the median pore diameter through partial sintering. The coatings were then cooled and etched in HF to obtain index gradation.

Several problems were proposed as the cause of the low thresholds observed for most of the films made from siloxane: impure or improperly prepared solutions, particulate or chemical contamination of the substrate, and the inability to completely eliminate carbonaceous residues produced during pyrolysis. Exhaustive studies of the distillation and filtration of the coating solution, and of a variety of techniques for cleaning substrates, were unsuccessful in increasing the thresholds, although it could readily be demonstrated that lack of attention to any of these details produced coatings with even lower thresholds. Three experimental results supported the hypothesis that carbon was the problem. (1) Thick crusts formed by evaporating the ethanol from a small volume of the solution turned black when they were baked at 400-500°C. (2) Analysis of a siloxane coating by secondary ion mass spectroscopy indicated that the carbon content increased with depth in the coating. (3) Thinning the films to improve the probability of carbon removal sometimes resulted in films with 355 nm, 0.6 ns damage thresholds as large as 9 J/cm^2 .¹⁹

Because siloxane coatings hold promise, we are continuing to study deposition of this material and believe it will be possible to eliminate residual carbon. We have produced a few, thick siloxane (500 nm) films with thresholds of 6 J/cm^2 . However, the transmittance spectra of

these coatings did not have the extremely large bandwidth that was observed in spectra of some of the earlier siloxane coatings. During our initial study of the etching of siloxane, we believed that index gradation occurred as a result of an attack on the silica material itself, and that the effect of etching was to increase the median size of pores near the air interface. Because thin coatings with high thresholds were not readily graded, and narrower bandwidth has been observed in thicker, etched films made by incorporation of oxidants to eliminate carbon, we now believe that one effect of etching films made from siloxane may be removal of constituents other than silica, that is, production of index gradation by removal of impurities from the front plane of the coating. Therefore, a successful technique for completely eliminating carbon may produce coatings whose response to etching is quite different from that of the initial films made from siloxane, so we cannot presently predict whether the index profile of a carbon-free film can be graded.

If a process can be found for producing pure silica through chemical reduction of siloxane, coatings made from this silica should find wide application in broadband AR coatings. Even in its present state, the material provides coatings with thresholds comparable to those of films made by vapor deposition.

B. Bulk phase-separated glass and films of phase-separated glass

Antireflecting surfaces on phase-separated glasses were produced by briefly immersing a figured optical component in acid. We found control of that treatment to be difficult.

The desirable characteristics of etched surfaces on phase-separated glass are their good resistance to laser damage and their extremely large bandwidth. Single-surface reflectance less than 1% across the entire transparency spectrum of a glass, from 350 nm to 2200 nm has been demonstrated.⁹ Other than the difficulty with their production, the principal undesirable characteristics are mechanical fragility and loss due to scattering, and the inability of phase-separated silicate glasses to resist coloration by intense 355-nm pulses. Some of these problems are inherent. The softness is associated with the wide bandwidth. Obtaining wide bandwidth requires etching a surface so that its refractive index profile varies rather smoothly from a value near $n = 1$ at the air interface to a value near the index of the glass. In such an etched surface, the glass content at the air interface is necessarily very low, and the surface is mechanically weak.

Similarly, the scattering loss is caused by the phase separation which is necessary to allow formation of a microporous surface. The scattering loss in bulk phase-separated glass varies with wavelength λ as λ^{-4} , and at wavelengths between 300 and 400 nm is usually in the range of $5 \times 10^{-2} \text{ cm}^{-1}$. The scattering loss can be reduced by using liquid-deposited films of phase-separated glass instead of bulk phase-separated glass. Such films were produced and they retained both the resistance to damage and the spectral bandwidth of etched surfaces on the bulk glass. However, phase separation of the liquid-deposited film occurred during heat treatment at 500 - 800°C, a treatment that could not be applied to some substrates. The difficulty of obtaining uniform etching is probably common to both films and bulk glass.

Therefore, given the inherent limitations of the phase-separated glasses, and the rapid progress being made with porous silica coatings, it is unlikely that the remaining problems with manufacture of large, optically-figured, antireflecting surfaces on etched, phase-separated glass will be solved unless a need arises for extreme spectral bandwidth.

C. Homogeneous, liquid deposited films

The study of homogeneous films deposited from liquids has not progressed to the point that a limiting problem can be identified. The initial films that we studied during 1978-1980 were made of single oxides such as TiO_2 and SiO_2 , or of complex glasses that had not been heated to produce phase separation, or of glasses that had been phase separated, but not etched. In most of these films, 1064-nm laser damage thresholds were comparable to those of vacuum-deposited films. The morphology of damage suggested the limiting problem causing low thresholds was inclusion of dirt in coating solutions, although hindsight now allows the possibility that it was partially due to formation of absorbing impurities during thermal processing.

The promise that solution chemistry might produce improved homogeneous coatings arises from a fundamental difference between solution chemistry and vapor deposition. The coating solutions are produced by reactions that reach a stable equilibrium. By contrast, reactive vapor deposition is a nonequilibrium process that has the potential for formation of incompletely oxidized films. In fact, after several years of study of vapor-deposited oxide coatings, we believe that many of the damage susceptible regions in these coatings are metal-rich

microvolumes. The evidence which best supports this hypothesis is the variation of damage morphology, damage threshold and spatially averaged absorption in films of Ta_2O_3 and TiO_2 deposited at varied partial pressures of oxygen.²⁰ In films deposited at optimum oxygen pressure, spatially averaged absorption was relatively low for thin films, typically about 10 cm^{-1} , and threshold level damage in these optimum films consisted of micron-sized pits separated by 100-500 μm . In films made at lower oxygen pressures, both the spatial density of damage micropits in threshold-level damage and the spatially averaged absorption increased as oxygen pressure decreased. In films made at sufficiently low oxygen pressure, the damage pits were so densely located that they merged and the film was uniformly removed during damage, and absorption was large. The very large, spatially averaged absorption in vacuum-deposited films made under severe oxygen depletion is known to result from nonstoichiometry. Since spatially averaged absorption was observed to be correlated with the spatial density of damage pits, it is reasonable to assume that the absorption measurement simply summed the absorption at a microscopic volumes with poor stoichiometry and that these volumes were also the sites at which damage first occurred. Because the damage threshold was not correlated with spatially averaged absorption unless the absorption was very large, it also seems that the absorbing microvolumes were always rather similar and that variation of oxygen pressure affected primarily only the number of absorbing volumes per unit area.

Oxide coating materials made by equilibrium chemical reactions have the potential for being stoichiometric at the molecular level, and their use may eliminate many of the absorbing defects in films. However,

liquid deposition has its own set of problems. It is difficult to exclude dirt and impurities from the solutions, although the recent studies of silica suggest these problems can be adequately treated by distillation and filtration. Liquid deposition of some oxides produces porous films that may require densification and the stress is very large in some of these films. Until adequate research is performed, it is not certain that better reflectors and polarizers can be made by liquid deposition, but we view liquid deposition as the technique most likely to provide multilayer coatings superior to those made by electron-beam evaporation.

D. Direct formation of antireflective surfaces on single-phase glasses

It would be highly advantageous to have a process for directly converting polished surfaces on single-phase materials like fused silica into antireflecting layers. The only technique that we investigated was that of etching the damage tracks left by passage of nuclear fragments. In this work by Hopper,²¹ etching such a track produced a cone shaped pit whose cone angle was determined by the difference in the etch rates of the damage track and the undamaged silica. Fused silica was exposed to the fragments obtained by bombarding a uranium foil with neutrons, and the damaged silica surfaces were etched with HF. The differential etch rate was about 4:1, and cones with the 0.4-0.5 μ m depth required to form broadband antireflecting surfaces had at the air interface diameters of about 0.2 to 0.25 μ m. Such cones were efficient scatterers of light, so the net transmission was only marginally improved, although specular reflection was greatly reduced. At present, we are not continuing study of this process, and are not aware of other candidate techniques for converting polished surfaces on fused silica into antireflecting layers.

Summary

Our study of porous coatings and surfaces was highly productive. It led to the development by Schott of Neutral Solution Processing which converts polished surfaces on borosilicate glasses into antireflecting surface layers, and to the development by Thomas of LLNL of a sol-gel antireflection coating for fused silica and crystals of KDP. Antireflecting surfaces made by these techniques have thresholds for laser-induced damage that are 2-3 times larger than thresholds of coatings that were previously available. Development of these coatings was crucial to the successful operation of the Nova laser.

During this study, we also began the investigation of several other coating techniques, but were unable to continue these studies and find solutions for the problems that were identified. Silica films made by chemical reduction of siloxane were mechanically strong, but we believe that the currently known procedure for making these films leads to production of carbon residues and resultant low damage thresholds. Antireflecting surfaces made by etching phase-separated glasses and films have the greatest spectral bandwidth of known single-layer films, but we do not have an etching process that yields spatially uniform antireflectance while maintaining surface figure. Homogeneous coatings made from liquids had only moderate resistance to damage, and we believe the damage was caused by inclusion of dirt and impurities in the coatings or by production of absorbing residues during thermal curing of the coatings. The only technique evaluated for direct conversion of silica surfaces into antireflecting surface layers was etching of damage tracks caused by irradiating the surface with nuclear fragments, and the porosity created by this process was sufficiently coarse to cause strong scattering of incident light.

Resolution of these problems should lead to antireflecting surfaces that are usable in both lasers and conventional optical systems. Homogeneous coatings deposited from solutions are particularly attractive because they may be stoichiometric.

The study of solution-deposited coatings for laser applications is a young and active field. Considering the progress that has been made, we anticipate rapid progress in solution of known problems and development of new coatings.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Acknowledgements

During the work described above, the author enjoyed collaboration with many colleagues at Lawrence Livermore Laboratory, principally W. H. Lowdermilk, Frank Rainer, J. E. Swain, I. M. Thomas, J. G. Wilder, W L. Smith, M. C. Staggs, S. E. Peluso, C. L. Vercimak, C. C. Weinzapfel, and B. W. Woods. He also gratefully acknowledges the contributions made by personnel at several corporations that participated in our study of porous surfaces and films: Corning Glass Works, Inc., Owens-Illinois, Inc., Hoya Optics, Inc., Westinghouse Electric Corporation, Optical Coating Laboratory, Inc., and Ohara Optical Glass, Inc. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

References

1. Cook, L. M., Mader, K.-H., and Schnabel, R., "Integral Antireflective Surfaces on Silicate Glass," U. S. Pat. Appl. 309,149, Oct. 6, 1981.
2. Cook, L. M., Ciolek, S., and Mader, K.-H., "Integral Antireflective Surface Production on Optical Glass," J. Am. Ceram. Soc. 65, C152, 1982.
3. Thomas, I. M., Wilder, J. G., Lowdermilk, W. H., and Staggs, M. C., "High Damage Threshold Porous Silica Antireflection Coating," Proceedings of the 1985 Boulder Damage Conference, to be published.
4. Lowdermilk, W. H., "Graded-index Surfaces and Films," SPIE Proceedings Vol. 387, pp. 1-24, 1983.
5. Milam, D., "Measurement and Identification of Laser-Damage Thresholds in Thin Films," SPIE Vol. 140, Optical Coatings-Applications and Utilization II, 52-61, 1978.
6. Lowdermilk, W. H., and Milam, D., "Laser-induced Surface and Coating Damage," IEEE J. Quant. Electr., Vol. QE-17, pp. 1888-1903, 1981.
7. Lowdermilk, W. H., and Milam, D., "Review of Ultraviolet Damage Threshold Measurements at Lawrence Livermore National Laboratory," SPIE Proceedings Vol. 476, pp. 143-162, 1984.
8. Lowdermilk, W. H., "Effects of Laser Radiation on Surfaces and Coatings", SPIE paper, to be published.
9. Minot, M. J., "Single-layer Gradient Refractive Index Antireflection Films Effective From 0.35 to 2.5 μ ," J. Opt. Soc. Am. 66, 515, 1976.
10. Lowdermilk, W. H., and Milam, D., "Graded-index Antireflection Surfaces for High Power Laser Applications," Appl. Phys. Lett. 36, 891, 1980.

11. Asahara, Y., and Izumitani, T., "The Properties of Gradient Index Antireflection Layer on the Phase Separable Glass," J. Non-Cryst. Solids, Vol. 42, pp. 269-280, 1980.
12. McCollister, H. L., and Boling, N. M., "Process of Making Glass Articles Having Antireflective Coatings and Product," U.S. Patent 4,273,826, 1981, Owens-Illinois, Inc., U.S.A.
13. Mukherjee, S. P., "Gel-derived Single-layer Antireflection Films with Refractive Index Gradient," Thin Solid Films 81, L89, 1981.
14. Mukherjee, S. P., and Lowdermilk, W. H., "Gel-derived Single Layer Antireflection Films," J. Non. Cryst. Sol., Vol. 48, pp. 177-184, 1982.
15. Cook, L. M., Lowdermilk, W. H., Milam, D., and Swain, J. E., "Antireflective Surfaces for High Energy Laser Optics Formed by Neutral Solution Processing," Appl. Opt., Vol. 21, pp. 1482-1485, 1982.
16. Wirtenson, G. R., Brown, N. J., and Cook, L. M., "Scaling up the Neutral Solution Anti-reflection Process," in Laser Induced Damage in Optical Materials: 1982, Bennett, H., E., Guenther, A. H., Milam, D., and Newnam, B. E., Eds., in press.
17. Smith, W. L., "Two Photon Absorption and Solarization in UV Glasses," 1982 Laser Program Annual Report, Hendricks, C. D., Ed., Lawrence Livermore National Laboratory, UCFI-50021-82, Section 7, pp. 34-38, 1983.
18. Yoldas, B. E. and Partlow, D. D., "Wide Spectrum Antireflective Coatings for Fused Silica and Other Glasses," Appl. Opt., Vol. 23, pp. 1418-1424, 1984.

19. Wilder, J. G., "Porous Silica AR Coating for Use a 248 nm or 266 nm," Appl. Opt., Vol. 23, 1448-1449, 1984.
20. Milam, D., Lowdermilk, W. H., Rainer, F., Swain, J. E., Carniglia, C. K., and Hart, T. T., "Influence of Deposition Parameters on Laser-Damage Threshold of Silica-Tantala AR Coatings," Appl. Opt., Vol. 21, pp. 3689-3694, 1982.
21. Hopper, R. W., Lawrence Livermore National Laboratory, Nov. 1982, unpublished.

Figure Captions

1. History of the measurement of 1064-nm laser-damage thresholds of porous surfaces and coatings. Boxes indicate the time span covered by tests of a particular coating or surface. Histograms indicate the number of thresholds measured. The samples were of four types: (A) etched surfaces of phase-separated glasses, (B) homogeneous films deposited from liquids, (C) etched glass films and (D) neutral solution processed surfaces on borosilicate glasses.
2. History of the measurement of 355-nm laser-damage thresholds for porous silica films and for graded-index surfaces made by etching nuclear-particle track damage in fused silica. All substrates were fused silica except for the one set that were KDP crystals.

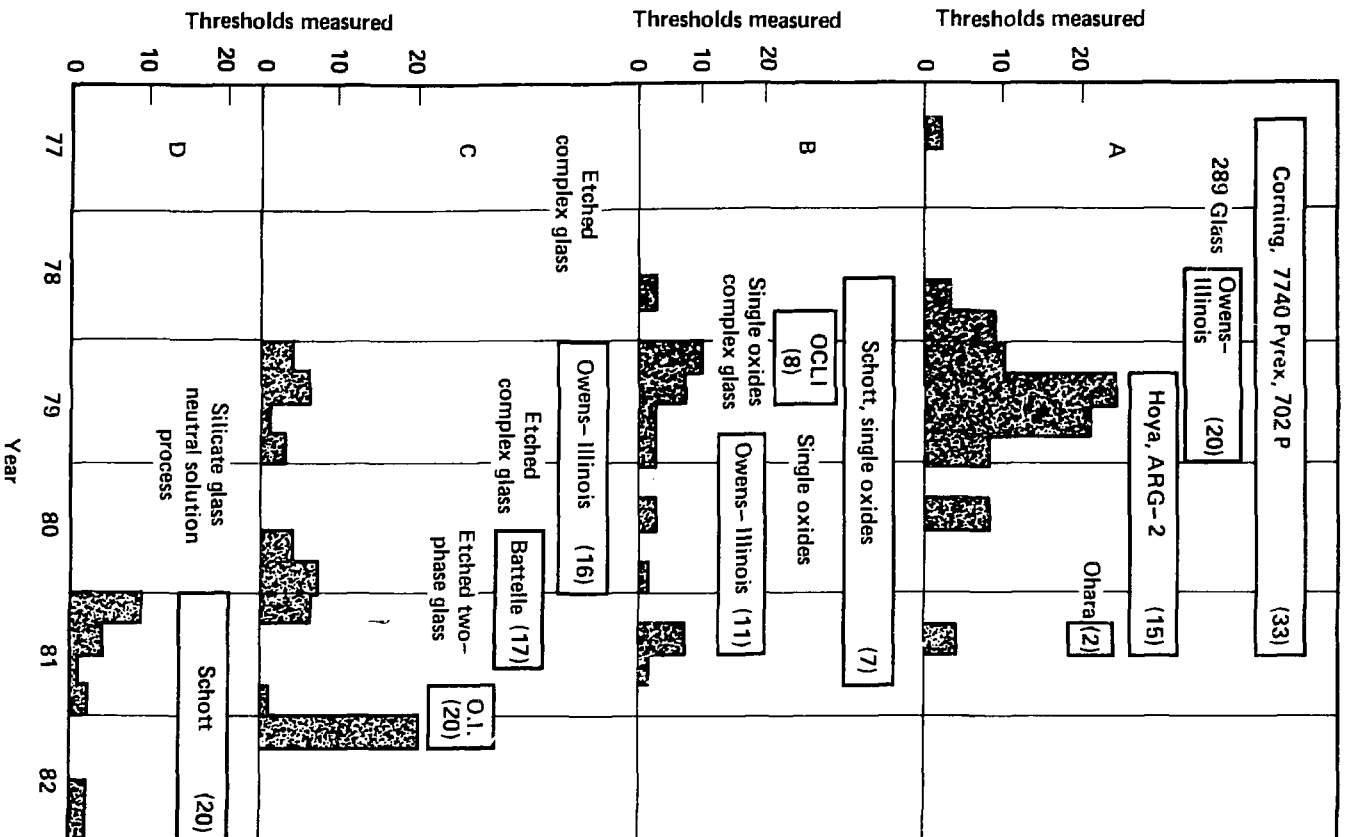


Figure 1

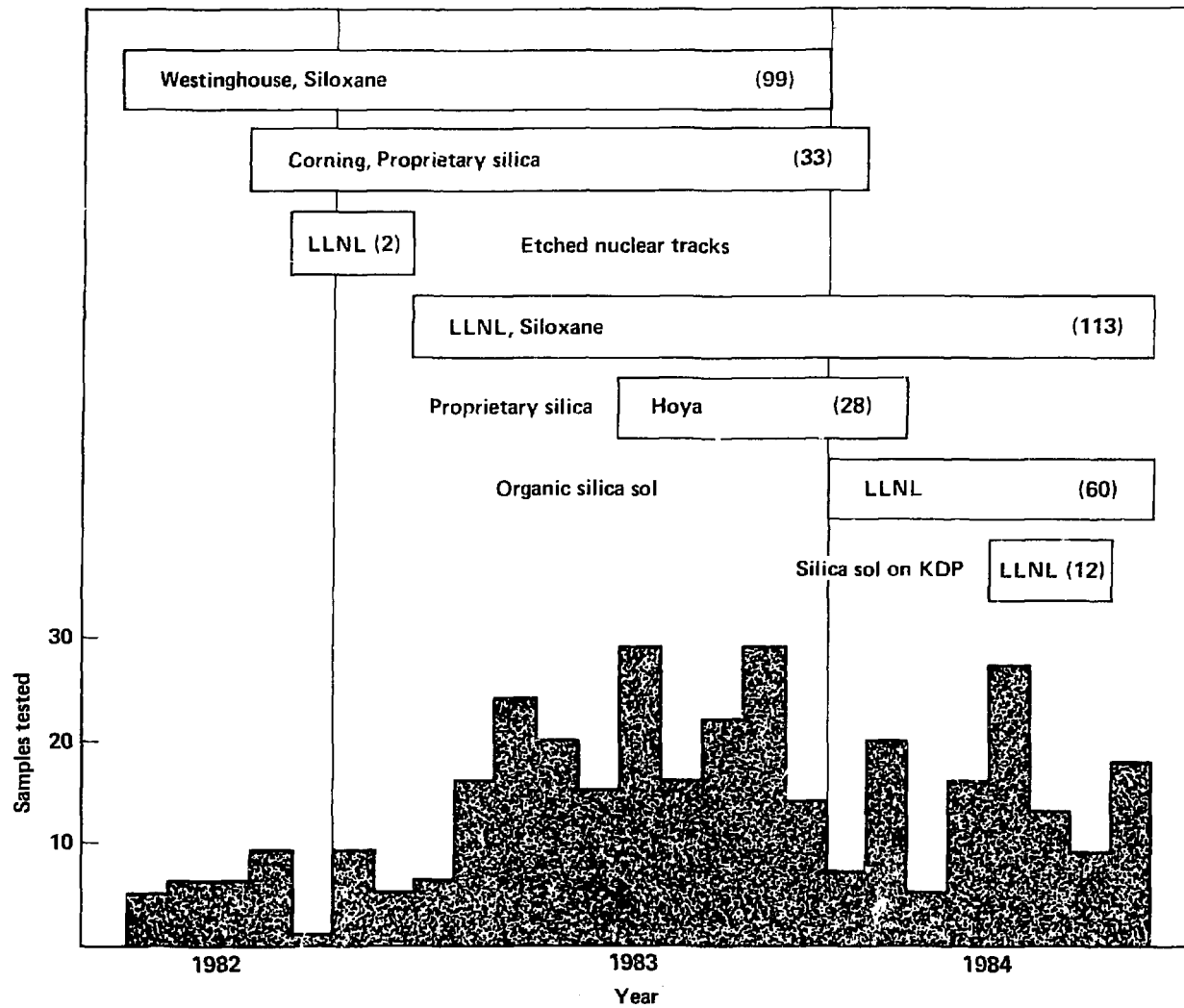


Figure 2