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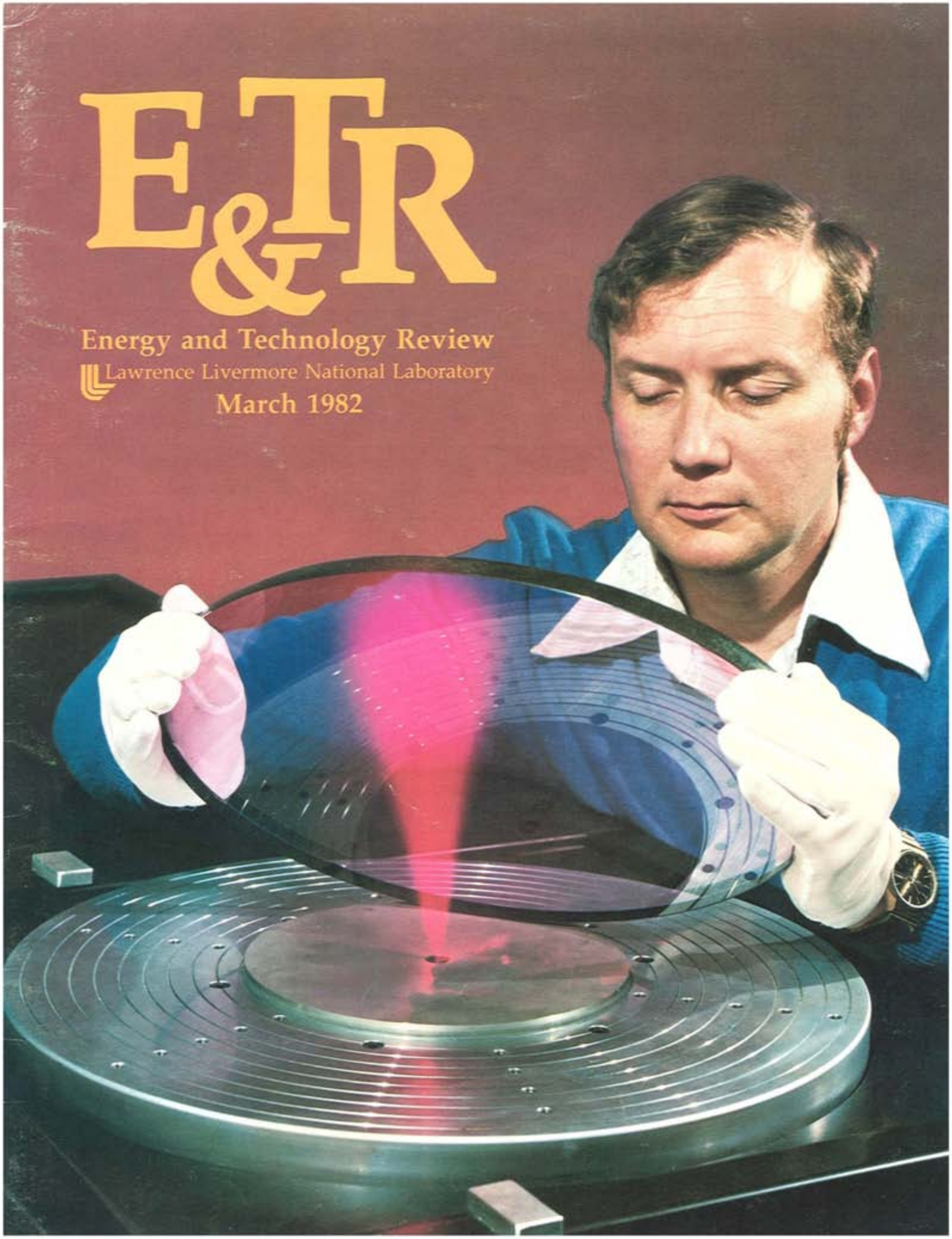


Damage-Resistant Antireflection Surfaces for High-Power Lasers

Because of their relatively low damage threshold, antireflection surfaces are critical components of high-power lasers. New methods of fabricating these surfaces promise greater damage resistance while preserving or enhancing their essential optical properties.

The power output of solid-state lasers is often constrained by the fact that antireflection and high-reflection optical components are subject to damage by laser light. This problem is particularly acute for the neodymium-glass lasers used in inertial-confinement fusion (ICF) research, as these lasers must generate the maximum possible power and energy. These neodymium-glass lasers contain lenses and windows with antireflection surfaces to prevent costly energy losses, reflectors to divide and turn the beam, and large polarizers, all of which are vulnerable to laser-induced damage.

Reflectors and polarizers produced by conventional techniques typically damage when subjected to fluences of 7 to 10 J/cm^2 delivered by 1-ns 1064-nm laser pulses. At present, the damage resistance of these components can be improved only through advances in conventional fabrication methods, as no other techniques are currently available. At the Laboratory, we are continuing research aimed at improving the damage resistance of all types of conventionally produced optical surfaces.

Antireflection surfaces are especially critical components of high-power lasers because they typically receive the highest fluence loading of all surfaces in the laser amplifier chain and have the lowest damage threshold. Their performance, therefore, is directly reflected in the overall system performance; doubling the damage threshold will double the power-output capability of the laser.

Optical surfaces in the Laboratory's Nova laser, for example, will require antireflection films able to withstand more than 10 J/cm^2 for 1-ns long pulses; coatings with a damage threshold this high have never yet been manufactured. Most commercially available antireflection surfaces fail at 5 J/cm^2. (In contrast, bare glass surfaces suffer damage at 16 J/cm^2.) Concerted efforts to increase the damage threshold of these surfaces by using alternative materials,

For further information contact David Milam (415) 422-5499.

The antireflection properties of conventional thin films result from the destructive interference of wavelets reflected from interfaces between film layers.

designs, and processing methods have, until now, met with little success. We are investigating several methods of producing unconventional antireflection surfaces with the damage-resistant properties required by the Laboratory's laser research programs.

Conventional Antireflection Surfaces

The character of unconventional antireflection surfaces may best be elucidated by first considering conventional surfaces. The conventional technique for altering the reflectance of a glass surface is to coat the surface with thin, discrete films of two or more transparent dielectrics that have different refractive indices. These films are condensed onto a glass substrate by placing the glass in a vacuum and bringing it into contact with a diffuse vapor of the coating material. In thin-film coatings produced for use at the 1064-nm wavelength of neodymium-glass lasers, the low-index material is usually silicon dioxide, and the high-index material is titanium dioxide, zirconium dioxide, or tantalum pentoxide.

The reflectance of a coated surface depends on the number and thickness of the deposited layers. A bare, polished glass surface reflects about 4% of incident light. Coating a glass surface with two- or four-layer antireflection films reduces its reflectance to less than 0.1%. Reflectance, on the other hand, can be increased to over 99% by coating the glass surface with 15 to 60 layers of the appropriate materials. The use of suitable materials can also produce surfaces that are highly reflective for light of a specific polarization.

The antireflection properties of conventional thin films result from the destructive interference of wavelets reflected from interfaces between film layers. Figure 1 shows a single-layer film deposited on a glass substrate. Light incident on such a surface is reflected in two waves, R_1 and R_2. When the refractive indices of the film layer (n_f), the glass substrate (n_g), and the ambient air (n_a) satisfy a certain

physical relationship, the reflected waves will be 180° out of phase and will cancel (i.e., sum to zero), producing zero reflectance (see box on page 15). As this condition cannot normally be satisfied by a real single-layer homogeneous film, these films are usually unable to reduce reflectance to zero.

Unconventional Antireflection Surfaces

We are investigating several techniques for producing unconventional antireflection surfaces. All of these are based on the fact that a glass surface can be etched to form a microporous layer with two principal characteristics. First, the micropores range in size from 0.5 to 100 nm, less than the wavelength of near-infrared or visible light. Such a layer behaves like a homogeneous layer with a low index of refraction. Second, the size of the micropores decreases with depth into the layer. This causes the mass density and index of refraction of the layer to increase with depth; such a surface is said to have a graded index.

Our interest in graded-index surfaces arises mainly from their high damage-resistance thresholds, but they also have other desirable properties. For incident light of a wavelength from 400 to 1000 nm, the reflectance of these surfaces is less than 0.5%, much lower than that of a surface with a discontinuous refractive index for the same range of wavelengths. Graded-index surfaces are also potentially much less expensive than conventional coated surfaces.

To understand the antireflection properties of graded-index surfaces, we can apply the same principles used to calculate the reflectance of a surface coated with a conventional thin film. We assume that the refractive index of the microporous layer increases smoothly in the direction normal to the surface, from the index of the air-glass interface to the index of the bulk glass substrate. This variation can be approximately modeled by a large number of small discrete steps; that is, the graded-index layer is treated as a large number of discrete thin layers (Fig. 2).

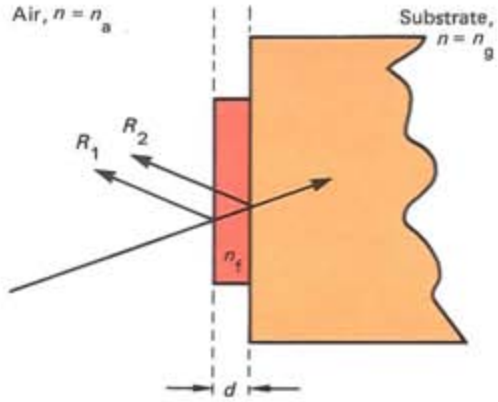


Fig. 1

Reflected waves at a glass surface coated with a single-layer thin film. The film has a refractive index n_f and an optical thickness $n_f d$. The glass substrate has a refractive index n_g. The external medium is air with a refractive index n_a. To achieve zero reflectance at some wavelength, the three indices must satisfy the condition $n_f = (n_a n_g)^{1/2}$. A beam of light incident on the film is reflected in two waves, R_1 from the surface of the film and R_2 from the surface of the substrate. The reflected waves sum to zero (i.e., are 180° out of phase) when the optical thickness of the film, n_f, is a multiple of quarter wavelengths.

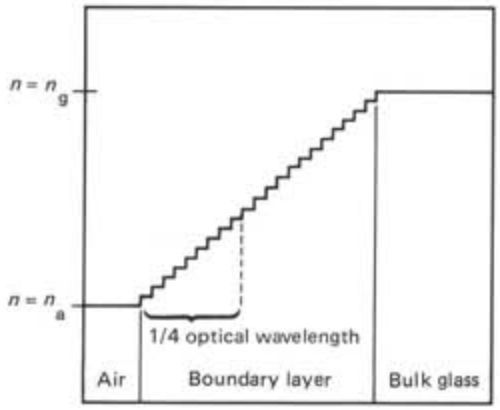


Fig 2

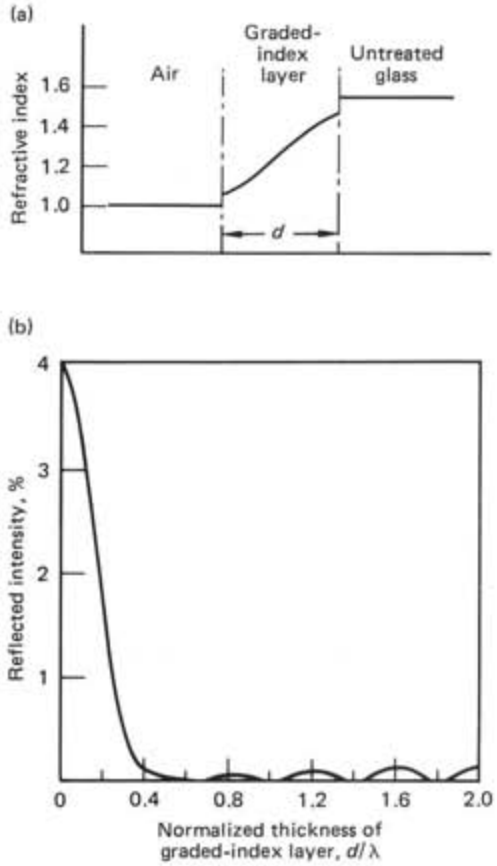
Simplified model of reflection from a graded-index surface. The index of refraction increases smoothly along the surface normal. This variation can be approximately modeled by a large number of small discrete steps. When light falls on the surface, wavelets R_n are reflected from the interfaces between the steps. If the optical thickness of the graded surface is more than half a wavelength, there will be a reflected wavelet R_1 (at an optical distance of one-quarter wavelength from R_n) that is 180° out of phase with R_n. Wavelets R_1 and R_n then sum to zero, as will other pairs. The net surface reflectance results from the partly phased sum of any wavelets that cannot be paired in this way.

When light falls on the surface, wavelets R_n are reflected from the interfaces between the steps. If the optical thickness of the microporous layer is more than half a wavelength, there will be a reflected wavelet R_1 (at an optical distance of a quarter wavelength along the normal from R_n; see box on page 15) that is 180° out of phase with R_n, and thus the pair of wavelets will sum to zero. The same consideration applies to other pairs R_2 and R_{n+1}, R_3 and R_{n+2}, and so on. The net surface reflectance then results from the partly phased sum of any wavelets that cannot be paired in this way.

Our simple model of a graded-index surface indicates that its reflectance is at a minimum when the optical thickness of the microporous layer is a

Fig. 3

(a) Refractive-index profile for a graded-index surface showing the profiles in air, the graded-index layer, and untreated glass; *d* denotes the thickness of the layer. (b) Exact calculation of reflectance vs depth for a graded-index surface having the index profile shown in (a). Reflectance is highly insensitive to the exact thickness, in contrast to the variation of reflectance with thickness for a single-layer discrete film.

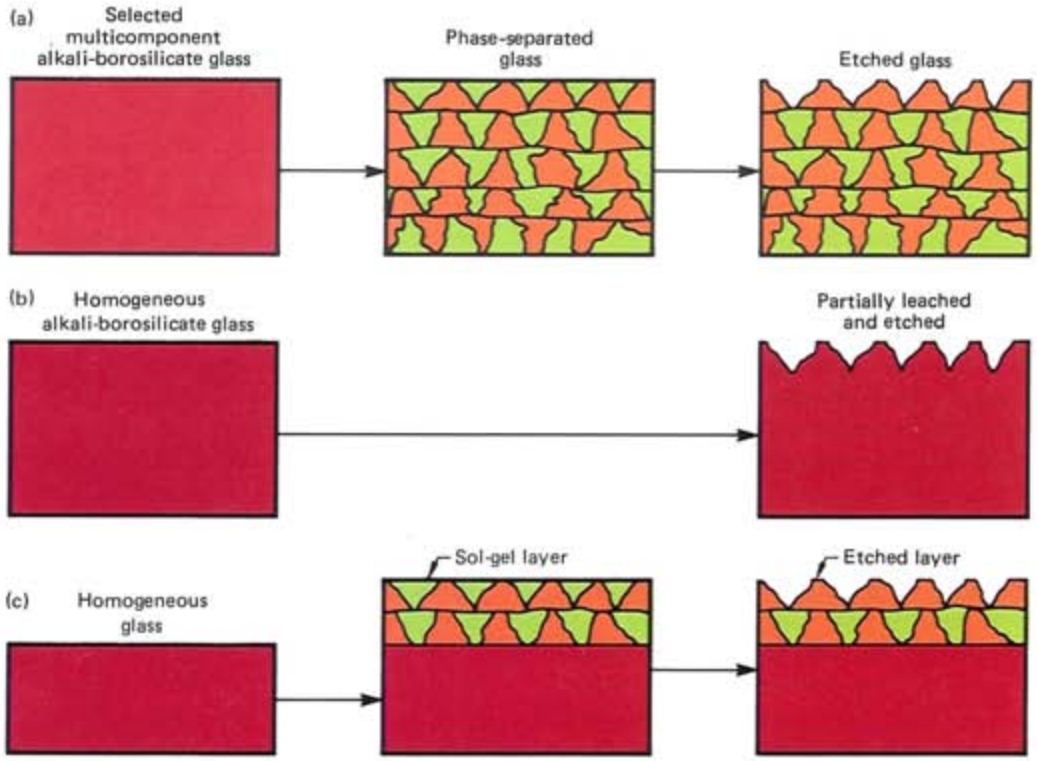


multiple of half wavelengths. Figure 3 shows the result of an exact calculation of reflectance as a function of the thickness of a real graded-index surface.[1] (The corresponding refractive-index profile is also shown.) As we would expect from the simpler model, reflectance is small for all thicknesses larger than a half wavelength and highly insensitive to the exact thickness. The latter is a point of considerable importance. Thickness insensitivity means that the low reflectance of graded-index surfaces is independent both of the wavelength and of the angle of incidence of the incident light. This is in marked contrast to the variation of reflectance with thickness for a single-layer discrete film (see figure in the box on page 15).

We are investigating three techniques for producing antireflection graded-index surfaces: etched phase-separated glass, neutral-solution processing, and etched sol-gel layers. These processes are illustrated in Fig. 4; Table 1 shows the relative advantages and limitations of each.

Fig. 4

Three techniques for producing graded-index antireflection coatings. (a) Phase-separated glass. Some alkali-borosilicate glasses tend to separate into interconnected silica-rich and silica-poor regions. Etching removes the more soluble low-silica phase, leaving a microporous surface layer about 1000 nm thick. (b) Neutral-solution processing. Homogeneous alkali-borosilicate glass is subjected to acid attack by neutral or weakly alkaline salt solutions, forming a porous low-index layer resulting from a combination of partial leaching and total dissolution (etching). (c) Etched sol-gel layers. A viscous liquid sol is polymerized to form a transparent elastic gel that is applied to a homogeneous glass surface. The surface is then heated to drive off residual organic material, leaving a thin microporous oxide layer. This layer is converted to an antireflection film by etching or by neutral-solution processing.



Etched Phase-Separated Glass

A commercial technique for producing graded-index surfaces was first developed by RCA Corporation, which introduced an etch process for soda-lime glass. The process proved difficult to implement on a commercial scale, however, and was abandoned as the fabrication of discrete coatings improved. A major advance in the production of graded surfaces followed the discovery that some alkali-borosilicate glasses tend to separate into silica-rich and silica-poor regions with characteristic dimensions of 1 to 100 nm. Because these regions are interconnected, etching the more soluble, low-silica phase leaves a microporous surface layer about 1000 nm in thickness. For etched Pyrex glass (Corning Code 7740), such surfaces have a reflectance of less than 0.5% for all wavelengths from 350 to 2500 nm.

We tested etched Pyrex glass and found that graded-index surfaces resist laser damage twice as well as conventional antireflection films.[1] However, the optical homogeneity of Pyrex is inadequate to allow its use in components of ICF lasers. Phase-separable glasses of adequate optical quality have recently been developed by Corning Glass Works, Owen-Illinois, Inc., and Hoya Optics, Inc. The Hoya glass is now a commercial product designated ARG2. Blanks up to 53 cm in diameter have been produced. For etched 5-cm-diam samples, transmission at 1064 nm is as great as 99.5%.

We used 1-ns, 1064-nm laser pulses to measure laser-damage thresholds for 66 etched samples of phase-separated glass from all three vendors. The measured thresholds[1] are shown in Fig. 5. The median damage threshold was 12 J/cm^2. For contrast, Fig. 5 also shows the measured thresholds of conventional discrete-layer antireflection films.[2]

We also tested a few etched samples with both 1- and 3-ns pulses. Their damage thresholds scaled as the square root of the pulse duration, as do the thresholds of bare polished glass surfaces. Damage thresholds for conventional films increase more slowly, or

Table 1 Characteristics of three types of damage-resistant antiflective surface produced by unconventional techniques.

Surface type	Advantages	Limitations
Graded-index surface on phase-separated glass	High laser-damage threshold. Reflectance insensitive to incidence angle or wavelength.	Mechanically fragile. Significant bulk scattering loss at short wavelengths. Poor ultraviolet transmission. Short etch time complicates fabrication.
Surface on homogeneous glasses formed by neutral-solution processing	High laser-damage threshold. Acceptable mechanical durability. Small bulk scattering loss. Extended etch time eases fabrication.	Reflectance somewhat dependent on wavelength and incidence angle. Poor ultraviolet transmission.
Graded-index surface formed by etching sol-gel layers	High laser-damage threshold. Reflectance insensitive to wavelength or incidence angle. Small bulk scattering loss.	Not highly developed. Mechanically fragile.

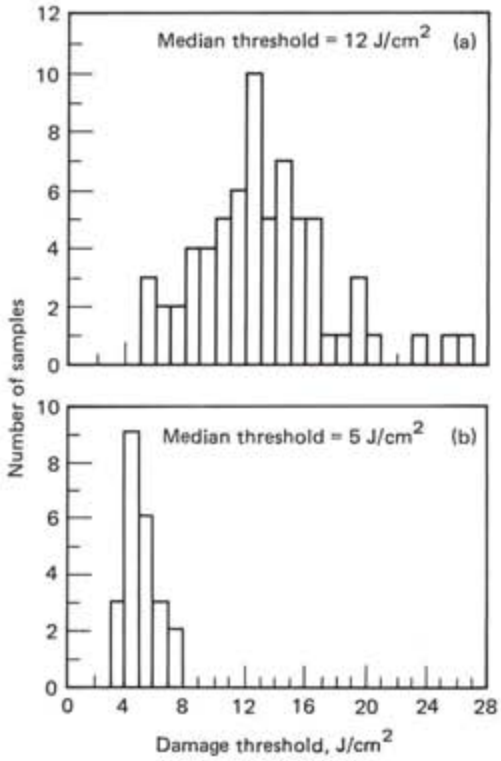


Fig. 5

Measured damage thresholds for 1-ns laser pulses with a wavelength of 1064 nm. (a) 66 samples of antireflection surfaces etched on phase-separated glass. (b) 23 conventional discrete-layer antireflection thin films. The median threshold of the etched surfaces is more than twice that of the conventional films.

not at all, as the laser pulse duration increases.

Etched surfaces on phase-separated glass thus have several advantages over conventional thin films. Surface reflectance is low and independent of wavelength or angle of incidence, and surface damage thresholds are high. They do have some disadvantages, however. Phase separation is peculiar to the silicate glasses, which transmit poorly at 355 nm, the third harmonic of neodymium-glass lasers.[1] Further, the phase separation leads to bulk scattering losses, which are significant at short wavelengths, where the glasses are nominally transparent, and the surfaces are difficult to prepare uniformly.

Neutral-Solution Processing

A second class of materials and surface films surmounts some of these difficulties while preserving most of the desirable features of etched surfaces on phase-separated glasses. Changes in reflectance can be produced by acid attack of homogeneous glass by neutral or weakly alkaline solutions of salts such as NaCl, LiCl, Na_2HAsO_4, and $NaC_2H_3O_3$. The reflectance change is caused by a porous low-index layer formed by the competing processes of partial leaching and total dissolution (etching). The structure of the layer is a system of pores, with mean radii of 60 to 300 nm, interconnected by channels. The porosity depends on the pH and composition of the solution. Because the glass is homogeneous, bulk scattering does not occur.

This technique for forming surface layers on homogeneous glasses is called neutral-solution processing. We studied films formed on BK-7 and BK-10 glass.[3] Samples 50 mm in diameter and 3 mm thick were immersed in a solution of 0.034 M Na_2HAsO_4 and 1.3×10^{-3} M Al^{+3} in water at 87°C. The surface layer developed at a rate of approximately 10 nm/h. Typically, 40 h are required to form a useful antireflection film. Because of this slow growth rate, reflectance can be easily reproduced.

The surface reflectance of a sample treated 39 h is shown in Fig. 6.[3] It shows a broad maximum at 580 nm and minima at 380 nm and 1040 nm. At 1040 nm, measured reflectance was 0.01% and transmission was 99.3%. The 0.7% loss is attributed to scattering loss at the surface. The reflectance of the untreated surface is also shown.

Surface layers formed by neutral-solution processing of homogeneous glass have reflectance characteristics intermediate to those of discrete single-layer films and those of etched phase-separated glass. Near-zero reflectance minima at 1040 nm and 380 nm may be accounted for by the existence of a homogeneous low-index layer. The spectrum, in fact, closely resembles that of the single-layer film (see figure in the box on page 15) except that the maximum reflectance of a single-layer film is equal to that of the bare glass. For the neutral-solution surface, the maximum reflectance is only 1.5% (although the precise value may be peculiar to this sample).

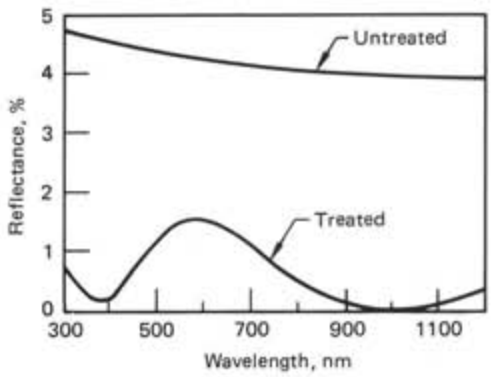


Fig. 6

Measured reflectance of a sample of homogeneous glass treated by neutral-solution processing. The reflectance of the untreated surface is also shown. The reflectance characteristics of the treated sample are intermediate to those of discrete single-layer films and etched phase-separated glass. The spectrum closely resembles that of the single-layer film, except that the maximum reflectance of a single-layer film is equal to that of the bare glass. For the neutral-solution surface, the maximum reflectance is only 1.5%.

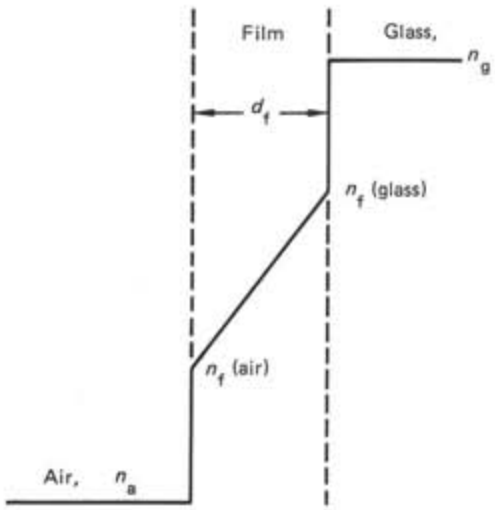


Fig. 7

Model of the surface-index gradation needed to explain the reflectance spectrum in Fig. 6. The refractive index varies along a surface normal with $n_f = 1.142$, $n_f(g) = 1.346$, $n_g = 1.507$, and $d_f = 210$ nm.

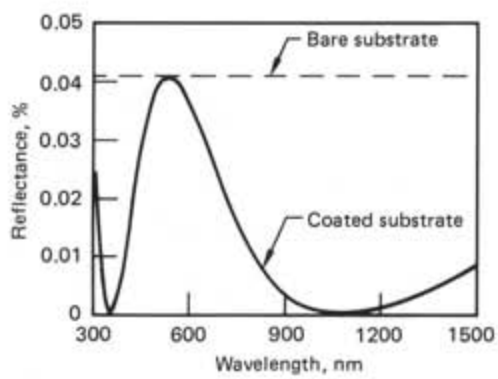
Calculating Surface Reflectance

The single-layer film deposited on a glass substrate (shown in Fig. 1 on page 11) has a refractive index $n_f d$ and an optical thickness $n_f s$ (the product of the refractive index and the thickness of the film). The refractive index of the glass is n_g, and the external medium is air with a refractive index n_a.

A beam of light incident on this surface generates two reflected waves, R_1 from the surface of the film and R_2 from the surface of the substrate (see Fig. 1). When the optical thickness of the film ($n_f d$) is an odd multiple of quarter wavelengths, the reflected waves will be 180° out of phase (i.e., will add destructively). The reflected waves will sum to zero if the various refractive indices satisfy the condition $n_f = (n_a n_g)^{1/2}$.

The figure (right) shows reflectance as a function of wavelength for a film satisfying this condition. (In this example, n_f is 1.22, n_a is 1.00, n_g is 1.507, and $n_f d$ is 266 nm.) Zero reflectance occurs for two wavelengths of incident light, λ_1 ($1/4\lambda_1 = 266$ nm $= n_f d$) and λ_2 ($3/4\lambda_2 = 266$ nm $= n_f d$). The values of λ_1 and λ_2, 1064 nm and 355 nm, respectively, are the points of zero reflectance on the curve. At the wavelength $\lambda_3 =$ 532 nm, the film is half an optical wavelength in thickness, and its presence does not alter the reflectance of the substrate's surface.

As the condition $n_f = (n_a n_g)^{1/2}$ is difficult to satisfy for conventional, single-layer homogeneous films, such films usually cannot reduce surface reflectance to zero. Recomputation of the curve in the figure using a larger and more realistic value of n_f would produce a curve of similar shape but with nonzero minima.



We have carried out more exact calculations[3] showing that the reflectance spectrum in Fig. 6 can be closely modeled by assuming that the refractive index varies along a surface normal (Fig. 7) with $n_f(a) = 1.142$, $n_f(g) = 1.346$, $n_g = 1.507$, and $d_f = 210$ nm. The assumed profile is in general agreement with the two-part process of surface formation: low-index material is formed by replacing metal ions in glass with H^+ or H_3O^+ from the solution and by etching, which tends to increase the mean pore size at the outside boundary and produce some gradation of density.

We damage-tested 15 antireflection surfaces formed on BK-7 and BK-10 glass by neutral-solution processing.[3] The median threshold for 1-ns, 1064-nm laser pulses was 12 J/cm^2, the same as the median threshold of graded-index antireflection surface layers on phase-separated glass. Two of these samples were also tested with pulses having durations of 3, 6, 9, and 20 ns. Over the whole range of pulse durations, the damage thresholds scaled as the square root of the pulse duration.

We have also established that antireflection surface layers can be formed by neutral-solution processing without altering the surface figure (i.e., surface contour) of polished glass components. That is, the distortion of a light beam transmitted by the processed surface is the same as the distortion caused by an untreated component. We have successfully used lenses treated by neutral-solution processing in the Laboratory's Shiva laser.

The median damage threshold [of sol-gel films] was . . . almost four times [that] of commercially available discrete-layer films and 30% greater than that of bare glass surfaces.

Etched Sol-Gel Layers

We are also studying a third type of antireflection surface that shows promise of overcoming a major limitation in the use of both phase-separated and homogeneous multicomponent silicate glasses to fabricate components for krypton-fluorine lasers (248 nm) or to transmit third and fourth harmonic light of neodymium-glass lasers (355 and 266 nm). At these ultraviolet wavelengths, the loss due to bulk absorption in silicate glasses is so large that it is irrelevant whether antireflection films can be formed to prevent surface losses. However, bulk absorption in thin layers of these glasses may be acceptably low, and techniques are available for applying thin layers of multicomponent silicate glasses to materials, such as fused silica, that have good ultraviolet transmission. The thin layers can then be converted into antireflection films by etching or by neutral-solution processing.

Layers of multicomponent inorganic oxide materials can be deposited by the sol-gel process.[4,5] This process consists of polymerizing a viscous liquid sol of alkoxysilane with other metal alkoxides or metal salts in alcohol solutions to form a transparent elastic gel. The polymerized liquid is applied to a glass surface that is subsequently heated to drive off residual organic matter, leaving an oxide layer. This layer is microporous, but can often be converted to a glassy solid by further heating. The porous nature of the initial film has been used to form low-refractive-index, single-layer aluminum oxide antireflection films on soda-lime glass. We and others have demonstrated the deposition of multicomponent borosilicate glasses.[6] We have used the sol-gel process to apply thin layers of phase-separable glasses to glass surfaces.[7] To date, the best results have been obtained by using glasses in the Na_2O-B_2O_3-SiO_2 system.

Test films were deposited on Pyrex (Corning Code 7740), BK-7 borosilicate glass, and fused silica. The substrate was suspended on a wire, immersed in the solution, and withdrawn vertically

at a rate of 5 cm/min. After each dipping the film was allowed to dry in air for 15 min. Up to ten layers were applied, and we estimate that each dipping added a thickness of 33 nm.

The films were dried overnight at 80°C in air and subjected to various heat treatments at temperatures ranging from 350 to 500°C. To form antireflection films, the films were leached in 0.5 wt% hydrofluoric acid solutions or in 0.6 wt% sodium fluoride in 0.16 *N* nitric acid. Leach times ranged from 15 s to 10 min.

We measured the reflectance (at a wavelength of 1060 nm) of films subjected to various heat treatments and leaching conditions. The results are summarized in Table 2. The reflectance values given in the table are the minimum values observed for the surface. Reflectance varied substantially over the surface, with typical maxima of 2%.

We used 1064-nm, 1-ns pulses to measure laser damage thresholds for 15 sol-gel films.[7] The median damage threshold was 21 J/cm^2. This is almost four times the median damage threshold of commercially available discrete-layer films and 30% greater than that of bare glass substrates. Etching of sol-gel layers is thus a promising technique for forming damage-resistant antireflection films, although much development work remains.

Table 2 Reflectance of sol-gel films, approximately 0.3 μm thick, etched in NH_4F/HNO_3 at 90°C. The film was composed of approximately 13% B_2O_3, 4% NaO_2, and 81% SiO_2.

Heat treatment			
Temperature, °C	Time, h	Leaching time, s	Reflectance, %
350	1.5	15	0.27
350	5.5	15	0.33
500	1.5	15	0.67
500	5.5	15	0.20
350	1.5	30	0.33
350	5.5	30	0.13
500	1.5	30	0.23
500	5.5	30	0.13

Conclusions

We have studied three unconventional techniques for forming damage-resistant antireflection surfaces on optical components of high-power lasers. All three have high laser-damage thresholds, a characteristic essential to ICF applications. We found that neutral-solution processing can produce antireflection surfaces for wavelengths adequately transmitted by borosilicate glass. Optical components fabricated by this process were successfully used in the Laboratory's Shiva laser. We are continuing efforts to bring all of these techniques to practical fruition.

Key Words: antireflection surfaces; graded-index surfaces; inertial-confinement fusion; lasers, neodymium-glass; lasers—solid-state; Nova; Shiva; thin-film optics.

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