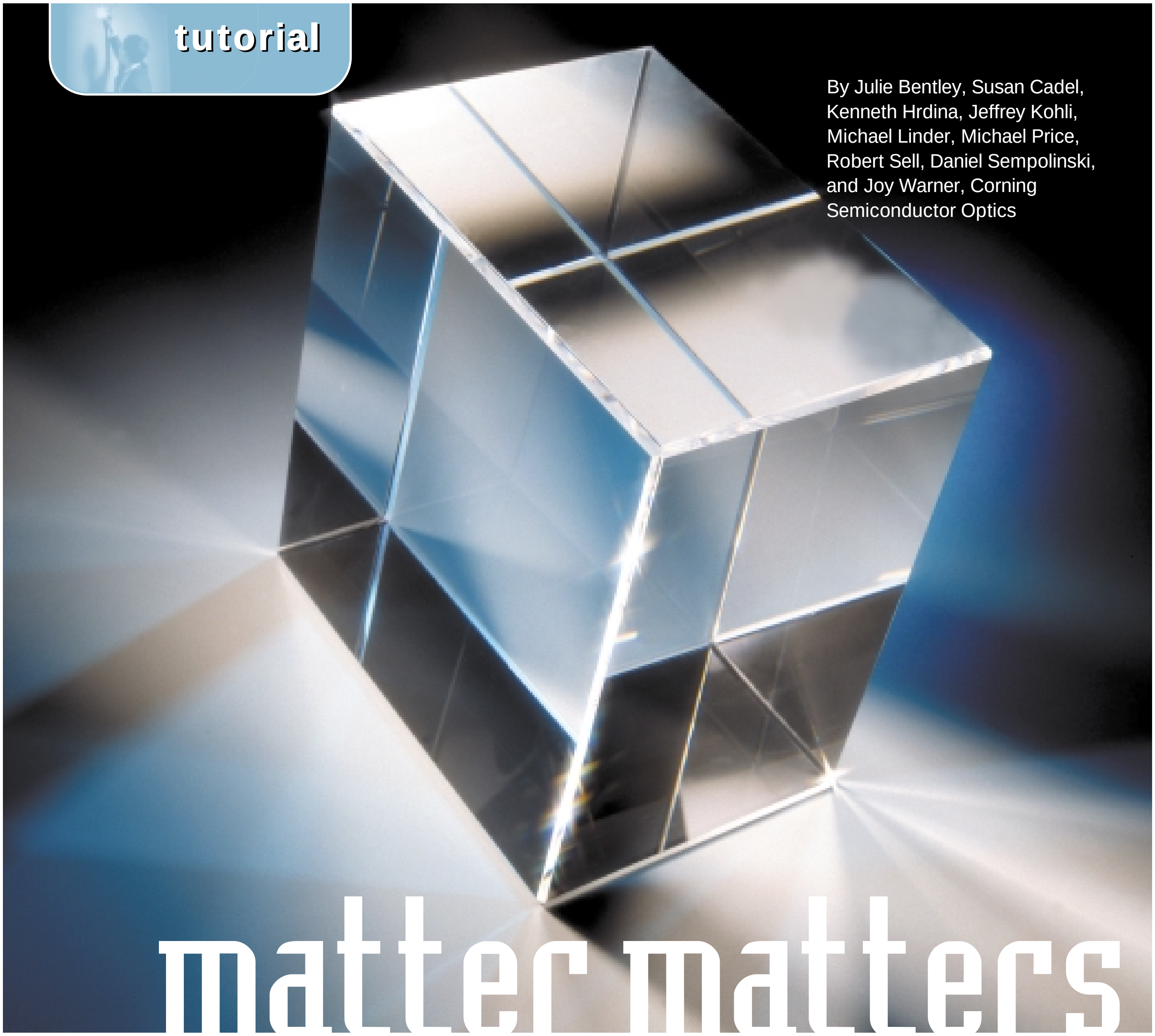
By Julie Bentley, Susan Cadel, Kenneth Hrdina, Jeffrey Kohli, Michael Linder, Michael Price, Robert Sell, Daniel Sempolinski, and Joy Warner, Corning Semiconductor Optics



matter matters

Optical materials rise to the microlithography challenge.

Optical materials are at the heart of the semiconductor industry. Microlithography projects a pattern from a photomask through an optical system to create IC chips using ultraviolet laser light. Optical inspection microscopes provide test capabilities for both masks and wafers at several different stages of the printing process. With the drive to smaller and smaller structures, the semiconductor industry continues its quest for better and better optical systems, and this in turn drives the requirements for the optical materials.

Printing smaller features on a chip requires improving the resolution of the optical system by increasing the numerical aperture and/or decreasing the exposure wavelength. For this reason, the wavelength of microlithographic tools has progressed from historic g-line (436 nm) and I-line (365 nm) to the recent KrF (248 nm) and ArF (193 nm) laser generations, with 157 nm slated to follow. Beyond 157 nm, the use of transmissive optical materials becomes impractical and the next generation of tools will require reflective optics and an extreme UV (EUV) light source at 13.4 nm.

The optical material requirements for these lithographies are highly dependent on whether the material is used for laser optics, illumination systems, photomasks, projection optics, or inspection tools. Common to all is a need for outstanding transmission (or reflection, in the case of EUV). Depending on the type of optic, this requirement can stem simply from the need for high throughput; however, in the case of projection optics, absorption also causes lens heating, which in turn introduces wavefront errors leading to image aberrations.

For a particular wavelength, transmission restricts the choice of available lens materials for an optical design (see figure 1). Furthermore, homogeneity of the refractive index and low birefringence are critical parameters that limit the material available for use in projection optics, while resistance to laser damage is more critical for laser optics and stepper illumination systems due to the high fluence on these components.

Historically, projection and illumination systems in steppers and inspection systems have used selected optical glasses or synthetic fused silica for 365-nm, and synthetic fused silica for 248-nm and 193-nm. CaF_2 is used for some elements at 193 nm, and it is the sole viable material at 157 nm. For reflective optics in EUV, materials with extremely low thermal expansion such as ULE glass (Corning Inc.; Corning, NY) or glass ceramics such as Zerodur (Schott Glass; Duryea, PA) are the materials of choice.

fused silica

Fused, or vitreous, silica is the material of choice for most 248-nm and many 193-nm applications because it provides an economical combination of optical transmission, laser damage resistance, and refractive index homogeneity. The industry also has a large cumulative body of experience in polishing this glass.

The physical properties of fused silica are controlled by thermal history and by trace levels of impurities and structural defects. It is a very viscous material compared to other common commercial glasses and must be processed at temperatures in excess of 1800°C. The high temperatures limit the options for working or homogenizing the glass without introducing metal contaminants, which can degrade UV transmission.

The tight lithographic specifications for UV transmission translate into the need to control metal contaminants at the parts-per-billion level. Key to meeting this purity requirement is the use of chemical precursors, such as organic siloxanes or $SiCl_4$, because these materials can be distilled to levels of very high purity.

The precursor vapor is normally fed into the hydrogen/oxygen or natural gas/oxygen flame, where it reacts to form a stream of fine silica particles. These particles can be captured, depending on the temperature of the deposition zone, as a dense glass or as a porous body. Both approaches use special thermal treatments such as reflow and slow anneals to control index homogeneity, birefringence, and changes induced by prolonged UV exposure.

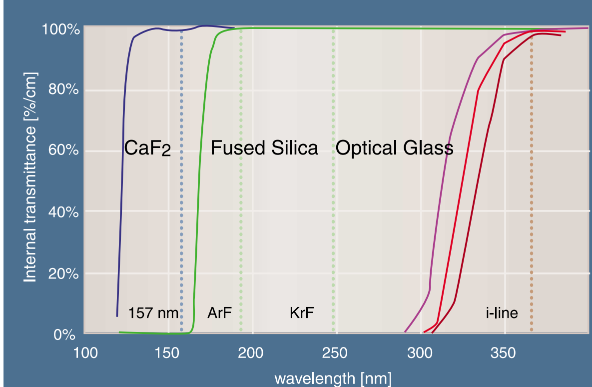


Figure 1 A range of materials is required to provide sufficient internal transmittance for all microlithography wavelengths.

Non-metallic contaminants also impact the optical properties of fused silica, in both positive and negative fashions. Molecular hydrogen provides benefits for laser damage resistance, acting as a passivating agent for induced transmission change. It performs this task mainly by reacting with and altering the absorption properties of the defects that occur during prolonged exposure to UV radiation so that they do not absorb light at the eventual exposure wavelengths. Concentration of molecular hydrogen is usually established during glass formation or in post-forming impregnation steps.

Recent materials studies have shown that the addition of fluorine improves transmission and laser damage resistance properties, especially at 157 nm, possibly by eliminating the strained bond sites that are most readily damaged under UV exposure.

Chlorine is detrimental to UV transmission. The chlorine-free precursors do not generate hydrochloric acid as a manufacturing byproduct or leave residual chlorine in the glass. If chlorine remains after forming or chemical drying, it has to be removed prior to consolidation with flushing treatments.

calcium fluoride

Although single crystals of various fluorides such as CaF_2, MgF_2, and so on are difficult to produce in high quality and quantity, they offer high deep-UV transparency, which results from their large bandgap. They are also highly resistant to laser damage, with transmission only weakly dependent upon laser fluence. Among these fluorides, CaF_2 is the most commonly used for microlithography applications.

Although CaF_2 exhibits cubic crystal symmetry, its optical behavior is not identical in all orientations. The photon wave vector introduces a term that effectively disrupts symmetry in the crystal, hence introducing intrinsic birefringence. Cubic crystals are optically isotropic only in the limit in which the wavelength of light is infinite compared with interatomic dimensions. At visible wavelengths this is an excellent approximation, but at UV wavelengths such as 193 nm, the atomic crystalline structure influences light differently for different propagation directions; thus, the intrinsic birefringence. Clocking CaF_2 lens blanks along different crystallographic orientations is a method to compensate for intrinsic birefringence in a lens barrel (see **oe***magazine*, March 2002, p. 23). In addition to intrinsic effects, stress-induced birefringence is also an important consideration that may vary with orientation and fabrication process.

Microlithography applications require CaF_2 lens blanks approximately 300 mm in diameter and more than 50-mm thick. The predominant method for producing these large crystals is the Bridgman or Bridgman-Stockbarger technique.

The critical nature of crystal quality dictates an extremely slow growth rate that allows elimination of trapped gases and the expulsion of impurities, as well as the reduction of slip and mosaic defects. Cooling or annealing the crystals after growth in a manner that controls thermal gradients minimizes these defects, as well as stress-induced birefringence and other optical inhomogeneities. Manufacturers typically grow crystals under high vacuum to eliminate ambient gas contamination, especially oxygen.

One of the most common types of imperfections in CaF_2 is dislocations. Dislocations are linear structures that occur in most crystalline materials as a result of the stresses exerted on the material during solidification and/or annealing. CaF_2 dislocations, however, are more complex due to the necessity of charge balance. Annealing eliminates dislocations by causing them to coalesce into 2-D structures called subgrain boundaries. X-ray analysis confirms that the crystallographic orientation of the CaF_2 structure shifts spatially across the subgrain boundary. Despite the orientation shift, subgrain boundary formation actually reduces stress within the CaF_2 crystal, decreasing stress-induced birefringence.

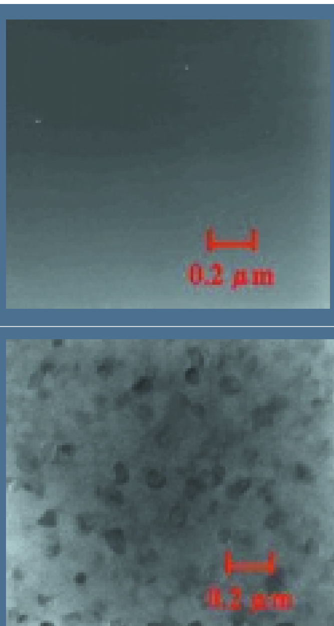


Figure 2 TEM shows the single-phase nature of glass (top) versus the multiphase nature of glass ceramic (bottom).

EUV Materials

The next reduction in wavelength after 157 nm will be to 13.4 nm for EUV lithography (EUVL). Unlike earlier reductions, this particular transition requires a major design shift in stepper optics from refractive to reflective. The change is dictated by the absence of material that can transmit at this low wavelength. The properties of the materials required—and hence, the choice of materials—are very different for EUVL reflective optics than for those used in deep-UV refractive optics.

In reflective optics, substrate materials should be purely passive. The incident light should reflect off of the multilayer coatings of the optics and the photomask without the introduction of any mechanical or optical distortion caused by the underlying substrate. To minimize distortion from the minute temperature changes and meet the EUVL specifications, the substrates must have a near-zero coefficient of thermal expansion (CTE) and low peak-to-valley (P-V) CTE variations. The extremely low CTE requirements are specified in parts per billion per degree kelvin (ppb/K).

Only two currently manufactured materials exist that meet this requirement on a regular basis: ULE and Zerodur. ULE glass is a single-phase, supercooled liquid with a CTE very near 0 ppb/K (see figure 2). Zerodur, on the other hand, contains an amorphous glassy phase with positive CTE, and a crystalline phase with negative CTE, to yield a net expansion near 0 ppb/K.

The demanding CTE requirements are forcing improvements in metrology as well as in materials. Schott has addressed this by improving the dilatometer techniques from 5 ppb/K to 1 ppb/K at last report. It is, however, desirable to measure the CTE non-destructively. We have shown refractive-index change in ULE to correlate with CTE changes such that we can use an interferometer to measure the coefficient with spatial resolution of less than 100 µm and precision of about 0.07 ppb/K.

Finished high-spatial-frequency roughness (HSFR) impacts the amount of reflected energy in the optical systems, which is equivalent to transmission for optical systems. The glass ceramic appears inherently more difficult to polish to the HSFR specification than the single-phase glass, which can be attributed to the mixture of phases with different properties. Optical manufacturers have already achieved the targeted 0.15-nm rms roughness on ULE, and improvements in procedures for polishing Zerodur are closing the gap. Advances in the coating process may also loosen the future HSFR specification.

Finished mid-spatial-frequency roughness (MSFR) is a critical parameter that impacts flare (spread in the central core of the point spread function) or image resolution. MSFR had been demonstrated as a problem in the past for ULE but not for Zerodur. The cause of the MSFR was found to be striae, a compositional inhomogeneity. Recent process improvements brought about by improved metrology tools have resulted in ULE with an eight-fold improvement in striae. The corresponding reduction in the risk of flare makes the material suitable for EUVL uses.

Several material properties impacting optical performance remain to be rigorously evaluated for EUVL acceptability. These include thermal hysteresis behavior, delayed elasticity, and temporal stability. Both materials appear acceptable for today's EUVL needs, but further improvements and investigations in both metrology and process are necessary for future next-generation lithography needs. **oe**

Julie Bentley is senior optical designer; Susan Cadel is manager market strategy; Kenneth Hrdina is associate development scientist; Jeffrey Kohli is project manager; Michael Linder is metrology manager; Michael Price is senior project engineer; Robert Sell is manager of marketing & strategy development; Daniel Sempolinski is development associate; and Joy Warner is product engineer at Corning Semiconductor Optics, Corning Inc., Corning, NY. For questions about this article, contact Cadel at 607-974-8531, 607-974-7210 (fax), or cadelsb@corning.com.

SPIE member