Calcium Fluoride Crystals

Blanks Offer Highest Transmission Rates at 193 nm and Below

The performance of microchips continues to double about every 18 months. The incredible progress that is being made in lithography and many other areas of technology owes a lot to calcium fluoride crystals. Low solubility and wide transmission make calcium fluoride extremely useful for a variety of different applications, including microlithography, mirror substrates for UV laser systems, windows, lenses and prisms for UV and IR applications.

FIGURE 1: **CaF_2 – blanks and processed lenses.**

Calcium fluoride (CaF_2) is an extremely unique optical substance that occurs naturally as the mineral fluorite (also called fluorspar). Besides its application in microlithography, this single-crystal material is often used today for a variety of infrared and ultraviolet wavelength applications, due to the fact that it is highly transmissive in these regions and exhibits extremely low birefringence. Out of all fluoride crystal materials (e.g. calcium fluoride, barium fluoride, magnesium fluoride, lithium fluoride), calcium fluoride is known to be one of the hardest materials. This is the reason why it is particularly well-suited for use in the manufacturing of a wide range of different lenses, prisms and mirror substrates. In addition, calcium fluoride is both physically stable and chemically inert, which means that windows made of it are highly resistant against any impact.

Calcium fluoride is commonly manufactured in different qualities or so called grades, e.g. for visible and infrared applications and for ultraviolet applications. UV grade calcium fluoride requires a much higher level of material purity than the materials for the infrared range and is therefore considerably more difficult to produce. It is manufactured using a complex precipitation process and is mainly used in advanced optical parts for microlithography and laser applications.

The most important quality features of calcium fluoride include excellent UV transmittance, a high laser damage threshold, low axial and radial stress birefringence, and high refractive-index homogeneity. The extremely high laser damage threshold of calcium fluoride has made it the material of choice for use in excimer laser optics. Furthermore, calcium fluoride has become very important as an ultraviolet optical material for integrated circuit lithography in beam delivery, illumination and projection systems that operate now down to 45 nm node.

From a Powder to a Crystal

Calcium fluoride blanks are manufactured in a wide variety of sizes to meet a customer's exact specification. The starting material is refined calcium fluoride powder that has to be as pure as possible. First, it is melted inside a furnace followed by the crystallisation process and then tempered down to room temperature. In course of the crystallisation process a temperature gradient "from liquid to solid" moves from the bottom to the top of the furnace taking several weeks.

At high temperature, calcium fluoride crystals are quite weak and react very sensitively to stress. For this reason, the temperature ramp-down must proceed very slowly to minimize thermal gradients. To further decrease the stress level, a secondary tempering cycle, the so called annealing, is often applied using a separate furnace, once the blank has been cut from the boule. This makes the process even more complex and can easily add several weeks to the overall manufacturing process.

Because the entire world's leading crystal manufacturers design and build their own furnaces, much of the proprietary information on calcium fluoride crystals resides in furnace design and process recipe. The latest generation of vacuum furnaces currently used allows for fabrication of calcium fluoride blanks in diameters of up to 350 mm and highest transmission rates at 193 nm and below.

A polished calcium fluoride surface can be expected to withstand several years of exposure to normal atmospheric conditions. Low solubility and wide transmission make calcium fluoride extremely useful for a variety of different applications, including mirror substrates for UV laser systems, windows, lenses and prisms for UV and IR applications.

THE AUTHOR

PETER MAUSHAKE

Peter Maushake is Product Manager Optical Materials at SCHOTT AG, Division SCHOTT Lithotec in Jena, Germany. Maushake studied Environmental Engineering at the department of Physical Technology of the University of Applied Sciences in Jena, Germany. At SCHOTT Lithotec he is responsible for product management and sales of fused silica and calcium fluoride as well as i-line glass for the European optics market.

SCHOTT AG
Division, SCHOTT Lithotec
Otto Schott Str.13
07745 Jena,Germany
Tel.: +49 (0) 3641/232-131
E-mail: peter.maushake@schott.com
Website: www.schott.com/lithotec

Calcium fluoride is able to withstand maximum temperatures of up to 800 °C in dry atmosphere. In fact, this material is used quite commonly in cryogenically cooled thermal imaging systems. Due to its high transmission, it is also used in spectroscopic windows and lenses.

The key to reduced loss of energy and lens heating it to minimize absorption. Thanks in particular to their low absorption, calcium fluoride crystals are frequently used in high power laser optics. Their polished surfaces remain stable and last for several years under working conditions. At 193 nm, the best grades of calcium fluoride approach an absorption of less than 0.0005 cm^{-1} (base 10). Depending on laser parameters (such as fluence), long-term tests reveal no significant change in absorption, even after billions of pulses. Because calcium fluoride is a crystalline material, it is unlikely to suffer from the compaction and rarefaction that is seen for example in fused silica.

Furthermore, homogeneity of refractive index as the other important parameter for lens material shows an index variation of less than 1 ppm (part per million) in the best grades of calcium fluoride.

Lithography Leads the Way

Due to its unique characteristics, calcium fluoride undoubtedly ranks as the material of choice for producing lithography lenses. As the relentless march to higher productivity semiconductors continues, optical technologists are pursuing shorter wavelength exposure sources in an effort to gain smaller linewidths and faster and smaller devices. Wafer exposure systems initially started with an exposure source wavelength of 436 nm. As technology advanced, the exposing wavelength rapidly moved to 405 nm, and then to 365 nm, the very limit of human eye visibility. The push for shorter wavelengths continued beyond visible limits to 248 nm using the krypton-fluoride (KrF) laser, and finally to 193 nm with the argon-fluoride (ArF) laser.

For a time, it appeared become the biggest market ever for calcium fluoride with the Fluorine (F_2) laser technology at 157 nm where only CaF_2 lenses could be used. However, in the meantime, this step has been removed from the roadmap and 193 nm technology is now the main application.

Today's steppers require blanks of up to 10 inches in diameter for lenses in the projection system. This places a strong demand on yield, in that defects generally limit the number of large blanks that can be cut from a single boule. Calcium fluoride is also used to produce optical elements. These are applied in the illumination optics, the beam delivery system and the laser itself, where they have to withstand highest energy loads.

THE COMPANY

Division SCHOTT Lithotec
Jena, Germany

SCHOTT AG, Division SCHOTT Lithotec in Jena, Germany, is a leading world-wide supplier of advanced materials and components with customer-orientated solutions focussing on optical and lithographic applications. As the only worldwide supplier SCHOTT Lithotec offers the entire range of optical materials and components for current and future lithography technology and has almost 50 years of experience in growing calcium fluoride crystals with diameters up to 350 mm.

FIGURE 2: **Octahedron showing the molecular structure of CaF_2.**

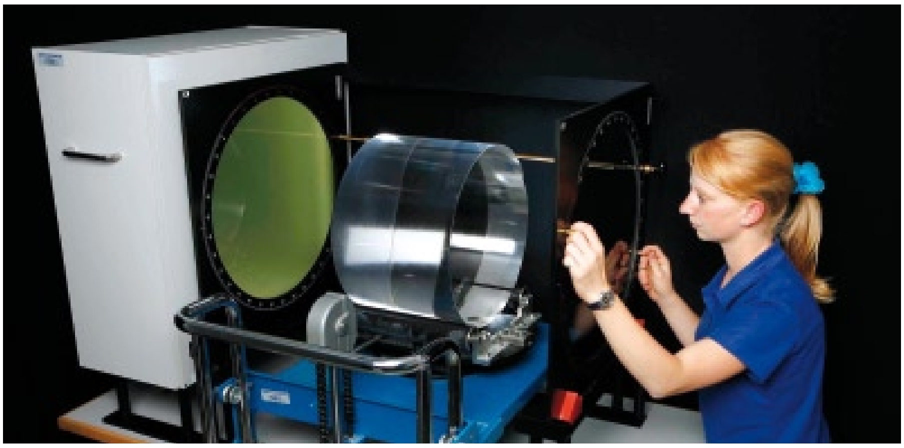

FIGURE 3: **Raw Crystal inspection in a cross polarizer.**

Advantages in optical performance for standard optics can be achieved with calcium fluoride in chromatically corrected optical systems for optics in the infrared and visual wavelength ranges (e.g. HDTV zoom lenses) in astronomy and photography, as well as in microscopy. Lenses used in commercial television cameras have now become one of the strongest optical markets for calcium fluoride crystals. Although this application is less demanding in terms of absorption at short wavelengths, it requires a substantial volume of material and, thus, competes with semiconductor applications.

Calcium fluoride is also used extensively for laser windows at UV wavelengths. This generally requires smaller sizes than the lenses used in microlithography.

Looking Forward

Today, it is extremely important that the various sectors of the semiconductor industry, such as device makers, tool suppliers, material suppliers, laser manufacturers, universities and national labs, share their understanding of calcium fluoride issues and solutions, so that each company does not have to define issues and invent solutions on its own. Customers are well-advised to discuss their exact needs and technical requirements with the crystal manufacturer and all other parties involved at a very early stage.

The industry has already achieved significant progress on calcium fluoride, yet the material still offers immense potential for further advancements. Thanks to increased furnace capacities and capabilities, material manufacturers will be in a much better position to come to consensus on and address with confidence the actual demand for calcium fluoride crystals. Improving yields and quality to an even higher level will remain the key challenge in the future. Leading crystal manufacturers already have programs in place aimed at upgrading the yields and should therefore be able to meet the demands of toolmakers in the future.