EMF
A Dynasil Company

THE SOLUTION TO COATING DLC ON CHALCOGENIDES

As manufacturers worldwide struggle to coat chalcogenides with diamond-like carbon, EMF's proprietary plasma-enhanced chemical vapor deposition process is tackling the toughest coating challenges.

Infrared optics are everywhere. Take a walk through your local shopping mall, visit a hospital or catch a flight at an airport, and you'll notice infrared (IR) thermometers and thermal cameras being used to measure the surface temperatures of objects and humans.

But the applications don't stop here. From pulse oximeters and machine vision systems to home security devices and self-driving cars, IR optics play an increasingly important role in more and more industries, including defense, space, astronomy, food safety, automotive, communications and healthcare.

IR devices measure temperature by detecting the emitted or reflected IR radiation from a surface. The warmer an object, the more IR light it will emit, with IR cameras detecting this energy and converting it into an electronic signal to generate a thermal image.

As part of this process, a lens will collect and focus the incident IR energy onto an array of sensors, making the optical performance of that lens a critical feature of any task, be it accurately determining temperature or creating a detailed thermal map.

HEAR & DLC COATINGS

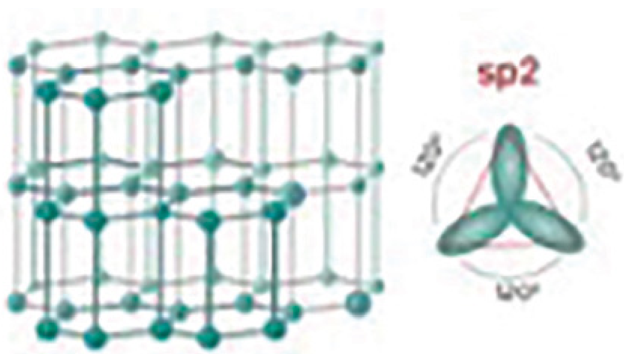
To ensure optimum performance, manufacturers typically apply a High-Efficiency Anti-Reflective (HEAR) coating to a lens surface to reduce the amount of reflected light and maximize the light transmitted to the sensors. While an HEAR coating comes at an incremental cost, it improves the efficiency of optical instruments, enhances contrast and reduces the scattered light that interferes with the optical performance of everything from telescopes to cameras.

Although an HEAR coating protects the lens, in certain applications, such as defense and security, oil and gas, firefighting, and space the optics are exposed to harsh environmental conditions including extreme temperatures, rapid and repetitive temperature changes, moisture, sand and dust, and humidity. To combat this, companies are turning to Diamond-Like Carbon (DLC) coatings.

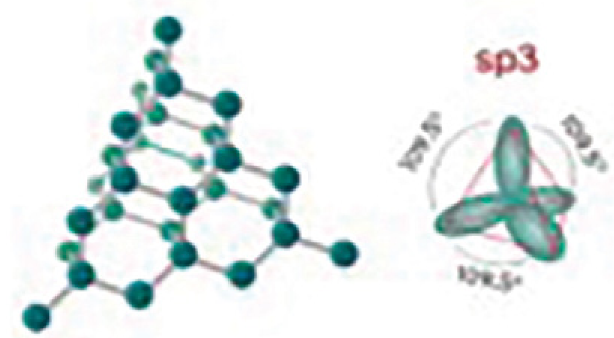
Similar to an HEAR coating, a DLC coating is transparent in IR wavelengths but, unlike an HEAR coating, it is virtually indestructible.

[CONTINUED ON NEXT PAGE]

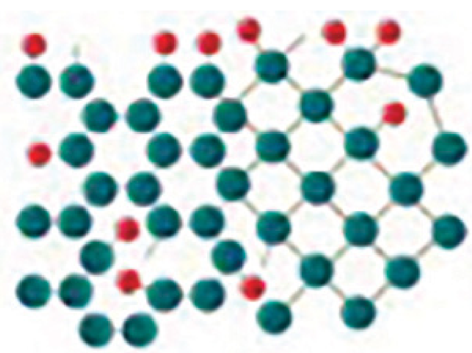
Graphite



Diamond



Diamond-Like Carbon



A DLC coating is an amorphous nano-composite carbon material that exhibits properties similar to that of natural diamond including low friction, high hardness, and high corrosion resistance. These exceptional properties give a DLC-coated optic excellent environmental protection, increasing its longevity and reducing the total cost of ownership.

Crucially, for manufacturers worldwide, optical coating solutions providers such as EMF, can apply long-lasting, defect-free DLC (and HEAR) coatings to virtually all IR materials, including well-known 'legacy' substrates like silicon (Si), germanium (Ge), zinc sulphide (ZnS), and zinc selenide (ZnSe).

However, in recent years, IR optical designers have shown an affinity towards the chalcogenide family of glasses that offer exceptional benefits but are highly temperamental.

COMMON INFRARED OPTICAL MATERIALS

Material	Wavelength Range	Type of Material
Silicon	1.1µm – 9µm	Metalloid
Germanium	2µm – 11.5µm	Metalloid
Sapphire	0.8µm – 18µm	Crystal
Zinc Selenide	1µm – 18µm	Crystal
Zinc Sulfide	1µm – 14µm	Crystal
Calcium Fluoride	0.15µm – 9µm	Crystal
Chalcogenides	0.8µm – 18µm	Amorphous Glass

— MEET EMF —

As the first company to offer optical thin film coatings in the US, EMF, a Dynasil company, has been a pioneer in the field since 1936. Home to 26 vacuum coating chambers, located across 2 state-of-the-art ISO 9001:2015 and ITAR certified facilities in New York, the company offers 40 million square inches of annual coating capacity, enabling high volume production as well as large format optical coatings up to 108" in diameter. EMF has more than 100 combined years of experience on virtually every substrate and also provides in-house metrology and MIL-standard testing.

Whatever your coating challenge, EMF is eager to help. Contact our team at +1-800-456-7070.

THE CHALCOGENIDE ADVANTAGE

Chalcogenide glasses are a well known family of materials that have been highlighted in academic papers, reports and book chapters for decades[1,2]. Typically described as 'remarkable', 'promising' and 'exceptional', these compounds of sulfur (S), selenium (Se), and tellurium (Te), exhibit a broad range of electronic, thermal and optical phenomena.

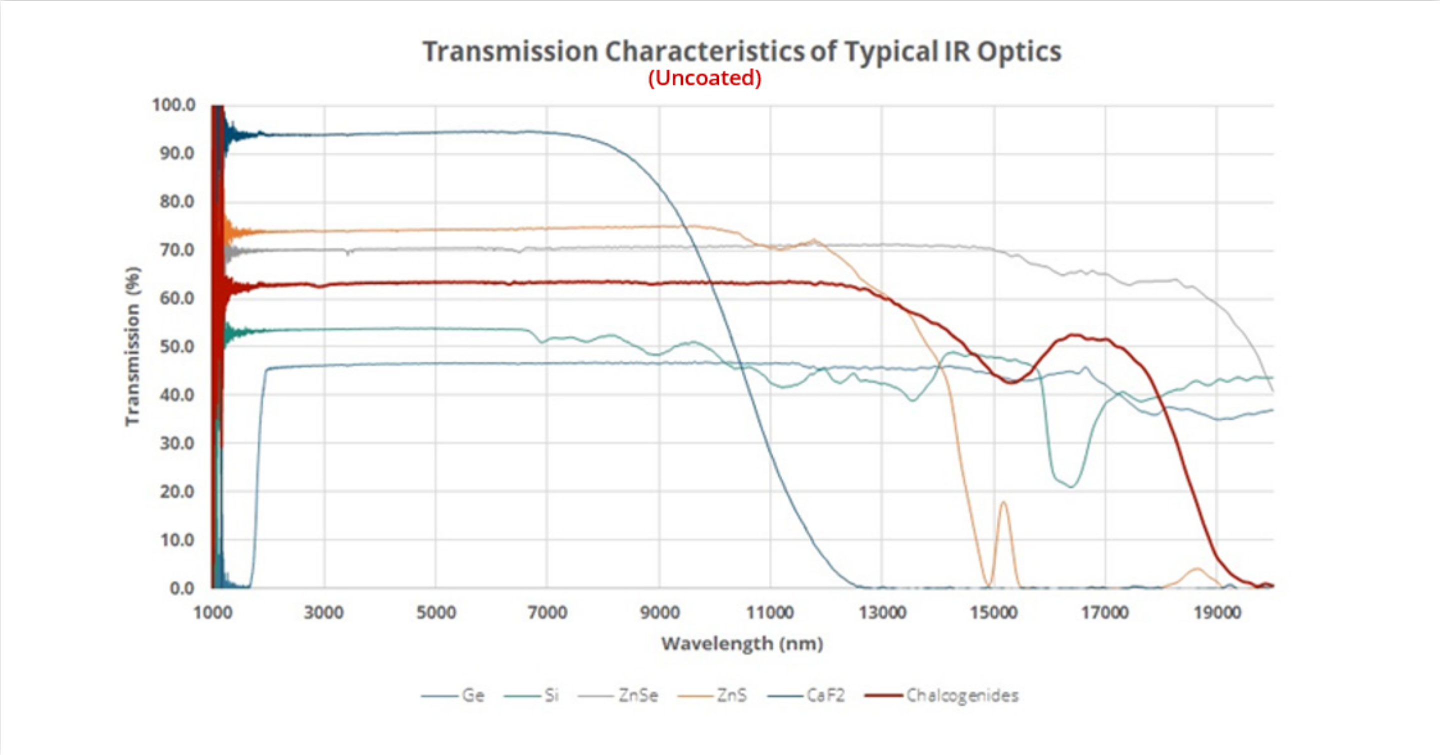
Properties such as refractive index, resistivity and melting temperature can be tuned by varying composition[3].

Thanks to this, chalcogenides have found great commercial significance. Arsenic trisulfide (As_2S_3) was commercial developed as early as the 1950s for mid-IR applications and since this time, the glasses have been used in numerous fields including data storage, lithium ion batteries and chemical sensing.

But importantly for optics manufacturers, these materials offer three key advantages over legacy materials.

Firstly, these amorphous glasses feature high transmission across the entire IR spectrum – from SWIR (0.9μ) to LWIR (14μ), transmitting further into the infrared than germanium and zinc sulfide substrates. Secondly, chalcogenides are athermal, meaning they are less likely to expand or contract with temperature changes, and have a stable refractive index across an operating temperature range of -40 ºC to +60 ºC.

[CONTINUED ON NEXT PAGE]



A third benefit of using chalcogenide glasses is cost. While germanium, silicon, zinc sulphide, and zinc selenide are precision cut with expensive diamond turning machines to form an IR lens, chalcogenides can be molded into the shape of the necessary optic. This mold can then be used repeatedly to create thousands of substrates opening the door to high volume production.

But, while chalcogenides offer many exceptional properties, they are more fragile and softer than legacy materials. These glassy materials can be attacked by oxygen and humidity, causing oxidation or hydrolysis of the surface[4], as well as many reactive gases and alkaline or oxidizing solutions[5].

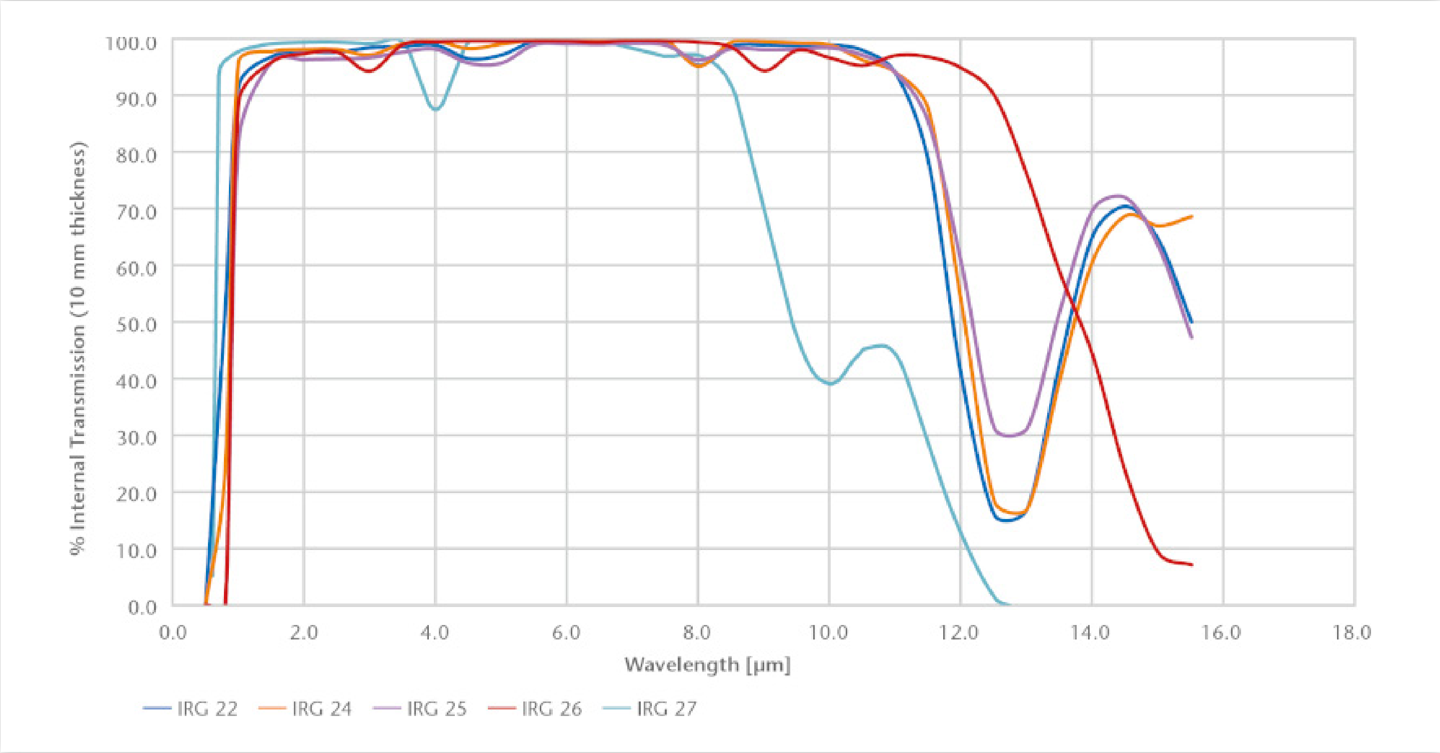
In addition, weak chemical bonding between atoms means that chalcogenides have poor mechanical properties, making them prone to scratches and other surface-layer defects. Clearly increasing the mechanical strength of these glasses would be beneficial for many applications, but to date, only a handful of researchers have investigated this, experimenting with heat treatments, for example, to alter these properties[6].

Given this, chalcogenides demand an extremely durable, protective anti-reflective coating, and, put simply, only a virtually indestructible DLC coating will do. And herein lies a key challenge.

COMMON IR CHALCOGENIDE GLASSES

Composition	$Ge_{33}As_{12}Se_{55}$	$Ge_{10}As_{40}Se_{50}$	$Ge_{28}Sb_{12}Se_{60}$	$As_{40}Se_{60}$	As_2S_3
Trade Names	IRG 22 IG2 AMTIR-1	IRG 24 IG4	IRG 25 IG5 AMTIR-3 BD-2	IRG 26 IG6 AMTIR-6 BD-6	IRG 27

TRANSMISSION PROPERTIES OF DIFFERENT CHALCOGENIDE GLASSES

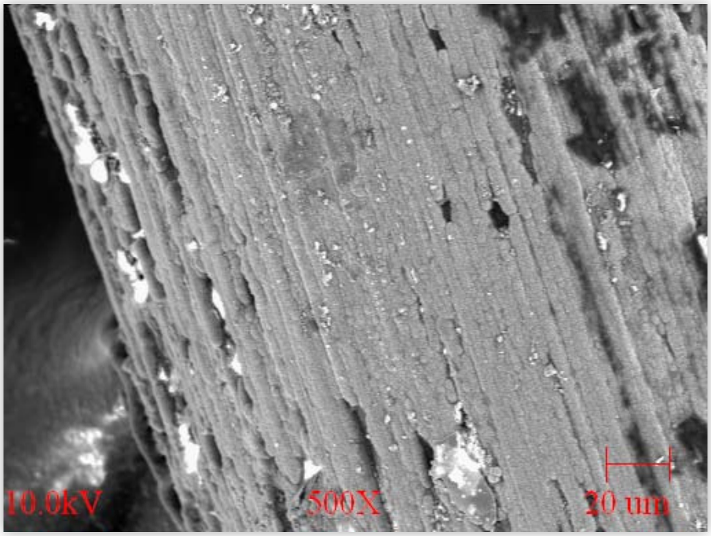


https://www.schott.com/en-us/products/ir-materials/technical-details

THE CHALCOGENIDE CHALLENGE

While diamond-like carbon provides a hard, anti-reflective coating to chalcogenide glass, the interface between the two materials often appears to lack the necessary adhesion for practical use. Researchers have been altering the composition of these glasses, adding small amounts of carbon to chalcogenides, to make surfaces more compatible with DLC[7]. But, in an industry setting, companies worldwide are still grappling with four common coating issues; non-uniformity, stresses, adhesion and pinholes. Surface-layer defects mean that consistently achieving uniform layers during coating is a real challenge. Spectral range is a function of coating thickness, so a non-uniform coating has a negative effect on the performance of the optic.

[CONTINUED ON NEXT PAGE]



Non-uniformity and stresses in a DLC coating

https://www.researchgate.net

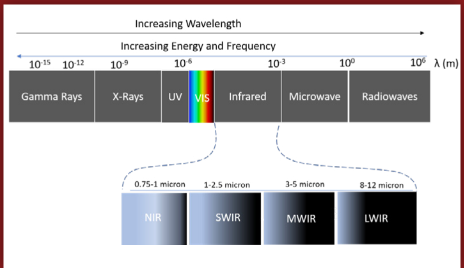
THE IR SPECTRUM AND ITS MANY APPLICATIONS

The IR spectrum is situated between the visible and microwave regions of the electromagnetic spectrum, with wavelengths spanning from 0.75 micron to 12 micron. Generally, infrared optics are categorized into four sub-bands: near infrared (NIR) short wave infrared (SWIR), mid wave infrared (MWIR) and long wave infrared (LWIR).

The NIR spectral band extends from 0.75 to 1 micron wavelengths and includes myriad applications including pulse oximeters that determine oxygen saturation on blood, LiDAR to map surroundings in self-driving cars, night vision goggles and remote control devices.

SWIR wavelengths, ranging from 1 to 2.5 micron, are critical for food and drug testing, non-destructive testing of packaged goods, counterfeit testing and medical imaging. Optical communications also operate at 1.3 micron and 1.55 micron.

Most thermometry takes place in either the MWIR or LWIR regions of the IR spectrum. The MWIR, from 3 to 5 micron, is more suitable for thermal measurements in, say, factories and airports, as ambient solar radiation cannot interfere with these readings. Meanwhile, the LWIR band, extending from 8 to 12 micron, is less sensitive to ambient noise, making it the region of choice for outdoor thermal imaging. This band is widely used in military surveillance, via cameras and drones, as well as reconnaissance operations.



Electromagnetic spectrum with infrared sub-bands

Application of infrared thermography in elevated skin temperature (EST) monitoring

The hard DLC coating is prone to residual stress, which develops during the coating process and can result in delamination. What's more, uncontrolled coating stresses often lead to a network of fine 'crazing' cracks on the coating, followed by larger cracks and ultimately coating failure. And due to the amorphous nature of

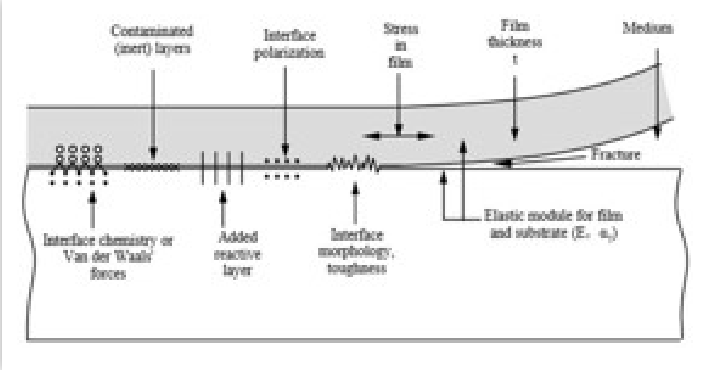
the chalcogenides, the interface between these glasses and diamond-like carbon lacks adhesion, which can also lead to delamination and failure between the base material and the coating.

Pinholes are a further issue, appearing as circular pockmarks on a coating surface. These defects emerge if the substrate isn't adequately cleaned or outgassed, as trapped air, liquid or solvents will then bubble through the coating. These defects create non-uniformity across the coating surface that will inevitably cause the optic to fail.

In addition, while the refractive index of DLC is a good match with legacy materials such as silicon and germanium, the same cannot be said for chalcogenides. A refractive index mismatch means that a multilayer coating must be carefully applied to the bare chalcogenide surface prior to coating it with DLC.

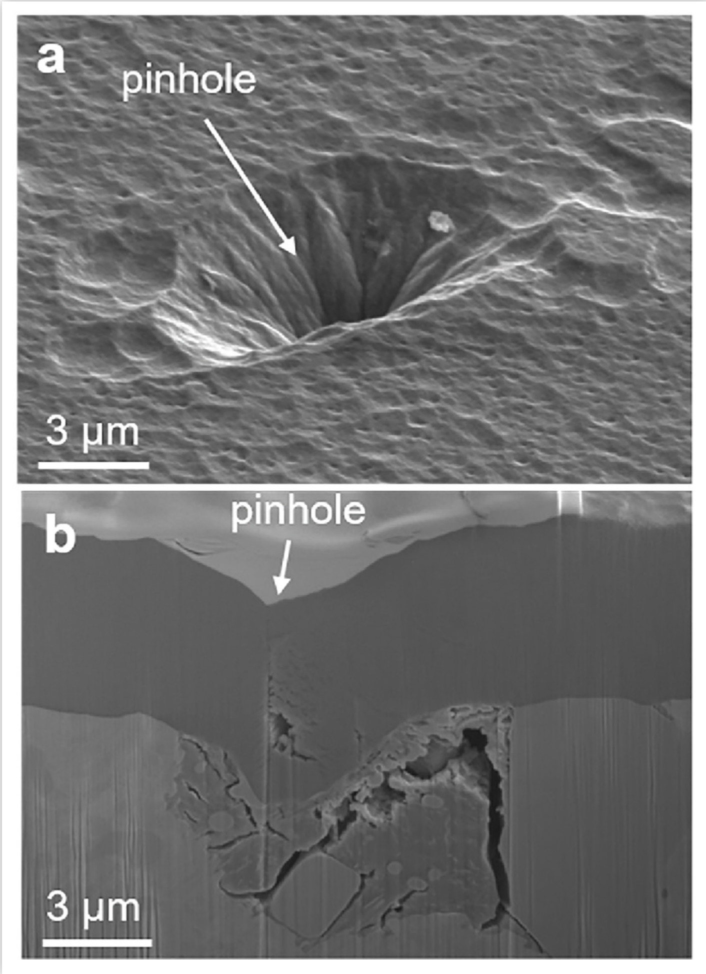
Given these issues, applying a high performance DLC coating to chalcogenide glasses is notoriously difficult to achieve. While some industry players have developed DLC coatings that optimize optical and environmental performance, developing processes to repeatedly deliver a robust coating in production volumes hasn't been easy.

Following extensive studies and years of ongoing effort, EMF has pioneered an ingenious and reliable process that eliminates these problems to deliver a DLC coating with virtually no defects.



Adhesion issues in DLC Coatings

https://www.researchgate.net



Pinholes in a DLC coating

https://www.researchgate.net

COATING CHALCOGENIDES WITH CONFIDENCE

In 2017, EMF designed a state-of-the-art DLC coating chamber based on a proprietary Plasma Enhanced Chemical Vapor Deposition (PE-CVD) process specifically with chalcogenides in mind. Company engineers defied conventional industry thinking and literally turned the deposition process upside down by designing the PE-CVD system to coat up, instead of down. Here, gases are injected from the bottom of the chamber and then evacuated close to the top – where the substrate being coated is suspended.

Whilst building the chamber, the engineers also opted for a cylindrical chamber geometry, rather than the typical box design. This design allows the plasma cloud to be radially symmetric with respect to the deposition plate resulting in a more uniform coating across the entire optic.

The chamber has an extra-large workspace to accommodate optics up to 14” in diameter.

The end result has been a system that virtually eliminates pinholes and minimizes processing defects. The upward gas flow in the cylindrical chamber ensures reactant gases evenly distribute throughout the chamber and undergo homogenous vapour phase reactions that deposit uniform thin films on the substrate. What’s more, the coat-up design combined with the chamber’s circular geometry means carbon flakes and other contaminants can’t settle into corners and later fall down onto the substrate, causing defects.

EMF’s custom-designed DLC coating chamber

EMF engineers also optimized the PE-CVD system’s numerous chamber inputs. Operating temperatures are minimized to reduce residual stresses in the coating while advanced process cooling controls have been integrated. Gas inputs and outlets are carefully positioned on the chamber, which also has forward and reflected RF power.

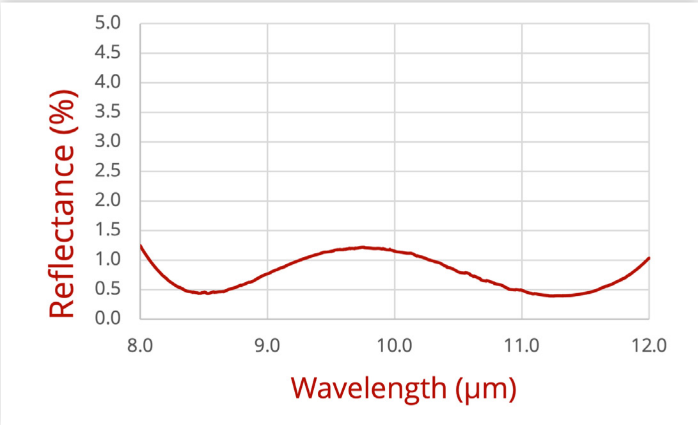
Witness samples of DLC-coated optics

And, special tooling and proprietary cleaning techniques have been provisioned.

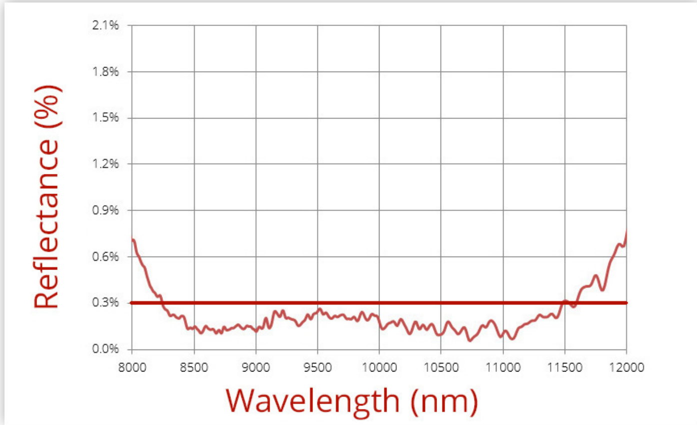
PERFECTING THE PROCESS

Thanks to their many decades of field experience, EMF engineers have honed the PE-CVD process to ensure that the correct number of DLC layers are deposited onto the chalcogenide, and in the necessary order, to deliver a robust IR optic. This also includes applying the all-important interstitial layer to phase match the refractive indices of the chalcogenide and DLC.

Getting the deposition processes right is the difference between success and failure– incorrect deposition can stress the coating and cause surface irregularities that lead to imaging problems. More importantly, these coatings stand up to the toughest military specs with EMF having coated thousands of chalcogenide-based optics for some of the most demanding commercial and military applications.

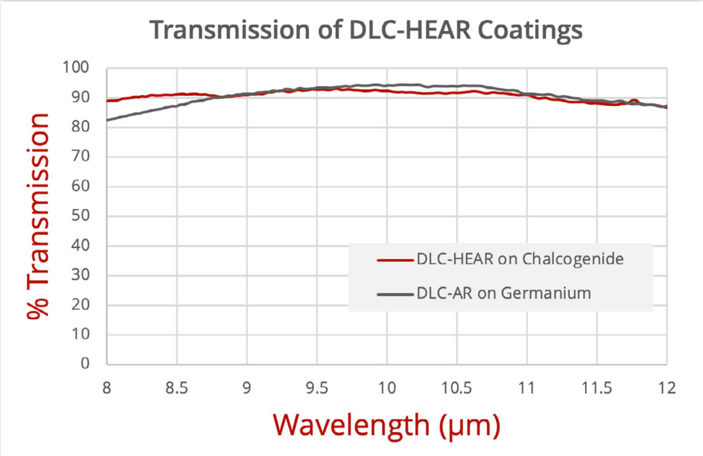


DLC: Rx ~ 1%



HEAR: Rx ≤ 0.3%

Typical on germanium, zinc selenide, zinc sulfide (multi-spectral) and chalcogenides at near normal AoI



MIL-Standard DLC Coatings

- Adhesion: Per MIL-M-13508C para 4.4.6 (fast pull)
- Abrasion: Per MIL-C-675C para 4.5.10. (severe abrasion, 40 strokes)
- Humidity: Per MIL-C-675C para 4.5.8. (Min 24 hours)
- Solubility: Per MIL-C-675C para 4.5.7. (24 hour immersion in water/salt)
- Salt Spray: Per MIL-C-675C para 4.5.9. (24 hours salt spray-fog test)
- Temperature Cycle: Per MIL-M-13508C para 4.4.4
- Wiper Test: No signs of removal when exposed to 5,000 revolutions sand/slurry mixture

EMF's customers include several US-based defense contractors including L3Harris, RPO and Leonardo DRS.

"It is always preferable to use a DLC process that coats up to ensure virtually pinhole-free coatings."

- Jadranka Lakic-Reljic,
Principal Quality Engineer, Leonardo DRS

"EMF has been an excellent vendor for us in a (coatings) world where we've had almost nothing but mediocre to abysmal vendors."

- Robert Benoit,
Optics Division Manager, L3Harris

THE EMF EDGE

Chalcogenide glasses are a well known family of materials that have been highlighted in academic papers, reports and book chapters for decades[1,2]. Described as 'remarkable', 'promising' and 'exceptional', these compounds of sulfur (S), selenium (Se), and tellurium (Te), exhibit a broad range of electronic, thermal and optical phenomena.

While EMF has pioneered PE-CVD to precisely coat chalcogenides, the company can also apply the process to legacy substrates, delivering a defect-free, durable optic that will stand the test of time in the field. In addition, the company offers full in-house metrology as well as MIL-standard testing including an in-house, purpose-built sand-slurry wiper testing system.

EMF has a track record of more than 99% on-time delivery and product quality. And, as part of its service commitment, the company offers an available 48-hour turnaround, available same day service, industry-leading technical and applications engineering support, and a zero-wait chamber reservation system.

In short, EMF offers a one-stop solution to all your coating needs with results that exceed optical spectral performance, and deliver substantial protection against harsh environmental conditions.

EMF'S INFRARED COATING CAPABILITIES

	SWIR 0.9 - 2.7 µ	MWIR 3.0 - 5.0 µ	LWIR 7.0 - 14.0 µ	MWIR-LWIR (MS) 3.0 - 14.0 µ
Glass	Y			
Sapphire	Y	Y		
Calcium Fluoride	Y	Y		
Silicon		Y		
Germanium		Y	Y	Y
Zinc Selenide	Y	Y	Y	Y
Zinc Sulfide	Y	Y	Y	Y (MS)
Chalcogenides IRG26, IG6, $As_{40}Se_{60}$		Y	Y	

REFERENCES:

1. Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium, 2007.
2. Furdyna, J. K., Dong, S. N., Lee, S., Liu, X., & Dobrowolska, M. (2019). The ubiquitous nature of chalcogenides in science and technology. In Chalcogenide: From 3D to 2D and Beyond (pp.1-30) Elsevier
3. Hewak, D.W. & Zheludev, N.I. & MacDonald, K.F.(2014). Controlling light on the nanoscale with chalcogenide thin films. Chalcogenide Glasses (pp.471-508)
4. M. Frumar, B. Frumarova, T. Wagner, G.K. Sujan, Amorphous and Glassy Semiconducting Chalcogenides, Reference Module in Materials Science and Materials Engineering, Elsevier, 2016.
5. Vlcek et al., (1991) The influence of the composition of the layers and of the inorganic solvents on photoinduced dissolution of As-S amorphous thin films, Journal of Non-Crystalline Solids, Volumes 137–138, Part 2, 1991, Pages 1035-1038.
6. Sharma et al., Impact of Morphology and Microstructure on the Mechanical Properties of Ge-As-Pb-Se Glass Ceramics, Applied Sciences, 20 April 2020.
7. Jun Ho Lee, Hyun Kim, Woo Hyung Lee, Min Chul Kwon, Yong Gyu Choi, Surface modification of chalcogenide glass for diamond-like-carbon coating, Applied Surface Science, Volume 478, 2019, Pages 802-805.