Ultra-Durable Phosphide-Based Antireflection Coatings for Sand and Rain Erosion Protection

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Abstract. Optical, mechanical, and erosion-protective characteristics of boron and gallium phosphide are evaluated as single films and within antireflection multilayers. These coatings are shown to combine broadband infrared transmission with environmental durability, specifically in relation to abrasion resistance and elevated temperature performance up to 500°C. Rain erosion protection of all common IR optical materials is demonstrated from single water jet impact and whirling arm tests. Protective characteristics in relation to solid particle impact are described.

Subject terms: phosphide coatings; optical and environmental properties; rain and sand erosion protection; antireflection coatings.

1 Introduction

Few existing materials have the required optical, thermal, and mechanical properties suitable for airborne applications in the infrared (IR), particularly in the 8- to 12-μm wave band. Current IR window materials such as forward-looking infrared (FLIR) ZnS and Ge exhibit acceptable optical properties. However, these materials have inadequate performance in relation to mechanical properties, in particular, they have poor rain and sand erosion resistance.

The use of hard, high-Young's-modulus transparent coatings is one of the most important methods of protecting optical components. Various coatings have been investigated for protecting FLIR ZnS and Ge, including coatings based on diamondlike carbon[1] (DLC) and the GeC family of coatings.[2]

DLC in thicknesses of 1 to 2 μm provides good abrasion resistance to IR windows, but offers minimal protection against high-speed rain impact.[3] Improvement in rain erosion resistance requires thicker coatings of a high-Young's-modulus material. Although DLC coatings have the required Young's modulus, an intrinsically high film compressive stress and the absorption coefficient limit the practical thickness of DLC to about 2 μm.

GeC films are not stress limited to the same extent as DLC and as such can be produced thick enough to provide some protection against erosion. However, GeC coating absorption is such that the thicknesses required for erosion protection incur intolerable optical loss for most applications.

One of the most promising coatings for use in extreme operating environments is diamond, which exhibits exceptional mechanical, optical, and thermal properties. Recent developments of various vapor deposition processes for producing polycrystalline diamond[4] seem to offer the possibility of providing synthetic protective coatings and bulk window materials. However, the prospect of obtaining low-scatter diamond protective coatings or bulk windows, of sufficiently good quality, seems to be at least several years away from becoming a commercial reality.

Phosphide-based coatings, in particular BP and GaP, have many of the desirable attributes of diamond, including high Young's modulus, hardness, high thermal conductivity, and an upper transmission limit[3] of at least 50 μm. BP coatings have demonstrated the best reported[3] performance to date in relation to rain erosion protection of FLIR ZnS and Ge. Moreover, the possibilities offered for ultradurable coatings utilizing the phosphides are extensive.[5]

Pilkington Optronics utilizes a variety of phosphide deposition techniques including reactive sputtering and plasma-assisted chemical vapor deposition. Analysis of the phosphide coatings produced show them to be near stoichiometric (within 10%) in composition, with an amorphous structure. These coatings exhibit a marginal deviation from stoichiometry, in that a few atomic percent (less than 3%) of hydrogen is incorporated during film growth. This hydrogen arises from use of hydride precursors.

This paper presents the current status and performance of Pilkington Optronics BP and GaP films, incorporated within antireflection multilayers, to produce low-loss, ultradurable protective coatings for all IR materials. Optical durability and erosion protection characteristics are described.

2 Optical Characteristics

2.1 *Spectrophotometric Assessment of BP and GaP*

Figure 1 shows representative transmission and loss IR spectra for BP and GaP deposited on multispectral zinc sulphide substrates. Substrate absorption has been deconvoluted. BP

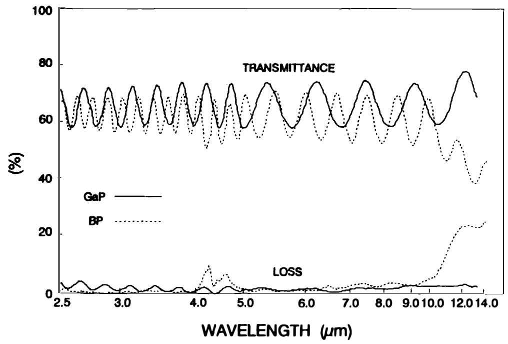


Fig. 1 Representative transmission and loss spectra for BP and GaP coatings (thickness of 10.1 and 6.6 μm, respectively) deposited on multispectral ZnS.

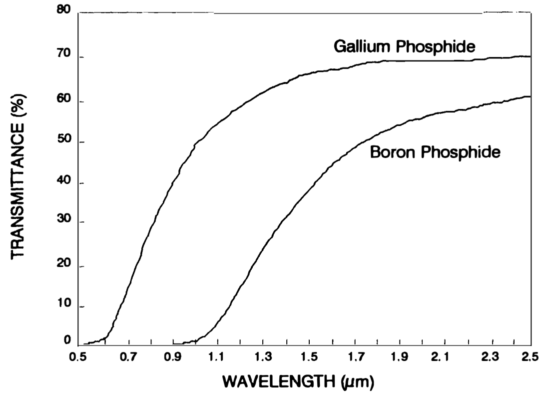


Fig. 2 Transmission edges of BP and GaP coatings (identical coatings to those shown in Fig. 1).

and GaP spectra shown in Fig. 1 correspond to film thicknesses of 10.1 and 6.6 μm, respectively. These show that transmission reduction results predominantly from reflection loss, which is a consequence of the relatively high refractive index of phosphides (typically $n = 2.9$ for BP and GaP). Incorporation of phosphide coatings into antireflection multilayers to reduce transmission loss is described in Sec. 2.3.

Figure 1 also highlights BP absorption features at 4.2, 4.5, and 13.0 μm. These are a consequence of B-H, P-H, and B-H-B stretching and bending modes arising from the incorporation of hydrogen from hydride precursors. GaP does not exhibit the same degree of resonant absorption because of the much reduced level of hydrogen present in the film growth process.

Visible and near IR transmission spectra of BP and GaP are shown in Fig. 2 (assessed from BP and GaP films shown in Fig. 1), indicating the transmission range of GaP extends to shorter wavelengths compared with BP. This is a consequence of GaP's larger bandgap.

Assessment of BP transmission for extended IR wavelengths was carried out by coating thin silicon wafers, which transmit over a wide IR range. To allow for the effects of Si substrate absorption, transmissions before and after BP coating were displayed as a ratio and multiplied by 0.5 (this provides a transmission trace at the 50% level).

Absorption features are observed as "dips" below the 50% line. This assessment was not intended as an accurate quantitative measurement, but serves to identify significant absorption features out to 50 μm. Figure 3 shows a typical spectrum, which emphasizes the broadband transmission capability of BP (film thickness 2 μm), with no fundamental cutoff occurring over the range 2.5 to 50 μm.

2.2 *IR Optical Loss of BP and GaP*

Analysis of average BP and GaP film optical loss, over the 8- to 11.5-μm wave band, shows that GaP has lower loss per micrometer of film compared to BP (typically a factor of 3 to 4). The primary reason for reduced GaP loss is a lower level of hydrogen incorporation into the film during the growth process, as described in Sec. 2.1.

Table 1 indicates measured absorption per micrometer for BP and GaP at specific CO_2 laser wavelengths. Absorption was measured using laser rate calorimetry.[6] The data show the extent of B-H-B induced resonance absorption in BP,

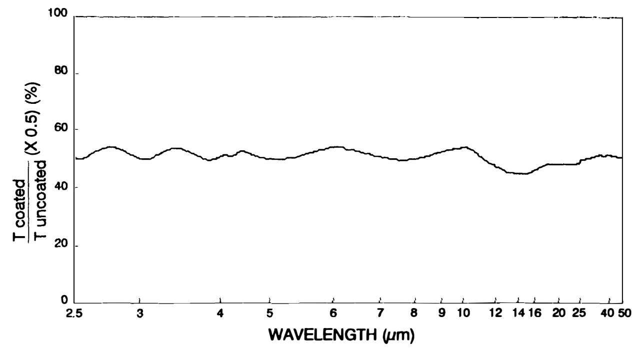


Fig. 3 Broadband IR performance of 2.0-μm-thick BP coating on Si wafer.

Table 1 Evaluation of phosphide coating absorption, at specific CO_2 laser wavelengths, using laser rate calorimetry.

WAVELENGTH (μm)	ABSORPTION (%/μm)	
	BP	GaP
9.24	0.48 ± 0.17	0.05 ± 0.05
10.21	0.54 ± 0.16	0.01 ± 0.05
10.59	0.80 ± 0.20	0.18 ± 0.07

associated with the tail of a broad absorption feature at 13 μm.

2.3 *Phosphide-Based Antireflection Multilayers*

BP and GaP films have refractive index values approximately equal to 2.9, as compared with 2.2 and 4 for ZnS and Ge substrate materials, respectively. This implies that a thick phosphide coating on ZnS has an effective optical admittance of 4.1 and 2.2 at the quarter- and half-wave points, respectively. Phosphide films on Ge substrates have effective admittances of 4.0 and 2.2 for the half- and quarter-wave positions, respectively. Consequently a quarter wave of refractive index 2.0 acts as an antireflection coating (ARC)

Table 2 Theoretical average transmittance and reflectance for Ge and ZnS substrates coated with BP or GaP and an antireflective overcoat of DLC or oxide. Theory includes film absorptions with averages evaluated for the 8- to 10-μm, 8- to 11.5-μm, and 8- to 12-μm range.

		OXIDE						DLC					
FILM	SUBSTRATE (1mm)	AVERAGE TRANSMITTANCE (%)			AVERAGE REFLECTANCE (%)			AVERAGE TRANSMITTANCE (%)			AVERAGE REFLECTANCE (%)		
		8-10	8-11.5	8-12	8-10	8-11.5	8-12	8-10	8-11.5	8-12	8-10	8-11.5	8-12
GaP	Ge	94.2	93.7	92.3	3.4	3.3	4.4	87.4	86.7	86.2	6.9	7.6	8.0
	ZnS	94.1	93.1	93.2	2.0	3.1	2.9	85.9	85.7	85.9	7.1	8.0	7.7
BP	Ge	90.0	85.0	82.4	2.5	3.0	3.1	84.9	80.9	78.3	4.6	5.0	5.4
	ZnS	87.7	83.4	79.7	4.3	4.5	5.3	82.6	78.6	73.2	6.8	7.4	8.3

for both types of substrate. DLC ($n=2.0$) or an infrared transmitting oxide ($n=1.8$) can be used to provide an antireflection overcoat layer close to the correct index.

Table 2 shows the theoretical transmittances and reflectances, over a range of wave bands, for each substrate type coated with a 10-μm-thick BP of GaP layer overcoated with either DLC or oxide antireflective layer.

Comparison between theoretical and experimental transmittance is shown in Figs. 4(a), 4(b), and 5 for DLC/BP (thickness = 11 μm)/Ge, DLC/BP (thickness = 13 μm)/Tuftran, and oxide/GaP (thickness = 10 μm)/ZnS, respectively. Excellent agreement is found.

3 Durability

3.1 *Knoop Hardness*

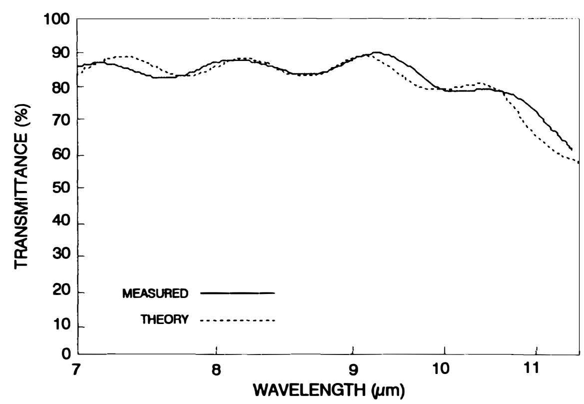
Knoop hardness measurements were made on a range of phosphide coatings on multispectral ZnS substrates, with the representative results shown in Fig. 6. As can be seen BP and GaP exhibit a high degree of hardness.

It was not practical to extrapolate these results to zero load with any degree of accuracy. Consequently, values are quoted for a 5-g load. For the BP and GaP, values of ~6000 and ~4000 kg/mm^2, respectively, were measured. For comparison, GeC coatings give a range of 1500 to 2500 kg/mm^2 for a 5-g load.

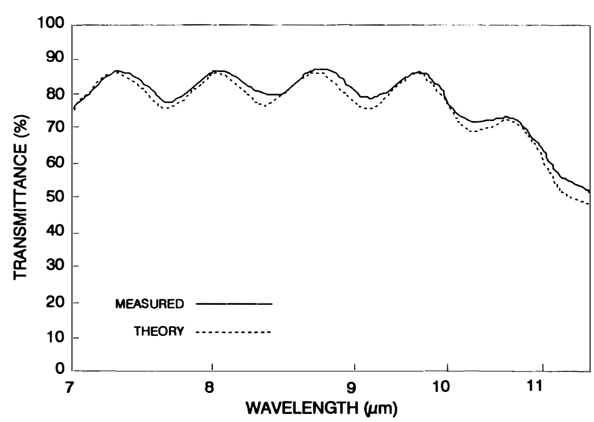
3.2 *Abrasion Resistance*

Coated samples were subjected to a severe abrasion test involving 100,000 wipes with a rubber blade in a slurry of sand and water (TS1888 specification; details described in Ref. 7). Note that DLC on germanium is required to pass 10,000 wipes in this test. DLC-coated ZnS will generally fail this test at 10,000 wipes. Table 3 indicates the range of phosphide-based coatings evaluated using this test. A pass in the test is achieved only if the sample shows no signs of marking or damage.

Table 3 reveals that all single BP layer phosphides and also antireflective multilayers on a range of substrate types



(a)



(b)

Fig. 4 Comparison between theoretical and measured transmittance for (a) DLC/BP (thickness = 11 μm)/Ge and (b) DLC/BP (thickness = 13 μm)/Tuftran.

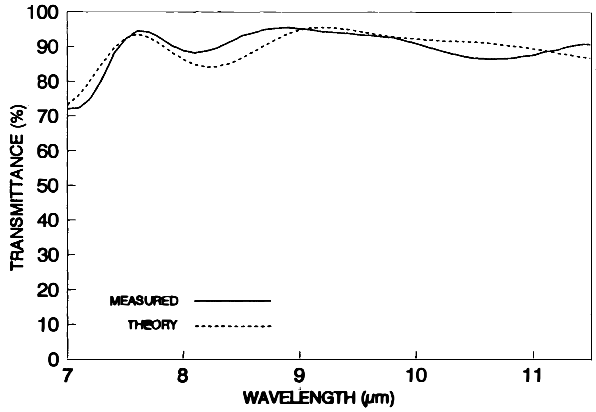


Fig. 5 Comparison between theoretical and measured transmittance for oxide/GaP (thickness = 10 μm)/ZnS.

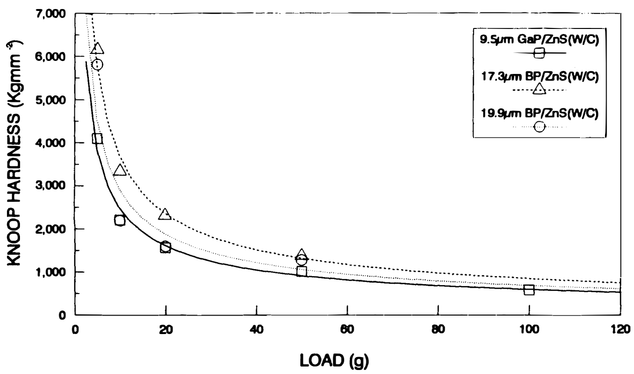


Fig. 6 Knoop hardness of typical BP and GaP coatings.

pass this very severe abrasion test. Moreover, a number of samples have been subjected to 250,000 wipes with no marking or damage. GaP layers achieve a pass for >60,000 wipes.

3.3 *Additional Environmental Tests*

Transmission measurements of GaP and BP have been performed at ambient and 500°C in air. Results indicate that the observed transmission loss (reversible on return to ambient) is entirely attributable to substrate loss and not film effects.

The transmittance of BP films has been measured up to 500°C in air, and this showed neither any transmittance fall (caused by the film) nor any long-term deterioration.

Table 4 summarizes environmental and durability tests (the appropriate MIL-F-48616 paragraph is quoted) passed by DLC/BP multilayer coatings. These include adhesion, abrasion, temperature, water solubility, and salt spray fog.

4 Rain Erosion Testing of Phosphide-Based Multilayers

4.1 *Water Jet Impact Assessment*

Water jet impact tests have been carried out to establish characteristic damage threshold velocities (DTVs) for phosphide-based coatings. The DTV refers to the maximum velocity at which a water drop or jet can impact a specified material without causing observable damage. DTV values reported here correspond to 10 impacts per site for at least two sites on the one sample.

Table 3 Range of phosphide-based coatings subjected to wiper blade slurry test. Passing the test requires no signs of damage of marking to the coating.

COATING TYPE	SLURRY TEST NUMBER OF WIPES
BP/FLIR ZnS	> 100,000
BP/Ge	> 100,000
DLC/BP/FLIR ZnS	> 100,000
DLC/BP/Ge	> 100,000
GaP/FLIR ZnS	> 60,000*
GaP/Ge	> 60,000*

The equipment used for this evaluation was supplied by the Physics and Chemistry of Solids Group at the Cavendish Laboratory, Cambridge, UK. A complete description of the equipment is given in Ref. 8. All measurements were carried out using an 0.8-mm jet, which is equivalent to a 6- to 3-mm drop size over the respective velocity range 150 to 400 m/s used.[9]

Multiple-impact (10 per site) evaluation was carried out, enabling a clearly defined DTV to be determined. Onset of damage is determined from Nomarski microscopy (typically 100× magnification) of the impact site.

This approach is in agreement with the findings of Hand,[9] Van der Zwaag and Field,[10] and Clapham and Hutley,[11] who conclude that multiple liquid jet impact on brittle materials does not change the DTV but emphasizes the transition between a damaged and undamaged state. Multiple-impact testing ensures that damage occurring in the substrate is accompanied by surface damage.

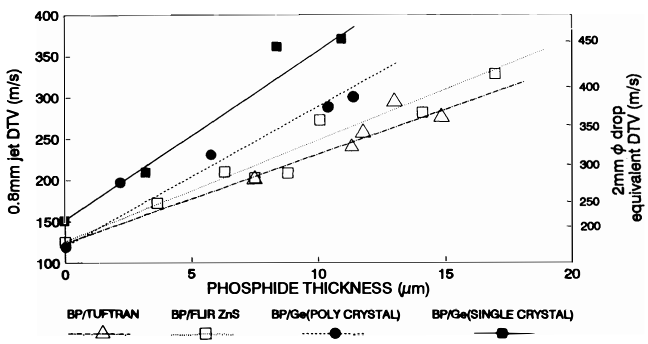
Figures 7(a) and 7(b) show DTV as a function of boron and gallium phosphide thicknesses, respectively, for a range of IR substrate materials (FLIR ZnS, Tuftran, and germanium). Results show the expected increase in DTV with increasing phosphide thickness,[10,11] where the degree of "stiffness" introduced to the underlying substrate increases with increasing film thickness, thereby minimizing the extent of tensile stressing within the substrate on water jet impact. This reduction in tensile stressing inhibits crack formation and hence erosion damage within the substrate.

Figure 8 shows a similar dependancy of DTV with increasing phosphide thickness when the phosphide is overcoated with an antireflective overcoat (examples include DLC and oxide overcoats).

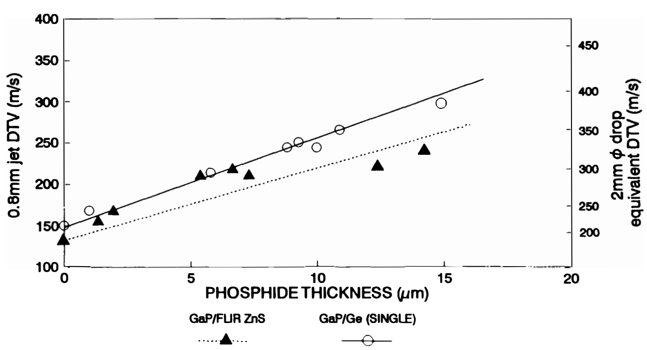
Figures 7(a) and 7(b) indicate that BP and GaP coatings on monocrystalline germanium substrates provide a greater DTV per micrometer of coating as compared with phosphide coatings on polycrystalline germanium and FLIR ZnS substrates. Furthermore, for the germanium case, this slope is dependent on the crystalline state of the substrate as poly or single crystal. Thus it is probable that a number of physical properties of the substrate influence the DTV of the phosphide-coated substrate. These include elastic constants, fracture toughness, presence of grain boundaries, and crystal orientations.

Table 4 Environmental/durability tests passed by DLC/BP multilayer coatings on germanium.

TEST	DESCRIPTION OF TEST	MIL-F-48616 RELAVENT PARAGRAPH
Adhesion	Rapid removal of adhesive tape	4.6.8.1
Humidity	49°C, 95% RH for 24hours	4.6.8.2
Moderate Abrasion	Rubbing with cheesecloth 1hr after humidity test	4.6.8.3
Temperature	Exposure to -61°C and +71°C for 2hrs at each temperature	4.6.9.1
Solubility&Cleaning	Immersion for >10 mins in trichloroethylene, acetone and ethyl alcohol	4.6.9.2
Severe Abrasion	20 strokes with a standerd eraser, with a force of 2.0-2.5 pounds continuously applied	4.6.10.1
Salt Solubility	24hr immersion in a solution of distilled water and salt	4.6.10.2
Water Solubility	24hr immersion in distilled water	4.6.10.3
Salt Spray Fog	24hr continuous exposure to a salt fog test	4.6.10.4



(a)



(b)

Fig. 7 Water jet impact damage threshold velocity (DTV) as a function of phosphide film thickness for (a) BP and (b) GaP deposited onto a range of substrate types.

Comparison of Fig. 7(b) with Fig. 7(a) shows that GaP provides less DTV per micrometer of coating as compared with BP. This suggests that the degree of stiffness imparted to the substrate is less for a given thickness of GaP as compared with BP.

The right-hand scales in Figs. 7(a), 7(b), and 8 show an equivalent 2-mm-drop-diam DTV, which has been extrapolated from 0.8-mm jet data using the correlations of Hand.[9] This allows some measure of comparison with the nominal 2-mm drop size utilized in whirling arm tests, reported in Sec. 4.2.

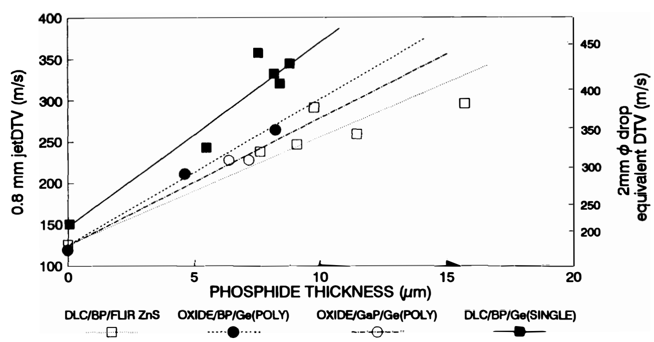


Fig. 8 Water jet impact damage threshold velocity (DTV) as a function of phosphide film thickness for BP or GaP incorporated into antireflection multilayers deposited onto a range of substrate types.

Validity of extrapolated DTV values for 2-mm equivalent drop sizes has been verified from measurements carried out using a hydrometeor impact facility at General Research Corporation (Advanced Technologies Division). This facility allows single water drop impact tests with accurately controlled water drop dimensions, measured just prior to impacting the specimen. Tests carried out on DLC/BP (thickness = 13 μm)/Tuftran samples utilizing 4- and 2-mm water drop sizes indicate DTVs of approximately 270 and 400 m/s, respectively.[12]

4.2 *Simulated Rain Erosion: Whirling Arm Tests*

4.2.1 *Whirling arm test facilities*

Rain erosion protective phosphide multilayers have been evaluated at two whirling arm rigs. The facilities are located at the Defence Research Agency Farnborough, UK [formerly Royal Aerospace Establishment (RAE)], and Wright Patterson Air Force Base, Dayton, Ohio [operated by University of Dayton Research Institute (UDRI)].

Test conditions at each facility are a 2-mm nominal drop size, 1 in./hr rainfall, normal incidence impact, 20-min exposure, and typical impact velocities of 211 or 223 m/s. A pass is achieved if the average transmission reduction (over the 8- to 12-μm wave band) is <4%.

Although the nominal test conditions are the same at RAE, the UDRI results are not. This is best demonstrated with DLC samples. A series of samples of DLC on germanium were produced in the same deposition run and some tested at 211 m/s in one rig and the remaining at the other facility. The results are shown in Fig. 9. Clearly UDRI is more severe. Further samples were tested at RAE at its maximum velocity of 223 m/s and the results of these tests are compared with the UDRI data in Fig. 10. This shows the average fall in transmission and the spread in results for both test rigs. UDRI at 211 m/s is more severe than RAE, even at 223 m/s. Also, the spread in UDRI results is greater even where the average falls are similar. The UDRI rig is therefore more severe in two respects—first the average transmission fall is larger, and second, there is greater variability in the results.

Adler[13] studied the drop size distribution of these two rigs and found that although the number of impacts per second is higher at RAE (and closer to natural rain), the drop size distribution is very extended at UDRI. This poor distribution may be reason for the measured variability at UDRI. Figure 11 compares the drop size distribution of the two rigs, and includes the distribution for natural rain.[14]

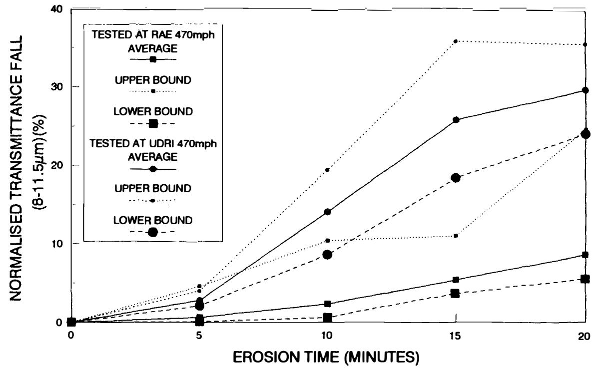


Fig. 9 Comparison of transmission losses at RAE and UDRI whirling arm rigs (v=211 m/s) for DLC on polycrystalline Ge.

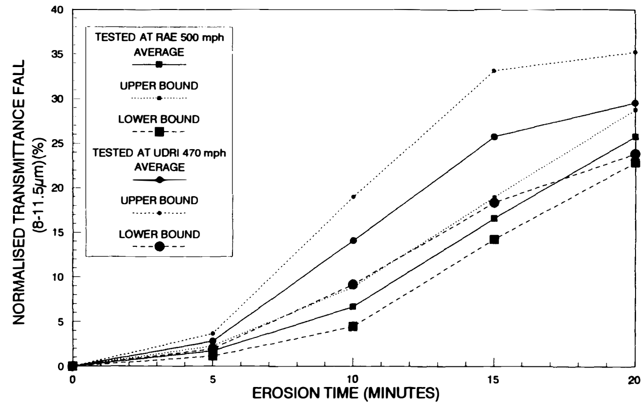


Fig. 10 Comparison of transmission losses at RAE (v=223 m/s) and UDRI (v=211 m/s) whirling arm rigs for DLC on polycrystalline Ge.

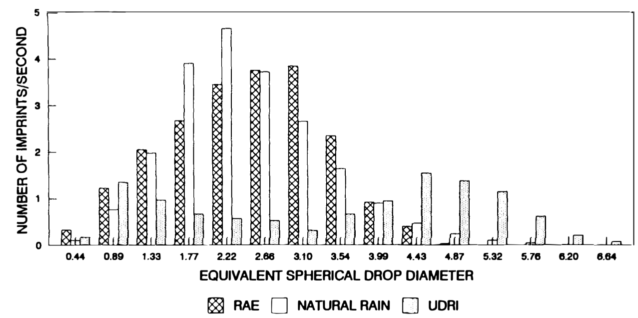


Fig. 11 Distribution of water drop sizes in RAE and UDRI whirling arm rigs. Distribution for natural rain indicated for comparison.

4.2.2 *Whirling arm performance of phosphide-based ARCs*

Table 5 indicates performance of a range of protective coating/substrate combinations at the two facilities. Table 5 also indicates typical BP thicknesses tested and associated change in average (8- to 11.5-μm) transmission. Passes (average transmission change <4%) are achieved for phosphide thicknesses >10 μm, and transmission reduction (8- to 12-μm wave band) is typically <1%.

Optical spectra for DLC/BP (thickness = 14.0 μm)/Tuftran and GaP (thickness = 10.7 μm)/FLIR ZnS before and after rain erosion testing at the UDRI and RAE facilities are shown in Figs. 12 and 13. There is no significant transmittance change, with observed wavelength shift resulting entirely from transmittance measurement at marginally different positions on the sample before and after evaluation.

Figure 14 shows the rain induced transmission decrease, as assessed on the UDRI facility, as a function of BP thickness for Ge substrates. The test conditions are 211 m/s velocity, 1 in./hr rainfall, and 2-mm nominal drop diameter at normal incidence. As expected, the erosion rate reduces with increasing BP thickness.

5 Sand/Dust Erosion Testing of Phosphide-Based Multilayers

5.1 *Sand/Dust Erosion: U.S. Defense Nuclear Agency Sand Erosion Facility*

Samples of DLC/BP (thickness = 12 μm)/FLIR ZnS were subjected to sand/dust testing at the U.S. Defense Nuclear Agency (DNA) sand erosion facility. This facility comprises a linear array of four oscillating spray nozzles that spray silica-based sand onto a nominal 7-in.^{2} plate. The nozzles are fed from individual fluidized beds. The plate holding the samples and the nozzles are then scanned, as shown in Fig. 15.

Samples were subjected to tests with a wide range of particle sizes (<177 μm) and velocities up to 206 m/s. In none of these did the DLC/BP-coated zinc sulphide show any significant transmittance fall. The maximum velocity assessed is seven times higher than the maximum velocity called up in the standard MIL-STD-810D sand/dust erosion test. For comparison, tests were carried out on thorium-fluo-

Table 5 Whirling arm test results for range of phosphide-based coatings.

		RAE				UDRI	
		ARM SPEED = 211m/s		ARM SPEED = 223m/s		ARM SPEED = 211m/s	
COATING	SUBSTRATE	PHOSPHIDE THICKNESS (μm)	NORMALISED TRANSMITTANCE FALL @10μm%	PHOSPHIDE THICKNESS (μm)	NORMALISED TRANSMITTANCE FALL @10μm%	PHOSPHIDE THICKNESS (μm)	NORMALISED TRANSMITTANCE FALL @10μm%
-	Ge	0	27	0	55	0	55
-	FLIR ZnS	0	3	0	15	0	15
DLC	Ge	10	10	0	30	0	34
BP	Ge	10	<1	N/T	N/T	10	<2
BP	FLIR ZnS	15	<0.5	14	2	N/T	N/T
DLC/BP	Ge	10	<0.5	14	<0.5	10	<2
DLC/BP	FLIR ZnS	N/T	N/T	15	2	N/T	N/T
DLC/BP	TUFTRAN	N/T	N/T	N/T	N/T	14	0.3
GaP	Ge	10	2	18	8	N/T	N/T
GaP	FLIR ZnS	11	3	18	8	N/T	N/T

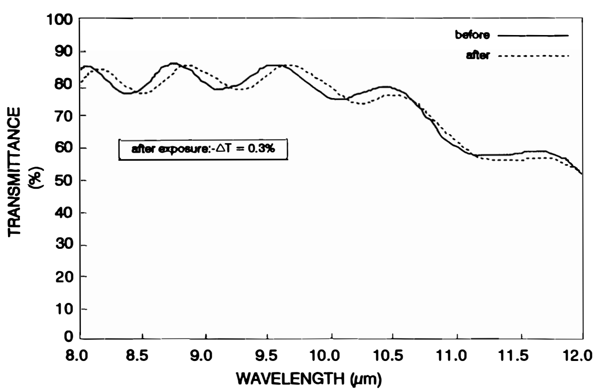


Fig. 12 Rain erosion testing of DLC/BP (thickness = 14 μm)/Tuftran using UDRI whirling arm rig (211 m/s, 20-min exposure).

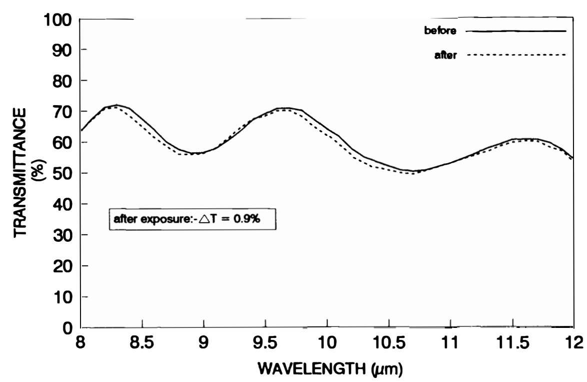


Fig. 13 Rain erosion testing of GaP (thickness = 10.7 μm)/FLIR ZnS using RAE whirling arm rig (211 m/s, 20-min exposure).

ride-coated zinc sulphide and DLC-coated FLIR samples from a range of suppliers. All tests were carried out at normal incidence.

Figures 16 and 17 show test results for 206 m/s velocity (53- to 74-μm particle size), and 45 m/s (149- to 177-μm particle size), respectively. In neither case is any fall in transmittance measurable for the DLC/BP samples, but significant reductions were measured for all other coatings.

5.2 *Pilkington Optronics Simulated Sand Erosion Facility*

Simulated sand erosion tests were carried out within Pilkington Optronics using a commercial beadblaster. This test method provides a relative assessment of the susceptibility to solid particle impact damage of a variety of substrate materials and the protection afforded by a range of durable coatings. As such, the method provides performance data to optimize coating deposition processes to maximize solid particle impact protection. Test conditions are indicated in Table 6.

A schematic diagram of the facility is shown in Fig. 18, with a sample inclination of 45 deg to the incident particle flux. The larger angle of incidence ensures that the rate of erosion is slowed sufficiently to enable the effect on optical transmittance to be evaluated.

A particle filtration system ensures that gross sample and holder debris produced during erosion is removed. Calibration of the equipment for the purposes of erosion testing was carried out using germanium disks to achieve reproducible IR transmission reduction as a function of erosion time. Germanium exhibits a high degree of erosion in a relatively short time, with a large transmission reduction, and as such is a useful calibration material.

Germanium disks are evaluated before and after a test sequence to ensure constancy of particle impact conditions. Reproducibility of erosion-induced transmission reduction with erosion time is typically ±5% in normalized transmittance.

Figure 19 shows normalized transmission reduction (assessed at a 10-μm wavelength) as a function of both erosion

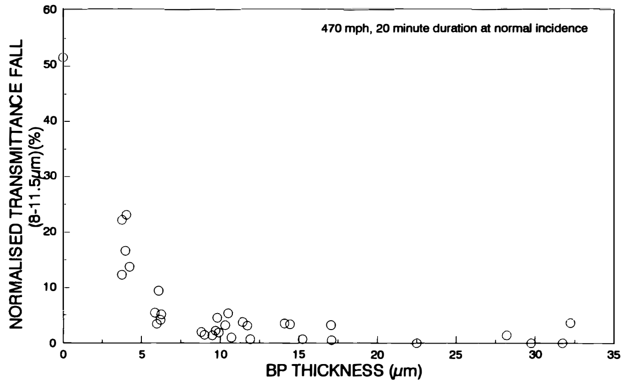


Fig. 14 Loss in transmittance as a function of BP thickness on Ge (as assessed on UDRI whirling arm rig).

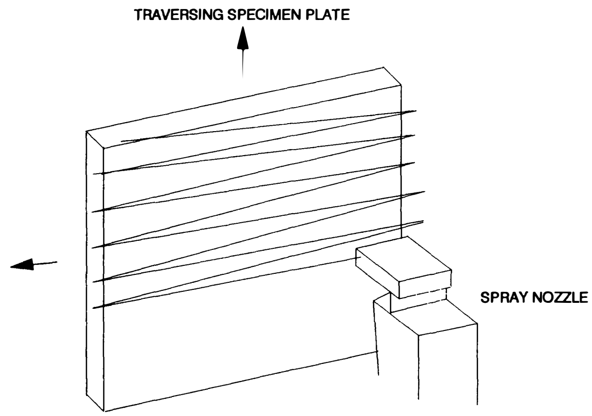


Fig. 15 Particle spray pattern for specimen plate translations at DNA sand erosion facility.

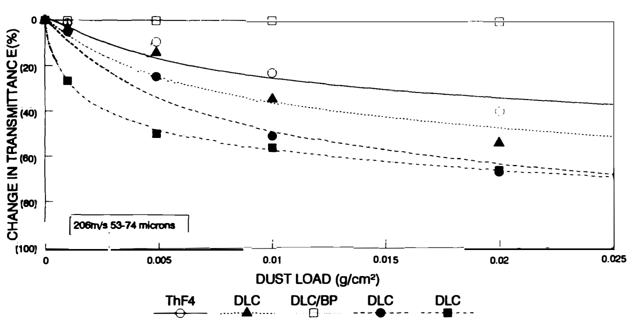


Fig. 16 Sand erosion tests at DNA for a range of coatings on FLIR ZnS substrates. Indicated DLC results are from three suppliers. Particle sizes range from 53 to 74 μm, impact velocity 206 m/s.

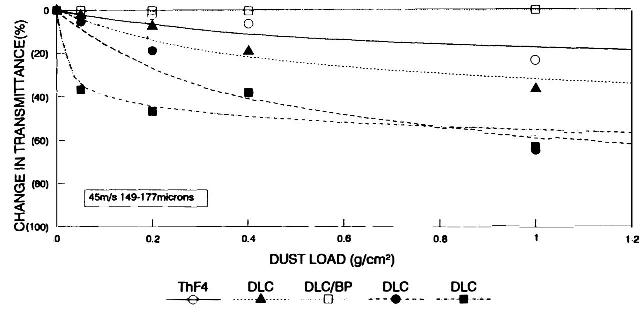


Fig. 17 Sand erosion tests at DNA for a range of coatings on FLIR ZnS substrates. Indicated DLC results are from three suppliers. Particle sizes range from 149 to 177 μm, impact velocity 45 m/s.

Table 6 Pilkington Optronics simulated sand erosion test specification.

Particle type	quartz bead
Particle size (μm)	45 - 80 (nom.)
Concentration (gm^{-3})	23
Air pressure (psi)	45
Air velocity (ms^{-1})	≈ 100
Flux ($gcm^{-2}s^{-1}$)	0.030
Angle of incidence	45°
Temperature	ambient

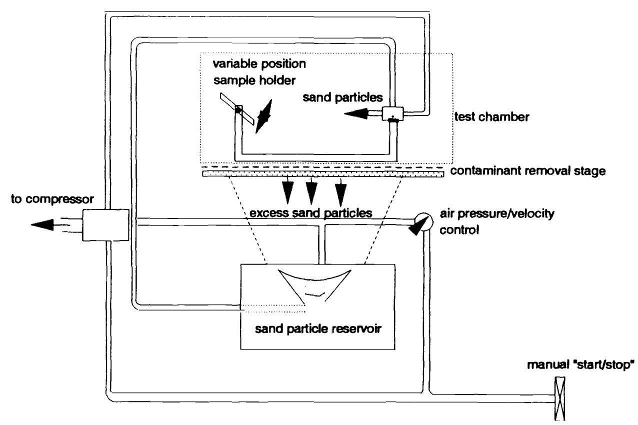


Fig. 18 Schematic of Pilkington Optronics simulated sand erosion test facility.

time and cumulative incident sand mass for Ge, FLIR ZnS, DLC/Ge, BP (thickness = 11 μm)/Ge, DLC/BP (thickness = 13 μm)/FLIR ZnS, GaP/(thickness = 10 μm)/Ge, and GaP/(thickness = 11 μm)/FLIR ZnS.

The time-stretched insert in Fig. 19 shows the rapid transmission reduction experienced by Ge and FLIR ZnS. Erosion in Ge and FLIR ZnS is characterized by gross roughening of the sample surface, primarily caused by pits formed at the intersection of cracks. Further roughening occurs with gross removal of material from the surface.

Figure 19 indicates the truly outstanding degree of protection provided by the DLC/BP multilayer to this severe sand erosion test. After a 12-min exposure (corresponding to 22 g/cm^2) normalized transmission was reduced by about 3%. This results primarily from a small degree of pitting at the coating surface, occurring at coating defects with regions between defects suffering no deterioration.

Preliminary work to assess the degree of solid particle impact protection as a function of BP thickness indicates that comparable levels of protection to those shown in Fig. 19

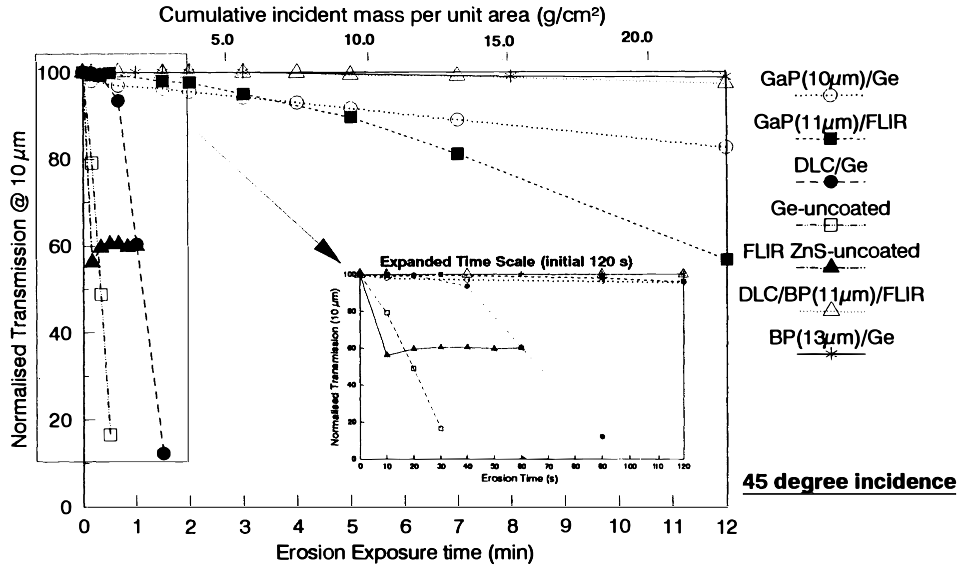


Fig. 19 Pilkington Optronics simulated sand erosion tests. Normalized transmission as a function of erosion time for DLC, BP, and GaP coatings on a range of substrate materials.

can be achieved with thicknesses significantly less than 10 μm. This result suggests that the critical coating parameters governing solid particle impact performance are hardness and adhesion and not stiffness, as is the case for rain impact performance.

Figure 19 indicates that although GaP coatings provide sand erosion protection for Ge and FLIR ZnS material, their performance falls short of that achieved with BP. The solid particle impact damage morphology for GaP coatings is different from that of BP, exhibiting surface roughening with minimal delamination of the coating from the substrate. This result may suggest that GaP films are not as intrinsically hard as BP, and are therefore more susceptible to removal of material at the coating surface as compared with BP.

6 Production Status

There are several programs with immediate requirements (or nearly so) for a production capability for coating a range of geometries and substrate materials with rain erosion protection coatings.

Because of the hazardous and unique nature of the processes utilized for phosphide coating growth, all production procedures must meet stringent health and safety requirements. Moreover, required tolerances in relation to coating thickness, uniformity, transmission, and durability demand tight control of the coating process. Pilkington Optronics has made the necessary capital investment to ensure the necessary health and safety and process control requirements are in place for production.

Because of the different deposition methodologies utilized for BP and GaP, each with unique difficulties, the BP process is at a much more advanced stage compared to GaP. BP can be considered to be in an advanced stage of preproduction with regard to coating of large-scale complex geometries on a range of substrate materials. GaP has been demonstrated, over small and flat substrate geometries, to have comparable durability and rain erosion protective characteristics to those of BP, for impact velocities up to 211 m/s, as assessed on the RAE whirling arm rig.

Note, however, that although the basic process is now repeatable, several details of the technology remain to be "bottomed-out," notably prevention of defects growing in the GaP films. As described in Sec. 4.2, this is the most probable reason for reduced rain impact protection at velocities >211 m/s, as assessed on the RAE whirling arm rig. Great strides have already been made in reducing the defect levels to achieve the performance quoted in this paper. Moreover, experience gained from scaling the BP process to larger and more complex geometries shows that this is a nontrivial activity requiring significant development activity.

BP is available now as a preproduction activity and is very close to full production on a number of complex geometries. Figure 20 illustrates the range of geometries and materials currently being BP coated on a preproduction basis. Shown in Fig. 20 are (1) trapezoidal Tuftran window (maximum dimension 6.5 in.), (2) 9-in.-diam hyper-hemispherical germanium dome, (3) 7-in.-diam FLIR ZnS dome, and (4) 3-in.-diam germanium window.

GaP still requires considerable effort toward scaling the deposition technology, and is probably a few years away from a full production capability.

7 Conclusions

BP and GaP are shown to be ultradurable coating materials that can be deposited as thick, low-optical-loss films.

A primary application for phosphide coatings is as rain and solid particle erosion protective coatings. Both materials exhibit exceptional rain erosion characteristics, with a performance unsurpassed by other coating materials. BP is shown to offer significant protection against solid particle impact.

GaP has a reduced loss over the 8- to 12-μm wave band compared to BP. The primary reason for this is the reduced level of hydrogen incorporation during the GaP growth pro-

Fig. 20 Range of materials and geometries DLC/BP coated on a preproduction basis.

cess. Preliminary solid particle impact assessment shows that although protection is provided, the performance level falls short of that obtained with BP.

Combining GaP and BP as a composite coating may offer a means of utilizing the advantages of both materials, i.e., thick low absorbing GaP to provide rain erosion protection and thin, hard BP for solid particle impact protection.

The BP coating process is at an advanced stage of preproduction on a range of substrate materials and complex geometries. The GaP coating process has been demonstrated over small-scale flat substrates, and requires development to enable large-scale complex substrate geometries to be coated.

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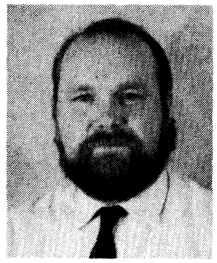

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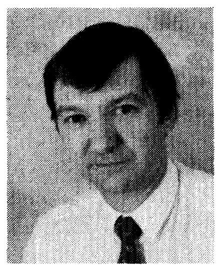

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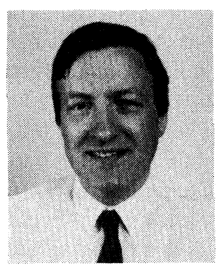

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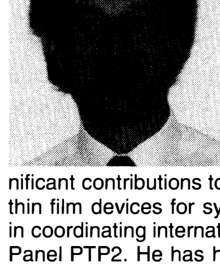

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