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Part I

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MULTILAYER COATINGS AND OPTICAL MATERIALS FOR TUNED INFRARED EMITTANCE AND THERMAL CONTROL

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ABSTRACT

Many thermal control applications require thin film coatings that emit or absorb strongly at near infrared and infrared wavelengths. One of the primary applications for these coatings is thermal control for surfaces and structures of spacecraft, which are exposed to solar radiation during at least 60% of their orbit, causing wide temperature fluctuations. Another recent application for this type of coating is infrared emissive imaging employing a fiber optic infrared scene projector. While single layer coatings can provide high emissivity in a broad wavelength band, multilayer coatings can be used to obtain higher emissivities over a narrow wavelength band. This band can be tuned to a specific range of temperatures and wavelengths. Coatings developed for thermal control have a reflective base layer, either ZrN or a refractory metal boride or silicide. These materials have increased durability compared to metal layers. The multilayer coating deposited over the based layer consists of an Al_2O_3/SiO_2 stack with high emittance at 300 K (9.8 μm), and solar reflectance near 0.6. Multilayer tuned infrared absorber/emitter coatings are applied to fiber optic infrared scene projectors. The coatings consists of a three layer $Si_3N_4/Cr/Si_3N_4$ absorber tuned at the 1.06 μm laser wavelength, and a six layer Cr/dielectric/Cr/dielectric/Cr/dielectric coating which emits strongly in either the 3 - 5 μm or the 8 - 12 μm infrared wavelength bands. Absorption bands of the coatings are independently tunable. All coatings are deposited by reactive DC and RF magnetron sputtering onto 2.5-in fiber optic faceplates. Either Si_3N_4, Si, or ZnS thin film dielectric materials were used in the emitter coatings. With an input laser power of 15 W, the coatings emit at a black body temperature 529 K, which compared well with predicted performance.

INTRODUCTION

Thin film coatings that absorb and emit optical radiation can be used to enhance the thermal emissive and absorptive properties of surfaces. Recent applications include solar control, thermal control of space structures, and infrared emissive displays. The coatings are designed to absorb or emit radiation to increase or decrease the temperature of a surface [1], reduce the transmittance of a window [2], or provide a detectable visual image [3]. For solar control, a high emissivity at visible and near infrared wavelengths, and high reflectance at infrared wavelengths is usually desired. Space structures experience large temperature fluctuations that must be moderated either by coatings applied to their surface or by compositional modification of the structure itself. Heat from power sources in these structures must also be dissipated. A new application for these high emittance coatings is for infrared displays, such as a fiber optic infrared scene projector [4].

Many types of thin film materials and coating layer designs are used to achieve the desired surface emittance performance. Single-layer coatings have been used extensively to provide emittance in a broad infrared wavelength band [5]. Very little selectivity and tuned emissivity, however, can be obtained by using single layer coatings. The emittance is entirely determined by the optical properties of the material, and is usually broadband in nature. These coatings take advantage of the various absorption and Restrahlen processes occurring in the

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material. Materials such as aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) absorb and emit at wavelengths in the mid and far infrared. Coating thicknesses as large as 20 μm are often needed to provide the specified emissivity (recall that the emissivity ~ coating thickness x absorptance) [6]. Single layer coatings can also be textured to enhance the solar absorptance and emissivity [7].

Interference effects in thin film multilayer dielectric coatings can be used to enhance the emissivity of a surface [3,5]. By using multilayer coatings, absorptances and emissivities greater than those of single layer coatings can be achieved. The design usually consists of a reflective base layer overcoated with a multilayer coating having layers with high and low refractive indices. The base layer material can be a metal or a conductive coating such as zirconium nitride (ZrN), but it must be reflective over the wavelength range of interest. The absorptance of the dielectric coating materials (such as Al_2O_3, SiO_2, Si_3N_4, Ta_2O_5, AlN, ZrO_2) should be low to enhance the interference effects.

Since these coatings must operate at high temperatures, and often hostile environments, the materials must be robust, abrasion resistant, and chemically resistant. They must be adherent to the surface and be able to survive multiple thermal cycles. The coating deposition process must be capable of uniformly coating large and complex surfaces. These requirements make many refractory metal borides and silicides attractive candidates for applications requiring protective coatings at high temperatures, and protective chemically-resistant coatings. The reasonably high reflectance of these materials at visible wavelengths, and metal-like reflectance at infrared wavelengths, make them attractive for use as base layers in multilayer coatings used for thermal control, tuned emittance, and solar control. Dielectric materials such as those mentioned above are durable and abrasion resistant.

This paper will focus on two multilayer coating concepts to provide (1) protective coatings for space structures, and (2) tuned emittance coatings for infrared fiber optic displays. The space structure coatings are constructed from a less-developed group of materials such as refractory metal borides and silicides and had specific solar absorptance and reflectance, and IR emissivity specifications. The tuned emissivity coatings are applied to fiber optic scene projector plates to create thermal image display.

COATING DEPOSITION AND CHARACTERIZATION

All coatings are deposited either by RF or DC reactive and nonreactive magnetron sputtering processes in a 28-in box coater. Three sputtering cathodes and an ion source are located in the base of the coating chamber. The planar magnetron sputtering cathodes supplied by Vacuum, Inc, US thin film Products, and Kurt Lesker hold either 15-cm or 5-cm diameter targets. Both Denton Model 101C and Commonwealth Mark II 10-cm ion sources are used for ion cleaning of substrates. The fiber optic screen assemblies are rotated above the targets in simple or double planetary motion. The thickness of the individual layers is controlled by using an Eddy model LM101 optical thickness monitor. The ultimate pressure in the chamber is 8×10^{-8} Torr, but coating depositions are typically performed at pressures near 1.5 mTorr. A 5 kW Sputtered Films model PS 600-4 power supply is used for most DC depositions. A 2 kW Eratron RF power supply was used for RF depositions.

In most cases, pure metal or semiconductor sputtering targets are used to deposit the coatings. Si_3N_4 coatings are deposited by sputtering Si from a 0.99999-pure Si target in mixtures of N_2 + Ar. The N_2 partial pressure is 0.75 mTorr. Argon is the primary sputtering gas for Cr, Al, Si, and ZnS coatings. The purity of the Cr, Al, and ZnS sputtering targets is 0.999, 0.99999, and 0.9999 respectively. Power supplied to the 15 cm Si target is 400 W (RF) for Si_3N_4 deposition, and 220 W (DC) for Si deposition. Power applied to the 5-cm Cr and Al

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targets is 400 W (DC), and 200 W (RF) is applied to the 5-cm ZnS target. VB_2, NbB_2, TaB_2, TiB_2, ZrB_2, and LaB_6 sources are used to deposit the boride coatings. WSi_2, $TiSi_2$, and $NbSi_2$ sources are used to deposit the silicide coatings. These sputtering sources are 2-in diameter, and 0.25-in thick, and are fabricated either by hot pressing or sintering, and have a purity of 0.999. All substrates are ion cleaned before deposition. To minimize the incorporation of impurities in the coatings, the chamber is pumped overnight before each coating deposition.

The transmittance and specular reflectance of the coatings is measured between 0.2 and 1.1-μm wavelengths with Perkin Elmer Lambda 12 spectrophotometer, and between 0.2 and 3.0-μm wavelengths by a Beckman UV/VIS 5270 dual beam spectrophotometer. Transmittance and specular reflectance between 2.5 and 50-μm wavelengths are measured by Nicholet 205 and 740 FTIR spectrophotometers. The solar reflectance and absorptance are then calculated from the weighted AM1 spectrum.

The coatings are designed using Filmstar™ optical design software. All layer thicknesses are expressed in optical thicknesses. The software uses the dispersion relations for the refractive index (n) and extinction coefficient (k) over the range of operating wavelengths. When possible, the optical constants measured for single layer coatings are used in the coating designs. When these aren't available, handbook values are used [8]. Little data are available for the optical constants of Cr between 8- and 12-μm wavelengths. The values of n and k are interpolated in this wavelength range. Ellipsometer measurements of optical constants of ZrB_2 coatings are made at 3- and 5-μm wavelengths. Sheet resistance is determined using the four-point van der Pauw technique. Coating thicknesses are measured by a Tencor alpha-step 200 profilometer.

Protective Coatings for Space Structures

Protective and thermal control coatings applied to space structures require a solar reflectance and absorptance, infrared reflectance, and high emissivity in specified wavelength bands. The entire coating should protect the space structure, while providing the required thermal control performance. Although the requirements for each type of space structure differ, generally a low solar absorptance (<0.3), high in-band emittance (>0.3), and infrared reflectance (>0.95) is desired. The goal for all space structures is to accomplish this with as little material as possible. In order to minimize the number of layers, and to achieved a broadband infrared reflectance the majority of coating designs used for this application are dielectric-enhanced metal layers (metal underlayer). In this case, the base layer is particularly important because it is in intimate contact with the structure. These coatings must also be resistant to atomic oxygen and solar wind.

Reflective metals typically used in enhanced coatings are not durable enough for protection of structures in space. While materials such as diamond-like carbon (DLC), diamond, BP, HfN, TiN, ZrN are being used extensively in wear applications, we report on the use and optical properties of a less-developed group of materials, refractory metal borides and silicides. These materials are semimetals, and show promise for a wide range of applications because of their hardness and high melting temperatures [9,10]. Based on measurements on bulk materials [3], thin-film boride materials such as VB_2, NbB_2, TaB_2, TiB_2, ZrB_2, and LaB_6, and silicides such as $TiSi_2$ and WSi_2 have the potential to display metal-like reflectivity at visible and infrared spectral regions. Melting temperatures for bulk NbB_2, TaB_2, TiB_2, and LaB_6 respectively are 3040 °C, 3040 °C, 3230 °C, 2720 °C [9]. The melting temperature for the silicides is near 2300 °C. The Knoop hardness of these materials ranges from 2000 to 4500 [9]. The reflectance of these materials at 0.55-μm wavelength ranges from 0.09 to 0.49, and from 0.54 to 0.91 at 1.06-μm wavelength. The reflectance at the 10.6-μm infrared wavelength is greater than 0.94, which is close to metallic reflectances. These materials are also resistant to chemical attack [10].

The properties described above make many borides and silicides attractive candidates for applications requiring protective coatings at high temperatures, and protective chemically-resistant coatings. The reasonably high reflectances make them attractive for use as base layers in multilayer coatings used for thermal control, tuned emittance, and solar control.

The VB_2 coatings were prone to oxidation. The coating was initially metallic in appearance, and oxidized after the reflectance measurements were made. As a result, no resistivity measurements could be performed on the coatings, although they (and the NbB_2 coatings) had the highest infrared reflectances measured of the samples tested.

Figure 1 shows measured reflectance spectra of the boride coatings at wavelengths between 0.4 and 2.6 µm. The NbB_2 coating displayed the highest visible - near IR reflectance ranging from 0.54 to 0.82, consistent with the infrared reflectance. The TaB_2 and ZrB_2 coatings had the lowest measured reflectances, ranging from 0.46 to 0.72. The reflectances of the LaB_6, TiB_2, and VB_2 coatings were intermediate.

The optical constants of two ZrB_2 coatings are measured at 3.39 µm and 5.0 µm wavelengths by ellipsometry. At 3.39-µm wavelength, n = 6.618, k = 5.95, and n = 8.261, k = 7.285 at 5.0-µm wavelength. The calculated reflectances are 0.716 at 3.39-µm wavelength, and 0.757 at 5.0-µm wavelength, which agree well with the measured reflectances. No coating displays outstanding solar reflectance, although these properties, listed in Table I, can be modified to some degree by a single or multilayer overcoat. The change in absorptance with a 1-µm-thick SiO2 overcoat is shown in the last column. These coatings compare favorably with other thermal control coatings. For comparison, the measured R_S and A_S for ZrN are 0.32 and 0.68 respectively. At room temperature, emittance was 0.16.

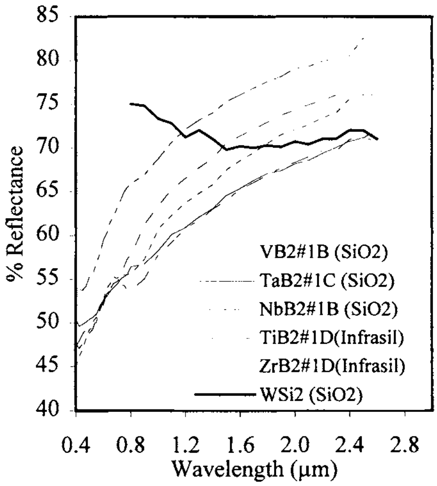

Figure 1. Reflectance spectra of boride and silicide coatings.

Table I. Properties of Boride and Silicide Coatings on Glass Substrates

Material	R @10.6 μm	Sheet Resistance (Ω/sq)	Coating (μ .cm)	Bulk (μ .cm)	R_S	A_S	A_{RT}	A_{RT} w/ overcoat
VB_2	0.91				0.56	0.44	0.085	0.13
NbB_2	0.91	14.3	552	68 - 100	0.42	0.58		
TaB_2	0.86	27.3	750	32	0.55	0.46	0.175	0.145
LaB_6	0.90	24.1	735		0.38	0.62	0.115	0.15
TiB_2	0.925	17.4	348	28	0.55	0.45	0.075	0.10
ZrB_2	0.90	3.32	208		0.51	0.49	0.10	0.16
WSi_2	0.98	4.0	40	25	0.52	0.48	0.02	

The design for a six-layer thermal control coating is shown in Figure 2. The design goals are to achieve a room temperature emissivity ≥ 0.3, a solar absorptance ≤ 0.3, and the highest possible reflectance at 10.6-μm wavelength. The coating is constructed using a ZrN base layer and SiO_2/Al_2O_3 dielectric layers. ZrN is used because the optical constants are well known [11]. The solar reflectance and absorptance are 0.67 and 0.33 respectively. The room temperature absorptance is 0.30 and the reflectance at 10.6 μm is 0.82. The coating is to be deposited onto glass and carbon-carbon substrates.

Fiber Optic Infrared Scene Projector

The fiber optic scene projector is an example of how multilayer coatings can be used to achieve very high absorptance. A scene projector absorbs incident laser or electromagnetic energy introduced into an array of optical fibers as the subject, and each fiber emits radiation in

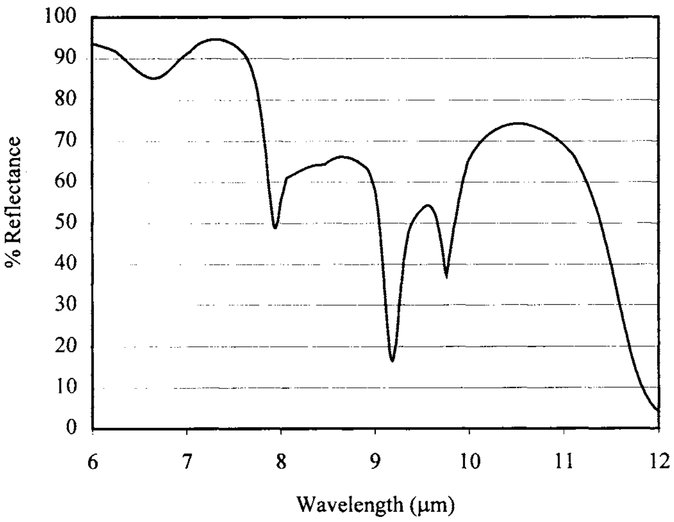

Figure 2. Design reflectance spectrum of six-layer thermal control coating.

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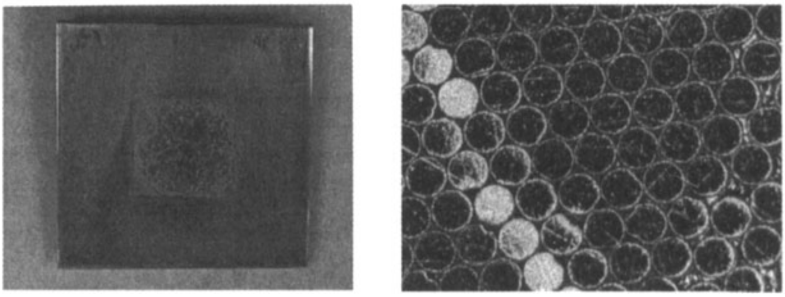
an infrared wavelength band as the image. The intensity of the incident radiation and the emissivity of the coating at the operating temperature determine the intensity and wavelength of emission. The scene projector being developed by the Naval Air Warfare Center and PNNL consists of a 2.5-in-square faceplate with a 1-in-square fiber optic array potted in the center (Figure 3). Each fiber forms a pixel in the display. The fibers are potted in the square array, planarized, and then the potting material removed to a depth of 20 μm to prevent cross talk between the fibers.

The optical fibers themselves are poor absorbers and emitters of electromagnetic radiation. To enhance the absorptance of the fibers, a multilayer coating that strongly absorbs incident radiation is first deposited onto the receiving end of the fibers. A two layer version of this coating, tuned to absorb strongly at wavelengths near 10 μm, was first introduced by Bly et al for ferroelectric detectors using nichrome metal layers and a lead fluoride spacer layer [3]. The coating employs multiple reflections in a dielectric spacer layer to achieve the high absorptance. The coating shown in Figure 4 consists of two distinct and independently-tunable designs; a lower multilayer coating which absorbs strongly at the 1.06-μm laser wavelength, and one that emits strongly between 3 - 5 μm or 8 - 12 μm infrared (IR) wavelengths. The six-layer coating that emitts strongly either in the 3 - 5 μm or the 8 - 12 μm wavelength bands is deposited over the three layer coating to create the display. The tip, or surface, of the fiber can reach a temperature of 529 K (256 °C) using this coating. Each coating will be described in detail.



a) b)

Figure 3. Picture of a) coated fiber optic scene projector array and b) closeup of coated fiber ends.

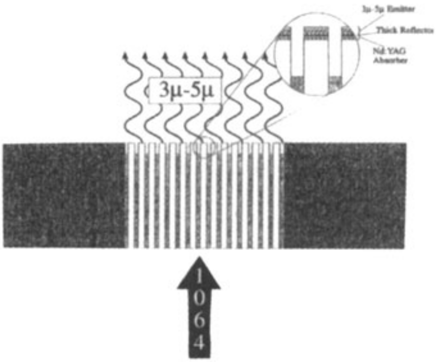


Figure 4. Structure of the fiber optic scene projector coating.

COATING PERFORMANCE

1.06-µm Absorber Coating

The coating applied first to the surface of the fiber optic array is used to absorb laser radiation introduced into the fibers. This radiation is the subject source for the scene projector. The coating is tuned to absorb strongly at 1.06 µm wavelength, but because this radiation is used only to heat the surface of the fiber, it can be designed to absorb at any wavelength transmitted by the fiber. The coating has three layers with the design S, 0.216H, 0.01M, 0.0016H, where chromium (Cr) was used as the metal (M) layer and Si_3N_4 is used as the dielectric cavity layer (H). S denotes the substrate. The design wavelength is 1.06 µm. Si_3N_4 hs used for the spacer layers instead of an oxide because it does not react with the Cr layers during deposition. Because the performance of this coating is very sensitive to the metal layer optical constants, the reaction between the Cr and the oxygen used to form an oxide layer would create a thin substoichiometric Cr-O layer, and could degrade the optical properties. Si_3N_4 is also very durable and transmits at wavelengths up to 8 µm. The design absorptance at this wavelength is 0.998.

Figure 5 shows that the measured optical absorptance at 1.06-µm wavelength was 0.995 ± 0.005, which very close to that of the design. Because the coating was totally reflective (no transmission due to the Cr layer) the absorptance (or emissivity) was determined by the simple relation: absorptance = 1 – reflectance, and emissivity ≈ absorptance [6].

Infrared Emitter Coating

Without the infrared emitter coating, the three-layer NIR absorber coating has a weak infrared absorptance of only 0.056. Because the NIR absorber and IR emitter coatings are decoupled by a thick Cr layer, the spectral position of both bands can be independently moved by adjusting layer thicknesses. The design for a coating with absorptance greater than 0.95 in the 3 - 5 µm wavelength band is 2.00M, 1.331H, 0.088M, 1.337H, 0.046M, 0.768H. Again, the materials are Cr (M) and Si_3N_4 (H). Figure 6 shows the measured absorptance of this coating compared to the design absorptance. The measured absorptance values range between 0.97 and 0.99 in the 3 - 5 µm IR wavelength band, differing only with the design values at the drop off at 3 µm wavelength.

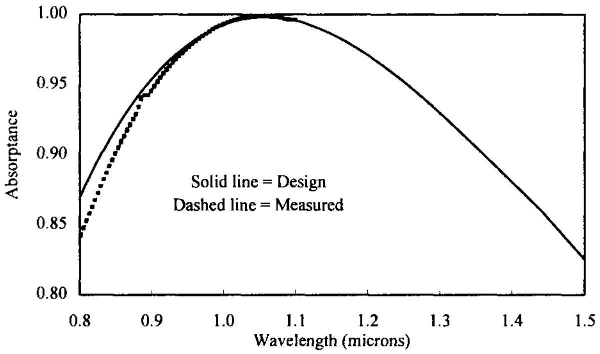


Figure 5. Near Infrared Absorptance Spectrum Of 1.06-µm Absorber Coating.

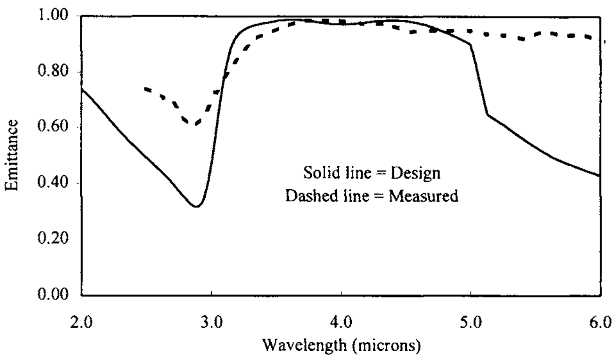


Figure 6. Infrared Absorptance Spectrum of 3 - 5 μm Emitter Coating.

The agreement between the design and measured IR absorptance is not as close as that of the lower wavelength absorber. The reason for the high absorptance values at wavelengths greater than 5 μm is not well understood, but may be due to the use of handbook optical constants for the Cr layer in the design. The optical constants for the magnetron-sputtered Cr layers have not been measured in the IR.

Both ZnS and Si are acceptable dielectric spacer materials for use in the 8 - 12 μm emitter coating. Both materials have very low absorptance in this wavelength region, and very different refractive indices (~2.25 for sputtered ZnS and ~3.8 for sputtered Si), which gives interestingly different coating designs. The optimized coating designs using these two materials and Cr metal layers are shown in Figure 7. The absorptance of the coating with ZnS spacer layers are considerably higher over the entire wavelength range, which indicates that low index materials are preferred for this application. For the ZnS design, the absorptance ranges between 0.85 and 0.99 between 8 - 12 μm wavelengths, and for the Si design, the absorptance ranges between 0.91 and 0.99. The regions of low absorptance are broader for the ZnS design.

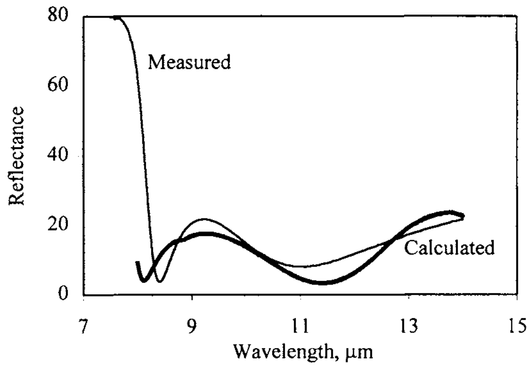


Figure 7. 8 - 12 μm emitter design using ZnS and Si spacer layers, and measured reflectance of coating with Si spacer layers.