

CVC Silicon Carbide Optical Properties and Systems (Preprint)

Colby A. Foss, Jr.

**Trex Enterprises Corporation
Advanced Materials Group
3038 Aukele Street
Lihue, HI 96766**

29 July 2005

Conference Proceedings

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

GOVERNMENT PURPOSE RIGHTS



**AIR FORCE RESEARCH LABORATORY
Directed Energy Directorate
3550 Aberdeen Ave SE
AIR FORCE MATERIEL COMMAND
KIRTLAND AIR FORCE BASE, NM 87117-5776**

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE (DD-MM-YYYY) 29 July 2005		2. REPORT TYPE Conference Proceedings (Preprint)		3. DATES COVERED (From - To) April 2004 - April 2005	
4. TITLE AND SUBTITLE CVC Silicon Carbide Optical Properties and Systems (Preprint)				5a. CONTRACT NUMBER FA9451-04-M-0085	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 65502F	
6. AUTHOR(S) Colby A. Foss, Jr.				5d. PROJECT NUMBER 3005	
				5e. TASK NUMBER DP	
				5f. WORK UNIT NUMBER DN	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Trex Enterprises Corporation Advanced Materials Group 3038 Aukele Street Lihue, HI 96766				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory 3550 Aberdeen Avenue SE Kirtland AFB, NM 87117-5776				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/DESE	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-DE-PS-TP-2006-1014	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release; Distribution is Unlimited.					
13. SUPPLEMENTARY NOTES Submitted for publication in SPIE Optics and Photonics, Session on Optical Materials and Structures TechnologiesII, Conference 5868, Proceedings Issue, San Diego, CA, 31 July 2005 - 4 August 2005. GOVERNMENT PURPOSE RIGHTS					
14. ABSTRACT The chemical vapor composites (CVC) process provides for the rapid manufacture of near net shape, reduced residual stress silicon carbide (SiC) suitable for high performance optics. The reduction or elimination of residual stress provides several key advantages: 1) increased growth rate, 2) high yields, and 3) near net shape deposition of complex geometries. Near net shape deposition allows for fabrication of spherical and aspherical optics without machining of the optical surface. Final surface figures of optical flats are typically better than 1/10λ (P-V) and a 2-5Å surface roughness. A comparison of ultraviolet spectrum reflectance of CVC SiC and that of single crystal SiC is discussed. The complex optical constants of CVC SiC in the mid-infrared spectrum are also presented.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 11	19a. NAME OF RESPONSIBLE PERSON Ryan Conk
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code)

CVC Silicon Carbide Optical Properties and Systems

Colby A. Foss, Jr.

Trex Enterprises Corporation Advanced Materials Group, 3038 Aukele Street Lihue, HI 96766

ABSTRACT

The chemical vapor composites (CVC) process provides for the rapid manufacture of near net shape, reduced residual stress silicon carbide (SiC) suitable for high performance optics. The reduction or elimination of residual stress provides several key advantages: 1) increased growth rate, 2) high yields, and 3) near net shape deposition of complex geometries. Near net shape deposition allows for fabrication of spherical and aspherical optics without machining of the optical surface. Final surface figures of optical flats are typically better than $1/10\lambda$ (P-V) and 2-5Å surface roughness. A comparison of ultraviolet spectrum reflectance of CVC SiC and that of single crystal SiC is discussed. The complex optical constants of CVC SiC in the mid-infrared spectrum are also presented.

Keywords: silicon carbide, chemical vapor composites, net shape deposition, optical properties.

1. INTRODUCTION

The chemical vapor composites process involves the addition of solid particulates into the chemical vapor deposition stream.¹ The addition of these particulates leads to an enhancement of deposit growth rate, and also an equiaxing of the grain structure. Conventional chemical vapor deposition (CVD) typically involves low growth rates, and an anisotropic grain structure which can be associated with high levels of residual stress.² In this paper we review the mechanical and thermal properties of silicon carbide derived from the chemical vapor composites process (CVC SiC), with emphasis on the consequences of these properties on lightweight mirror applications. We also discuss the optical properties of CVC SiC in the ultraviolet and mid-infrared spectral ranges.

2. MECHANICAL AND THERMAL PROPERTIES OF TREX CVC SiC

Table 1 summarizes the room temperature mechanical and thermal properties of CVC SiC. The density (ρ) is effectively theoretical,³ and the Young modulus (E) higher than many other materials used in mirror structures, including non-CVD SiC.⁴

The room temperature coefficient of thermal expansion (α) of CVC SiC is also low amongst common mirror materials, though at 2.3 ppm/K higher than ultra low expansion glass (ULE).⁴ The thermal conductivity (K) of CVC SiC is lower than that of beryllium (Be, 216 W/m/K),⁴ and also CVD SiC (300 W/m/K).⁵ The high thermal conductivity of CVD SiC is likely due to larger grain dimensions along the direction of growth. We have found that chemical vapor deposited SiC (grown without solid particulate addition) shows anisotropic conductivity; thermal conductivity is higher along the direction of grain orientation.

Table 1. Room Temperature Properties of CVC SiC

Property at 298.15 K	Current Data with Statistics
Density (g/cm ³)	3.18 ± 0.04
Porosity	nil
Grain Size (microns)	5-20
Flexural Strength (MPa)	433 ± 8
Young's Modulus (GPa)	456 ± 22
Poisson Ratio	0.21
Hardness (HV, kg/mm ²)	2850
Fracture Toughness (MPa m ^{1/2})	3.39
Electrical Resistivity (Ω cm)	Less than 1.5 to greater than 1000
Thermal Conductivity (W /m/K)	140 ± 3 > 200 achievable via post deposition heat treatment.
Coefficient of Thermal Expansion (ppm/K differential value at 300 K)	2.33 ± 0.04
Heat Capacity (J/kg/K)	680.8 ± 0.2

For lightweight mirror applications, which require as low a mass as possible while still maintaining precise optical form, high Young modulus and low mass density are desirable. The relevant material property thus cited is often the specific stiffness E/ρ . For mirror applications that involve significant changes in temperature, a low coefficient of thermal expansion is desirable. Also, to minimize distortion due to temperature gradients a high thermal conductivity is desirable. The ratio K/α defines the thermal stability factor. Candidate mirror materials can be organized in a map defined by the plot of E/ρ versus K/α . This is shown in Figure 1.

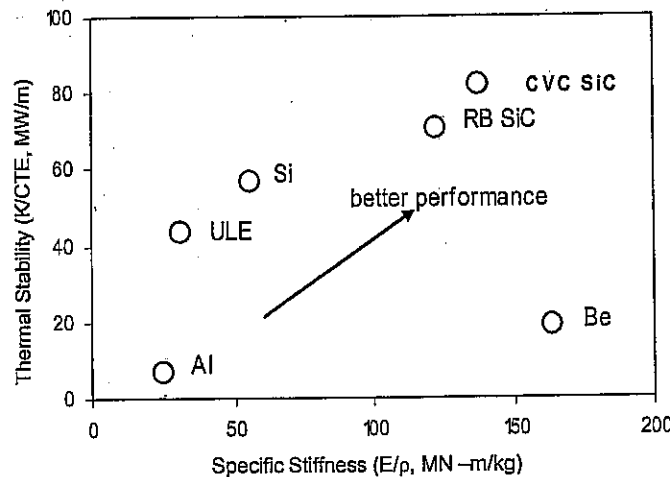


Figure 1. Comparison of selected mirror materials according to thermal stability and specific stiffness. Adapted from Baley, et al., reference 4.

Figure 1 demonstrates that CVC SiC possesses a very favorable combination of mechanical and thermal properties. While its specific stiffness is not as high as that of Be, it is superior to Be in terms of thermal stability.

Figure 2 shows the coefficient of thermal expansion of CVC SiC for the temperature range 20 K – 300 K. The CTE drops to very low values under cryogenic conditions. This is consistent with the diminishing contribution from anharmonic potential terms as the temperature decreases.⁶

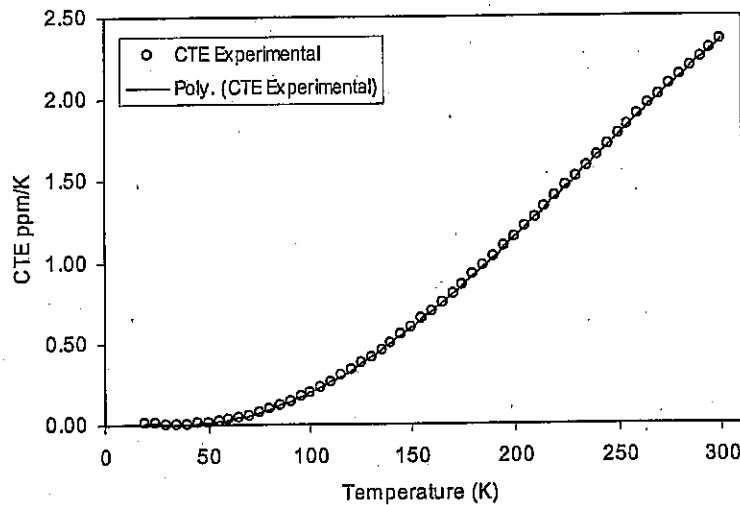


Figure 2. The coefficient of thermal expansion for CVC SiC as a function of temperature.

The curve in Figure 2 can be fit to the following polynomial equation:

$$\text{CTE} = -1.791 \times 10^{-10} T^4 + 1.234 \times 10^{-8} T^3 + 4.977 \times 10^{-5} T^2 - 3.60 \times 10^{-3} T + 0.0663 \quad (1)$$

where T is in Kelvin units. Equation 1 yields CTE values at 300 K and 20 K of 2.34 ppm/K and 0.014 ppm/K, respectively.

3. OPTICAL PROPERTIES OF TREX CVC SiC

Figure 3 shows the ultraviolet range reflectance of single crystal SiC (solid curve) calculated from literature optical constants⁷ and experimental reflectance values for CVC SiC obtained by France and McCandliss.⁸ In spite of the fact that CVC SiC is polycrystalline, the reflectance data agree within error. These data pertain to normal incidence. In the ultraviolet region, the reflectance is generally less than 50%. Thus, for UV applications, CVC SiC must either be coated, or perhaps the reflecting element designed for grazing incidence.

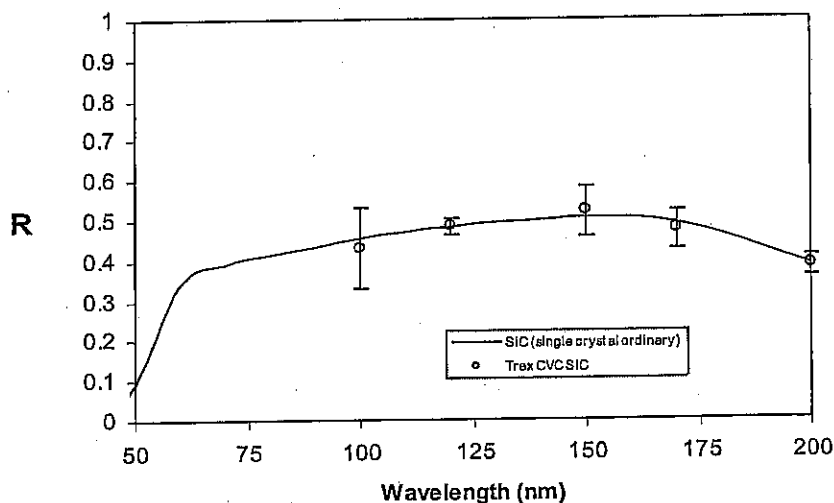


Figure 3. Ultraviolet region reflectance data for CVC SiC (open circles with error bars) and single crystal SiC.

We recently obtained the complex optical constants for CVC SiC in the mid-infrared spectral range. These data were measured using spectroscopic ellipsometry. Figure 4 shows the real refractive index n and absorption coefficient k as a function of wavelength.

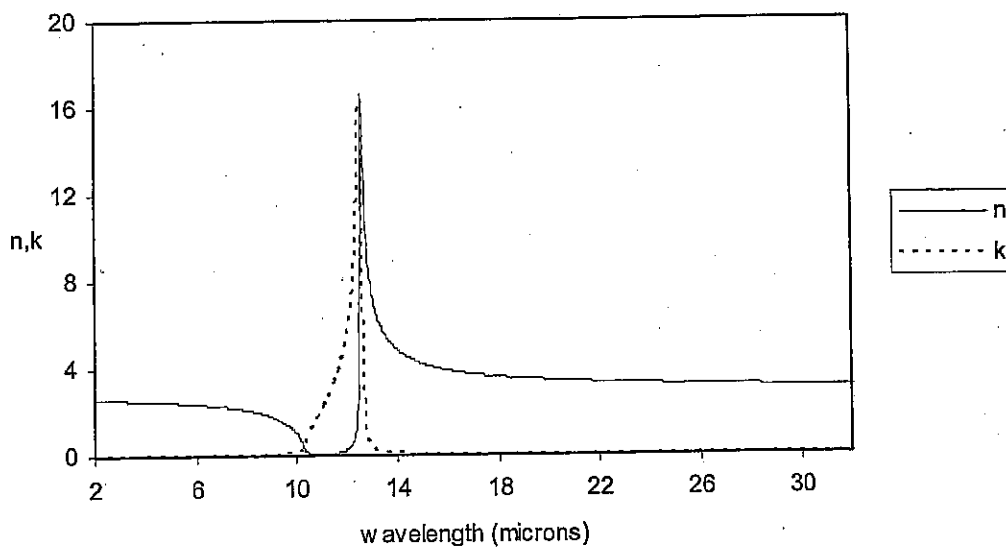


Figure 4. Infrared optical constants for CVC SiC. The solid curve shows the real index of refraction, n . The dashed curve corresponds to the absorption coefficient, k .

The major feature in these data is the absorption band centered at $\lambda = 12.6 \mu\text{m}$ (or in wavenumber convention, 796.8 cm^{-1}). This absorption band is seen in other types of SiC, and has been identified with the transverse optical phonon mode ω_{TO} .⁹

The real refractive index and absorption coefficient constitute the complex index of refraction $\tilde{n}$, via

$$\tilde{n} = n + ik \quad (2)$$

where $i = \sqrt{-1}$. The complex index of refraction is related to the complex dielectric function via $\tilde{\epsilon} = \tilde{n}^2$. The n and k curves in Figure 4 can be restated in terms of the real and imaginary components of $\tilde{\epsilon}$, and fit with complex function

$$\tilde{\epsilon} = \epsilon_{\infty} + \frac{\epsilon_{\infty}(\omega_{LO}^2 - \omega_{TO}^2)}{\omega_{TO}^2 - \omega^2 - i\Gamma\omega} - \frac{f\omega_p^2}{\omega(\omega + i/\tau)} \quad (3)$$

where in the first and second terms on the right hand side the infinite frequency dielectric constant $\epsilon_{\infty} = 6.774$, the transverse optical phonon frequency $\omega_{TO} = 796.8 \text{ cm}^{-1}$, the longitudinal optical phonon frequency $\omega_{LO} \approx 972 \text{ cm}^{-1}$, and the oscillator damping factor $\Gamma = 5.5 \text{ cm}^{-1}$. The frequency of the incident light is given by ω .

The third term on the right hand side of the equation is necessary to account for metal like character, most likely imparted by free electrons introduced by nitrogen atoms that contaminate our process. The plasma frequency ω_p is multiplied by a factor f , which addresses the effective mass of the free electron. The best fit of the data required that $f\omega_p^2 = 1.13 \times 10^{28} \text{ sec}^{-2}$, and the mean lifetime $\tau = 1 \times 10^{-15} \text{ sec}$. The term τ corresponds to the average time between consecutive collisions of the electrons with lattice atoms.

One interesting result of the ellipsometric study is that the complex index of refraction data could be fit by a single equation. This is consistent with a material that is structurally isotropic. Studies on other SiC samples required two equations, one for the incident light component parallel, and one for the component perpendicular to the sample surface.⁹ Thus, in addition to optical microscope images of CVC SiC material, we have both thermal conductivity and infrared ellipsometry data that confirm an equiaxial grain structure.

From the real refractive index and absorption coefficient functions and the well-known Fresnel equations, we can calculate the reflectance spectra of CVC SiC. At normal incidence, the maximum reflectance (96.2%) occurs at $\lambda = 11.84 \text{ }\mu\text{m}$. The range over which the normal incidence reflectance exceeds 90% is rather limited ($10.78 \text{ }\mu\text{m} < \lambda < 12.49 \text{ }\mu\text{m}$). Even at high incidence angle ($\theta = 75^\circ$), the reflectance over most of the mid-infrared spectrum does not exceed 80%, and this increase is limited to the s-polarized component of the incident light (see Figure 5). Thus, for most infrared applications, reflective coatings will be necessary.

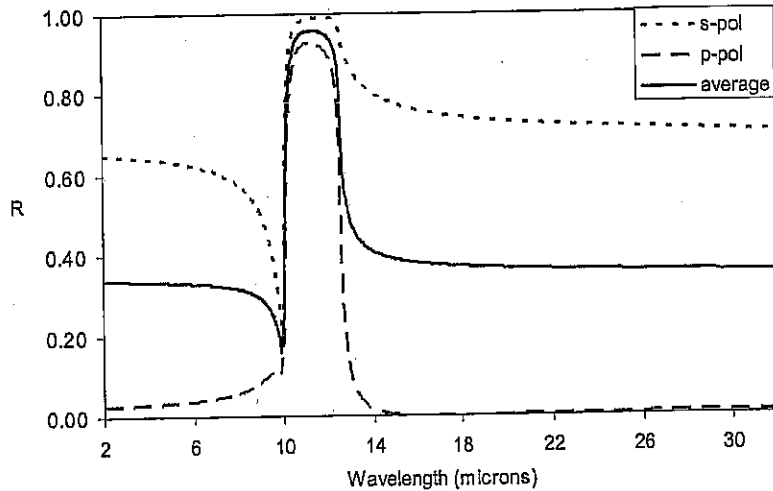


Figure 5. Infrared reflectance calculated with Fresnel's relations and experimental n and k from Figure 4.

4. MIRROR FABRICATION AND PERFORMANCE

Figure 6 shows the peak to valley (P-V) surface figure as a function of aspect ratio (AR, mirror diameter divided by thickness) for various flat CVC SiC mirrors. The fabrication of these mirrors involved deposition of a rough disc geometry, machining to the appropriate thickness and diameter, and diamond slurry polishing. For these mirrors, the surface roughness after polishing was typical less than 10 Å rms.

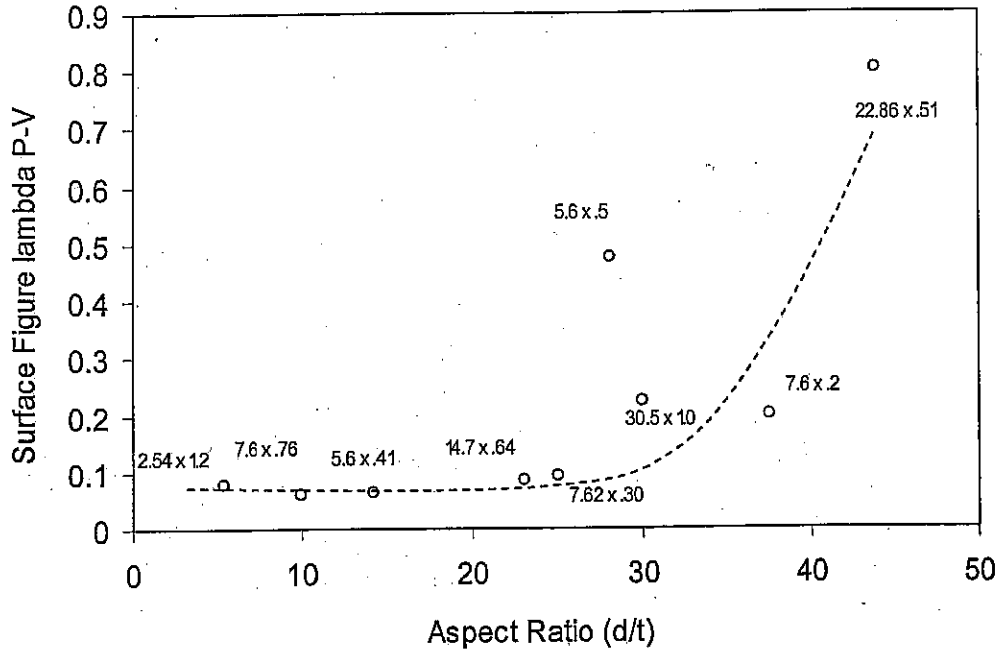


Figure 6. P-V surface figure as a function of mirror aspect ratio. For aspect ratios below ca. 25, mirrors maintain a surface figure better than 0.1 λ (where $\lambda = 632.8$ nm helium-neon interrogation wavelength). All dimensions are given. As diameter x thickness in centimeter units.

The surface figure is at or below 0.1 λ for mirrors whose AR value is ca. 25 or less. As AR increases above 25, the structure becomes too flimsy and the surface figure increases rapidly. The areal density (AD) for any flat monolithic mirror is given by $AD = \rho t$ (where ρ is the material density in kg/m^3 and t is the mirror thickness). Assuming that an aspect ratio of 25 is the upper limit that can maintain tenth wave figure, we can define a limiting areal density function $AD_{0.1}$ for solid disc CVC SiC mirrors

$$AD_{0.1} (\text{kg m}^2) = \frac{\rho}{AR_{0.1}} d = \frac{3210}{25} d = 128.4 d (m) \quad (4)$$

where $AR_{0.1}$ is the highest aspect ratio that achieves sufficient structural stiffness to maintain tenth wave figure. Since the density of SiC is 3210 kg m^{-3} , the limiting areal density is a function linear in the mirror diameter with slope 128.4 kg m^{-2} . Thus, for solid disc mirrors made of CVC SiC, the areal density may be expected to increase rapidly with diameter. A one meter diameter mirror thick enough to hold tenth wave would weigh at least 100 kg. A two meter diameter mirror would be over 400 kg. In spite of the high specific stiffness of CVC SiC, solid disc structures would be restrictively heavy, at least for airborne and space applications.

In order to reduce areal density, CVC SiC material can be removed via machining, even if for designs where the facesheet and rib walls are very thin. Figure 7 shows a 15.2 cm diameter, 0.60 cm thick CVC SiC disc that has had material removed via machining. The facesheet and rib thickness are 0.15 cm. The 12 full triangular rib elements have effective aspect ratios of 19. The partial triangle elements at the perimeter have aspect ratios of 16. The total mass and

areal density are 0.163 kg and 8.98 kg/m², respectively. The machining of the rib backing structure removed approximately 53% of the total mass.

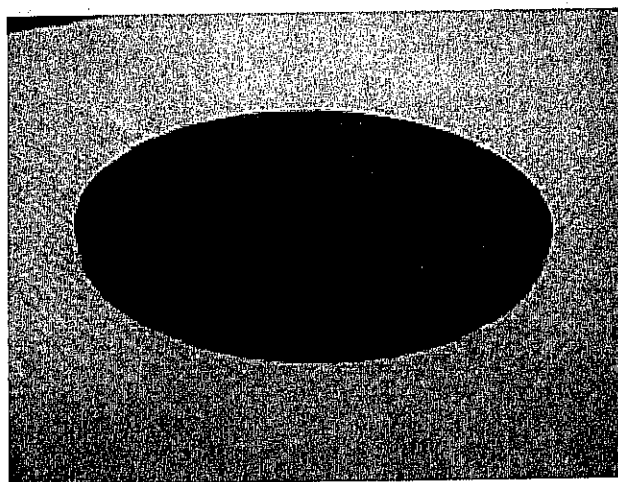


Figure 7. CVC SiC mirror blank with machined rib backing structure. $d = 15.2$ cm $t = 0.6$ cm Areal Density 8.74 kg/m² Element aspect ratios 18.8, 15.7

Lightweight mirrors machined from solid discs of CVC SiC are technically feasible, but may not be cost effective in the case of large aperture structures. Attaching a thin facesheet to a preformed ribbing structure is an alternative strategy, assuming that issues of bonding and CTE differences are effectively addressed. **Figure 8** shows an image of a 20.3 cm diameter 0.051 cm thick mirror facesheet that was machined from CVC SiC. While such a high aspect ratio structure ($AR = 398$) cannot be expected to hold tenth wave surface figure upon polishing (it did not), it provides a good example of the amenability of CVC SiC to machining. Also, it should be noted that the surface roughness after polishing was found to be 1.85 Å rms.



Figure 8. Ultra-thin facesheet $d = 20.3$ cm, $t = 0.051$ cm. Roughness 1.85 Å rms (12.21 Å P-V)

Finally, the CVC process can be employed to produce near net shape structures such as powered mirrors. **Figure 9** shows a 25.4 cm diameter one meter radius of curvature spherical concave mirror structure, before and after polishing. The part was grown on a precisely machined convex graphite substrate. After deposition, the back surface was

machined to bring the total thickness to 0.3 cm. The areal density is ca. 9.5 kg/m². After polishing, the surface figure was 0.202 λ (P-V). This surface figure is surprisingly good given the high aspect ratio the structure (AR = 85).

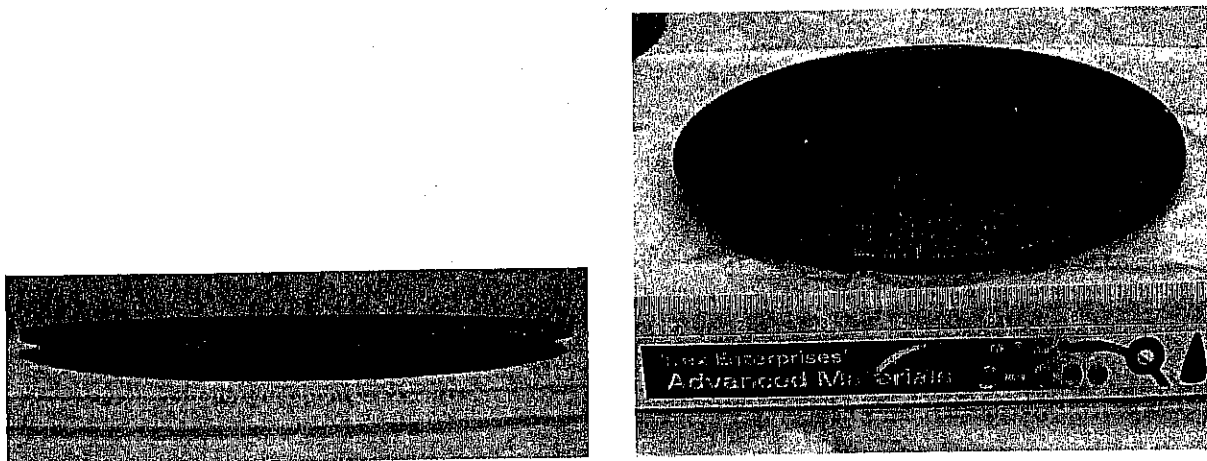


Figure 9. Thin curved mirror fabricated via near net shape deposition $d = 25.4$ cm $t = 3$ mm Radius of Curvature 1.0 m. Left: Post deposition, prior to backside machining and polishing. Right: after polishing. Surface Figure 0.202 λ P-V.

5. CONCLUSIONS

Silicon carbide prepared via the chemical vapor composites process has mechanical and thermal properties that are highly favorable for lightweight mirror technology. Low residual stress is associated with isotropic grain structure, which is achieved via addition of solid particulates into the chemical vapor stream. Isotropic grain structure leads to isotropic thermal and optical properties. CVC SiC mirrors show ultraviolet region reflectance in agreement with R calculated from single crystal optical constants. The intrinsic infrared reflectivity of CVC SiC high only over a limited wavelength region, namely the transverse optical phonon band centered at 13 μ m. Low residual stress allows for net shape deposition and machining of very delicate structures, including ultrathin facesheets and all-CVC SiC ribbed mirrors.

Acknowledgments

The work reported in this paper was supported in part by the Missile Defense Agency, the Space and Missile Defense Command, and the Air Force Research Laboratory (SBIR).

REFERENCES

1. P. Reagan, A.N. Scoville, and R. Leaf US Patent 5,348,765. September 20, 1994.
2. W.D Nix and B.M. Clemens "Crystallite coalescence: a mechanism for intrinsic tensile stress in thin films" *Journal of Materials Research* **14**, 3467-3473, 1999.
3. R.G. Weast (Ed) *Handbook of Chemistry and Physics*, p B-143 Chemical Rubber Company, Boca Raton, FL, 1982, 63rd Ed.

4. M.A. Ealey, J.A. Wellman, and G. Weaver, "CERAFORM SiC: Roadmap to 2 Meters and 2 kg/m² Areal Density" in M.A. Ealey, R.A. Paquin, and T.B. Parsonage (Eds), *Advanced Materials for Optics and Precision Structures*, pp 53 - 70, SPIE, Bellingham, WA, 1997.
5. The thermal conductivity of CVD SiC was taken from the website <http://www.cvdmaterials.com>, last accessed 6 July 2005.
6. N.W. Ashcroft and N.D. Mermin *Solid State Physics* Ch 25, Saunders College Publishing, Fort Worth TX, 1976.
7. E. Palik *Optical Constants of Solids* p 587 Academic Press, New York 1985.
8. K. France and S. McCandliss, Johns Hopkins University, unpublished results.
9. T. Tiwald, J.A. Woollam, S. Zollner, J. Christiansen, R.B. Gregory, T. Wetteroth, S.R. Wilson, and A.R. Powell "Carrier concentration and lattice absorption in bulk and epitaxial silicon carbide determined using infrared ellipsometry" *Physical Review B*, **60**, 11464-11474, 1999.