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CHEMICALLY VAPOR DEPOSITED SILICON CARBIDE (SiC) FOR OPTICAL APPLICATIONS

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In this paper we present important physical, thermal, mechanical, and optical properties of cubic (β) silicon carbide produced via a bulk chemical vapor deposition (CVD) process developed at CVD Incorporated. This CVD SiC has been identified as the leading mirror material for high energy synchrotron radiation because of its high thermal conductivity, low thermal expansion, high polishability, and high reflectance in the vacuum UV. However, it has been difficult to obtain high quality, monolithic, CVD SiC mirrors in large sizes, i.e., greater than 10–20 cm. Recently, CVD Incorporated has been successful in scaling an SiC CVD process to produce large monolithic pieces of SiC up to 60 cm (24 in.) in diameter and plates up to 76 cm (30 in.) long by 46 cm (18 in.) wide with thicknesses up to 13 mm (0.5 in.). The properties of this material that make it attractive for optical applications, such as synchrotron optics, will be discussed.

1. Introduction

Silicon carbide (SiC) is currently used for high temperature engineering application, such as reaction tubes and furnace components in semiconductor processing chambers, heating elements, refractory ware, abrasives, and coatings for wear and corrosion resistance [1–3]. Most of the bulk SiC available today is made by sintering and/or hot-pressing powders of SiC. These sintered/hot-pressed forms of SiC are usually porous and multiphased materials that, when polished, do not make a good optical surface. Recently, there has been growing interest in producing bulk SiC via the chemical vapor deposition (CVD) processes. This technology allows the production of material which is theoretically dense, with superior mechanical and thermal properties, and which is highly polishable. The CVD SiC's high stiffness-to-weight ratio, strength, thermal conductivity, hardness, and low thermal expansion coefficient make it an excellent material for optical substrates, such as synchrotron mirrors.

Silicon carbide is widely considered to be the material of choice for mirror optics in vacuum ultraviolet (VUV) and X-ray applications. For example, mirrors for deflecting synchrotron radiation in large electron-storage rings must withstand high X-ray flux without degradation or excessive thermal distortion, which affects transmission and energy resolution. The relatively low thermal expansion coefficient and excellent thermal conductivity of CVD SiC give it a high ranking in such applications [4–6]. Also, the high polishability of CVD SiC (< 3 Å rms) minimizes losses due to stray light [4,7]. In addition to its utility in synchrotron beam lines, SiC has applications in UV telescopes/instruments for space astronomy because of its high normal incidence reflectance ($> 40\%$ above 60 nm) [8].

The primary limitation to the application of CVD SiC has been the unavailability of large monolithic pieces for the fabrication of mirrors. To overcome this limitation, SiC optics are usually made of a composite material which consists of a hot-pressed or reaction-bonded SiC substrate coated with a thin CVD SiC film. These composites do not have the resistance to thermal distortion of CVD SiC. Recently CVD Inc., has developed a CVD technology for fabricating large monolithic pieces of polycrystalline β-SiC. The SiC material is free of microcracks and/or voids, resulting in high polishability, strength, stiffness, and thermal conductivity.

The CVD SiC produced was characterized to determine physical, thermal, mechanical, and optical properties. These material characterization measurements include thermal conductivity, coefficient of thermal expansion (CTE), heat capacity, flexural strength, Young's modulus, hardness, density, chemical purity, crystalline structure, surface finish characteristics and reflectivity.

2. Discussion of material characterization results

A discussion of the results of characterization studies on CVD SiC is presented in this section. These measurements were made at CVD, Inc., the University of Dayton Research Institute (UDRI), and a number of other commercial laboratories. As previously mentioned, the CVD process developed was scaled from a small research furnace to a pilot-plant furnace and finally to a manufacturing facility. Characterization measurements were performed on CVD SiC produced in all three CVD chambers during the scaling process. In addition, material from various runs (lots) was also tested to determine the ability of the CVD process to consistently reproduce a β-SiC material.

2.1. Chemical and physical properties

Trace-element analysis of material grown in the research furnace was performed using proton induced X-ray emission spectroscopy (PIXE) at Element Analysis Corporation, Tallahassee, FL. In this technique high energy protons are accelerated into the sample and collide with core shell electrons to create X-rays which are characteristic of the particular atoms present in the sample. Impurity levels as low as parts per billion can be detected by this technique, with the exception of elements with atomic weights lower than carbon. All heavier elements, with a few exceptions, can be detected. The following impurities, in weight percent, were detected in CVD SiC produced in two deposition runs. From the first run the impurities detected were 1.2 ppm Mn, 7.3 ppm Fe, 1.0 ppm Co, 0.64 ppm Ni, and 5.5 ppm Cu. Similarly, the following impurities were detected in a sample from another run: 0.6 ppm Mn, 3.9 ppm Fe, and 1.5 ppm Zn. From these data it is concluded that the CVD SiC produced is 99.999% pure, excluding H, He, Li, Be, B and free C.

The density of CVD SiC was measured at room temperature using the Archimedes immersion technique. In this technique, a SiC sample is hung by a fine thread in a beaker of water and weighed. This weight is compared to the weight of the sample before immersion. The density of SiC material produced in two depositions in a research CVD chamber was 3.213 ± 0.013 g/cm^3 and 3.212 ± 0.033 g/cm^3. The density of single crystal cubic SiC is 3.21 g/cm^3; therefore, within the uncertainty of the measurement (1 part in 10^3), the CVD SiC is theoretically dense.

The microstructure of the SiC has been evaluated using X-ray diffraction and optical microscopy. Diffraction analysis performed at CVD Inc., using a Siemens D500 X-Ray Diffractometer, indicates that the material is polycrystalline β-SiC with crystallites that are randomly oriented. These results were confirmed at UDRI and ES Laboratories, Wrightstown, NJ. Fig. 1 shows a typical diffraction pattern from material grown in the research furnace. Similar patterns have been obtained for material produced in the pilot plant and manufacturing CVD facilities using optimized CVD conditions. All of the diffraction peaks in fig. 1 were identified as cubic SiC.

The current technical literature suggests that preferential growth of CVD materials can occur on certain crystallographic planes under conditions of high temperature and/or low growth rate (low gas concentration) [9]. We have observed similar behavior of CVD-grown SiC. For example, at low deposition rates, i.e. < 1 μm/min, there is a strong preferential growth in the (111) and (220) directions in the temperature range

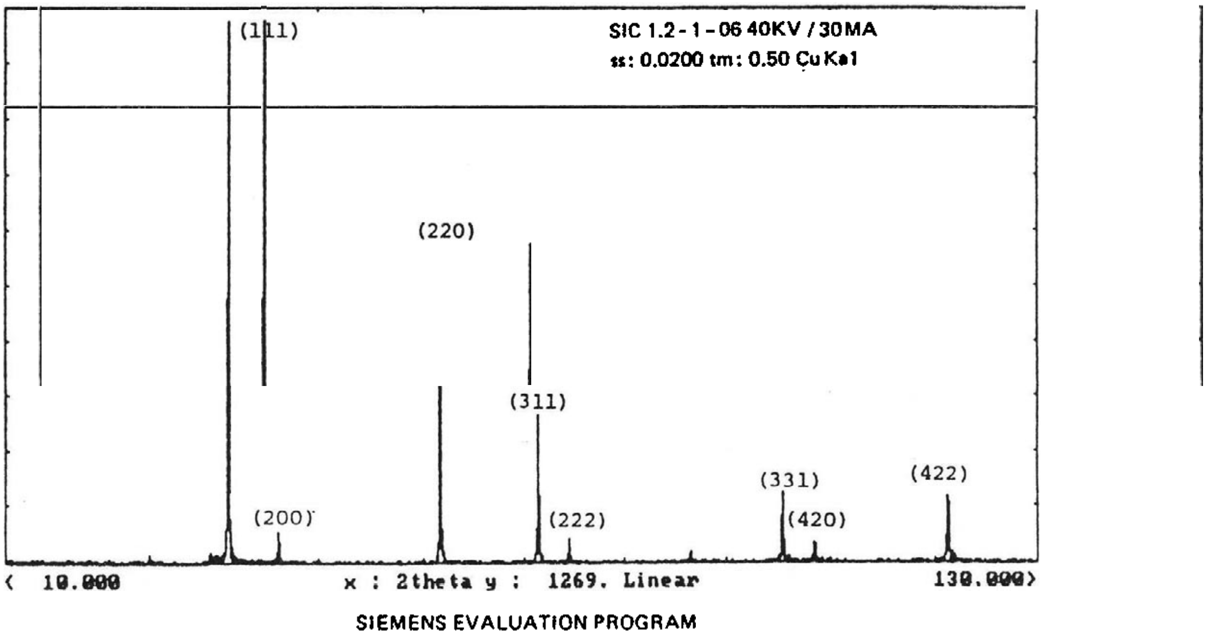

Fig. 1. Typical X-ray diffraction pattern for polycrystalline CVD SiC produced in the research furnace (Run 1.2.1-6). Notice that all of the peaks are identifiable as cubic (fcc) SiC peaks. The relative intensity of the peaks also indicates no preferred orientation.

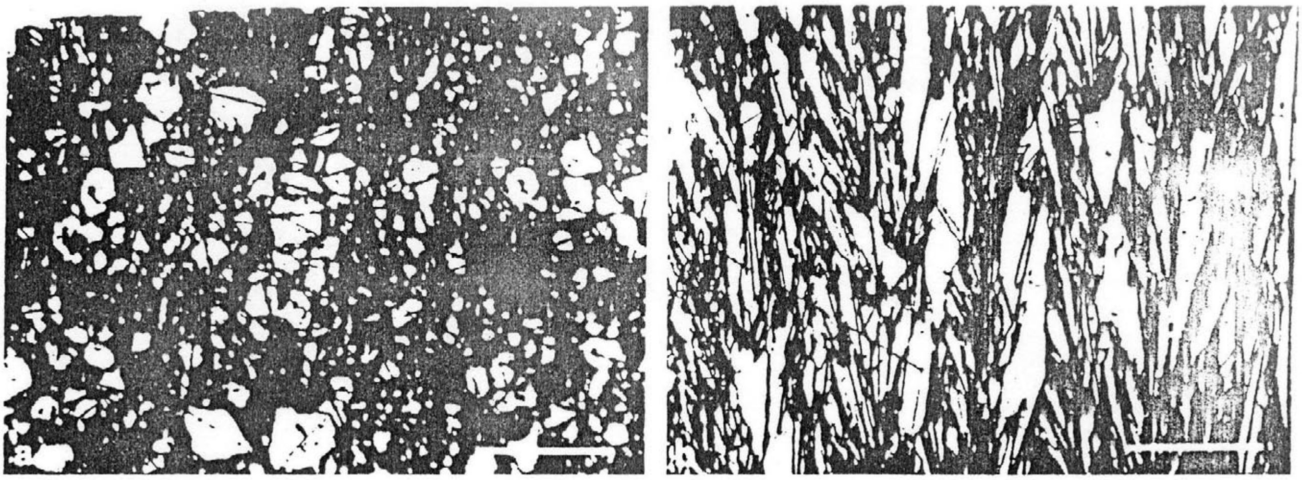

Fig. 2. (a) Typical micrograph of KOH-etched CVD SiC surface perpendicular to growth axis (320 ×) and (b) typical micrograph of KOH-etched CVD SiC surface parallel to growth axis (160 ×). Notice the columnar growth structure, which is commonly observed in CVD deposited materials. The marked bar in micrograph (a) indicates 60 μm and the bar in (b), 120 μm.

1300–1450 ° C. It is important to understand the sensitivity of the crystallographic orientation of the material to growth rate (furnace conditions) for CVD SiC, since many of the physical, mechanical, and thermal properties depend on the microstructure.

Figs. 2a and 2b are typical optical micrographs of CVD SiC. The material was polished and then etched in molten potassium hydroxide before the micrographs were taken. Fig. 2a shows the as-deposited SiC surfaces (surface perpendicular to growth axis). The average grain size is approximately 10 μm. Fig. 2b is a cross section of the material (surface parallel to growth axis) and shows the growth to be columnar. We have observed that the grains originating at the substrate, where nucleation initially occurs, are small and then increase in size with distance from the substrate. This is typical for most CVD deposited materials [1,9].

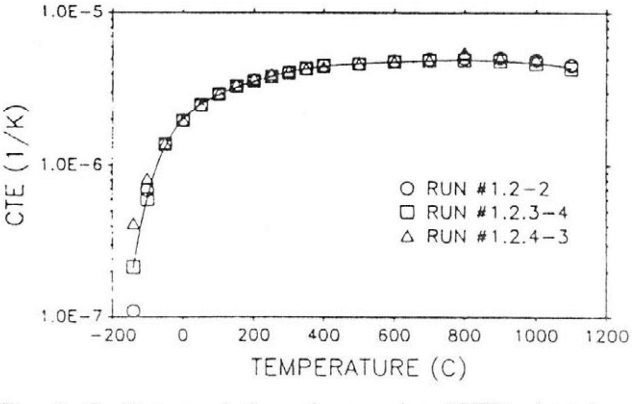

Fig. 3. Coefficient of thermal expansion (CTE) plotted vs temperature for various samples of CVD SiC. Material from Run 1.2-2 was produced in a small research CVD furnace, Run 1.2.3-4 in a pilot-plant facility, and Run 1.2.4-3 in a manufacturing facility. The uncertainty in the measured value of CTE is $\pm 2 \times 10^{-7}$ K^{-1}.

2.2. Thermal properties

A number of samples of CVD SiC were tested at CVD Inc. and UDRI to determine the coefficient of thermal expansion (CTE). The CTE measurements were made using differential dilatometers over the temperature range 123 to 1375 K (− 150 to 1100 ° C). Fig. 3 shows results of CTE measurements made on CVD SiC produced in three runs, one each from the research furnace (Run 1.2-2), the pilot plant furnace (Run 1.2.3-4), and the manufacturing facility (Run 1.2.4-3). Calibration runs performed on the dilatometer used to make these measurements (Theta Industries, Inc., Model Dilatronic IR) indicate that the uncertainty in the measurement of CTE is about 2×10^{-7} K^{-1} for the sample

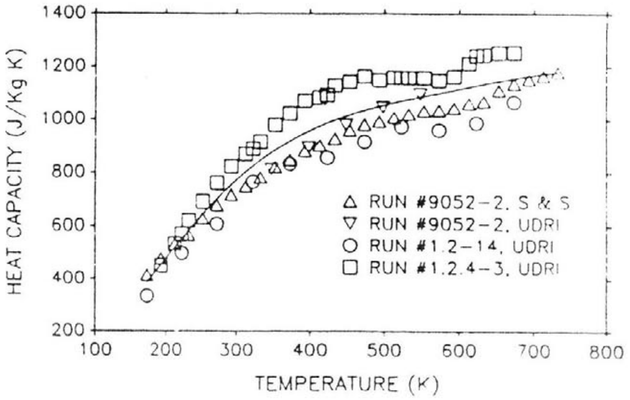

Fig. 4. Heat capacity of CVD SiC measured by a differential scanning calorimeter (DSC). Measurements were performed at UDRI and Skinner and Shermal Laboratories (S&S) using a sapphire standard. Note good agreement in data at low temperatures and deviations observed at higher temperatures. Solid line drawn through points in a least-squares 5th-order regression fit to all the data.

length used (40 mm). Notice that these data (fig. 3) show that the CTEs of CVD SiC from various runs and various CVD chambers are equal within the uncertainty of the measurement. This demonstrates the reproducibility of the CVD process, with respect to CTE, that can be achieved during scaling from a small research furnace to a manufacturing facility.

The heat capacity of several samples of CVD SiC, produced in various runs, was determined using a differential scanning calorimeter (DSC), with sapphire as the reference material, over the temperature range 173 to 733 K (−100 to 460°C). These measurements were performed at UDRI on a Dupont Model 910 DSC and at Skinner and Sherman Laboratories (S&S), Waltham, MA, on a Dupont Model 1090 DSC. The results are shown in fig. 4. Note that the UDRI data and the S&S data for samples from the same run (9052-2) agree at low temperatures but deviate from each other at higher temperatures. Also notice (see fig. 4) that the UDRI data for Runs 1.2-14 and 1.2.4-3 differ slightly from that of Run 9052-2 at low temperatures and differ significantly at high temperatures. We do not know, at this time, whether these differences are due to uncertainties in the measurement (calibration errors) or differences in material properties. The solid line in fig. 4 is a least-squares 5th-order regression fit to all the data.

The thermal diffusivity of CVD SiC was measured at UDRI by the flashlamp technique. In this method the front face of a small (13 mm × 13 mm × 2.5 mm) specimen plate is irradiated with an energy pulse from a Xenon flashlamp, and the resulting temperature rise of the rear surface of the specimen is measured and recorded. An Armco iron standard is used to calibrate the apparatus immediately before and after each run. By using these data to solve the heat flow (diffusion) equation (edge effects are ignored), the thermal diffusivity can be determined. Fig. 5 shows the average measured thermal diffusivity of CVD SiC samples produced in the research furnace in Run 1.2-14 and the manufacturing facility in Run 1.2.4-3. The error bars represent the standard deviation in the measured values for two samples from each run. The solid line is a least-squares 2nd-order regression fit to the data. Notice that the diffusivity increases as the temperature decreases from 298 K (25°C) to 83 K (−190°C). Also notice that the values for the two runs differ. The reason for this difference is not clear at this time. However, the deposition temperature in Run 1.2.4-3 was higher than in Run 1.2-14. The higher temperature would produce material with larger grains and, therefore, fewer grain boundaries. It may be that thermal diffusion across grain boundaries is much lower than through the SiC crystallites. More work needs to be done to better understand the relationship between the thermal diffusivity and deposition conditions and microstructure of the deposited SiC.

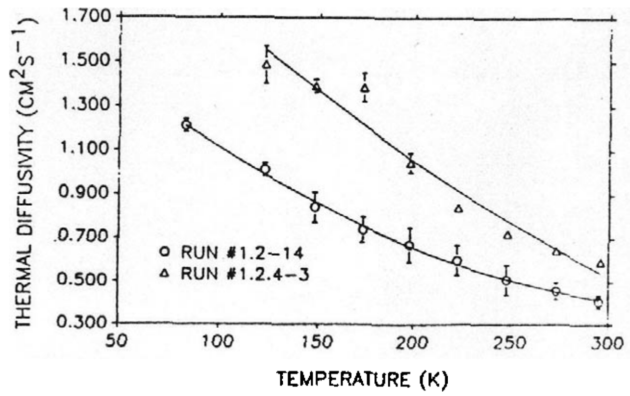

Fig. 5. Thermal diffusivity of CVD SiC measured at UDRI a using flashlamp technique. Solid lines are least-squares 2nd-order regression fits to data. Error bars represent the standard deviation for measurements made on two samples from Run 1.2-14 and Run 1.2.4-3. The deposition temperature was higher in Run 1.2.4-3, which may account for the observed (measured) difference in diffusivity.

The thermal conductivity is simply the product of the density (ρ) heat capacity (c_p), and thermal diffusivity (α_d). Knowing the values of ρ, α_d, and c_p at specific temperatures, one can calculate the thermal conductivity. If we assume that the density of CVD SiC does not change appreciably over the temperature range 80 to 300 K, we can use the heat capacity data of fig. 4 and the thermal diffusivity data of fig. 5 to determine the thermal conductivity. For example, the thermal conductivity for CVD SiC from Run 1.2.4-3 varies from 122 to 160 J m^{-1} s^{-1} K^{-1} as the temperature increases from 122 to 296 K.

2.3. Mechanical properties

The hardness of CVD SiC material produced in the research furnace, the pilot-plant furnace, and the manufacturing facility was measured using both Knoop and Vickers indentors, under loads ranging from 300 g to 1 kg. The average hardness value for 80 samples tested was 2463 ± 152 kg/mm. There was no significant difference between the Knoop and Vickers hardness values, for the various loads used.

The fracture toughness critical flaw intensity value, K_{IC}, of CVD SiC was measured for material produced in the small research furnace, the pilot-plant furnace, and the manufacturing facility. The K_{IC} values determined using the Vickers microfracture technique [10] did not vary substantially under various loads or from sample to sample. The average K_{IC} value using the Vickers microindentation method for 42 samples tested was 3.3 ± 0.3 MPa$\sqrt{m}$. This value agrees quite well with others reported in the literature for CVD-grown SiC having an average grain size of 10 μm [1].

The flexural strength of CVD SiC was measured at CVD Inc., and UDRI using a four-point flexure test.

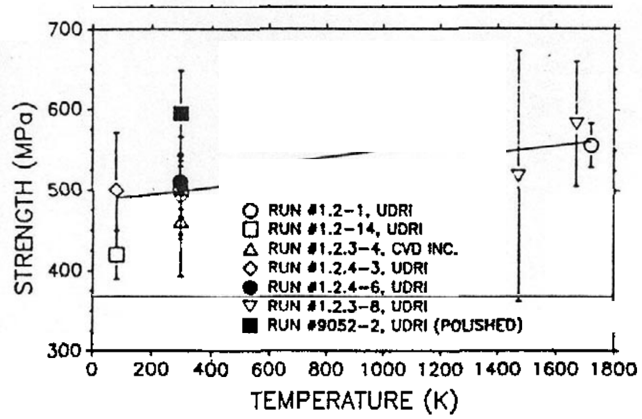

Fig. 6. Flexural strength (four-point loading) of CVD SiC as a function of temperature. All samples had a 0.4 μm rms surface finish except for point ■, which was optically polished. The solid line is a least-squares linear regression fit to data, excluding point ■.

The results are shown in fig. 6. Tests were performed at 79 K (−194°C), 295 K (22°C), 1473 K (1200°C), 1673 K (1400°C), and 1723 K (1450°C) using material grown in the research furnace (Runs 9052-2, 1.2-1, and 1.2-14), the pilot-plant furnace (Runs 1.2.3-4 and 1.2.3-8) and the manufacturing facility (Runs 1.2.4-3 and 1.2.4-6). The tests at CVD Inc., were made using an Instron Model 1122 Universal Testing Instrument on 20 beams 50 mm long by 6.4 mm wide by 2 mm thick, and the tests at UDRI were made using an Instron Model 1123 Universal Testing Instrument on five to ten beams (from each run) 50 mm long by 6.4 mm wide by 3.2 mm thick. All of the beams were prepared with a surface finish of 0.4 μm rms, except for beams from Run 9052-2 (point ■ in fig. 6), which were optically polished. The solid line in fig. 6 is a least-squares linear regression fit to the data, excluding point ■. The flexural strength results suggest that the strength increases with temperature. This effect has been observed previously for CVD SiC and is attributed to small plastic deformation that occurs at crack tips at higher temperature [1].

The room-temperature flexural strength of the polished beams prepared from material grown in Run 9052-2 (point ■ in fig. 6) is higher than any of the others. This is attributed to the optical finish on the faces and edges of these beams. As a result, the average flexural strength of these beams is the most indicative of the intrinsic room-temperature strength of CVD SiC.

The sonic and flexure elastic moduli of CVD SiC were measured for 30 samples (beams). The sonic modulus was measured at UDRI using a GrindoSonic, MK3 (J.W. Lemmens, Co.), and the flexure modulus was measured at CVD Inc., using an Instron Model 1122 Universal Testing Instrument. There was essentially no difference in the modulus determined by these methods using material from the research furnace and the pilot-plant facility. The measured sonic modulus was 467 ± 9 GPa for 10 beams tested, and the flexure modulus was 461 ± 16 for 20 beams tested.

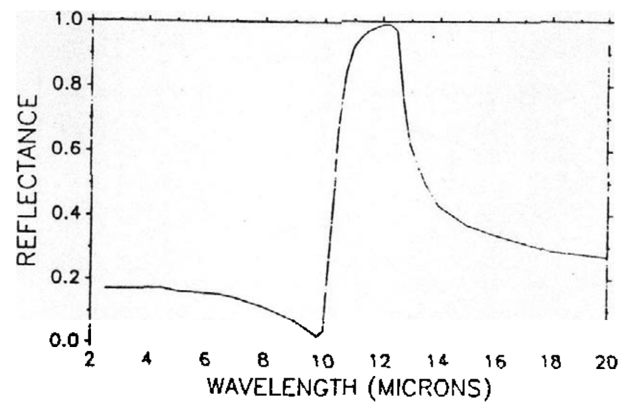

Fig. 7. Normal incidence IR reflectance of polished, uncoated CVD SiC. Notice the high reflectivity at 11–12 μm.

2.4. Optical properties

As mentioned in the section 1 and shown above, CVD β-SiC is a theoretically dense, single phase, high purity, homogeneous material. These characteristics make it attractive as an optical material due to its high polishability and thermal stability. The CVD β-SiC has been polished to < 10 Å rms by several optical houses. United Technologies Optical Systems (UTOS), West Palm Beach, FL, has routinely achieved finishes of < 8 Å rms and Carl Zeiss, FRG, has recently obtained a finish of 3 Å rms "without much effort" [11]. These results indicate that CVD SiC is highly polishable and, therefore~~, is suitable for mirror applications where low~~ surface scatter is required.

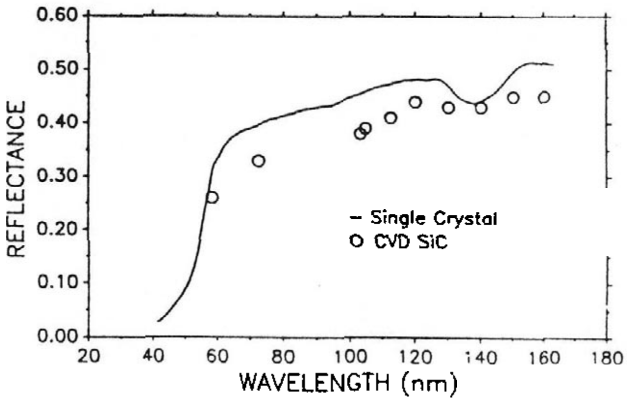

Fig. 8. Normal incidence VUV reflectance polished, uncoated CVD SiC. The solid line represents the calculated values for single crystal SiC using refractive index and extinction coefficient data from ref. [12]. The SiC sample had a surface finish (polish) with a microroughness of 8.8 Å rms.

The VUV and IR reflectances of CVD SiC were measured and compared to the reflectance of single-crystal SiC calculated from refractive index and extinction coefficient data. The normal incidence IR reflectance in the wavelength range of 2.5–50 μm was measured at CVD Inc., using a Perkin–Elmer Model 1330 IR spectrophotometer outfitted with a reflectance measuring accessory, and these data are shown in fig. 7. The experimental data in fig. 7 are consistent with that calculated for single crystal SiC [12]. The VUV reflectance of CVD SiC was measured by Acton Research Corporation, Acton, MA, at normal incidence. These data are shown in fig. 8 (O points) along with the calculated reflectance for single crystal SiC (solid line) using refractive index and extinction coefficient data available in the literature [12]. The CVD SiC sample used in these measurements was polished flat to 0.049 μm rms and had an average microroughness of 8.8 Å as measured on a Wyko profilometer.

3. Conclusions

A scalable CVD process has been developed to produce a theoretically dense, high purity β-SiC which possesses superior properties for optical applications. Large monolithic disks of CVD SiC up to 60 cm (24 in.) in diameter and plates up to 76 cm (30 in.) long by 46 cm (18 in.) wide are currently being produced with thicknesses up to 13 mm (0.5 in.). The CVD SiC technology is currently being scaled to 1.5-m-diameter optics.

Numerous material characterization measurements performed throughout the CVD process development and scaling have allowed for optimization of the CVD process conditions in a number of CVD reactors, producing a homogeneous material ideal for optical components. In addition, important scaling laws and processing issues were identified which will be used in further efforts to scale the process to much larger sizes.

Important physical, thermal, mechanical, and optical properties of CVD SiC have been measured. These results show that this material is theoretically dense, highly pure, single phase (cubic) SiC which can be optically polished to ≤ 3 Å rms. The material is homogeneous with respect to CTE and has a very high elastic modulus (460 GPa), high strength (600 MPa) and hardness (2500 kg/mm^2), and relatively high heat capacity (700 J kg^{-1} K^{-1}) and thermal conductivity (160 W m^{-1} K^{-1}). All of these properties are beneficial for optical applications and were optimized by adjusting the CVD conditions during the SiC process development and scaling. The CVD SiC is a good candidate material for current and future optical applications, such as synchrotron mirrors, where durability, strength, high stiffness-to-weight ratio, good thermal distortion resistance, and thermal stability are required in material that can be finished to extremely high optical tolerances (low surface scatter).

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