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EVALUATION OF CVD SILICON CARBIDE FOR SYNCHROTRON-RADIATION MIRRORS*

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ABSTRACT

Chemical vapor deposited silicon carbide (CVD SiC) is a recent addition to the list of materials suitable for use in the harsh environment of synchrotron radiation (SR) beam lines. SR mirrors for use at normal incidence must be ultrahigh vacuum compatible, must withstand intense x-ray irradiation without surface damage, must be capable of being polished to an extremely smooth surface finish, and must maintain surface figure under thermal loading. CVD SiC exceeds the performance of conventional optical materials in all these areas. It is, however, a relatively new optical material. Few manufacturers have experience in producing optical quality material, and few opticians have experience in figuring and polishing the material. The CVD material occurs in a variety of forms, sensitively dependent upon reaction chamber production conditions. We are evaluating samples of CVD SiC obtained commercially from various manufacturers, representing a range of deposition conditions, to determine which types of CVD material are most suitable for superpolishing. At the time of this writing, samples are being polished by several commercial vendors and surface finish characteristics are being evaluated by various analytical methods.

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Introduction

The development of silicon carbide (SiC) as a mirror material has proceeded slowly since the initial investigations by Choyke, Rehn, and co-workers in the mid-1970's[1,2] which showed that the material had great potential for high power applications in adverse environments. The reasons for the slow pace of development are twofold: (1) Chemical vapor deposited (CVD) SiC occurs in a variety of forms, not all of which are capable of being superpolished, and (2) very few commercial optical houses have experience in working with such a hard material. Most suppliers of the CVD material have no experience in producing optical quality material for UV and x-ray applications where smoothness and low scatter are of utmost concern; the material has been developed mainly for use in the nuclear fuel industry and as a coating for high-temperature applications in corrosive environments. There are, however, a number of vendors in this country, and also throughout the world, who have the capability to produce the CVD material on a commercial basis. The material that has been the subject of previous low-scatter measurements was polished at Westinghouse in Pittsburgh and is not available on a commercial basis. Because of interest in SiC as a synchrotron radiation (SR) mirror at the National Synchrotron Light Source (NSLS), we have undertaken a study to determine the suitability of CVD SiC supplied by various manufacturers for SR mirrors. At the same time, we are evaluating the capability of various optical polishing firms in producing a smooth finish on the CVD samples. Because of the unknowns involved, this is an iterative process, in that the polishers may not be able to produce a

smooth finish because the material is not suitable, not because the polishing technique is faulty. We expect to be able to converge upon a polishable material and a successful polishing technique. We are guided in the development of polishing techniques for SiC by previous reports that only simple techniques are necessary for production of low scatter finishes on SiC[2] using fine 0.25 micron diamond powder and bowl-feed techniques[3,4].

Silicon Carbide Material

Mirrors for use in SR sources are subject to extremely hostile operating conditions. Rehn and Jones[5] have enumerated the characteristics required of mirrors suited for SR beam lines and have reviewed typical operating conditions inside a high energy, high current storage ring. Mirrors for use at normal incidence must be ultrahigh vacuum compatible, must withstand intense x-ray irradiation without surface damage, must be capable of being polished to an extremely smooth surface finish, and must maintain surface figure under thermal loading. Silicon carbide was proposed as a candidate mirror substrate by Choyke and co-workers[1] for use as a SR mirror and also as a high power laser mirror substrate. It meets all of the above requirements and, in many cases, exceeds the performance of conventional metal and glass optics in these areas. SiC has a weight advantage over metal mirrors, owing to its high specific stiffness[1], so that large aperture mirrors could be fabricated from SiC at a significant saving in weight and thickness. CVD SiC has been shown to be polishable to a supersmooth surface finish, the best examples of which show surface roughness on the order of 3Å rms[6]. Of particular interest to the far ultraviolet community is its high intrinsic reflectivity at normal incidence in the region 500Å to 1000Å, higher than any other known material[6,7].

SiC is available in a variety of forms. In addition to the CVD material, other types of the ceramic form include hot-pressed, reaction bonded, sintered-alpha, and recrystallized. These forms encompass various compositions, densities and grain sizes, and they may be formed and shaped with varying degrees of difficulty with the usual ceramic forming processes[8-10]. These other forms do not lend themselves toward superpolishing, owing to their grainy nature, but they may be used as substrates for coating with the CVD material. In this way a large mirror can be fabricated with all the thermal and mechanical properties of the bulk material, but with only the surface containing the more expensive polishable material. In some applications where extremely smooth surfaces are not required, i.e., visible and infrared mirrors, the polished substrate may be suitable when coated with a high-reflecting coating.

Substrate Vacuum Properties

The suitability of the substrate material for SR mirrors is dependent upon its UHV compatibility. We measured the UHV properties of two of the substrate materials: sintered-alpha and recrystallized. The sintered-alpha material was manufactured by the Carborundum Corporation; the recrystallized material was manufactured by Norton. The percentage volume density for these materials is shown in Table I. The recrystallized material is quite porous, being only 82% dense, while the sintered-alpha material is nearly fully dense. The latter contains surface pits and volume voids evident in Fig. 1, but the voids are not interconnected. Samples of each material were cleaned and degreased and placed inside a UHV test chamber. Subsequent to a mild bakeout of about 50°C, the chamber reached its base pressure in the low 10^{-10} Torr range with no evidence of virtual leaks

or outgassing for each material. Thus, despite the porous appearance of both substrates, they meet the UHV compatibility requirements of the NSLS[11].

Coating Properties

The substrate pieces used in this study consist of 1" diameter by 3/8" thick disks of sintered-alpha SiC supplied by Carborundum Corporation, Buffalo, New York. Several pieces were sent to each of two CVD suppliers: Raytheon Company, Research Division, Waltham, Massachusetts and General Atomic Company, San Diego, California. One side of the pieces at Raytheon was polished before coating. The Nomarski micrographs in Fig. 1 show the porosity of the uncoated polished and as-fired surfaces of the sintered-alpha material. Scratch marks are evident on the polished surface, since the polish in this case was only intended to remove the overall roughness from the as-fired surface. The disks were coated at Raytheon in a static-flow reaction chamber under a variety of reaction conditions. SEM micrographs in Fig. 2 reveal a range of surface microstructure from highly faceted crystalline deposits, with individual crystals several microns in height and width, to a disordered, rather amorphous, flat deposit. Figure 3a. is the corresponding Nomarski photograph of the most crystalline sample of Fig. 2. The extreme contrast between bright and dark areas is from the well-defined angles and slopes of the crystal faces. Similarly, Fig. 3b. is the corresponding Nomarski photograph of the amorphous deposit, indicating a diffuse, less faceted microstructure. The SEM photographs of these surfaces are similar to those appearing in Chin, et al[12], in which is presented a systematic study of surface morphology of CVD SiC deposits under varying deposition conditions. The variable studied were substrate temperature, H_2 to CH_3SiCl_3 ratio, and deposition chamber pressure. Faceting was observed at high substrate temperatures, high H_2 to CH_3SiCl_3 ratios, and lower deposition

chamber pressures. Smooth, featureless deposits were observed at lower substrate temperatures, lower H_2 to CH_3SiCl_3 ratios and at higher deposition chamber pressures when adatoms are expected to have lower mobility than in the other case, thereby inhibiting migration to dislocation sites and edges, preventing new nucleation sites for new crystal growth.

Polished CVD SiC

Two coated samples were polished at Raytheon to a standard "inspection" finish. The samples represent extremes in the deposition conditions and are, in fact, the reverse face of the samples shown in Fig. 3. The polished faces are shown in Fig. 4. Although the polishing method was not meant to produce the best possible finish, inspection of the micrographs reveals many more scratches on the more crystalline material. This is perhaps a result of individual crystals being torn away from the surface and being dragged across it[13]. Additional polishing is under way to determine if the smoother of these two deposits results in the smoother polished surface, according to the conclusions of Franks and Stedman[14].

The samples provided by General Atomic were coated in a fluidized bed bed reactor under conditions designed to produce a featureless deposit. Three coated samples are shown in Fig. 5. One surface of each piece was polished at General Atomic. SEM photographs of the polished side of sample #25 reveal it to be completely featureless. Oblique illumination with a focused microscope illuminator in Fig. 6 reveals longitudinal striations along the surface in addition to diffusely scattered light from the image. The latter effect may be caused by light scattered from the unpolished substrate surface after passing through the thin coating layer which is about 0.001" thick, or by scattering within the bulk of the coating layer.

Should this prove to be the case, then the microscope illuminator test is not a good way to characterize thin CVD deposits. The nature of the longitudinal striations is also under investigation.

Sample pieces, both coated and uncoated, were sent to four optical firms who indicated their interest in evaluating the SiC material for polishing suitability. None has any previous experience in polishing the material. One of the firms declined to continue after an initial inspection of the material. The three other firms: Applied Optics Center Corporation, Burlington, Massachusetts; Astron Developments Ltd., Teddington, U.K.; and Karl Lambrecht Corporation, Chicago, Illinois are actively engaged in developing polishing methods for the substrate and coating materials. Quantitative analysis of the polished material using total integrated scatter and surface profilometry will be carried out when the results of the polishing efforts warrant it. Presently, Nomarski microscopy and visual inspection is sufficient to judge the quality of the surfaces. The process of deposition and polishing is an iterative one, in that the inability to bring the first run of samples to a superpolish may be because the material is not entirely suitable. The next iteration should produce a more nearly ideal material.

Additional Considerations

In developing a SiC mirror material, we are concentrating on a particular substrate-coating configuration. Specifically, we are looking for a thin coating of CVD material, on the order of 0.010" thick, deposited on a thick substrate that is ground and figured nearly to the desired shape. Our test samples are, however, flat surfaces much smaller in size than any usable mirror would be. Machining of the substrate can be done using standard diamond grinding techniques familiar to the ceramic industry. Large substrates can be

accommodated on commercial machines: 20" diameter pieces can be handled easily. The cost of a large mirror substrate made from sintered or reaction-bonded material is generally much less than for the same size piece made entirely from the CVD material. The CVD process is slow, and the time required to build up a thick deposit can become expensive. With a substrate already machined to nearly the correct figure, the amount of polishing needed on the coating can be minimized. Large substrates could be accommodated in large CVD reaction vessels, provided that the deposition process can be scaled up in size after it succeeds for the smaller test pieces. The present size limit on CVD material that is suitable for superpolishing is about 30 mm x 30 mm square(13). This material is produced several millimeters thick and the size appears to be limited by cracks in the surface caused by stresses generated in the thick material(13). A thin coating of CVD material on a thick substrate with matching thermal expansion properties should eliminate stress-induced cracking as a size-limiting process. Any of the SiC substrate materials listed in Table I would provide a suitable matching substrate.

SiC has shown great promise as a mirror material for SR beam line use. In a worst-case test situation, Zietz, Saile and Haelbich(15) showed that, of several candidate mirror materials exposed to the high energy flux from DORIS, only the CVD SiC survived without any apparent surface damage. They showed that this material is capable of withstanding the harsh environment in a high energy SR source. Large substrate-quality pieces of SiC can be fabricated at present, and the CVD material is available commercially, but it has yet to be shown that it can be polished satisfactorily on a commercial basis.

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Table I

Thermal Properties of SiC and Related Substrate Materials at 20°C Unless Otherwise Noted.

Material	Volume Density (%)	Thermal Conductivity (W/cm °C)	Thermal Expansion x10^{-6} (°C^{-1})
SiC - sintered α[10]	96-98	.87†	4.8†
SiC - reaction bonded	100	2.0[16]†, 1.04[17]*	5.0[17]
SiC - CVD	100	2.0[6], 0.7[16]	4.9[16]†
SiC - β (crystal)[18]		0.255	4.8†
SiC - recrystallized	82		
SiC - hot pressed	96-98		
Cu		3.9	17
Si		1.7	4.4
Graphite-pyrolytic (parallel a-axis)		8	2-4

† = average from 20°C to about 1000°C

* = 600°C

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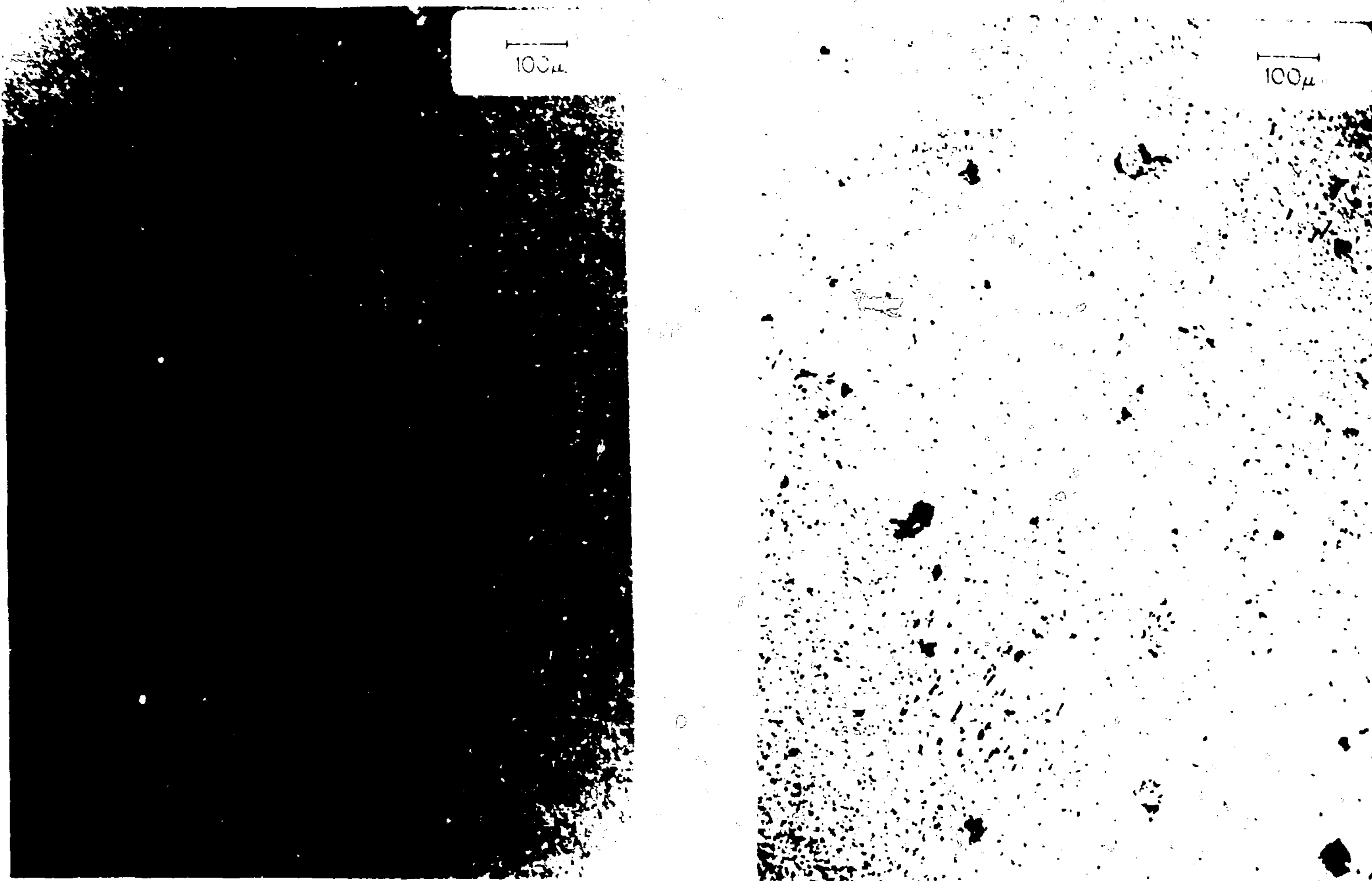
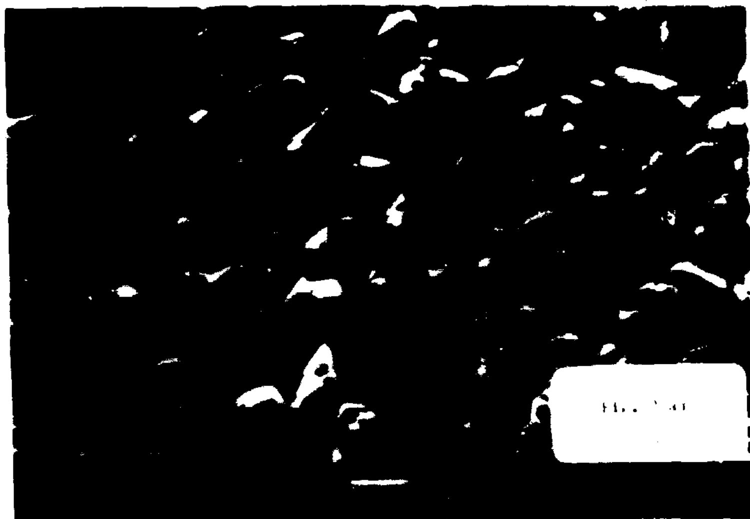
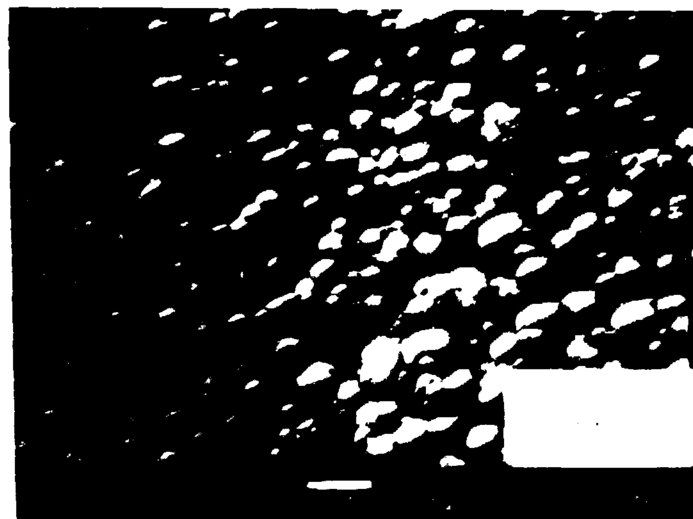


Fig. 1. Nomarski micrographs x80 of sintered-alpha SiC surfaces:

a. unpolished, as-fired surface.

b. lightly polished surface, showing polishing scratches and substrate pits and voids. The material is 96% dense and is UHV compatible.





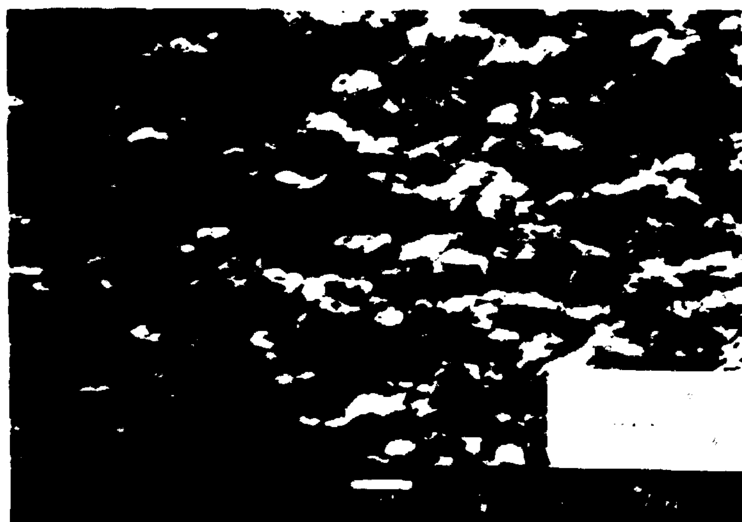
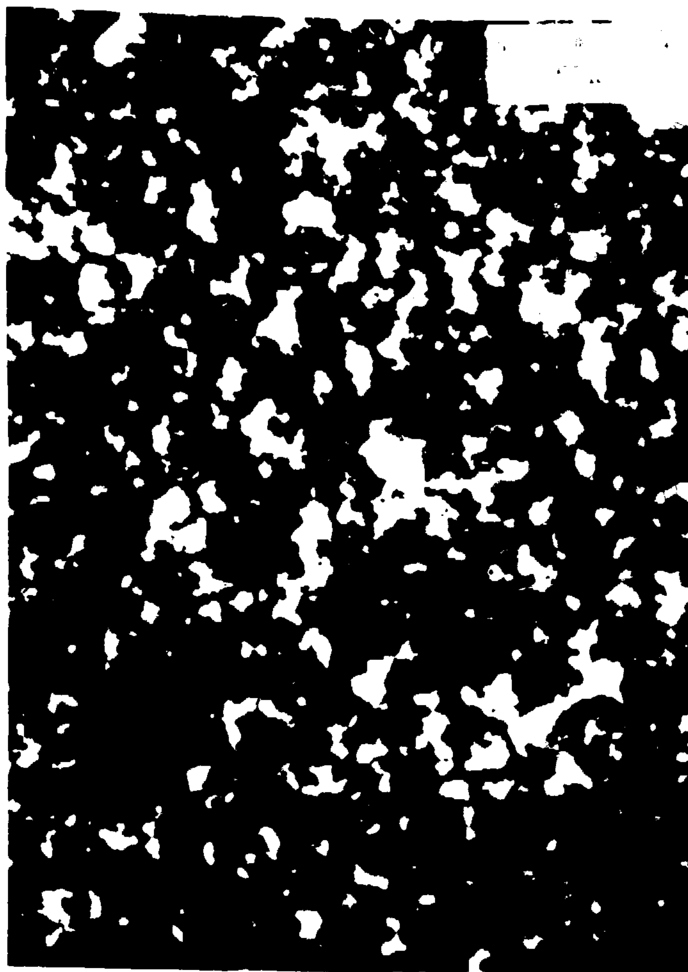


Fig. 2. SEM photographs of unpolished CVD SiC samples obtained from Raytheon. The surface microstructure ranges from highly faceted and crystalline to disordered and amorphous as a result of different reaction chamber deposition conditions.



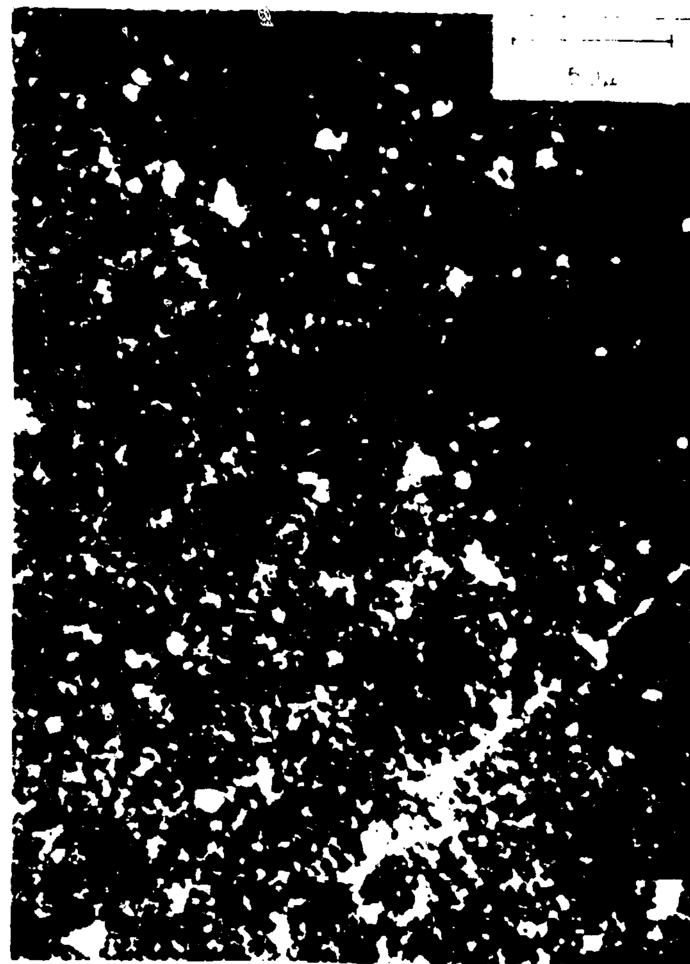


Fig. 3. Nomarski micrographs of unpolished CVD SiC, x400:

a. the most crystalline of the Fig. 2 samples. The extreme contrast between dark and light regions is a result of well-defined slopes of the crystal faces.

b. the most disordered, amorphous surface in Fig. 2.

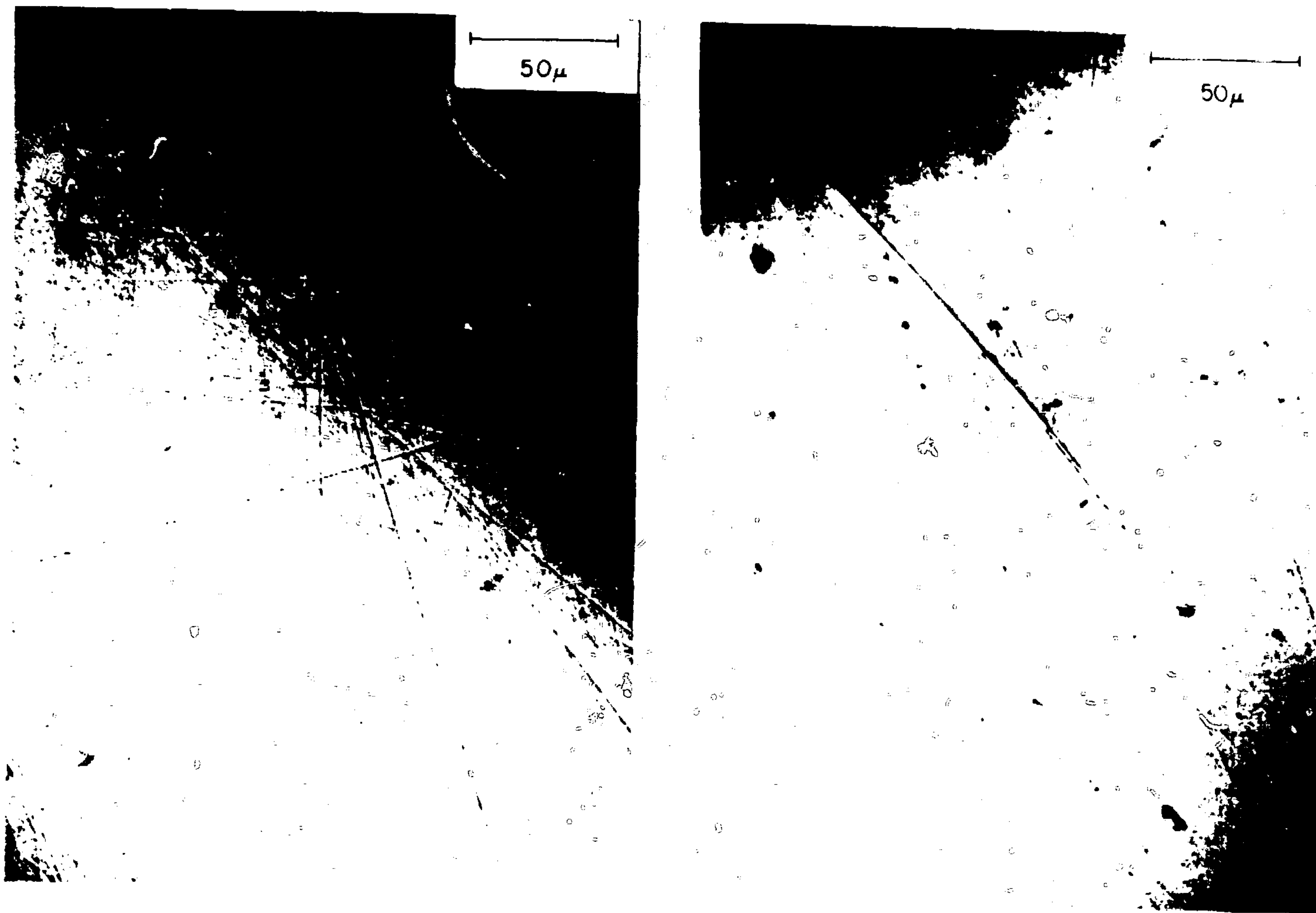


Fig. 4. Nomarski micrographs of the polished faces of the CVD samples shown in Fig. 3, x400:

a. Polished highly-faceted material shows a large number of scratch marks.

b. Polished amorphous surface results in fewer scratch marks, indicating this material may be more suitable for fine polishing.

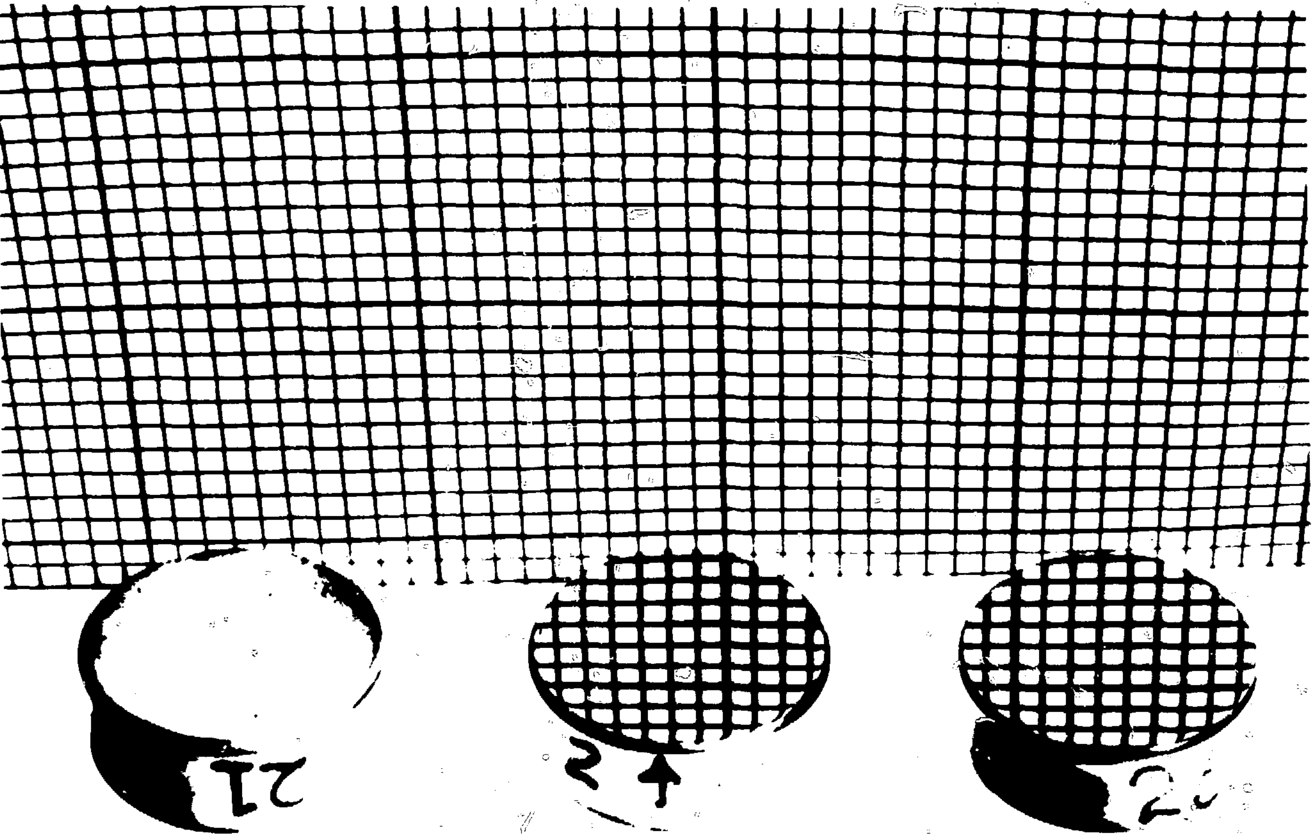


Fig. 5. Samples coated with CVD SiC by General Atomic Company. The substrates are 1" diameter by 3/8" thick, made from sintered-alpha SiC. An unpolished surface is shown on the left; the other two pieces are polished and appear nearly featureless under the SEM.

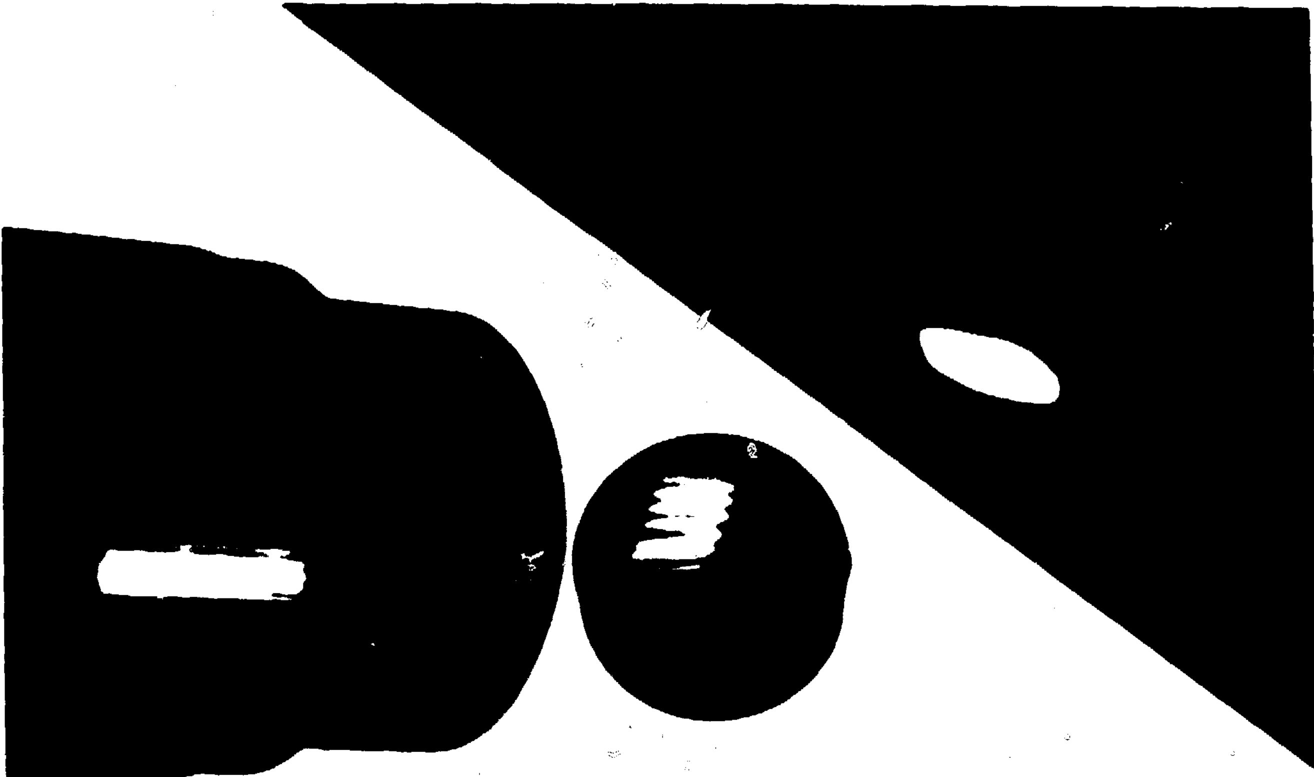


Fig. 6. Microscope illuminator is focused onto one of the polished surfaces in Fig. 5. Striations are evident that do not appear in the SEM photos at high magnification. Some of the diffuse scattering may be from the rough substrate reflecting through the semitransparent 0.001" thick coating layer.

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