Structural Analysis of Silicon Carbide Deposited by Gas-Phase Selective Area Laser Deposition (SALD)

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Abstract: Silicon carbide deposited by the gas-phase Selective Area Laser Deposition (SALD) process underwent extensive structural analysis in this investigation. The silicon carbide material was locally formed from a gas precursor mixture of tetramethylsilane and hydrogen, at a deposition temperature of approximately 1100°C and maintained by a closed-loop laser control system. Ground powder samples of the SALD silicon carbide material were examined by Magic Angle Spinning-Nuclear Magnetic Resonance, X-ray Diffraction and Transmission Electron Microscopy. The results from these analytical tools show a significant level of twinning in the SALD SiC material which explains the significant differences between the NMR and X-ray spectra.

Introduction: Gas-phase Selective Area Laser Deposition (SALD) is a laser-driven chemical vapor deposition (CVD) process that locally forms the desired solid material in the laser beam heated zone. A schematic of the process is found in figure 1. Silicon carbide has been repeatedly deposited from a gas mixture of tetramethylsilane (TMS, $Si(CH_3)_4$) and hydrogen in several SALD-based techniques, such as SALDVI and SALD Joining[1-4]. The SALD SiC material, as well as other, similar CVD SiC deposits, was previously revealed to be the beta, face-centered cubic crystalline polytype through x-ray diffraction analysis (XRD)[5-7]. Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) was performed on SiC SALD samples as a secondary identification tool but the resulting spectra showed significant deviation from the expected beta silicon carbide pattern. Further investigation using fine structure XRD pattern modeling and transmission electron microscopy (TEM) dark field imaging and selective area electron diffraction methods were undertaken to reconcile the initial XRD findings and the MAS-NMR results. The explanation focuses on the nano- and sub-nanometer structure in the SALD SiC material, specifically the formation of twins.

Experimental: The SALD silicon carbide material was fabricated using a continuous wave Neodynium:YAG laser (λ = 1.064 microns) directed into a stainless steel vacuum chamber. The gas precursor environment was a 1:2 ratio of TMS to hydrogen and the deposition temperature was approximately 1100°C, as maintained by the closed-loop temperature control program. After the silicon carbide deposited onto a silicon carbide substrate, the SALD material was broken off and ground to a powder with a mortar and pestle. This powder then underwent the various investigative procedures.

The magic-angle spinning method is the necessary technique for NMR analysis of inorganic solids. Until the early 1970's, NMR spectra of inorganics suffered from broad peak structure and high background noise due to orientation effects and nuclear interactions[8]. This was addressed by spinning the sample at an angle of 54.7° to the applied magnetic field. The magic angle orientation mitigated these secondary interactions and the resulting NMR spectra have sharper peaks and lower background noise. The SALD silicon carbide powder samples were packed into a zirconia pencil rotor and spun at the magic angle at a 5 kHz spinning rate in a Chemagnetics CMX300 NMR spectrometer. The spectrometer utiziled a commercial double-bearing 7.5 millimeter MAS probe with the following acquisition parameters: 90° pulse width for ^{29}Si, 40 kHz spectral width and Fourier transformation with 40 Hz line broadening. The chemical shifts presented in the spectrum are relative to the silicon environment in liquid TMS using an external sample of solid tetrakis-trimethylsilyl-silane (TTMS) as the secondary reference.

The x-ray diffraction experimental patterns were acquired with a Bruker 5005 x-ray diffractometer using a copper source. The x-ray diffraction pattern modeling originated from a computer simulation program that was devised to replicate x-ray diffraction patterns of dominantly beta silicon carbide. Based on considerations of the amount, type and manner of production of stacking faults in the material morphology, the diffraction simulation produces patterns by selecting the type and frequency of stacking errors in the beta polytype sequence, ABCABC[9,10]. This simulation generates 1000 silicon-carbon layers to form a supercell, with the layers labeled A, B or C depending on the atom position determined for the specific layer. The type of layer created depends on three user-controlled variables that set the probability of forming a stacking fault in a regular cubic lattice, the likelihood of whether the initiated fault continues and the distribution of faults in a certain region. After 15 supercells are formed, the model calculates structure factors and d-spacings in the 15000 layer structure for (hkl) planes in the 2θ range of interest. Diffraction intensities are evaluated on per volume basis, making the calculations independent of the supercell size. In the SALD SiC investigation, the 30° to 45° 2θ region was modeled to examine the background intensity surrounding the (111), 35.6° peak, the intensity of the (200), 41.6° peak and possible shifts in the peak positions.

TEM dark field imaging and selective area electron diffraction were performed on a Phillips EM420 unit with an accelerating voltage of 100 kilovolts.

Results: The typical SALD silicon carbide x-ray pattern is found in figure 2, with three dominant peaks at approximately 35.6°, 60° and 72°. The NMR spectra of SALD SiC (A), a 50/50 weight % alpha/beta SiC powder physical mixture(B), a 100% beta SiC powder standard (C) and a 100% alpha SiC powder standard (D) are shown for comparison in figure 3. The x-ray diffraction modeling results appear in figure 4. The black line pattern is from an experimental SALD SiC sample, while the gray line pattern represents the attempt of the computer model to match the experimental result. The accompanying stacking fault data that the model produced in replicating the experimental pattern is found in table 1. TEM bright field and electron diffraction images are presented in figures 5 and 6 respectively. The zone axis of the diffraction pattern from the FCC silicon carbide is [110].

Discussion: As mentioned previously, the SALD SiC XRD pattern indicates the 3C, beta polytype crystal structure, although the 4th main peak at 41.6° is not significant. The NMR patterns, which are discussed more fully in another publication[11], show significant variation of the SALD SiC from the one dominant peak pattern of the beta powder standard NMR spectra. Although the SALD pattern appears to be a mixture of the alpha and beta standards, the characteristic shape could not be reproduced by physically mixing the 2 polytypes in various ratios, including the 50:50 weight % combination in figure 3D. Because the NMR probes the local chemical environment at the Angstrom level, the SALD results point to a change in the atomic structure and order from the pure beta stacking sequence. The XRD modeling data support this hypothesis. The fine detail of the SALD XRD pattern shows a broad hump before the 35.6° peak and a very broad, low intensity peak at 41.6°. The model output pattern shows excellent correlation to the experimental pattern and the raw data indicates a significant presence of 1, 2 and 3 layer stacking faults, over 75% of the faults generated. The stacking sequences for these faults, i.e. AA'AA'AA' for 1 layer, ABA'B'AB for 2 layer and ABCB'A'C' for 3 layer, correspond to hexagonal alpha polytype regions of 2H, 4H and 6H respectively. These faults are twin structures, with a 180° rotation of orientation across the twin plane. Further modeling efforts showed that as the quantity of faults was reduced, the intensity and sharpness of the 41.6° peak increased.

The physical evidence of twins was provided by the TEM analysis. Twins are indicated in TEM bright and dark field images by alternating contrast bands in the twinned regions. This contrast alternation arises from the 180° phase orientation rotation of adjacent regions. Similarly, the electron diffraction patterns show diffraction spot reflections across the twin plane. These reflections are the result of two diffraction patterns superimposed onto one image again due to the orientation rotation caused by the twin. Multiple spots occur at expected diffraction positions except along the twin plane, which produces only one spot per position because the plane acts as the mirror plane. Streaking of the diffraction spots also points to the presence of twins. The TEM images in figures 5 and 6 show these anticipated features. The twin plane from the diffraction pattern in figure 6 is a (111) type as is typical in FCC materials. The twin bands in figure 5 range from .5 nanometer to several nanometers across. This is consistent with the belief that stacking disruptions led to the unique NMR results for the SALD SiC material. These twin features were widespread throughout the TEM SALD silicon carbide samples.

Conclusions: SALD silicon carbide is a bulk face-centered cubic crystalline material that shows a significant level of twinning in the stacking structure. These twin features are in effect alpha polytype, hexagonal domains on the Angstrom/nanometer scale. The presence of the alpha regions in the bulk material is the source of the unique NMR spectra and x-ray diffraction fine structure for the SALD silicon carbide material.

Acknowledgments: The authors would like to acknowledge Dr. Vijay Pujar and Dr. Sean Xie for their aid and effort during this project, as well as the partial funding support of the Office of Naval Research, grant # N00014-95-1-0978.

Figures and Tables

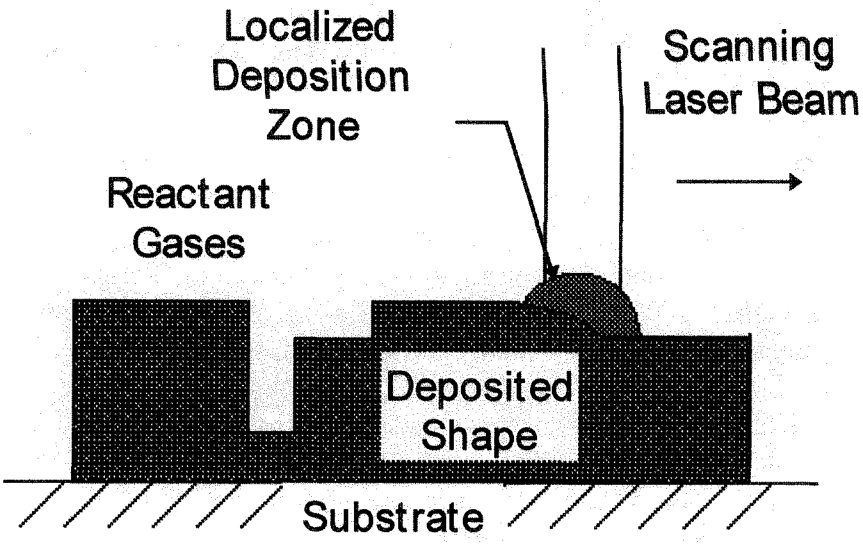

Figure 1: Schematic of Selective Area Laser Deposition (SALD) Process

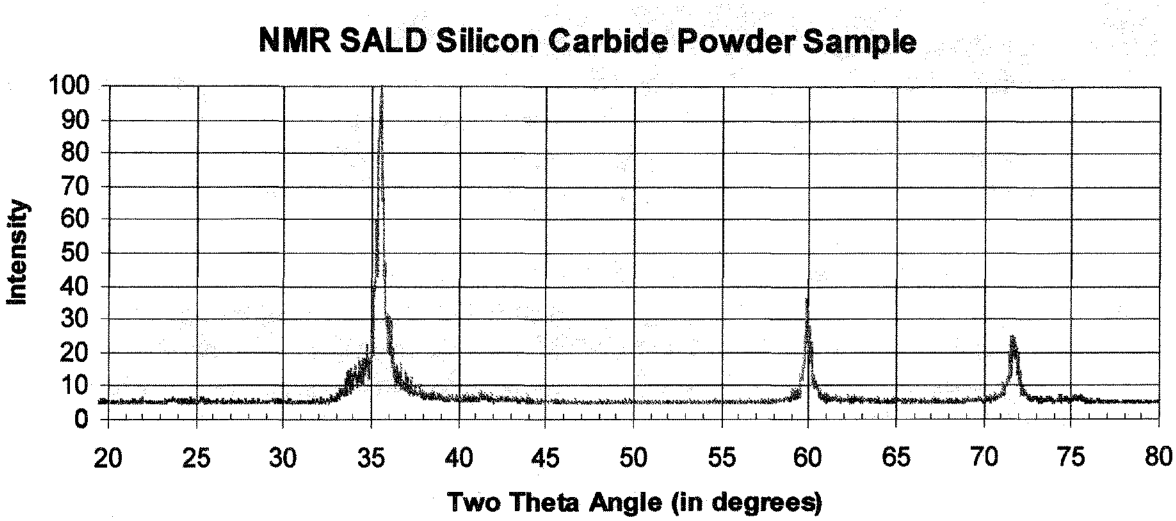

Figure 2: Powder X-ray Diffraction Pattern for Typical SALD Silicon Carbide Sample

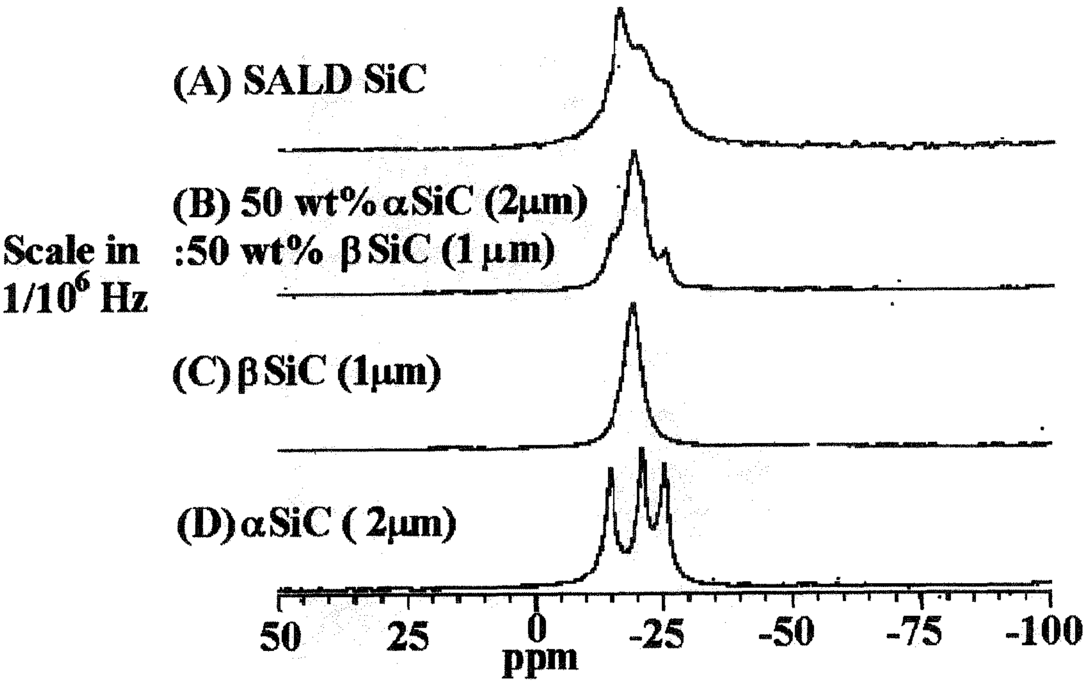

Figure 3: Magic-Angle-Spinning Nuclear Magnetic Resonance Spectra for SALD Silicon Carbide (A), 50/50 Weight % Alpha/Beta SiC Powder Mixture (B), 100% Beta Silicon Carbide Powder Standard (C) and 100% Alpha Silicon Carbide Powder Standard (D)

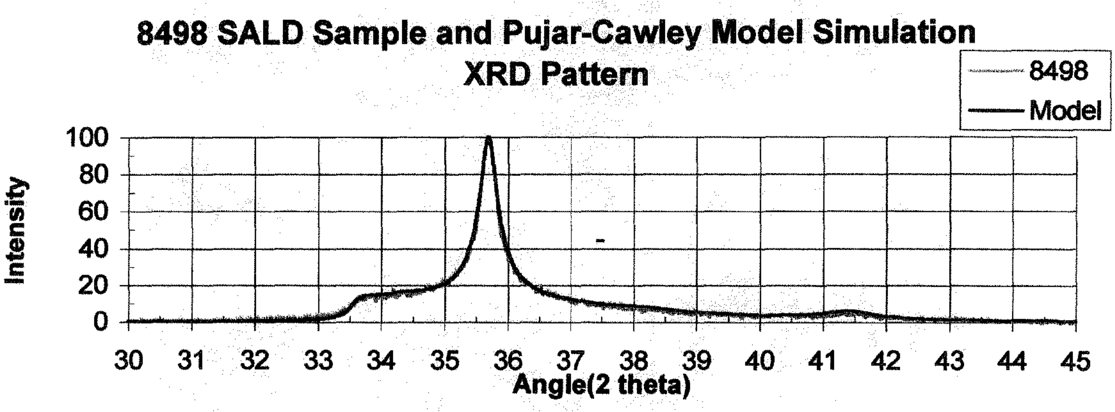

Figure 4: XRD Computer Model Simulation of Experimental SALD Silicon Carbide Pattern

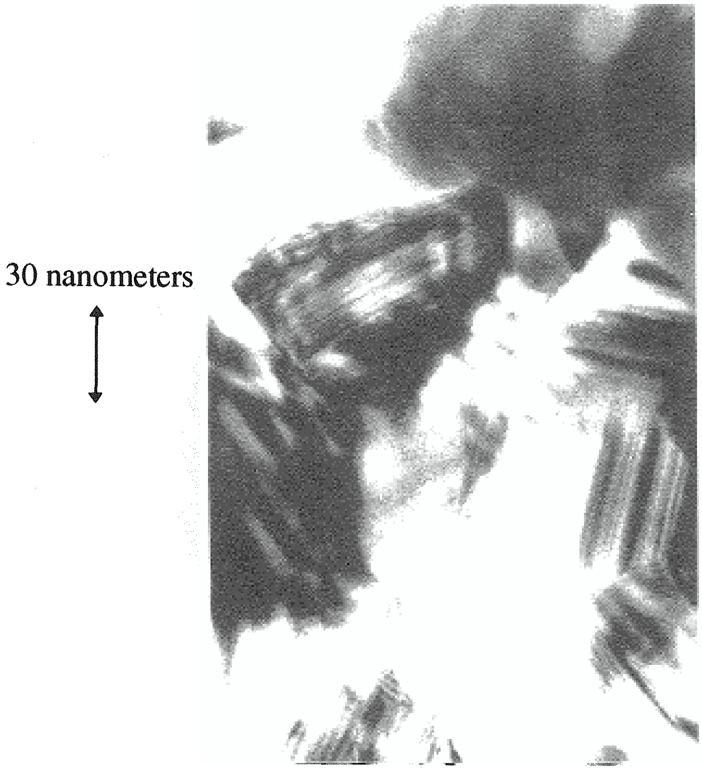

Figure 5: Bright Field TEM Image of Twin Bands in SALD Silicon Carbide

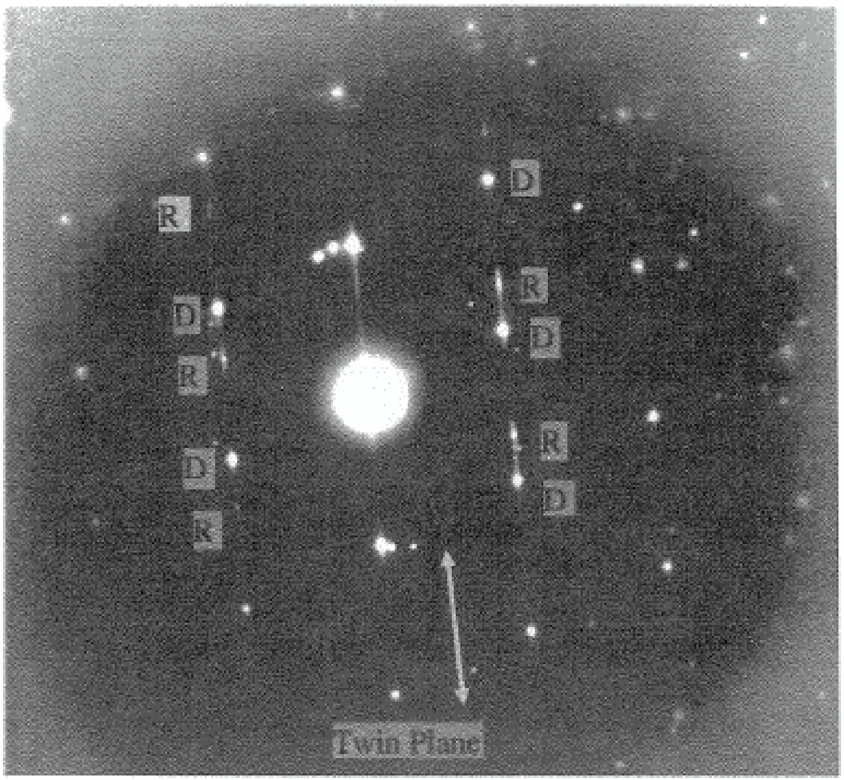

Figure 6: Electron Diffraction Pattern for SALD Silicon Carbide, Camera Length = 684 cm, [110] Zone Axis
(D = Diffraction spot, R = Reflected spot)

Fault Width	Frequency	Normalized Frequency
1	1160	0.2548
2	1121	0.2463
3	1133	0.2489
4	485	0.1065
5	233	0.0512
6	119	0.0261
7	63	0.0138
8	22	0.0048
9	20	0.0044
10	23	0.0051
11	26	0.0057
12	19	0.0042
13	14	0.0031
14	10	0.0022
15	6	0.0013

Table 1: Raw Fault Data from XRD Simulation Model Shown in Figure 4 (Note: 4552 Total Number of Faults)

Footnotes

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