# Selective Area Laser Deposition of Silicon Carbide

**James V. Tompkins and Harris L. Marcus**

*Center for Materials Science and Engineering*
*The University of Texas at Austin*

## Abstract

Selective Area Laser Deposition (SALD) is a Solid Freeform Fabrication approach which uses a moving laser beam to deposit solid material from a precursor gas. We have achieved a deposition rate of 1.5 mm/min for silicon carbide within the focused laser beam, sufficient for constructing three dimensional objects. Use of tetramethylsilane vapor yielded freestanding rods and uniform single layers. Critical issues include the effect of nucleation rate on material quality, thermal shock complications, and non-uniform growth.

## Selective Area Laser Deposition

The ability to develop a mature Solid Freeform Fabrication industry depends in part on materials processing technologies which can quickly and inexpensively produce three dimensional objects. Currently, many of the established rapid prototyping systems employ solid materials (often as powders) [1,2,3], and liquids (especially photopolymers) [4] for rapid prototyping applications.

Selective Area Laser Deposition (SALD) uses gas exclusively to produce solid material [5]. In this method, a focussed laser beam causes a precursor gas to chemically react to produce solid material only where the beam strikes a substrate. As the beam moves over the substrate, it leaves behind a trail of the material, which one may use to build up a solid object.

SALD offers several advantages. It can use a relatively simple mechanical system since it doesn't require precision powder or liquid delivery systems. SALD also offers spatial resolution which is not limited by powder grain size or finite thicknesses of powder layers. Further, depositing from a gas minimizes the porosity inherent with powders, suggesting full strength, structural parts are possible. SALD is not limited to successive planar cross sections of uniform composition. In principle, it offers a nearly unlimited ability to produce internal variations in composition by switching precursor gases, or possibly even to create internal voids or ducts.

The largest obstacle to making objects from gases is the low growth rates associated with conventional chemical vapor deposition (CVD), usually on the order of 100-1000 um/hr. SALD requires a deposition process with a much higher growth rate. Other important requirements are a deposit profile which is uniform both along and perpendicular to the scanning direction, and a good interface between scan lines.

## Silicon Carbide

Previous work on SALD investigated the pyrolysis of acetylene to deposit carbon [6]. This research focused on silicon carbide, as its extreme hardness and high melting temperature (2540 C) limit the conventional machining or casting of parts. Most silicon carbide parts are sintered at high temperature and pressure from silicon carbide powder with boron added as a binding agent. The rapid production of fully dense objects from silicon carbide without the costly processing steps and without the impurity of a binder material demonstrates unique advantages of the SALD process.

This study used tetramethylsilane ($Si(CH_3)_4$) as a precursor to deposit silicon carbide. It is a liquid which boils 26 C, giving a vapor pressure close to one atmosphere at room temperature, and makes a safe, convenient source of vapor. High purity tetramethylsilane is commonly used as a nuclear magnetic resonance (NMR) standard, making it readily available.

## Experimental Procedure

Fig. 1 shows a schematic of the SALD system. All depositions occurred within a vacuum chamber flushed with nitrogen and evacuated to a 5 mTorr base pressure. All experiments used tetramethylsilane vapor at 125 torr, drawn from a flask of liquid at room temperature outside the chamber. The chamber was not heated.

To selectively deposit silicon carbide, we used the focussed infrared beam from a 25W $CO_2$ laser. A 4.5 W beam focussed to a diameter of 1mm on an unheated substrate gave a bright plume of light at the substrate surface , indicating the presence of a thermal plasma [7]. We did not measure temperature within the plasma, although rough visual estimates are in excess of 1000 C.

The deposition chamber was translated on a computer controlled X-Y table, with the substrate moving relative to a fixed beam. Scan rates varied from 0 (stationary) to 400 um/sec. A stationary beam produced rods of material roughly the same diameter as the laser beam. The growth rates reported below came from dividing the resulting rod length by the elapsed time.

Alumina substrates were used because of their high temperature resistance and their lack of both silicon and carbon. Both solid sheets and powders were

tried, with powders having the advantage that they allowed a lower laser intensity to initiate growth. This is possibly due to greater absorption of the beam through internal reflection, or lower thermal conductivity.

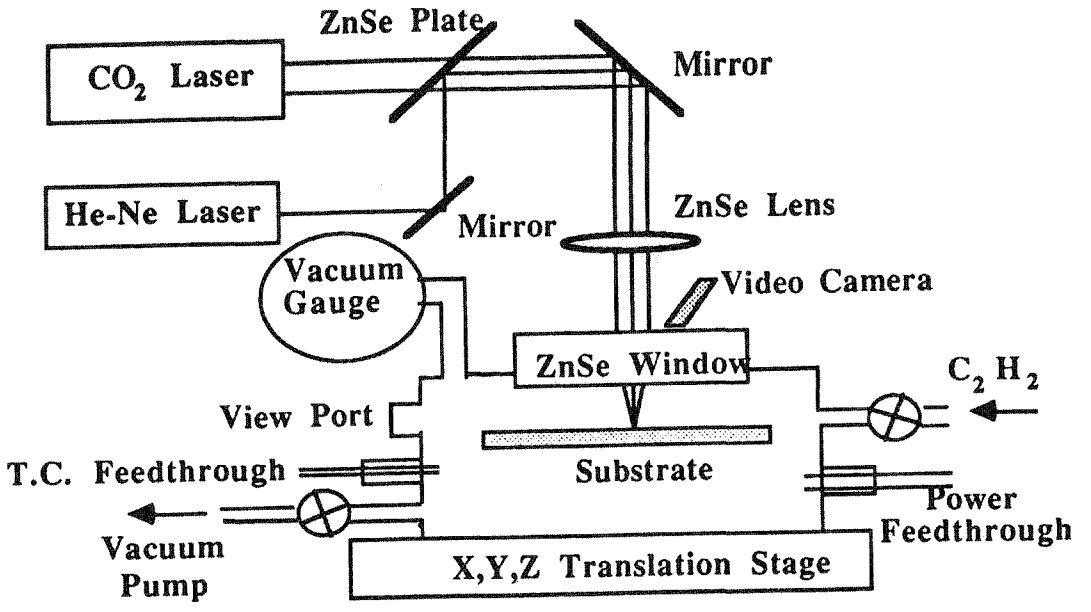


Fig 1. SALD System, Zong *et al* [8]

Results

The above conditions led to growth of a glossy black material. Measurement of rods grown in a stationary beam indicated growth rates of 1.5 mm/min, or 90,000 um/hr. This is approximately 180 times greater than the 470 um/hr [9] to 510 um/hr [10] reported for conventional CVD of silicon carbide from tetramethylsilane in hydrogen.

Several analytical results for the deposited material were consistent with those for amorphous silicon carbide. X-ray diffraction studies of the resulting material indicated that the material was amorphous, with no crystalline silicon, graphite, or silicon carbide peaks present. The material was also found to be harder than polycrystalline alumina in a scratch test. Auger spectra of the deposited material were compared qualitatively with a hot-pressed silicon carbide standard and showed a silicon to carbon ratio within six percent of the standard. In an additional experiment, samples placed in a furnace at 850 C in air for twenty hours showed a unmeasurable (0.001 g) weight loss while a similar quantity of graphite was completely consumed in less than two hours.

Slow scanning of the laser beam (20 um/sec) produced curved or articulated rods, showing that growth could be produced at least 45 degrees from the vertical direction of the laser beam. Faster movement of the beam (100-400

um/sec) gave a uniform line of material on the substrate surface. Rastering of the laser beam produced a square deposit as seen in Fig. 2. The interface between successive scans cannot be discerned after sputtering of the surface.

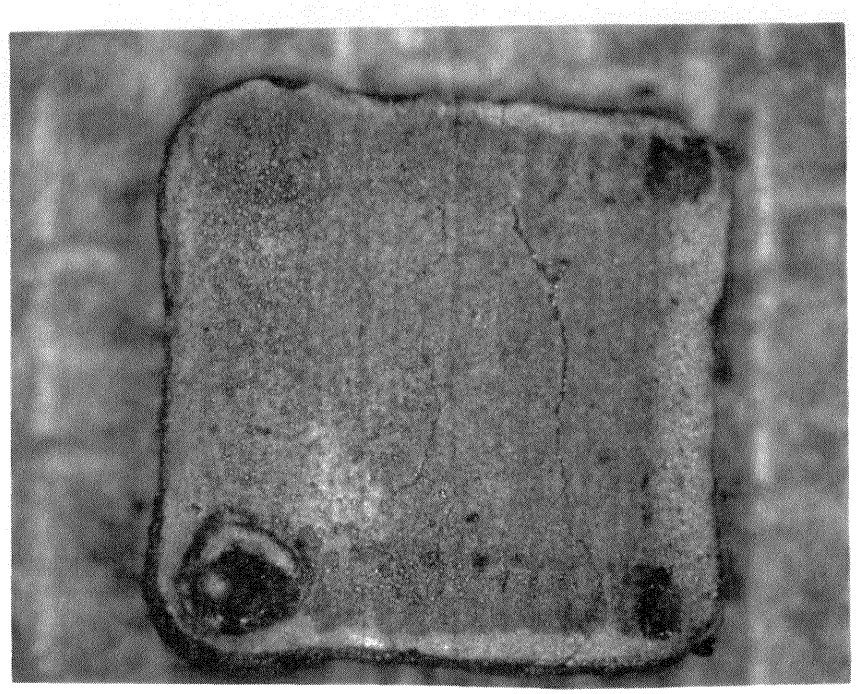

Fig. 2 Square from 3X3mm Raster, 400 um/sec, 100 um Line Spacing

Discussion

The material deposited from tetramethylsilane appears to be amorphous silicon carbide. The material is a very shiny black, and under a microscope interference colors indicate a very thin film which we believe is a self passivating layer of silica associated with residual oxygen in the system. We also hypothesize that the presence of the thermal plasma contributes to the high growth rates in a manner related to plasma enhanced CVD, although the higher partial pressure of tetramethylsilane and lack of hydrogen gas may also be responsible. Another factor may be the opportunity for diffusion of reactant to the deposition point in three dimensions, instead of the conventional diffusion through a boundary layer.

The nearly stoichiometric silicon to carbon ratio was remarkable. Tetramethylsilane contains four times the stoichiometric amount of carbon. However, the carbon is contained in methyl groups, and the molecule contains just enough hydrogen atoms for the methyl groups to ideally leave as methane. We anticipate that adding excess hydrogen would lower the carbon content further, possibly at some expense to the growth rate.

The apparent amorphous character of the material was not expected, however, we may speculate on its origin. The high growth rate would be consistent with a rapid nucleation rate during deposition. The large number of nucleation sites might occur due to the high concentration of tetramethylsilane or due to the actived species in the thermal plasma. A large number of nucleation siteds would prevent the growth of large, ordered crystals in the material. The absence of an X-ray diffraction pattern for crystalline beta-silicon carbide is consistent for amorphous material or very small crystals. SEM images of the material showed rounded structures without facets expected of crystalline material as seen in Fig. 3. For high resolution in SFF applications, the glassy, isotropic nature of amorphous material might be an advantage, since facets or preferred growth directions interfere with smooth planar growth.

After a short inert ion sputter in a Scanning Auger Microprobe, the oxygen content in the deposited material was below the detection limit. The low oxygen content was encouraging, indicating an absence of a $SiO_x$ phase in the bulk material. Although alumina was chosen to isolate the material from possible sources of carbon or silicon, alumina is susceptible to decomposition at high temperature, yielding free oxygen.

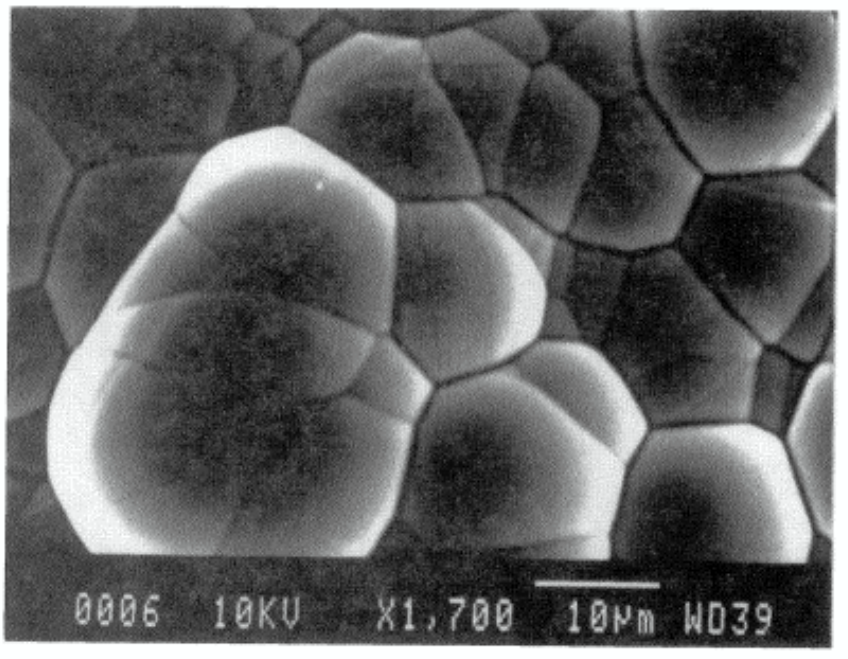


Fig. 3 SEM of SALD Silicon Carbide Rod, 4.5 Watts

We encountered two obstacles when we attempted to deposit thick or multiple layers of silicon carbide to produce three dimensional objects. First, when scanning over an existing layer, the steep, rapidly moving temperature gradient caused severe cracking in the underlying layer. The thermal shock combined with any residual stresses in the first layer cannot be resisted by the thin silicon carbide, even though silicon carbide has a good thermal shock resistance for a ceramic material. Several approaches may have to be employed in the future to alleviate this problem: First, the entire deposition area may be heated to a high temperature, reducing the thermal gradient needed. Secondly, a deposition chemistry which can use a lower temperature may be employed.

Another problem encountered is non-uniform growth in thick or multiple layers. Although the uniformity in a single layer seems quite good, the smallest projection from the surface becomes excessively hot during subsequent heating with the laser beam. This rise in temperature accelerates growth, making any microscopic projection unstable for extended growth. This is separate from the problem of localized growth due to a nucleation barrier observed by Zong in the SALD of pyrolytic carbon [11].

## Conclusion

We have successfully produced silicon carbide rods and single layers using the SALD process, demonstrating its potential as a rapid prototyping tool as well as a method for producing structural parts. The lack crystallinity may be explained by the extremely high growth rates achieved, and may be desirable where high resolution is needed. Thermal shock considerations may be solved in the near future using proposed techniques, but the instability of microscopic irregularities in the first layer will require further study.

The authors acknowledge the support of ONR grant N00014-92-J-1514 in funding this research. The assistance of Britton Birmingham and Steve Lin in this work is greatly appreciated.

## References


[1] Proceedings of the Solid Freeform Fabrication Symposium, edited by J.J. Beaman, Harris L. Marcus, David L. Bourell, and J. W. Barlow, The University of Texas at Austin, Austin,Texas, August 6-8, 1990

[2] Proceedings of the Solid Freeform Fabrication Symposium, edited by Harris L. Marcus, Joeseph J. Beaman,David L. Bourell, and Richard H. Crawford, The University of Texas at Austin, Austin,Texas, August 12-14, 1991.

[3] Proceedings of the Solid Freeform Fabrication Symposium, edited by Harris L. Marcus, Joseph J. Beaman, Joel W. Barlow, David L. Bourell, and Richard H. Crawford, The University of Texas at Austin, Austin,Texas, August 3-5, 1992.

[4] Jacobs, Dr. Paul F., and Jan Richter, "Advances in Stereolithography Accuracy", Proceedings of the Solid Freeform Fabrication Symposium, edited by Harris L. Marcus, Joeseph J. Beaman,David L. Bourell, and Richard H. Crawford, The University of Texas at Austin, Austin,Texas, August 12-14, 1991.

[5] Zong, G., Yves Jacquot, W. Richards Thissell, and H.L. Marcus, "Solid Freeform Fabrication Using Selective Area Laser Deposition", Plasma and Laser Processing of Materials, edited by K. Upadhya, The Minerals, Metals, and Materials Society, 1991.

[6] Zong, G., J.V. Tompkins, W.R.Thissell, E. Sajot, and H.L. Marcus, "Processing Problems Associated With Gas Phase Solid Freeform Fabrication Using Pyrolytic Selective Area Laser Deposition", Proceedings of the Solid Freeform Fabrication Symposium, edited by Harris L. Marcus, Joeseph J. Beaman,David L. Bourell, and Richard H. Crawford, The University of Texas at Austin, Austin,Texas, August 12-14, 1991, p.271

[7] Radziemski, Leon, and David A. Cremers, Laser Induced Plasmas and Applications, Marcel Drekker Inc., New York, NY, 1989 pp 327-9

[8] G. S. Zong, R. Carnes, H. G. Wheat, and H. L. Marcus, "Solid Feeform Fabrication by Selective Area Laser Deposition", Proceedings of the Solid Freeform Fabrication Symposium, edited by J.J. Beaman, Harris L. Marcus, David L. Bourell, and J. W. Barlow, The University of Texas at Austin, Austin,Texas, August 6-8, 1990

[9] Figueras, A., S. Garelik, J. Santiso, R. Rodroguez-Clemente, B. Armas, C. Combescure, R. Berjoan, J. M. Saurel, R. Caplain, "Growth and Properties of CVD-SiC Layers Using Tetramethylsilane", Materials Science and Engineering, Volume B11, Nos 1-4, January 15, 1992, pp 83-88.

[10] Figueras, A., R. Rodroguez-Clemente, S. Garelik, J. Santiso, B. Armas, C. Combescure, A. Mazel, Y. Kihn, J. Sevely, "Influence of H2 Partial Pressure on the Morphology and Crystallization of SiC Layers Obtained by LPCVD Using Tetramethylsilane", Journal de Physique IV, Colloque C2 Supple. au Journal de Physique II, Volume I, September 1991, pp C2-225-232

[11] Zong, G., J.V. Tompkins, W.R.Thissell, E. Sajot, and H.L. Marcus, "Processing Problems Associated With Gas Phase Solid Freeform Fabrication Using Pyrolytic Selective Area Laser Deposition", Proceedings of the Solid Freeform Fabrication Symposium, edited by Harris L. Marcus, Joeseph J. Beaman,David L. Bourell, and Richard H. Crawford, The University of Texas at Austin, Austin,Texas, August 12-14, 1991, p.271