

Advances in Selective Area Laser Deposition of Silicon Carbide

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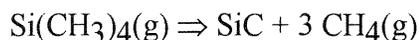
Abstract

Selective Area Laser Deposition (SALD) is a Solid Freeform Fabrication (SFF) technique which uses a scanning laser beam to produce solid material by locally decomposing a gas precursor. In this work, a focused CO₂ laser beam strikes a substrate in the presence of tetramethylsilane (TMS) or diethylsilane (DES), producing silicon carbide objects with high density and no binder phase. Recent investigation has yielded growth rates up to 2.7mm/min in the beam area, and has eliminated previously noted contamination of the optics by a byproduct which mass spectroscopy identifies as silicon dioxide. This paper reviews a cause of non-uniform growth and demonstrates the addition of hydrogen and reduced scan speeds to make multilayer parts. In addition, it presents a method for in-situ measurement of height of deposited material.

Introduction

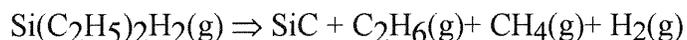
Selective Area Laser Deposition [1] describes a rapid prototyping process in which a moving laser beam causes localized decomposition of a precursor gas, creating solid material. A computer containing specifications for a three dimensional object controls the motion of an x-y table, which moves the beam relative to a substrate surface. The moving area heated by the beam dictates where material will be added, building up solid material (metal, ceramic, glass, etc.) in the desired shape for either prototype or structural parts.

This paper reviews recent progress in SALD employing tetramethylsilane (Si(CH₃)₄) and diethylsilane (H₂Si(C₂H₅)₂) to produce silicon carbide. Pyrolysis of tetramethylsilane has been investigated by Figueras et al in the growth of silicon carbide films [2]. Tetramethylsilane decomposes according to the following overall reaction:



The reaction proceeds exothermically, with an enthalpy change of -73.75 kcal/mole [3].

We also considered an alternative precursor, diethylsilane. The molecular formula for diethylsilane suggests the following overall reaction:



Diethylsilane offered the possibility of lower deposition temperatures, as both the hydrogen and ethyl groups display less electronegativity and should ease decomposition relative to the methyl groups in tetramethylsilane.

A previous paper reports the fabrication of single layer silicon carbide objects from tetramethylsilane by Selective Area Laser Deposition [4]. Thermal shock and uneven growth posed the greatest obstacles to the production of larger, more general shapes. The investigation of rod growth with a stationary beam produced growth rates of up to 1.6 mm/min. The following describes the most recent advances in producing more complex, multilayer silicon carbide objects, including increased growth rates, more even growth, and reduction in the effects of residual oxygen on the process.

Apparatus

The equipment setup (Fig. 1) varies somewhat from early SALD work [5]. Vapor drawn from a flask containing liquid tetramethylsilane (vapor pressure 755 Torr) or diethylsilane (85 Torr) at ambient temperature fills a vacuum chamber. A computer controlled x-y table supports a CO₂ laser and associated optics which produce a focused beam passing through a ZnSe window into the chamber. A firmly packed powder bed within the vacuum chamber serves as a substrate. Movement of the table scans the beam over selected areas of the substrate, where

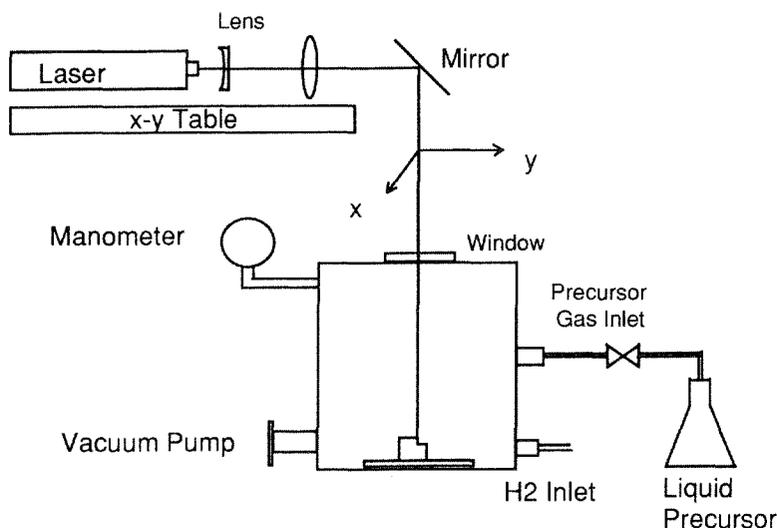


Fig. 1 SALD System Schematic

pyrolysis of the tetramethylsilane or diethylsilane produces silicon carbide. In a departure from the earlier system, we have added a small fan with a brushless DC motor inside the chamber to provide forced convection to the deposition area similar to that in a flowing gas system.

Experimental Procedure

The vacuum chamber underwent multiple cycle purges with nitrogen to base pressures of less than 10^{-2} Torr. The system did not undergo a bakeout between trials. The substrate consisted of firmly packed 16 μ m silicon carbide powder. Powder provides greater absorption of the beam, as well as less conduction of heat away from the deposition point, assisting in initiation of the SALD process.

Precursor gas pressure ranged from 20-140 Torr for tetramethylsilane. The upper limit reflects previous problems experienced with fogging of the ZnSe window by decomposition products at higher pressures. An equilibrium vapor pressure of 85 Torr at room temperature limited diethylsilane pressures to 85 Torr or less. Where indicated below, we also added chromatograph grade hydrogen gas at pressures up to 100 Torr.

Two successive ZnSe lenses acted to focus the beam from the CO₂ laser, producing an estimated 400um spot size (1/e²). Previous measurements of absorption by tetramethylsilane provided a pressure/absorption correction factor to achieve a constant intensity at the substrate surface of six watts regardless of pressure. Trials for diethylsilane represent the first investigation for this precursor, and considerations outlined below prevented the acquisition and use of correction curves for uniform power at the surface.

Scanning of the laser beam typically took place at 80-100 um/sec. We have not thoroughly investigated a full range of scan speeds, and future work will address the determination of an optimal scan speed. All scanning patterns consisted of parallel lines with a spacing of 100 um.

Results

As seen in Fig. 2, we observed growth rates as high as 2.7 mm/min. The previous maximum rate of 1.6mm/min occurred at 80 Torr of TMS. Rates had previously decreased at pressures over 80 Torr, due in part to clouding of the ZnSe window by precipitation of a reaction byproduct. The data shown apply to rods grown with a stationary beam for 5 minutes in pure tetramethylsilane.

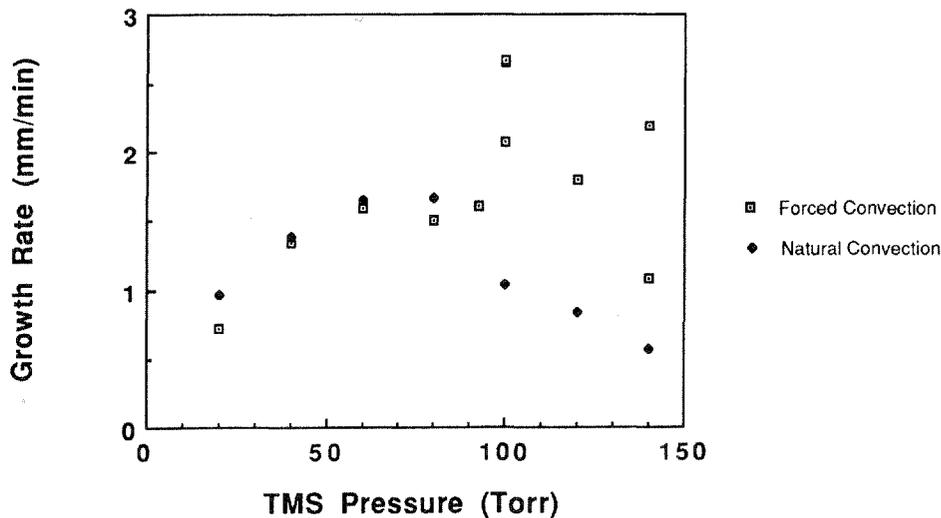


Fig. 2 Growth rate vs. TMS pressure

The improvement in the rate may have resulted from the addition of a forced convection component in the mass transport mechanism. The variation seen in growth rates probably results from an irregular flow pattern from the small fan; for example, a small lateral displacement relative to the fan might greatly affect the flow velocity. The difficulty of exactly reproducing the positioning of the deposition point relative to the small fan used in these experiments

probably accounts for much of the scatter observed in rate data. Mode hopping in the laser, resulting in fluctuations in output power as described later in this paper, may represent an additional source of variation.

Airflow from the fan offers an additional benefit: in previous SALD experiments, natural convection from the heated area carried a relatively undiluted stream of heated reaction byproducts upward along the beam path, ultimately striking surfaces on optical components such as the ZnSe window. At these surfaces, a solid material precipitated from the gas, leading to absorption of the beam. The addition of forced convection dispersed this stream of waste gas leaving the deposition site, greatly reducing clouding of the optical path.

Trials with diethylsilane did not show significant growth except at very low pressures. Observation of the substrate showed no heating of the surface even at the highest available laser settings (30 Watts). Only at pressures below 10 Torr did the beam have a noticeable effect on the surface, and at 10 torr a small amount of growth occurred. We interpret this as an indication of very strong absorption of the 10.6 μm wavelength, requiring further investigation. Although the laser could not deliver the desired six watts to the substrate surface, growth of silicon carbide at pressures below 10 Torr suggest that solving the absorption problem may allow diethylsilane to serve as a suitable precursor.

The issue of growth rate represents a critical concern in the development of SALD technology. The data shown above for tetramethylsilane represents nearly a doubling of the growth rate over that previously reported. Fig.3 shows an example of a 3-D silicon carbide object. The scale of the object, approximately one inch, indicates the capability of SALD in its current state. The three horizontal appendages contain a 1mm thick layer of deposited silicon carbide. This material has a durable and solid feel, but definitive density and strength data require further investigation.

As mentioned above, previous work had revealed a problem with contamination of the optics in the chamber due to a byproduct of the deposition reaction. Mass spectroscopy using electron impact ionization identified the solid byproduct precipitating on the reactor walls as well as on the ZnSe window as pure SiO_2 . Based on this information, three steps have eliminated the contamination problem: drying the substrate in vacuum for 24 hours prior to deposition, redesigning the precursor flask to eliminate exposure to oxygen-bearing vacuum grease, and adding hydrogen gas. Hydrogen acts to getter any available oxygen to form water, which adsorbs onto the chamber wall. Adding hydrogen to the tetramethylsilane has dramatically reduced the formation of silicon dioxide, and experiments involving up to twenty hours of deposition have not resulted in any visible fogging of the optical components. However, hydrogen slows the deposition rate significantly: 100 Torr of hydrogen reduces the rate by approximately a factor of five. Future work will investigate the minimum pressure of hydrogen needed as a function of tetramethylsilane pressure to prevent silicon dioxide formation.

Although silicon carbide generally has excellent thermal shock resistance for a ceramic material, thermal shock also presented difficulties in SALD, specifically in the growth of multiple layers of material. Scan rates of 400 $\mu\text{m}/\text{sec}$ produced solid single layers of material, suitable for analysis by XRDS, SEM, scanning auger spectroscopy, or for annealing experiments in a furnace. However, deposition of a second layer resulted in severe thermal shock caused by the steep, moving thermal gradient, fracturing the original layer. Reducing the scan speed to 80-100 $\mu\text{m}/\text{sec}$ reduces this problem. Two separate contributions may account for this: first, the initial layer of material has greater thickness and therefore greater strength; and second, the

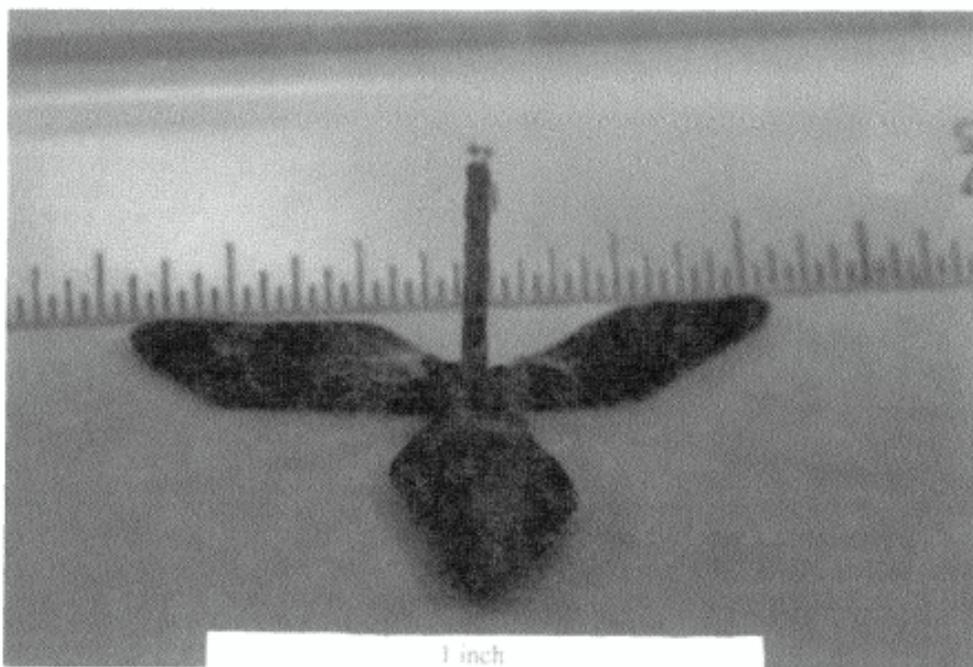


Fig. 3 “Stirrer” created in 3 hours 15 minutes from tetramethylsilane.

slower scan rate induces a proportionately lower thermal shock on the material. Thermal shock under current conditions no longer interferes with growth of multiple layers of silicon carbide.

The requirement to heat the deposition surface from above with laser radiation as opposed to heating the substrate from below as in conventional CVD creates a unique challenge in SALD: any projection above the planar surface of the material suffers less conduction into the underlying solid, causing it to retain more of the incident energy. This causes it to grow faster, and an unstable situation exists which we refer to as preferential growth. An instability in deposition rate identified during rod growth compounds the problem by actually initiating projections along the deposition path. During growth rate measurements using a stationary beam, an unexpected periodic variation appeared in rod diameter, referred to hereafter as “beading”. Fig. 4 shows an extreme case of this. This instability may also exhibit itself in the growth of single or multiple layers of material, but became directly observable during the growth of rods. Beading results from several physical phenomena. Birmingham [6] identified small periodic fluctuations in the CO₂ laser, and later showed that the associated shift in wavelength caused by mode hopping created a dramatic shift in absorption by the gas. Further, he showed that reflectivity of the silicon carbide powder and deposit also varied sharply in the region in which the CO₂ laser's mode hopping occurred. The period of the beading events corresponds very closely with the established period of mode hopping in the CO₂ laser.

We employ two approaches to minimize the problem of localized growth: reducing the scan rate reduces the thermal gradient between the substrate surface and the underlying material, reducing heat flow into the substrate. Also, the addition of hydrogen increases the rate of

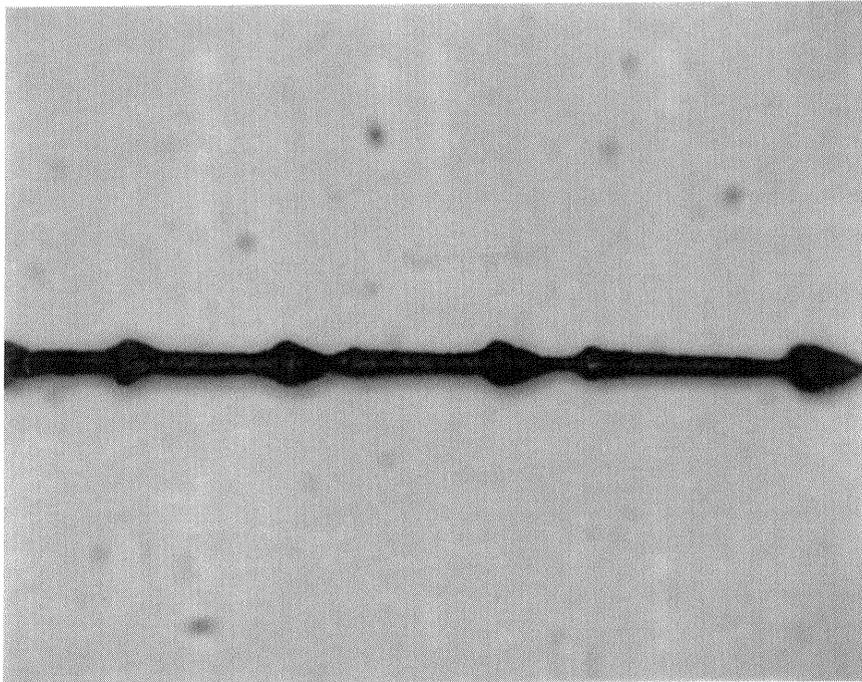


Fig. 4 Example of “beading” occurring during rod growth

etching (reverse reaction) of silicon carbide at the higher temperatures experienced by projections on the surface. Although these approaches reduce preferential growth, the answer ultimately lies in the use of precursors with lower deposition temperatures to further reduce the thermal gradient in the material, and hence conduction into the substrate. Such precursors exist but require complex and critical handling procedures. In addition, SALD requires a laser with a wavelength appropriate to the chemical and physical properties of the material produced.

In-situ deposition thickness measurement approach

Development of an in-situ deposition thickness measurement technique is critical to control the height of the different shapes built up by the SALD process. One method consists of using the scattered energy of the He-Ne laser focused beam to make an image of the spot. This method is easier than the interferometric methods and does not require polished surfaces, nevertheless its sensitivity may approach that of medium accuracy interferometry. This system is shown schematically in Fig. 5.

Measuring principles

The He-Ne laser beam is focused onto the surface of the growing object by the lens L1. When the surface is exactly at the focal plane of the lens, a large fraction of specular reflection light is backscattered and collected by the lens L2 to project the spot image onto the position-sensitive detector (PSD). When the deposit grows, the spot image moves along the detector which is an optoelectronic sensor that provides continuous position data of a light spot traveling over its surface. An aperture is used in front of L2 to improve the resolution by decreasing the

spotsizes. Knowing the displacement d along the detector we can estimate the growth G by the following formula:

$$G = (X \sin \alpha / X') * d$$

$(X \sin \alpha / X')$ is a ratio associated with the position of the lens L2.

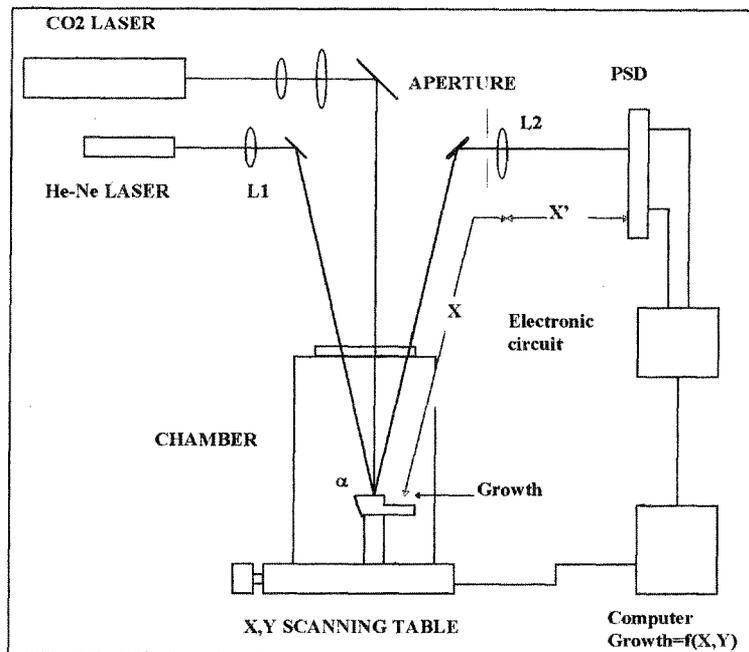


Figure 5
Schematic of the deposition thickness measurement system

The Detection

When a light spot falls on the PSD, an electric charge proportional to the light energy is generated at the incident position (Fig.6). This electric charge is driven through the resistive P-layer and collected by the electrodes. Since the resistivity of the P-layer is uniform, the photocurrent collected by an electrode is inversely proportional to the distance between the incident position and the electrode.

The following formulas give us an estimation of the incident position depending on the two outputs I1 and I2.

$$\begin{aligned} I_1 &= I_0(L-d)/2L \\ I_2 &= I_0(L+d)/2L \end{aligned}$$

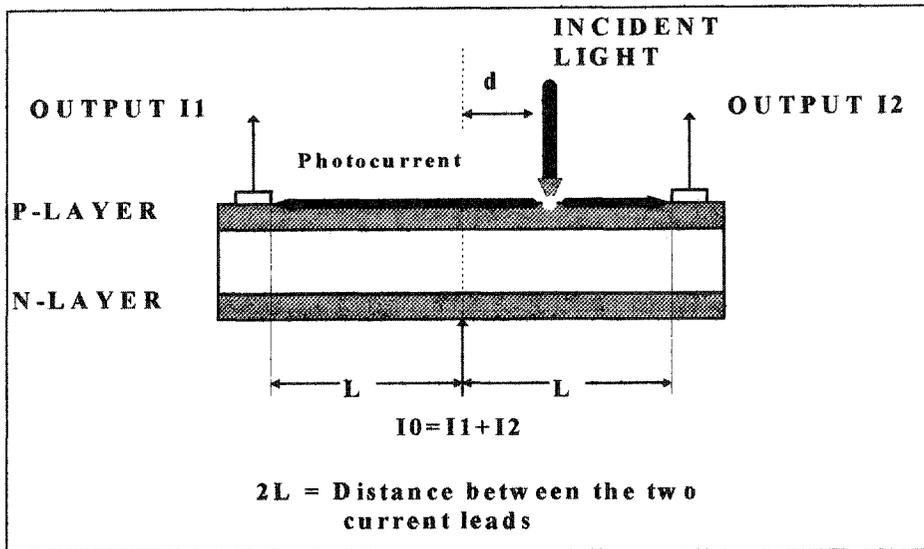
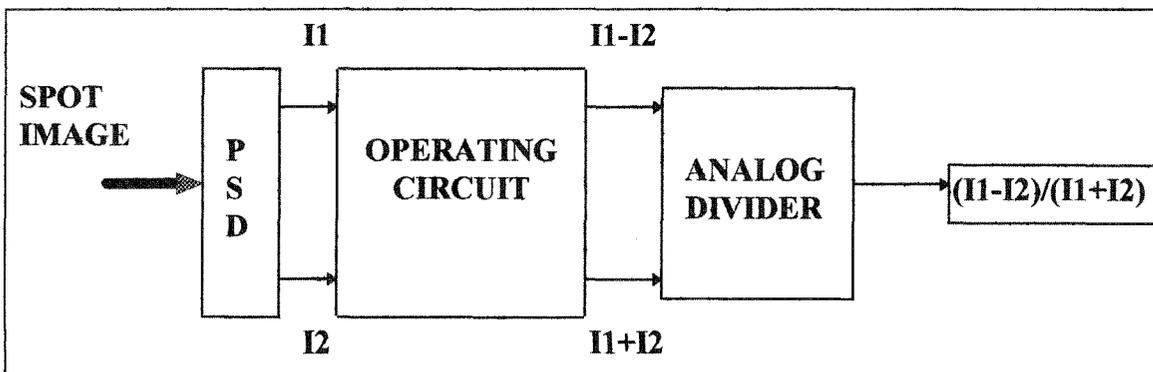


Figure 6
Schematic of the position-sensitive detector

One of the most important problems that we met is the specular reflection on the rough surface of the silicon carbide, which causes a variable incident intensity of the spot image (I_0 variable). To avoid that problem an operating electronic circuit was built in order to calculate the ratio: $(I_2 - I_1)/(I_2 + I_1) = d/L$ which is independent of the reflected light intensity.



Finally we have :

$$G = (X \sin \alpha / X') * L * (I_2 - I_1) / (I_1 + I_2)$$

Results

Initially, different measurements were made by changing the ratio ($X\sin\alpha/X'$). The spot was directly projected onto a fluorescent screen. The smallest displacement d resolvable was $d = 0.5$ mm which corresponds to $30\ \mu\text{m}$ of growth with a ratio of $(X\sin\alpha/X') = 0.06$. The PSD will be used to improve the position resolution of the spot image. A detected spot displacement of $150\ \mu\text{m}$ is possible with such a detector which corresponds to a resolvable $10\ \mu\text{m}$ of growth for the same ratio $(X\sin\alpha/X') = 0.06$. The dynamic range linearity (Fig.7) and errors (Fig.8) were estimated by placing a sample that was a flat surface of silicon carbide at the plane $G = 0$ and moving the sample in the Z direction.

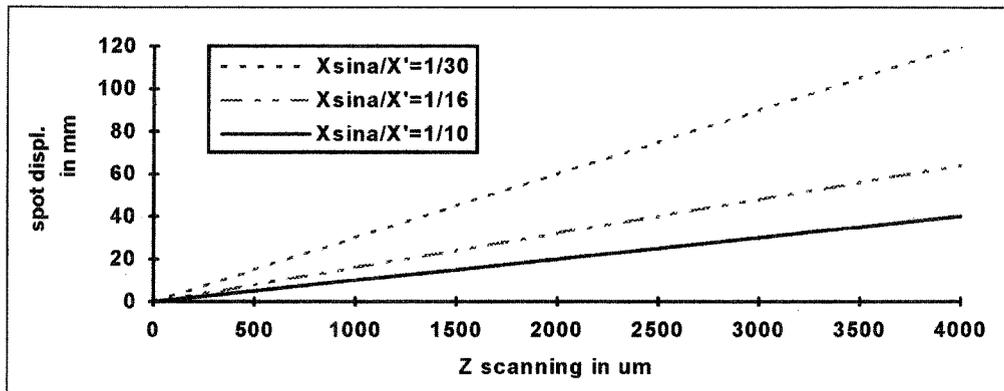


Figure.7
The displacement of the spot (mm)
function of the Z-scanning

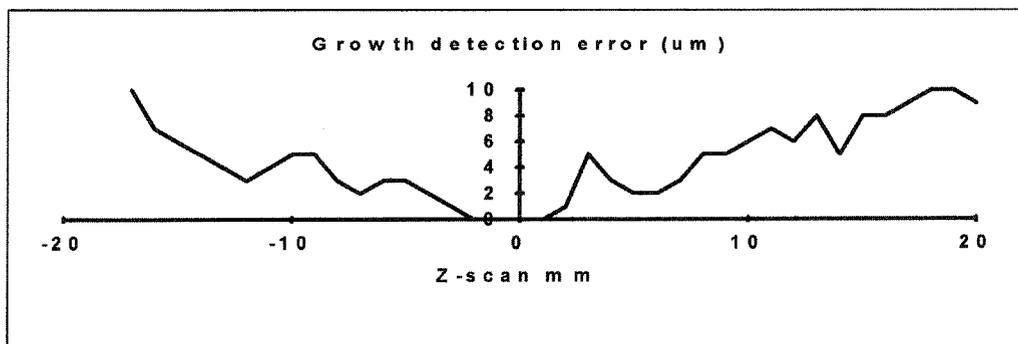


Figure.8
Growth detection error in μm

Conclusion

The above paper describes continuing progress toward a SALD technology capable of producing prototype as well as structural parts. The current process already yields dense silicon carbide free of the glassy binder phases which typically compromise high temperature resistance. The alternative precursor, diethylsilane, shows incompatibility with CO₂ lasers, but growth at low pressures with a greatly attenuated beam indicates its potential for lower deposition temperatures. The process continues to produce higher growth rates, and thermal shock and contamination of the optical path no longer pose significant obstacles in the practical matter of producing large scale parts. Additionally, an in-situ method for measuring height of the material following deposition represents a step toward actively controlling the uniformity of deposition height in spite of variations in deposition rate. The ability to produce solid objects on a useful scale (approximately 1 inch) in a matter of hours represents a substantial advance in the area of SALD.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of ONR grant N00014-92-J-1514 and Texas ATP grant 351.

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