Processing Problems Associated with Gas Phase Solid Freeform Fabrication Using Pyrolytic Selective Area Laser Deposition

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Abstract

Concerns critical to selective area laser deposition are discussed. Variables affecting deposition rate, dimensional control, and surface uniformity are analyzed. Localized growth results in undesirable morphology, and contributing factors are cited. Catalytic powders increase nucleation rate and provide superior temperature profiles resulting in good surface uniformity. Specific process control devices are investigated.

1. Introduction

Selective area laser deposition (SALD) is a solid freeform fabrication (SFF) process in which a laser beam interacts with a precursor gas to selectively deposit material. The laser beam is scanned by a computer program to produce a three dimensional object in a manner analogous to selective laser sintering [2,3]. The pyrolytic SALD of arbitrary three-dimensional shapes presents unique problems and issues which are quite different from those of selective layer sintering or thermal CVD thin film process. The key issues in an SALD process are dimensional control, deposition rate, deposit surface uniformity, and deposit properties. This paper identifies the processing problems associated with gas phase SFF using SALD and discusses the progress made in solving them.

2. Dimensional Control in Pyrolytic SALD

Deposition induced by laser heating is characterized by localization or area selectivity. The spatial resolution in a SALD process depends upon laser spot size and intensity, scanning speed, thermal properties of the substrate and deposit, and type of chemical reactions involved. When a substrate is heated by a focused laser beam, the surface temperature profile is different from the Gaussian beam intensity profile, decreasing gradually with distance from the center depending strongly on the thermal properties of the surface [4]. Excellent localization of deposited films can be obtained since deposition rates depend strongly on the surface temperature. Interestingly, the deposition area can be smaller than the focused laser beam since the local energy flux controls the local temperature.

Pyrolytic SALD experimental results showed that increasing laser power decreases the spatial resolution for the steady state growth [5]. This dimensional control can be understood by referring to Figure 1. The surface temperature distribution is a Gaussian function and the reaction occurs over that part of the Gaussian profile which is above the threshold temperature, I_T. The Gaussian temperature distribution on a given substrate surface depends on the laser power input when the laser beam is fixed on the substrate . The higher the laser power, the higher the peak temperature and the broader the Gaussian temperature distribution for a constant beam scan speed. The variation in the Gaussian temperature distribution is also a strong function of the laser scanning speed [6].

The dimensional control ability in the SALD can also be achieved by optical means. When the substrate surface is placed in the focal plane of the laser beam carbon rods grow in uniform

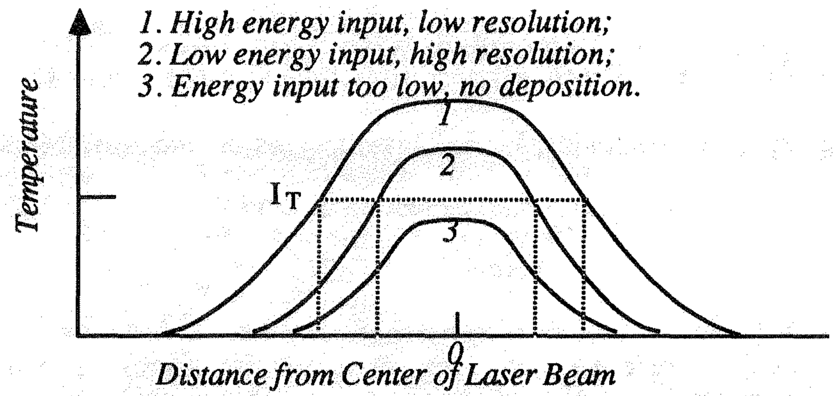


Fig. 1 Temperature distribution on a surface irradiated by a Gaussian laser beam.

diameter along the axis of the laser focus (Fig. 2a). After growing out of the regime of focus length, rods change their diameter according to the laser beam width (Fig. 2b) modified by the reduced energy density. The change in energy density could be adjusted by increasing laser power of the defocused laser impinging on the sample. To accomplish this a laser control system was designed. This control of laser power is also necessary to compensate for local variations in thermal or optical properties or geometry, or to adjust for different scan rates. This is currently accomplished by altering the length of laser bursts with a voltage controlled pulse width modulator. By varying the duty cycle of the laser bursts (0-100%), the average power supplied to the substrate is varied in a linear fashion. Voltage control is compatible with many types of computer I/O cards and software. In addition to addressing the above problems, being able to program laser power output makes it convenient to run experiments such as ramping power to find a level that gives an optimum deposition rate. Laser power requirements for each point in the deposition path might be predicted from a mathematical model of the object to be fabricated, but a more likely alternative would be to use a closed loop type of process control which measures temperature or growth rate itself during deposition. This will be discussed in a following section.

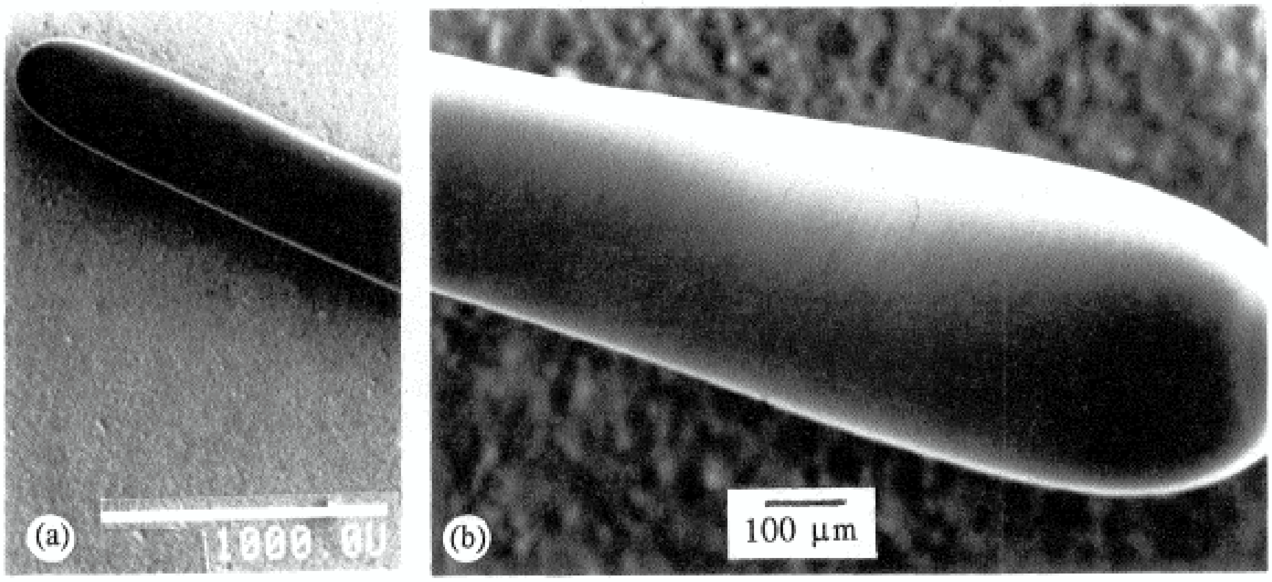


Fig. 2 Carbon rod deposited from acetylene on alumina substrate, **(a)** at focus plane of the laser beam, **(b)** at near-under-focus of the laser beam.

3. Nucleation and Instabilities

In a SALD process, the preferred line morphology is a flat-topped microstructure with constant thickness and width along the line. However, this morphology has not been achieved to date. Figure 3a shows a line deposited on an alumina substrate. The desired localized growth was observed. There are many probable reasons responsible for its nonuniform morphology, such as poor, nonuniform surface preparation, unsatisfactory control of process parameters, instabilities inherent in the SALD process, including the changes in thermal and optical conditions that occur when the deposited layer replaces the substrate as the deposition template, and the heat released during the exothermic decomposition of acetylene.

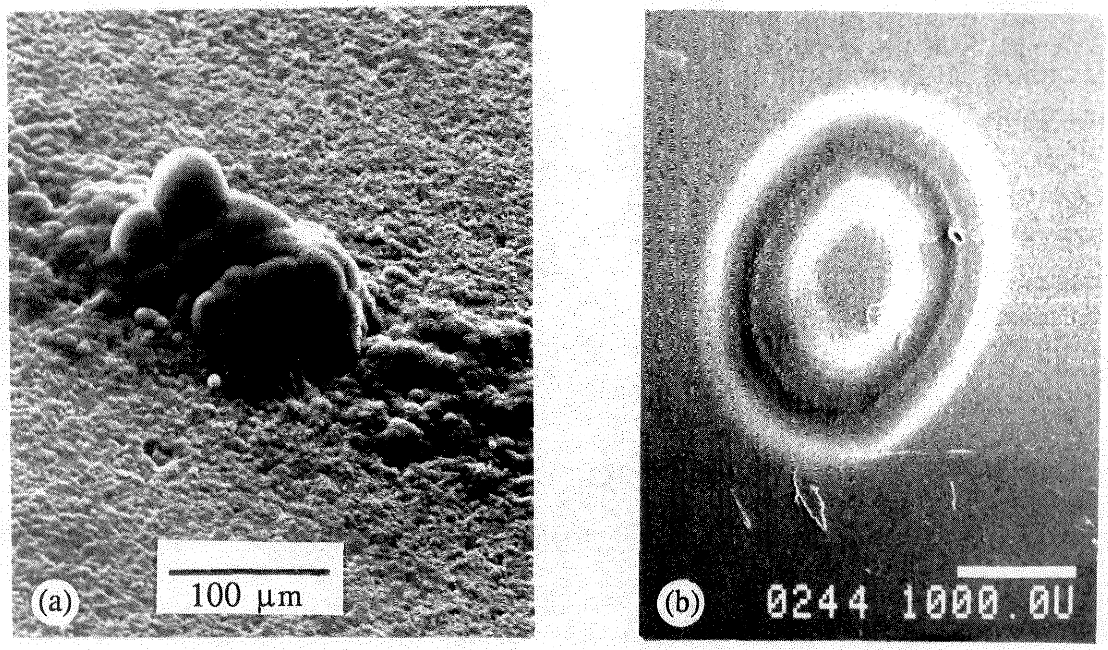


Fig. 3 **(a)** Nonuniform carbon line deposited on an alumina substrate from C_2H_2; $p_{C_2H_2}$=200 Torr, λ=10.6μm, P_{tot}=5W, **(b)** Foreign impurities on the substrate surface are the nucleation sites for the nodular growth.

The nucleation sites for the nodular growth are often foreign impurity inclusions such as shown in Figure 3b or localized defects [7] on the substrate surface. Therefore, uniform surface preparation is critical for controlled SALD. When the laser beam scans over a large area on the alumina substrate surface at room temperature, preferred nucleation at locations of defects in the substrate surface can produce a low nucleation density as shown in Fig.4a. The defects in Fig. 4a are not clearly defined, but may be chemical, crystallographic, or morphological in nature. The deposited carbon absorbs more CO_2 laser power than alumina does due to the lower reflectivity and since deposition rates are very sensitive to the surface temperature, the growth of the nucleus is more favorable than the formation of new nucleus in the subsequent scans. Also, nucleation at other sites may in certain operating conditions be suppressed by local gas depletion due to the fast nodular growth. Figure 4b shows a dramatic case where nodular growth inhibits growth of the bulk material.

It is obvious that a choice of substrate must be made to control the nucleation density to get the initial uniform deposition layer for the gas phase SFF using SALD.

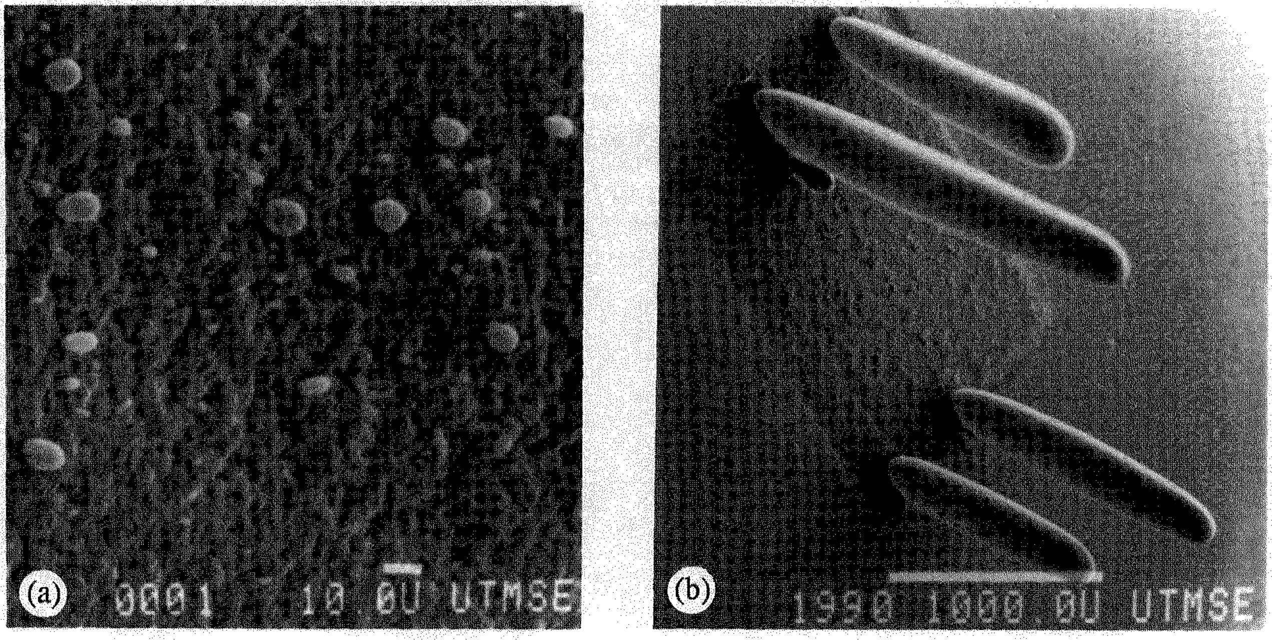


Fig. 4 (a) Initial stage of carbon deposit nucleation on alumina from acetylene (after three scans); scanning speed 508µm/sec, step = 127µm. **(b)** Nodular growth of carbon deposit on alumina from acetylene.

4. Approaches to Improve the Uniformity in SALD

4.1. The competition between nucleation and growth

The nucleation effects of SALD of a strip are different from those of SALD of a rod since prevailing conditions differ. In the former case of deposition of a strip there is steady-state competition between forward growth on the strip itself and nucleation on the bare substrate in front of the leading edge of the strip (Fig.5); while in deposition of a rod only nucleation on the bare substrate is initially important.

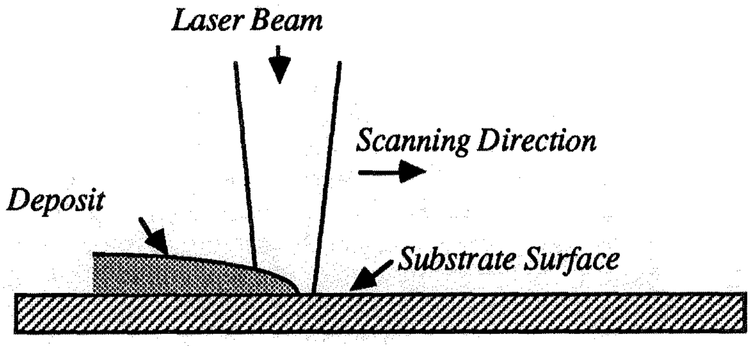


Fig 5 Schematic for deposition of a strip.

During the dwell time of the laser beam, the growth on the deposited strip and nucleation on the substrate will occur. If the growth rate is higher compared to the nucleation rate, the deposited film under the laser beam will grow more rapidly at the expense of nucleation due to the nucleation site being 'starved' for reactants. Therefore, to achieve uniform deposition, the nucleation rate must approximate the growth rate. Any approach which helps nucleation compete against growth will be useful in improving the uniformity in SALD.

4.2. Catalyst enhanced nucleation

Surface reaction rates can be altered by gaseous additions or surface modification which affect the catalytic behavior of the substrate. For example, the nucleation and growth rate of ZnS has been shown to increase markedly when the zinc precursor vapor reactant contained a small amount of aluminium or copper [8] and some species, such as Si and SiC, can help in the nucleation of diamond and increase its growth rate [9]. Therefore, one way to promote the nucleation may be a catalyst enhanced nucleation approach.

In this paper, nucleation and renucleation refer to classical nucleation theory as well as catalyst-assisted nucleation and renucleation. Nucleation refers to the initial deposition of material onto the substrate, whereas renucleation refers to subsequent nucleation on the outer surface of each layer as the part is being grown or configured. Catalytic deposition in this case is a process in which the presence of specific atoms or species on the target surface and/or in the gas phase reaction zone participating in surface reactions increases the deposition rate. These foreign atoms or species may be active in the deposition process in the way catalysis is defined in a chemical sense or some fraction of them are incorporated into deposits and participate in the local bonding.

The nucleation is usually impeded by the nucleation barriers. Such barriers are often viewed as detrimental to the uniformity of deposits. There is a difference between nucleation barriers due to physical effects and those due to chemical effects. However, according to the above definition of catalytic deposition, any approach, which can lower or eliminate the nucleation or renucleation barrier due to either physical effects or surface chemical effects, is a catalyst-assisted nucleation or renucleation approach. The mechanisms of heterogeneous catalysis at a molecular level are not available to date, though the surface reaction kinetics equations have been derived from the models such as Langmuir-Hinshelwood model [10]. Assuming that the reaction is not controlled by the flux of reactive species to the reaction zone, the deposition rate is given by the Arrhenius equation. This establishes that the catalyst must decrease the activation energy of the reaction.

When a thin layer of pure SiC powder was used as the substrate, a uniform carbon layer can be deposited. Figure 6a shows the renucleation of carbon deposits on the deposited layer. Uniform multi-layer deposition was achieved (figure 6b) with multi-scanning over the uniform first layer. Free-standing carbon blocks and rings have been made using this local catalyst-temperature enhanced nucleation approach, as shown in the figure 7. In addition the use of a thin layer of powder as the substrate makes it easy to remove the objects from the substrate.

4.3. Localized temperature enhanced nucleation

Increasing the temperature in the front of the leading edge of the strip can also increase the nucleation rate, over a range of temperatures as discussed earlier, and thus improve the uniformity. One of the approaches is to reduce the thermal conductivity of the substrate material by using powder for a substrate. In the case of fine particles with no convective flow in the gas the effective thermal conductivity is given by [11]

$$k_e = \frac{k_s \ (1-\varepsilon)}{1+ \ \varphi \ k_s/k_g} \qquad (1)$$

where k_s and k_g are the thermal conductivities for the solid and gas, respectively, e the volume fraction of gas in the powder substrate, φ a constant which is about 0.034. The heat conductivity of the powder is lower than its bulk material. The powder substrate makes the temperature distribution more localized and results in better resolution.

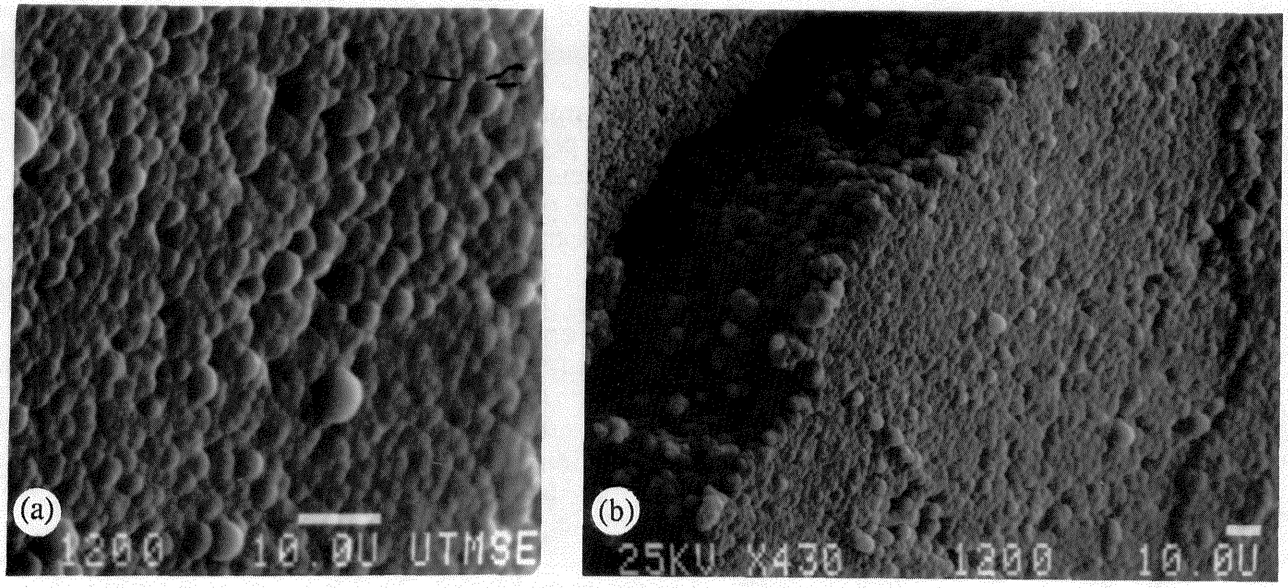


Fig. 6 Uniform renucleation **(a)** and multi-layer **(b)** of carbon deposits by SiC powder catalyst assisted nucleation approach. $p_{C_2H_2}$=700 Torr, λ=10.6μm, P_{tot}=5W.

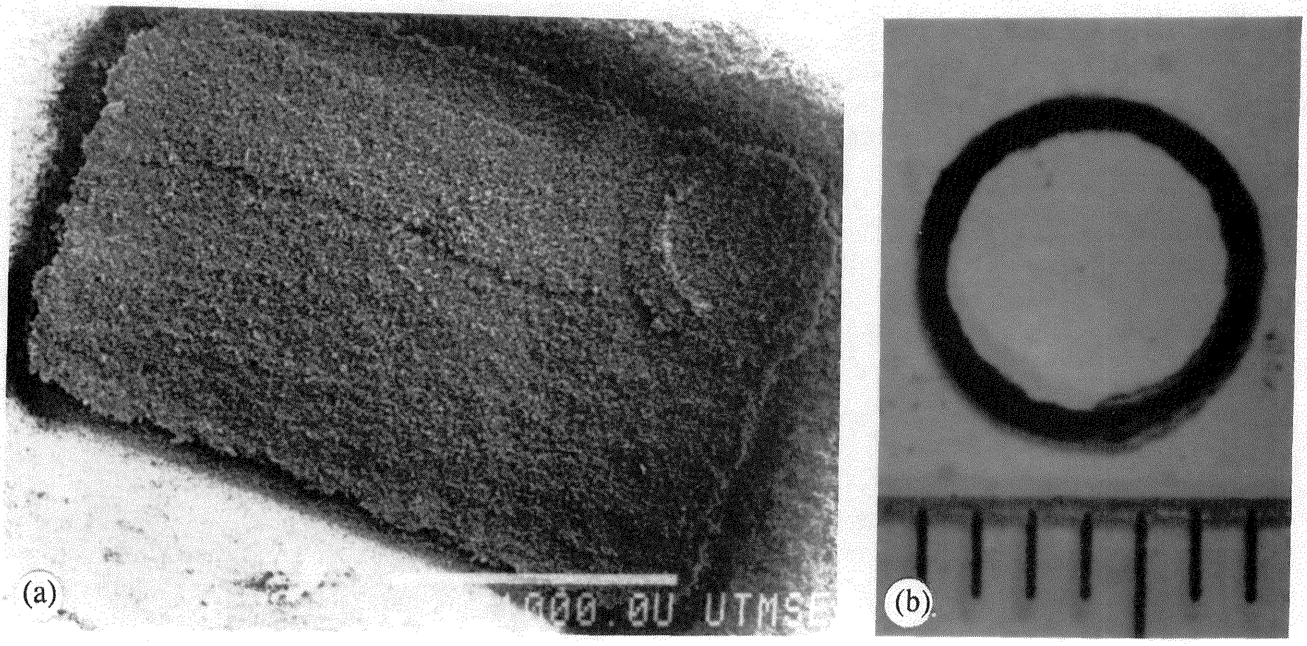


Fig. 7 Free-standing carbon block **(a)** and ring **(b)** made by SiC powder catalyst assisted nucleation approach. $p_{C_2H_2}$=700 Torr, λ=10.6μm, P_{tot}=5W.

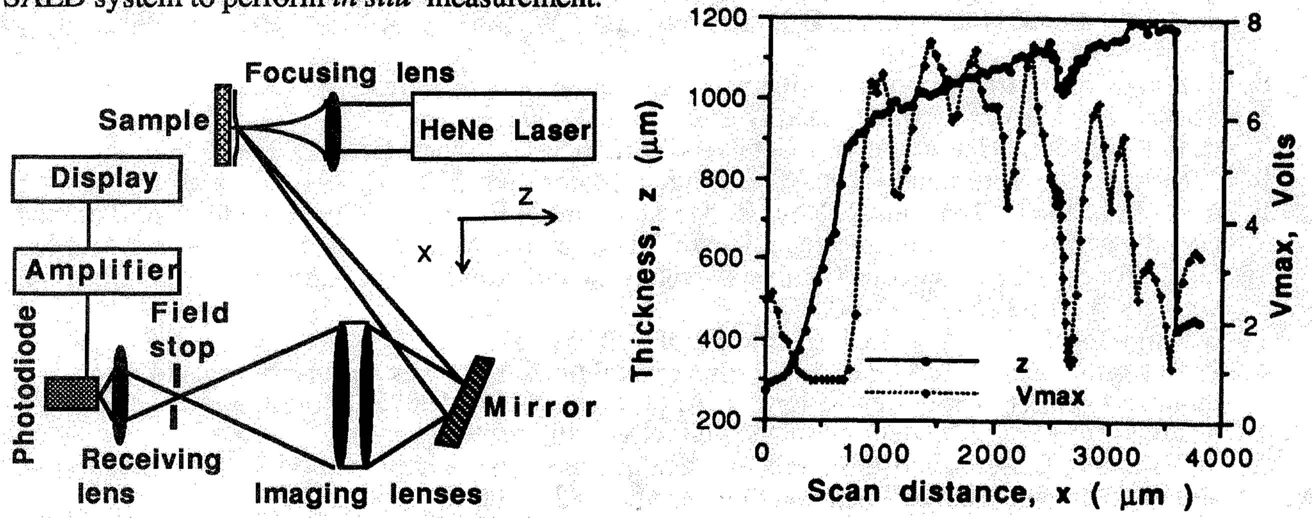
Since catalytic materials may have high thermal conductivity, which is not desired for SALD, catalytic powder substrates should be an improvement over a solid catalytic substrate and should help nucleation compete with growth resulting in a more uniform deposition.

When a 0.5 mm thick high-pressure pressed solid SiC was used as the substrate, no carbon deposit was observed. The experimental conditions tested with no success included laser powers from four to twenty-five watts, substrate temperatures from 20 to 400 C, C_2H_2 pressure of 500 Torr, and scanning speeds from 0.1 to 1 mm/s. This may be due to the high reflectivity of the solid SiC surface and the high heat conductivity of solid SiC relative to the SiC powder as defined by equation (1). This demonstrates the advantages of using a powder as the substrate.

5. *In Situ* Deposition Thickness Measurement for Process Control

In the pyrolytic SALD, within the kinetically limited regime the deposition rates depend exponentially on temperature which depends sensitively on the local surface properties and geometry of the sample. Thus, a small variation in a processing parameter may result in a very large variation in deposition rates. Even with the best possible modeling, it seems that it will not really be possible to accurately control the SALD process in this kinetically limited regime without some form of very sensitive dynamic feedback system. In the mass transport regime, however, the deposition rate is nearly temperature independent. This regime will give the relative easily controlled SALD process together with higher deposition rates.

Optical methods for the measurement of changes in surface height are among the most sensitive and rapid diagnostic tools available. The rate of spatial variation of a solid surface during deposition or removal of material has been measured using ellipsometry, interferometry, reflectance, transmission techniques, and laser spot-imaging techniques [12-16]. Of all these techniques, the laser spot-imaging technique seems to be the most suitable one to be modified and added to the SALD system to perform *in situ* thickness measurement and closed-loop thickness control. Fig. 8a shows an experimental arrangement for the thickness measurement using the scattering of a HeNe laser beam to detect the vertical movement of the laser spot. The height of the sample is determined by the displacement the maximizes the photodiode signal. Fig. 8b shows a typical surface roughness profile of a carbon deposit for a line scanning measurement together with the record of the maximum intensity change of the scattering HeNe laser beam. A resolution of about 5 μm was achieved using this set-up. A modification of this system will soon be added to the SALD system to perform *in situ* measurement.



(a) (b)

Fig. 8 (a) Experimental arrangement for the measurement of deposition thickness in SALD, (b) A line scanning measurement of the surface roughness of a carbon deposit.

6. Summary

Selective Area Laser Deposition poses many unique challenges as well as advantages when compared to alternative processes. Strong temperature dependencies allow high resolution, provided laser power and spot size give the proper temperature profile on the substrate surface. Variations in local thermal conductivity and geometry are additional complications. To fabricate three dimensional objects , a flat topped deposit with constant thickness and width is required. This in turn requires the nucleation rate approximate the localized growth rate. Catalytic powders provide the necessary nucleation to get an initial uniform layer of deposition, and also give better heat transfer conditions. Finally, the expected exponential temperature dependence which allows high resolution also implies sensitivity to local temperature differences and has resulted in a proposed method to monitor *in situ* growth rate .

Acknowledgement

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