SYNTHESIS OF POWDERS AND THIN FILMS BY LASER INDUCED GAS PHASE REACTIONS

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ABSTRACT

Laser induced gas phase reactions have been used to produce highly controlled powder and thin film reaction products. Powders of Si, Si$_3$N$_4$ and SiC exhibit presumed ideal characteristics for consolidation into dense ceramic parts. Individual powder characteristics can be manipulated with this process while being highly efficient in terms of materials utilization and energy consumption. The CVD process permits physical, electronic and crystallographic properties to be controlled. Resulting amorphous Si films exhibit superior properties.

INTRODUCTION

This paper will review the principal features of two laser driven gas phase chemical reactions that are being investigated at M.I.T. Powders are formed$^1$ in one and thin films in the other.$^2$ Both processes yield materials having superior, technologically important properties on a laboratory scale and we believe that they can be developed to operate in economically viable manners.

Reactant gases are heated by absorbing IR photons in these processes. They differ from photochemical reactions induced by ultraviolet or visible wavelength photons because absorption of single or multiple IR photons generally leaves the molecules in vibrationally or rotationally excited electronic ground states where they will ultimately dissociate when sufficient energy has been adsorbed. With the high gas pressures used, and the combination of the anharmonicity, the sparseness of the rotational structure and high dissociation
energy of the SiH$_4$ molecules, it is unlikely that collisionless unimolecular multiphoton reactions can be induced. Thus, these reactions basically proceed as thermal reactions with a Boltzmann distribution of energies. Even if collisions and other relaxation processes occur, these reactions may differ from conventional reactions because the short times and rapid heating rates may result in different intermediate states. Our investigation has proceeded on the premise that these laser induced reactions will differ from conventional reactions in the level of process control and the process conditions that can be achieved uniquely with them and that they will have value because of the superior properties of the resulting powders and films.

We have modelled$^{3,4}$ these processes simply as thermal processes described by the laser energy absorbed by the reactant gas stream, the heat capacity of all species, and latent heats of reaction. The absorption of laser energy is generally presumed to terminate progressively as the reaction proceeds. There are in fact important differences between this simple model and actuality.

The powder and CVD laser driven reactions permit important process attributes to be achieved. For both, these include:

1. highly controlled atmospheric conditions;
2. cold wall reaction vessels;
3. unusually rapid heating and cooling rates;
4. precise control of process variables;
5. accessibility to the reaction with process diagnostics.

For the laser CVD process, the ability to establish the substrate temperature at a level that is different from the gas reaction temperature is an important feature.

LASER INDUCED POWDER SYNTHESIS

Process Description

Powders have been synthesized with crossflow and counterflow gas stream-laser beam configurations and with both static and flowing gases. Most of the process research has been conducted with the reaction cell shown schematically in Fig. 1.

In a crossflow configuration, the laser beam having a Gaussian shaped intensity profile orthogonally intersects the reactant gas stream possessing a parabolic velocity profile. The laser beam enters the cell through a KCl window. The premixed reactant gases, under some conditions diluted with an inert gas, enter through a 1.5 mm ID stainless steel nozzle located 2-3 mm below the laser beam. A coaxial stream of argon is used to entrain the particles in the gas.