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Laser techniques for studying chemical vapor deposition

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Chemical vapor deposition (CVD) is widely used to produce thin films for microelectronics, protective coatings and other materials processing applications. CVD involves flowing a reactive gas (often diluted in a carrier gas) through a reactor containing a heated substrate. Chemical reactions occur that deposit a solid film on the substrate. Gaseous reaction products and any unreacted starting materials flow out of the reactor. CVD processes are run under a wide variety of conditions, including atmospheric to sub-Torr pressures, and temperatures ranging from room temperature to several thousand degrees. There are a number of related materials processing methods, including plasma etching and deposition processes in which a glow discharge is used to create reactive chemical species instead of, or in addition to, a heated substrate.

Despite the large number of applications, however, little is known about the fundamental chemistry and physics of most CVD processes. CVD recipes have generally been determined empirically, but as process requirements become more stringent, a more basic understanding will be needed to improve reactor design and speed process optimization. In situ measurements of the reacting gas are important steps toward gaining such an understanding, both from the standpoint of characterizing the reactor and testing models of a CVD process. Optical diagnostics provide a nearly-ideal means for probing the gas phase during deposition. They are non-intrusive, selective, sensitive, and can provide high spatial resolution within the strong temperature and concentration gradients that can be present in CVD processes. Laser-based techniques, ranging from light scattering for flow visualization to laser-induced fluorescence spectroscopy, are thus valuable tools for studying materials processing technologies such as CVD.

Our work, a coordinated program of experimental and theoretical research in the fundamental mechanisms of CVD, illustrates the application of laser techniques to the understanding of a CVD system. We have used a number of laser-based techniques to probe CVD systems and have compared our measurements with predictions from computer models, primarily for the silane CVD system. The silane CVD model solves the two-dimensional, steady-state boundary layer equations of fluid flow coupled to 26 elementary chemical reactions describing the thermal decomposition of silane and the subsequent reactions of intermediate species that result in the deposition of a silicon film. A detailed description of this model can be found elsewhere.[1–3] In a horizontal channel-flow reactor, we have used pulsed UV laser Raman spectroscopy to measure gas temperatures and silane number density as a function of position in the reactor, temperature and gas composition.[4] We also used laser-induced fluorescence spectroscopy (LIF) to monitor Si_2 [4] and Si atoms[5] relative densities as a function of such variables. The laser measurements of gas-phase species compare favorably with the predictions of the model, indicating that the model contains a good description of the gas-phase processes in this CVD system. Details of these experiments and comparisons can be found in the full papers.[4,5]

In addition to the work on the silane system, we have done laser velocimetry measurements in a vertical tube reactor,[6] flow visualization experiments and Raman measurements of gas temperatures for a rotating disk reactor,[7] Raman measurements of SiH_2Cl_2 and WF_6 under

CVD conditions,[8] and LIF measurements of HSiCl[9] and Si atoms[10] during the CVD of silicon from SiH_2Cl_2.

Other researchers have also used optical diagnostics to study materials-processing technologies. In addition to the methods mentioned above, these include optical emission spectroscopy, infrared absorption spectroscopy (including diode laser methods), optogalvanic spectroscopy, and CARS (coherent anti-Stokes Raman Spectroscopy). The reviews by Gottscho and Miller[11], Dreyfus, et al.[12], and Wormhoudt, et al.[13] cover many of these topics, although these papers do not cover the most recent results.

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