CHEMICAL VAPOUR DEPOSITION ENGINEERING - ADVANCED CVD RESEARCH AT THE UNIVERSITY OF UPPSALA

JAN ENGQVIST
Thin Film and Surface Chemistry group, Department of Inorganic Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden
Present address: Sandvik Coromant, Gimoverken, Box 100, S-740 52 Gimo, Sweden

Introduction

Thin films of different materials play an important role in fundamental science, as well as in the field of applied materials and solid-state technology. By means of thin-film materials many new phenomena in chemistry, physics, biology and medicine have been detected and investigated. Microelectronics, sensors, solar cells, metal cutting and forming, corrosion protection and biocompatibility are well-known examples of thin-film applications.

With the increased demand for tailor-made, well-defined and high-purity materials with precisely controlled properties, vapour deposition techniques based on chemical reactions have increased in importance. The common name for these techniques is chemical vapour deposition (CVD), which is a process whereby a solid material is deposited from a vapour by chemical reactions on, or in the vicinity of a substrate surface. The chemical reactions are usually initated and maintained by heat (thermally activated CVD, TACVD), but can also be induced by photons (e.g. laser-assisted CVD, LCVD), electrons, ions or a combination of these as in plasma-assisted CVD (PACVD).

The CVD process usually consists of several sequential steps such as (*i*) mass transport of reactants in the vapour, (*ii*) homogeneous reactions, (*iii*) adsorption of the reactants, (*iv*) surface diffusion, (*v*) surface reactions, (*vi*) desorption of reactants and (*vii*) mass transport of the reaction products. Finally, solid-state reactions may also take place during the deposition process. The crystal structure, microstructure, morfology, defect content, etc. and thus the properties of the substrate/film material are then the result of the interplay between the reactions mentioned above.

Surface analysis in CVD processes

In order to tailor the desirable film properties and achieve an improved process control, a mechanistic understanding of the nucleation and growth process is needed. A classical approach is to apply chemical modeling concepts to get a hint of the important reaction steps. In chemical modelling the plausible elementary reaction steps are listed and the corresponding rate equations are written. The drawback of this approach is that a CVD process usually involves too many reaction steps and that more than one rate equation can predict the measured deposition rate in an acceptable way. Another approach is to try to isolate important reaction steps by using different analytical techniques in-situ during the deposition process. However, many CVD processes are working at high pressures (above 1 Torr) and at elevated temperatures, which excludes direct use of electron spectroscopic techniques.

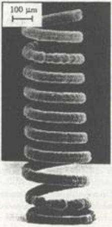
An alternative is therefore to perform the process under UHV conditions in order to enable surface analysis. Examples of reaction steps which can be investigated by this type of studies are, adsorption of reactants, surface reactions and desorption of reaction products. An advantage with this type of studies is that well-characterized surfaces is used. The UHV environment also offers high-purity conditions where the influence of various contaminants can be eliminated. In addition, under these conditions the deposition process is controlled by the surface reactions and not by a combination of heterogeneous and homogeneous reactions. CVD under UHV conditions has opened a new material processing area and completely new materials can be grown by this technique.

It is important to note that results obtained under UHV conditions cannot directly be applied to explain reaction mecanism in "high-pressure" CVD processes. Another important issue which must be considered is that the analytical technique itself seriously can influence the surface chemistry. Most analytical techniques are based on the principle that the surface is bombarded by high-energetic photons, electrons or ions. This bombardment may affect the chemistry and give misleading information which in the worst case can lead to wrong conclusions.

An alternative route to study surface reactions in CVD is to actually deposit the film in a CVD reactor under true deposition conditions and quickly interrupt the growth process. The film is then transported under vacuum by a special transfer system to the UHV chamber for surface analysis. In the analysis chamber, adsorbed molecules can be studied by various techniques (AES, ESCA etc.) to determine the type of species present on the surface as well as their concentrations.

Selective deposition by laser-assisted CVD

CVD is usually considered as a large-area deposition technique. However, the use of lasers in CVD is one way to achieve area selective deposition. In LCVD the laser beam activation of the chemical reactions is based on pyrolytic (thermal) and/or photolytic excitation mechanisms. In the photolytic process, the



Crystalline boron spring deposited by LCVD.

laser beam is used for excitation of species which can be activated by a proper selection of precursor molecules, substrate material and laser wavelenght. In thermal LCVD the laser beam is used as a local heat source. The beam is focused onto the substrate surface and induces a temperature increase which initiates and maintains the CVD process. However, a high temperature is only reached locally in the centre of the laser spot on the surface and the temperature decreases rapidly in the lateral direction. Thus, deposition will only take place in that small spot and selective deposition is achieved.

In conventional CVD, selective deposition can be attained on patterned substrates or in combination with a mechanical mask. LCVD, however, offers the unique possibility of depositiong lateral resolved material structures. By moving the laser beam or the substrate, structures smaller than 1 µm can be produced in a single step using a so-called direct writing process. Moreover, a spectacular use of LCVD in the future may be fabrication of very complicated material structures. By moving the laser beam, not only in two, but in three dimensions, truely free standing 3D-structures can be produced.