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Modeling and simulation of Chemechal Vapor Deposition (CVD) process Metal coating

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ABSTRACT

Chemical vapour deposition (CVD) is a widely used method for depositing thin films of a large variety of advanced materials. Applications of CVD range from the fabrication of microelectronic devices to the deposition of protective coatings but also optoelectronic films, decorative coatings.

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Introduction

Chemical vapor deposition (CVD) is a process whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The solid material is obtained as a coating, a powder, or as single crystals. By varying the experimental conditions—substrate material, substrate temperature, composition of the reaction gas mixture, total pressure gas flows, etc.—materials with different properties can be grown.

A characteristic feature of the CVD technique is its excellent throwing power, enabling the production of coatings of uniform thickness and properties with a low porosity even on substrates of complicated shape. Another characteristic feature is the possibility of localized, or *selective* deposition, on patterned substrates. CVD is employed in many thin film applications. It is, for instance, used in the microelectronics industry to make films serving as dielectrics, conductors, passivation layers, oxidation barriers, and epitaxial layers. The production of optical fibers as well as wear-, corrosion-, and heat resistant coatings with this technique is well known. Other CVD applications are the preparation of high temperature materials (tungsten, ceramics, etc.) and the production of solar cells, of high temperature fiber composites, and of particles of well-defined sizes. Recently, high-Tc superconductors have also been made by this technique. Since oxygen activity in the vapor can be precisely controlled during the deposition, no annealing in oxygen is needed to achieve superconductivity.

Important Reaction Zones in CVD

In CVD, gaseous reactants are admitted into a reactor (see Fig.1). Near or on a heated substrate surface, a chemical reaction of the following type occurs:

Gaseous reactants → Solid material + Gaseous products

Because of the gas flows as well as the temperature used in CVD, five important reaction zones are developed during the CVD process . The properties of CVD materials are affected by the interacting processes occurring in these reaction zones. In a CVD process, a main gas flow (the reaction gas mixture) passes over the substrate/coating surface. For fluid dynamical reasons, a more or less stagnant boundary layer occurs in the vapor adjacent to the substrate/coating. During the deposition process, the gaseous reactants and the gaseous reaction products are transported across this boundary layer. In reaction zone 1 as well as in the main gas stream, homogeneous reactions in the vapor may occur. These reactions may lead to an undesirable homogeneous nucleation resulting in a flaky and non-adherent coating. In some cases however, these reactions, when not accompanied by homogeneous nucleation, are favorable to the CVD process.

The heterogeneous reactions occur in the phase boundary vapor/coating (zone 2). These reactions determine, in many systems, the deposition rate and the properties of the coating.

Relatively high temperatures may be used during CVD. This means that various solid state reactions (phase transformations, precipitation, recrystallization, grain growth, for example) may occur during the process (the zones 3 - 5). In zone 4, which is a diffusion zone, various intermediate phases may be formed. The reactions in this zone are important for the adhesion of the coating to the substrate.

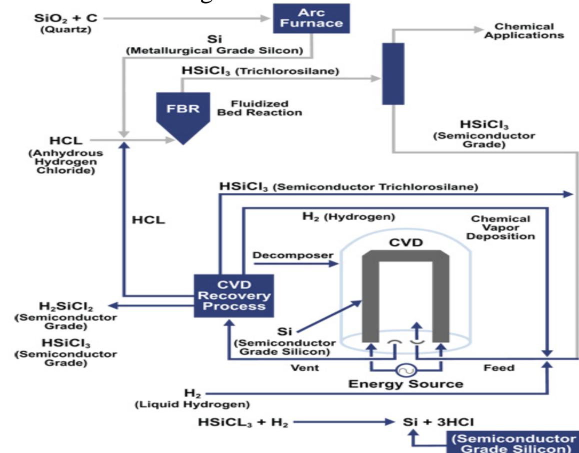

Fig.1. Chemical vapor deposition process

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Design of CVD Experiments

Every CVD experiment is unique. However, some general aspects in designing CVD experiments can be given. The design is usually an iterative procedure. For instance, the choice of the reaction gas mixture affects the design of the CVD system, the cleaning procedure, the adhesion of the coating, etc.

CVD processes frequently proceed by complicated chemical reaction schemes. However, use of overall CVD reactions enables a classification to be made.

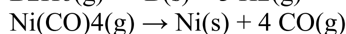
Thermal decomposition reactions or pyrolytic reactions mean, in this case, that a gaseous compound AX is thermally dissociated into A (a solid material) and X (a gaseous reaction product).

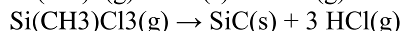
$AX(g) \rightarrow A(s) + X(g)$

Use of thermal decomposition reactions normally results in relatively pure coatings. Examples of some thermal decomposition reactions are given below:

$SiH_4(g) \rightarrow Si(s) + 2\ H_2(g)$

$B_2H_6(g) \rightarrow B(s) + 3\ H_2(g)$


$Ni(CO)_4(g) \rightarrow Ni(s) + 4\ CO(g)$


$Si(CH_3)Cl_3(g) \rightarrow SiC(s) + 3\ HCl(g)$

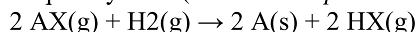
Processes like carburizing and nitriding may also be classified in this category of reaction. In carburizing, for instance, a carbon-carrying vapor species, e.g., methane, is allowed to react at/on a heated surface.

Methane then decomposes in principle according to:

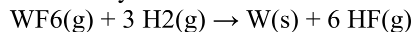
$CH_4(g) \rightarrow C(s) + 2\ H_2(g)$

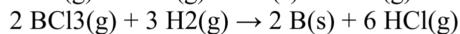
The deposited carbon reacts immediately with the substrate yielding a solid solution of carbon in the substrate and/or—if they exist—carbides of the substrate material.

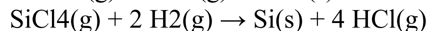
Reduction reactions, where hydrogen acts a reducing agent, are frequently used (see also *Coupled reactions* below).


$2\ AX(g) + H_2(g) \rightarrow 2\ A(s) + 2\ HX(g)$

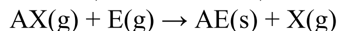
Straightforward reduction reactions have been almost exclusively used in the CVD of elements.


$WF_6(g) + 3\ H_2(g) \rightarrow W(s) + 6\ HF(g)$

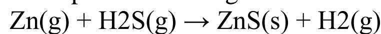

$2\ BCl_3(g) + 3\ H_2(g) \rightarrow 2\ B(s) + 6\ HCl(g)$

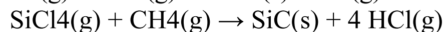

$SiCl_4(g) + 2\ H_2(g) \rightarrow Si(s) + 4\ HCl(g)$

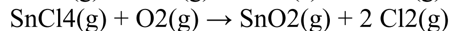
Exchange reactions mean that an element E replaces another element, for instance X, in the molecule AX according to:


$AX(g) + E(g) \rightarrow AE(s) + X(g)$

Examples of exchange reactions are:

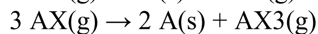

$Zn(g) + H_2S(g) \rightarrow ZnS(s) + H_2(g)$


$SiCl_4(g) + CH_4(g) \rightarrow SiC(s) + 4\ HCl(g)$


$SnCl_4(g) + O_2(g) \rightarrow SnO_2(g) + 2\ Cl_2(g)$

Disproportionation reactions are rarely used in CVD. Disproportionation means a reaction where the oxidation number of an element both increases and decreases through the formation of two new species. CVD of A from AX can be obtained in disproportionations like:

$2\ AX(g) \rightarrow A(s) + AX_2(g)$


$3\ AX(g) \rightarrow 2\ A(s) + AX_3(g)$

$4\ AX(g) \rightarrow 3\ A(s) + AX_4(g)$

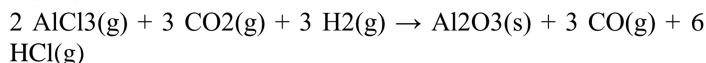
Examples of disproportionation reactions are.

$2\ GeI_2(g) \rightarrow Ge(s) + GeI_4(g)$

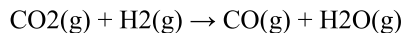
$2\ TiCl_2(g) \rightarrow Ti(s) + TiCl_4(g)$

$2\ SiI_2(g) \rightarrow Si(s) + SiI_4(g)$

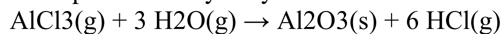
Coupled reactions are often used in CVD. For instance, CVD of Al_2O_3 from $AlCl_3$, CO_2 and H_2 can be described in an overall reaction:


$2\ AlCl_3(g) + 3\ CO_2(g) + 3\ H_2(g) \rightarrow Al_2O_3(s) + 3\ CO(g) + 6\ HCl(g)$

where the reaction in which water is formed:

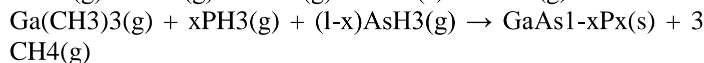

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

is coupled to the hydrolysis reaction:


$AlCl_3(g) + 3\ H_2O(g) \rightarrow Al_2O_3(s) + 6\ HCl(g)$

Other examples of overall coupled CVD reactions are:

$TiCl_4(g) + NH_3(g) + \frac{1}{2}\ H_2(g) \rightarrow TiN(s) + 4\ HCl(g)$


$Ga(CH_3)_3(g) + xPH_3(g) + (1-x)AsH_3(g) \rightarrow GaAs_{1-x}P_x(s) + 3\ CH_4(g)$

Simulations

A DSMC code (Icarus) developed at Sandia National Laboratories was used to determine the velocity field of the gas jet for the three test conditions. It was also used to analyze the interaction between the gas jet, the vapor flux and a polygonal approximation to a cylindrical fiber. We first simulated the expansion of a helium gas jet from a choked nozzle in the absence of a cylindrical substrate. The flow field was determined at the substrate location and used in a second model to analyze the interaction of the flow with the cylindrical substrate. The inputs to the substrate interaction model were the velocity of the gas flow and the vapor flux at the position of the substrate (determined from the preceding analysis). Previous simulations have indicated that the vapor atoms reach the velocity of the gas jet a short distance from the source and thus the aluminum vapor atoms were input at the same velocity as the helium. The average trajectories of the helium and aluminum atoms and the helium velocity in the axial direction were determined for a region near the cylindrical substrate.

The use of a rarefied gas jet to alter vapor atom trajectories has allowed the coating of regions on a circular cross section that were not in the line-of-sight of the vapor source. The degree of non-line-of-sight deposition and thus the coating thickness uniformity was a sensitive function of the gas jet flow conditions. For a fixed background pressure in the region of deposition, an increase in coating uniformity was observed as the jet's Mach number was reduced.

DSMC analysis has indicated that the observed NLOS coating is a result of binary collisions between carrier gas and vapor atoms in the flow. The analysis shows that gas jet streamlines flow around the substrate. Scattering from the carrier gas streamlines allows the aluminum vapor atoms to diffuse out of the flow and impact parts of the substrate that are not directly viewable from the source.

The transport of vapor atoms in a gas jet depends on several factors: the Mach number (or kinetic energy) of the gas jet and vapor atoms, the Knudsen number of the gas jet and vapor atoms (The Knudsen number, Kn, is defined as the ratio between the mean free path in a flow to the characteristic length of a body immersed in the flow.

As the Mach number DVD gas jet varied from 0.433 to 0.039, Kn for Al–He scattering was estimated to change to 0.6 to 0.3) and the mass of the two atom types present. High gas jet Mach numbers (>0.3) and small Knudsen numbers (<0.1) promote vapor atom transport close to the gas jet atom flow trajectories since collisions between vapor and gas jet atoms occur frequently and are energetic. This results in limited vapor atom diffusion perpendicular to the streamline and, for the fiber case, leads to a low deposition flux contribution via scattering. When the Mach number is reduced and/or the Knudsen number increased (Knudsen numbers much greater than one are not desired since vapor atoms may then be carried past the fiber without scattering from the streamlines), collisions between the carrier gas and the vapor atoms occur less frequently and the

momentum of the carrier gas is lowered (Knudsen numbers much greater than one are not desired since vapor atoms may then be carried past the fiber without scattering from the streamlines).

To estimate the coating thickness around the circumference of the fiber in the simulation, we computed the aluminum vapor density at a distance less than 10 Am from the surface of the cylindrical substrate. This distance was small compared to the mean free path and the fiber diameter. The results are plotted as a function of the radial position on the substrate's circumference in Fig. 5. As the Mach number was decreased, the predicted uniformity of the aluminum coating around the fiber's circumference improved.

This result was similar to that seen in the experimental study, Fig. 2.

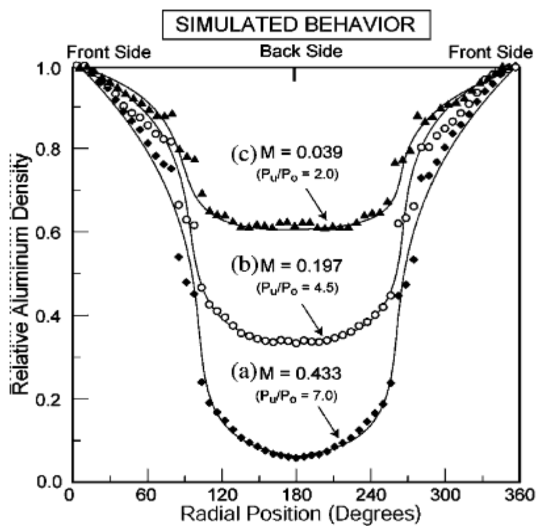


Fig.5. Plot showing the relative aluminum density above the fiber surface as a function of radial position on the fiber for a gas jet Mach number of (a) 0.433, (b) 0.197 and (c) 0.039. Note the general increase in uniformity as the Mach number was decreased compared well with the experimental observations.

Conclusion

Coatings of aluminum having good uniformity (backside coating thickness >70% of front side coating thickness) have been produced on stationary, non-rotated, cylindrical substrates using a increased pressure CVD technique that incorporates the use of a gas jet. The thickness uniformity around the fibers circumference was a sensitive function of the gas jet Mach number. Low gas jet Mach numbers led to the highest uniformity since binary collisions between the gas jet and the aluminum atoms promoted diffusive transport that resulting in online- of-sight coating.

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