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► **To cite this version:**

Anne-Lise Thomann, Constantin Vahlas. Functionalization of, and Deposition on Complex-Shaped Surfaces: Vacuum Processes, Materials, Models, Challenges, and Methods. Chemical Vapor Deposition, 2011, 10.1002/cvde.201100101 . hal-01288652

HAL Id: hal-01288652

<https://hal.science/hal-01288652>

Submitted on 12 Mar 2024

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Functionalization of, and Deposition on Complex-Shaped Surfaces: Vacuum Processes, Materials, Models, Challenges, and Methods

The application of coatings and the deposition of thin films on topologically complex surfaces provide the corresponding materials with either functional or structural properties and hence with targeted multifunctionalities. Such activities concern numerous application fields which reflect or support most of the societal concerns such as conservation of the environment, energy efficiency, transportation, security and safety, information and communication, infrastructure and construction, health and well-being, including food science, water management, sports industry, and ageing of the population. Examples come from the transportation sector (vehicle structure and motor, namely turbine blades and vanes), microelectronics (trenches and vias), glass industry (moulds), energy storage and conversion, heterogeneous catalysis, micro- (and nano-) electro-mechanical systems (MEMS), optoelectronics, biomaterials, nuclear materials, and protection of cultural heritage. Targeted properties of use in these applications are corrosion and/or oxidation protection, electrical functionalities, catalytic activity, biocompatibility or anti-fouling, wetting, mechanical functionalities such as adhesion, hardness and/or wear resistance, together with a durability compatible with the lifetime of the part.

The increasing complexity and miniaturization of such systems, combined with more severe specifications and targeted high added value, require highly elaborated processes for the deposition of films on these surfaces. The use of wet processes for deposition on, and functionalization of, large surfaces is well implemented, and can be applied for the treatment of moder-

ately complex parts. Sol-gel, for example, is an environmentally compatible technique which is expected to replace electrodeposition of Zn–Ni coatings for the replacement of Cd in components in the aeronautics sector. Wet techniques attain their limits, however, when the surfaces to be treated present aggressive aspect ratios and/or require deposition of uniform films or uniformly distributed nanometer-size objects (particles, tubes). On the other hand, dry (vacuum) techniques a priori better meet the constraints originating from the conformal functionalization of complex surfaces.

A complex surface can be defined with regard to a process implying a heterogeneous transfer, such as the functionalization or the deposition of a film. Such a process implies a gaseous phase which is in contact with the surface and provides the species which are responsible for its modification. In such a case, three types of physico-chemical phenomena may take place simultaneously, depending on the nature of the process:

- Homogeneous transfer or transport; convection, ballistic transfer, diffusion.
- Eventually, activation of the source species leading to their transformation prior to attaining the surface. This is the case, for example, of the thermal decomposition of a molecular compound, or of the gas ionization in plasma.
- Heterogeneous transfer, properly speaking; adsorption, condensation, chemical deposition. . .

Many times, a surface acquires a complex character with regard to the targeted application, when the charac-

teristic lengths covered by the laws which control these phenomena become comparable with the characteristic dimensions of the surface (2D roughness) or of the porosity (3D). In such a case, a –sometimes strong– coupling occurs between the surface topology and the above-mentioned phenomena. In general, such coupling is the source of difficulties in controlling the process and, consequently, in the quality of the final product (e.g., film homogeneity).

Such a definition of surface complexity can be met at different scales, ranging from the nanometer to the centimeter, and can originate from the curvature, the porosity, or from the roughness. Scanning electron microscopy (SEM) images of Figure 1 illustrate such surfaces. Micrograph A presents a high (800 °C) temperature resistant fiber from an “E-glass”-type tissue.^[1] Such tissues are being coated with functional materials such as TiO₂, as shown in the micrograph. Micrograph B presents a porous steel structure. The open porosity is 70% and pore size is 10 μm.^[2] Deposition of a catalytic coating on the surface of the fibers, or of the pores of the two structures, would allow the use of these market materials in applications requiring different types of catalysts (treatment of gaseous effluents, launched systems. . .). Micrograph C presents particles of a metallic alloy powder composed of Al, Co, Cr, Ni, Ta. This powder is the raw material for the preparation of bond coatings applied by plasma torch on turbine blades. It has been shown that the deposition on the surface of such particles of platinum group elements prior to their use ensures the homogeneous distribution of these doping elements within the

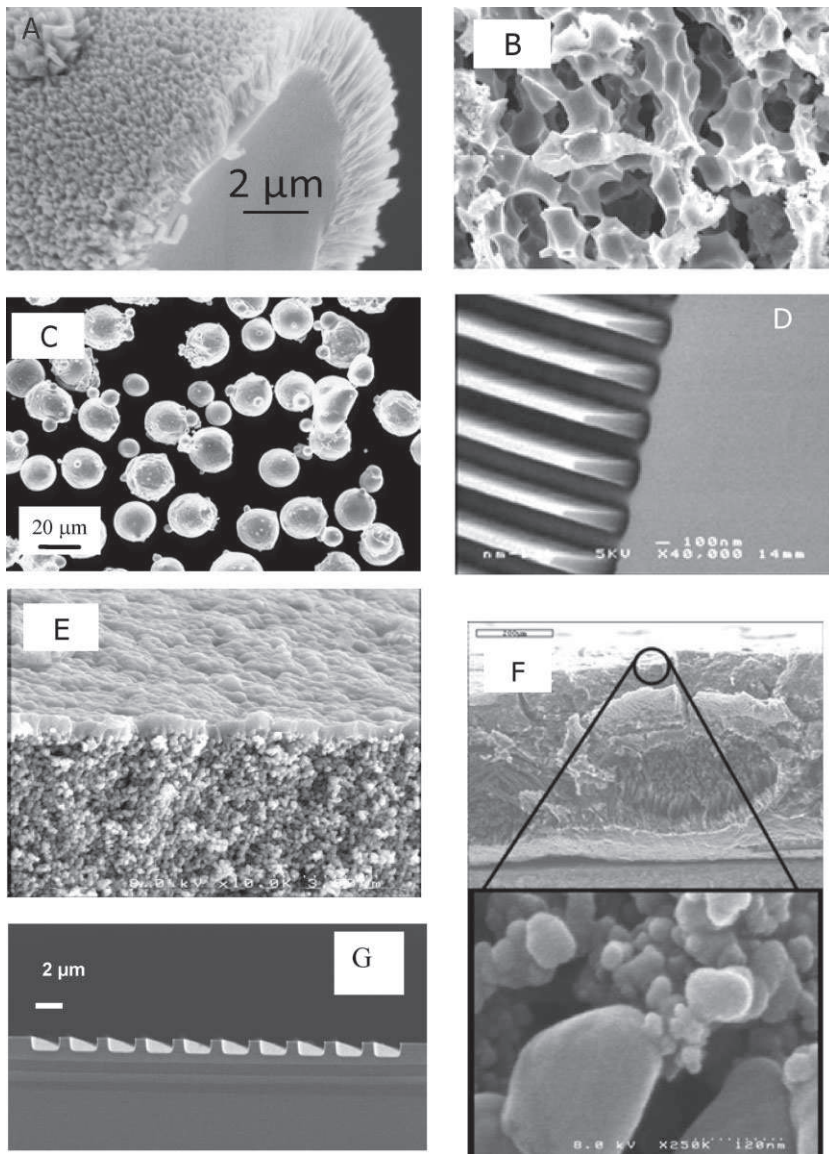


Fig. 1. SEM images of materials containing surfaces with complex geometry. Information on each material is provided in the text. Figures reproduced with permission: A) Copyright 2009, Elsevier; B) Copyright 2007, Elsevier; C) Copyright 2003, Elsevier; D) Copyright 2000, Elsevier; E) Copyright 2001, Elsevier.

bond coating and improves its properties.^[3] Micrograph D illustrates a SiO_2 etch on Si, performed by inductively coupled plasma (ICP) in a feasibility study of lithography by nanoprinting. Patterns are 50 nm distant and etching depth is 800 nm.^[4] Micrograph E shows the upper part of an alumina-based, asymmetric, highly porous membrane. This membrane serves as a support to a plasma enhanced (PE)CVD film which confers to the material selectivity with

regard to gaseous or ionic species.^[5] Micrographs F present a porous material composed of a carbon tissue coated with carbon and Teflon[®] particles. This material serves as an electrode in proton exchange membrane fuel cells. Plasma sputtering techniques are used to ensure diffusion of the catalyst (Pt) in this complex medium where, in order to be active, it forms nanometer-size aggregates on carbon.^[6] Finally, micrograph G illustrates low aspect ratio trenches

etched in a silicon wafer. These kinds of substrates are developed for 3D material synthesis and may serve as models for the study of thin film growth.^[7]

An analogous situation prevails in the antinomic case where the objective is the partial functionalization of the surface or even the loss of conformity, such as the filling of trenches or the preparation of composite materials by chemical vapor infiltration. The large variety of vacuum techniques permits dealing with these requirements. It has to be recalled here that there is no universal technique compatible with all specifications. The challenge in materials engineering consists in selecting the appropriate technique and then in tuning the process with regard to the targeted objectives. CVD and PVD are the two families of dry techniques which were historically distinguished, considering their proper characteristics (directionality, surface chemistry...). They allow responding to both material (microstructure, adhesion, purity...) and process (temperature, pressure, thickness...) requirements. In response to today's (and a fortiori tomorrow's) requirements which are more and more restrictive, each family makes its own progress (atomic layer deposition (ALD), pulsed pressure metal-organic (PP-MO)CVD, high power impulse magnetron sputtering (HiPIMS)). Moreover, advanced hybrid processes mix both kinds of techniques, a simple illustration being in-situ plasma cleaning (etching) of a substrate surface followed by thermally or plasma-activated CVD.

The above elements reveal the existence of commonly met problems in the surface processing community which go beyond particular materials and deposition techniques. With the aim of joining the efforts to investigate phenomena occurring during deposition on complex-shaped surfaces, a French research laboratory group (CNRS Groupement de Recherche 2008–2011), entitled "Mécanismes de dépôts par voie gazeuse sur des Surfaces à Géométrie Complexe" (SurGeCo, <http://surgeco.grenoble-inp.fr/>) was created. Among

the different actions undertaken within SurGeCo, can be mentioned the development of a model patterned silicon substrate and the creation of a session dedicated to complex substrates during the "Materials2010" Conference held in Nantes (France) in October 2010.

This special issue contains contributions from the above session together with those from research groups in New Zealand, and the United States. It features the latest research in the deposition and functionalization of complex surfaces by various vacuum deposition techniques. The first three papers focus on the comparison between various gas-phase deposition techniques for the coating of substrates such as powders, nanotubes, nanoparticles, or sub-micrometer patterns. Performance of conventional CVD is presented against that of modified CVD methods like MOCVD, PECVD, or supercritical fluid chemical deposition (SFCD). In the same way, the ability to coat complex surfaces with PVD techniques, for example pulsed laser deposition (PLD) or magnetron sputtering deposition (MSD), is discussed.

The synthesis of proton exchange membrane fuel cell (PEMFC) electrodes is studied by P. Brault and A. Caillard from the University of Orleans. This system, composed of a porous carbon support (tissue, fibers, etc.), a gas-diffusion layer, and a catalyst phase (nanoaggregates of transition metals) is quite complicated and requires the investigation of the deposition process onto various kinds of complex surfaces. First, the authors discuss the possible processing of carbon nanotubes and nanofibers or mesoporous carbon to be used as supports, by CVD and PECVD techniques. Then they present the performance of catalyst nanoclusters deposited by either MSD or MOCVD. At the present time, the entire system (porous support + gas-diffusion layer + catalyst) is fabricated by various different techniques, including liquid phase ones. The original idea followed by the authors in this work would be to develop a hybrid process (CVD and PVD) exclusively based on gas-phase techniques.

As explained by Majimel and co-authors from the University of Bordeaux, coating of nanofibers and nanoparticles can also be carried out by a quite different technique using precursors in a particular state. This deposition method is called SFCD. It involves solvents in a supercritical state, allowing for convenient dissolution of many metallic precursors which can thus be used for chemical transformation. In the paper, a detailed comparison is done between SFCD and CVD in terms of experimental conditions, reactor geometry, process mechanisms, and finally characteristics of the metallic coating. It is concluded that SFCD may be an interesting alternative to CVD, especially for the coating of complex substrates.

In order to compare CVD and PVD processes, Thomann et al. (universities of Orleans and Toulouse) use silicon micropatterned substrates that have been especially designed to investigate the ability of gas-phase deposition techniques to coat submicrometer and micrometer patterns (trenches, blocks, and holes). Three deposition techniques, namely MOCVD, PLD, and MSD are tested for the processing of Al film, a well-known material with significant applications potential. The results reveal that, in addition to the investigation of conformity aspects, such model substrates permit the gaining of insight into the growth parameters and could, thus be an efficient tool for the comparative study of deposition processes. For instance, the directionality of the atom flux arriving at the substrate can be studied. In this paper, differences between MSD and PLD films are evident, although both processes are known to be highly anisotropic.

In the next paper from El-Mel et al. from the University of Nantes, the anisotropy of the atom flux coming from the sputtered target in MSD is utilized to synthesize aligned ZnO nanowires. In this case, what is usually considered as a drawback (especially for the synthesis of conformal deposit onto complex surfaces), is proved to be a discriminant advantage. Arrays of nanowires parallel to the substrate are successfully deposited by MSD selec-

tively on the top of silicon nanolines prepared by laser interference lithography. The size and dimensions of the nanowires can be controlled; they are determined by those of the nanoline template patterns.

The next two articles deal with the optimization of CVD experimental parameters with the aim of processing conformal coatings. Conformality can also be promoted through the activation of the gas phase, or by properly selecting the nature of the film. In the first paper, Siriwongrungson and co-workers from the University of Canterbury perform deposition of TiO₂ on nano- and micro-patterned Si and Si₃N₄ substrates by PP-MOCVD. The thickness uniformity is studied by statistical conformality measurements on a single pattern of the substrate. Very good conformality is obtained in the entire range of investigated deposition parameters. Conformality and film microstructure is found to be independent of deposition conditions, and this result is attributed to the unique mass transport regime created in PP-MOCVD. It is concluded that PP-MOCVD permits the defining of a new parametric window for the synthesis of conformal coatings.

To reach the same objective, Supiot et al. from the University of Lille choose to ionize the gas phase. Deposition of organosilicon polymers by PECVD and remote (R)PECVD on micropatterned silicon substrates is investigated. The deposition rate at various locations on the patterns (bottom, top, side wall) is measured and compared with values obtained from a 3D growth model. Again, the coating characteristics are used here, in comparison with the simulation results, to gain insight into the thin film growth mode.

When conformal films are required, the technique that gives the best results, whatever the nature and scale of the substrate complexity, is ALD. In their paper Brizé et al. from the Grenoble institute of technology study the deposition of TaN from pentakis(dimethylamido)tantalum (PDMAT) and NH₃ on various nanopatterned substrates. A

detailed thermodynamic study shows that the precursor is fully decomposed and that deposition occurs from its fragments. Under optimized deposition conditions, conformal deposits are obtained even on patterns exhibiting aggressive aspect ratios. On complex substrates such as nanowires, the ALD TaN layers are found to be perfectly uniform, and even follow the roughness and irregularities of the surface.

The mechanisms involved in ALD are simulated by Adomaitis et al. at the University of Maryland, by coupling ballistic transport and ALD surface-reaction models. Predictions are compared with previously published experimental studies of ALD in nanopores. As mentioned by the authors, this work gives the baseline for the further development of models dedicated to deposition onto more realistic surfaces. The utility of such physically based models would be to determine optimal precursor exposure levels for ALD nano-manufacturing operations.

The last two papers deal with the comparison between experiments and simulations in two different, though equivalent in principle, CVD processes: Infiltration of fibers to synthesize ceramic matrix composites or carbon fiber-reinforced carbons; and deposition onto powders by fluidized bed CVD. In the former, Ros et al. at the University of Bordeaux develop a 3D Monte Carlo code based on the random walk technique. This tool is able, not only to simulate a deposition run, but also to determine important process parameters such as the effective diffusion tensor and the reaction rate of the medium. This model is first validated on a slit pore and then applied to the densification process of fibers. The paper also reveals that the model is valuable for the study of deposition onto a structured surface by PVD techniques such as RPECVD. The development of such versatile models would be of great interest to compare CVD and PVD processes.

In the latter contribution, Reuge et al. from the University of Toulouse investigate fluidized bed CVD of silicon

from silane onto agglomerates of TiO₂ submicrometer particles. Experiments and simulations indicate that the deposition zone is limited to several millimeters, and that very high local deposition rates exist. From these results, optimized deposition conditions are defined which should limit the powder agglomeration process. The authors conclude that *“Such an approach, combining experimental and modeling analysis, is of interest for all the researchers working in gas-phase deposition processes on micrometer-size and nanometer-size objects forming agglomerates (micro- or nano-fibers, nanotubes, nanowires, micro- nanoparticles)”*.

The papers gathered in the present issue provide a comprehensive overview of the main features of PVD and CVD coatings, related to the involved growth mechanisms. They illustrate the ability of each technique to perform deposition onto various types of substrates such as nano-objects, porous media, powders, micropatterns, etc. It is, for example, clearly stated that CVD is very suitable for deposition into porous materials, or for homogenous coating of powders; ALD is the very best technique to obtain conformal films on patterns of very aggressive aspect ratio, and PVD techniques give rise to anisotropic atom fluxes. Depending on the required final properties or designs, features at the substrate surface (patterns, roughness, porosity, etc.) may have to be reproduced or, on the contrary, modified. Conformality may not be the goal to reach! Papers in this issue show that very interesting new materials can be produced using anisotropic processes.

The reported examples show that combination of various gas-phase techniques may be the only way to synthesize complex materials that are requested at the present time to ensure cocktail or upgradeable properties. Deposition process solutions that will be developed in the future to build such intelligent materials may be hybrid or multi-stage. Because their deposition conditions and growth modes are different, PVD and CVD methods are

complementary, and will allow the synthesis of a wide range of functional materials.

In the frame of very complex material synthesis, the research field on deposition onto complex substrates will be of particular relevance. In terms of process improvement, the aim will be to reach a precise control of the film characteristics in order to tailor specific properties. This objective will only be achieved in a sustainable way, however, if deposition mechanisms have been elucidated and monitored with regard to the targeted specifications. As is reported in this issue, complex substrates are now developed to serve both for material development and for process investigation.

An important point for further research in the field of deposition onto complex surfaces is the coupling of simulations with experiments. Indeed, since the in-situ analysis of the growing surface at topologically different locations is extremely difficult if not impossible, the only way to validate growth mechanisms and predict coating features will be to compare simulations with a posteriori film characterization.

It has been a great pleasure to work on this issue dedicated to the deposition onto complex-shaped surfaces. We are indebted to Professor Michael L. Hitchman for the opportunity he gave us to coordinate these interesting manuscripts, to all the authors for their high-level contributions, and to the referees for their constructive reviews. Last but not least, we thank the Journal's staff with a special mention to Mrs Heather Elliott for patiently assuming the role of converging point among authors, reviewers, and editors.

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