Nanostructured Films and Coatings

Edited by

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Preface

The NATO Advanced Research Workshop on Nanostructured Films and Coatings (Santorini, Greece, June 28-30, 1999) successfully reviewed the state-of-the-art of many topics in this rapidly growing high-tech area. Nanostructured films and coatings may possess unique properties due to the size and the interface effects. They find many advanced applications such as electronics, catalysis, protection, data storage, optics and sensors. The focus of the Workshop was placed on the synthesis and processing; advanced characterization techniques; properties (including mechanical, chemical, electronic, thermal, catalytic, and magnetic); modeling of intralayer and interlayer interfaces; and applications.

Nanostructured films can be synthesized by vapor phase and solution chemistry methods. Solution approach allows the complex and hidden surfaces to be coated since it does not have the limitation of line-of-sight deposition as in the vapor methods. Vapor deposition such as sputtering, chemical vapor condensation and solution chemistry such as sol-gel, electrodeposition and electroless deposition were reviewed. Template-mediated approach was also discussed. Thick coatings were prepared using thermal spraying of nanostructured powders. Increasing attention is given on the use of liquid precursors for thermal spraying.

Advanced characterization techniques of nanostructured films and coatings were addressed. These included, for example, magnetic domain imaging; structural and residual stress study using synchrotron radiation techniques; and surface chemistry using surface FTIR. It was noted that some conventional techniques may not accurately determine the structure of nanostructured alloys and composites, and new techniques need to be developed for better characterization of nanostructured materials.

Enhanced material properties of nanostructured films and coatings were reported in many areas. The understanding and control of the intralayer and interlayer interfaces in multilayered, multifunctional nanostructured films and coatings are critical to the optimization of material properties and performances. Tailor-design of interfaces in these materials through modelling and experimental efforts is receiving growing interest.

The participation in the Workshop was by invitation. This NATO ARW publication includes most of the invited lecture and invited poster papers.

We would like to acknowledge the significant contribution of the organizing committee: Lawrence Kabacoff (USA), A. K. Vasudevan (USA), Lynn K. Kurihara (USA) and Alexei Romanov (Russia). We gratefully acknowledge the major financial support of this ARW by the NATO High Technology Program, and the co-sponsorship by the International Field Office (Europe), U.S. Office of Naval Research; European Research Office of the U.S. Army; European Office of Aerospace Research and Development, and U.S. Air Force Office of Scientific Research, U.S. Air Force Research Laboratory. We thank Yannis Papaioannou, Tourlite International (USA) for his assistance with the travel and lodging for the participants, and many others who provided their support in the preparation and conduction of the Workshop. We also thank Deborah K. Chow for the editorial assistance with the proceedings.

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GAS PHASE SYNTHESIS OF NANOSTRUCTURED FILMS AND COATINGS

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1. Introduction

Nanocrystalline materials have become increasingly important both in fundamental and applied research because of their interesting properties which are altered compared to conventional microstructures due to effects of grain size and due to the disordered atomic structure of the interfacial regions. For many years the research was concentrated on the synthesis and properties of nanocrystalline materials in bulk form which were prepared by consolidation and sintering of nanocrystalline powders prepared by wet chemical, gas phase and mechanical routes. Recently, as a response to the need of constantly improving the properties and performance of thin films and coatings, a potential for nanocrystalline materials in the area of novel synthesis and microstructures of films and coatings was identified. Many different techniques for the preparation of thin and thick films are readily available both for industrial applications and basic research and provide an excellent base for the development and application of new methods. The potential of nanocrystalline films and coatings can be identified in a wide range of technologies based on friction and wear properties, other mechanical properties such as superplasticity, and thermal conductivity for thermal barrier coatings, and optical, magnetic, electronic and catalytic properties.

In principle many different structures in thin films such as multilayers in electronic materials and for magneto-resistance effects (GMR, TMR etc.) should be included in a complete review of the topic of nanostructured films and coatings, because the characteristic dimensions are in the nanometer regime. However, it is beyond the scope of this paper to give a complete overview of all these structures and the corresponding processing techniques which are available for the synthesis of thin films and coatings. Therefore, the reader is referred to the literature on physical and chemical vapor processing techniques [1, 2]. Nevertheless, for the understanding of gas phase synthesis processes presented in the following sections it is worthwhile to note that the physical and chemical vapor deposition routes (PVD, CVD) have achieved a high degree of control and excellent reproducibility. Therefore, these techniques are widely spread in both research and production. The PVD and CVD techniques have capabilities to design materials at the atomic level by depositing atomic building units in a layer by layer growth to obtain atomically sharp interfaces between chemically or structurally dissimilar materials. In particular the design of semiconductor interfaces and magnetic multilayers has led to sophisticated artificial materials and unique applications associated with the well-defined nanostructures. As a disadvantage for production on a large scale, the processes for controlled growth are relatively slow.

G.M. Chow et al. (eds.), Nanostructured Films and Coatings, 1–10.

Additionally, the microstructures which can be obtained include single crystalline, epitaxial layers and columnar grain structures depending on the crystallographic relationships between the substrate and the growing film and the synthesis conditions (temperature, pressure, growth rate etc.). However, based on the knowledge of nanocrystalline materials in bulk form, it is anticipated that novel microstructures with grain sizes in the nanometer regime, controlled porosity with narrow size distributions and control of the chemical composition and the elemental distribution on the scale of the nanometer sized grains will open new areas of application. In this paper the opportunities for the growth of films and coatings with nanometer sized microstructures based on chemical vapor processing is reviewed.

2. The Chemical Vapor Synthesis Process

The process for film growth is based on the Chemical Vapor Synthesis (CVS) which has been described in detail in the literature [3]. The CVS technique itself is similar to the process of Chemical Vapor Deposition (CVD) which is widely employed to prepare thin films and coatings at a high level of control. The conditions for CVD growth have been determined for many materials systems and detailed knowledge exists for the dependence of the growth rate as a function of precursor partial pressure and temperature as well as other quantities influencing the growth of films on substrates. In the simplest form of a hot wall reactor the substrate is located in a cylindrical reactor tube heated with an external furnace. Other activation source such as microwave plasma can be employed as well. The complex growth process includes multiple steps such as decomposition of the metalorganic precursor molecules, gas diffusion to the hot substrate, deposition of the atomic species on the surface of the substrate and surface diffusion of the species to energetically favored sites on the surface such as steps and kinks. The growth rate of a film on a substrate depends on many parameter. It is shown schematically in Figure 1 as a function of the inverse temperature and the partial pressure of the precursor. Several distinct growth regimes can be identified in the dependence on the precursor pressure: (1) a regime in which the growth rate depends linearly on the precursor partial pressure; (2) a regime in which the growth rate on the substrate ceases to increase with increasing partial pressure and (3) a regime in which a rapid decrease at the highest partial pressures occurs. The best conditions for CVD growth are in the initial linear regime because the precursor decomposes and the reaction products are solely deposited at the surface of the growing films. Over a wide range of pressure no change in the mode of growth is observed and conditions for stable growth are given. In the plateau regime additional formation of nanoparticles occurs in the gas phase and consequently the growth rate of the film does not increase with increasing precursor partial pressure. At the highest partial pressures film growth is further suppressed and most of the precursor is transformed into nanoparticles because fewer precursor molecules reach the substrate surface. While this regime is not desirable in conventional film growth because of the incorporation of the nanoparticles into the films, this regime is used for the formation of nanoparticles by CVS. In this process the particles are collected from the gas phase after exiting from the hot wall reactor and can be processed further by consolidation and sintering.

The temperature dependence of the growth rate by CVD shows a similar behavior: (1) film growth occurs in the first two regimes with surface reaction control and gas diffusion control as rate determining steps. At higher temperatures the film growth rate decreases rapidly due to the homogeneous formation of nanoparticles in the gas phase. Therefore, optimum conditions for particle formation in the gas phase, i.e. CVS, require high temperatures and high precursor partial pressures.

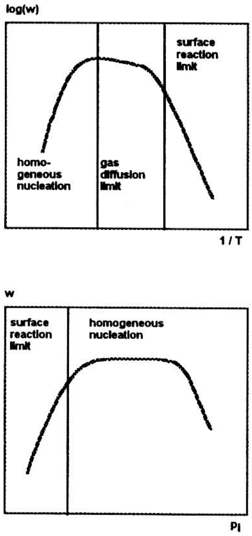

Figure 1: Schematic dependence of the film growth rate on a substrate by CVD growth as a function of the inverse temperature (top) and the precursor partial pressure P_i (bottom).

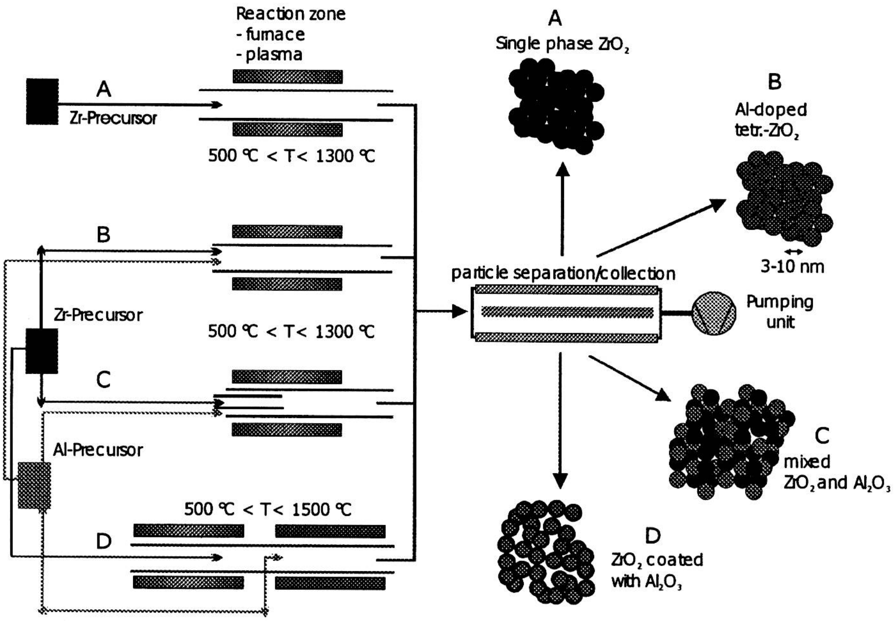

Figure 2: Opportunities of the CVS processing for the synthesis of nanocrystalline oxides with different elemental distributions of Zr- and Al-ions in the individual nanoparticles and the corresponding geometry of the various reactor designs.

The opportunities which result from the unique design of a hot wall CVS reactor for nanoparticle synthesis are illustrated schematically in Figure 2. The design is applicable in general for many materials systems, but as an example the consequences for the microstructure of the nanoparticles are shown for the ZrO_2/Al_2O_3 system, which is immiscible according to the equilibrium phase diagram. By changing the reactor geometry it is possible to synthesize oxide nanoparticles with different elemental distributions of the Zr- and Al-ions: crystalline and amorphous Al-doped zirconia, mixed pure oxides and coated nanoparticles. The possibility to control the elemental distributions within the nanoparticles opens many opportunities for the engineering of properties.

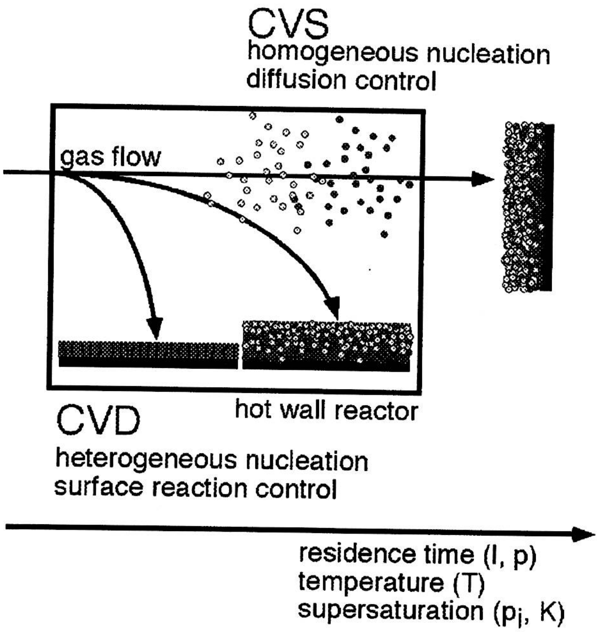

Figure 3: Various synthesis techniques based on chemical vapor processing: CVD for pure film growth with epitaxial or columnar grain structure, CVS for homogeneous formation of nanoparticles and CVD/CVS for nanoparticle deposition on a substrate with instantaneous sintering.

An interesting opportunity arises by the careful control of the synthesis parameter in the regime where CVD growth coincides with nanoparticle formation in the gas phase. At high precursor partial pressures and high temperatures, i.e. at high growth rates, it is possible to incorporate nanoparticles into the growing film, thus increasing the film growth rates compared to pure CVD growth. It has been demonstrated that nanoparticles which are formed in the gas phase can be deposited on the surface of a substrate held at high temperatures. Depending on the processing temperature it is possible to obtain porous or dense nanocrystalline coatings. The complete range of possibilities from epitaxial and columnar coatings grown by CVD, nanoparticles in the gas phase by CVS and the intermediate range of CVD/CVS as discussed above is summarized in Figure 3, highlighting the relationship between the different techniques. An important feature of the CVD/CVS regime is the high growth rate, because the total rate is determined by the sum of the film growth (CVD) and the