Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B2-2-MoA

CVD Coatings and Technologies II
Moderator: Raphael Boichot, Grenoble-INP/CNRS, France

1:40pm **B2-2-MoA-1 Synthesis of Rare Earth Silicate Coatings by CVD**, ***Arthur Derrien (derrien@lcts.u-bordeaux.fr)**, L. Lager, J. Roger, J. Danet, S. Jacques,* LCTS, CNRS, Univ. Bordeaux, France

Rare earth silicates (RESiO) are increasingly studied due to their optical and electrical properties. They are also chemically inert and have numerous crystalline structures allowing their properties to be adjusted depending on the required application. They are used in various fields such as lasers, sensors, microelectronic components or solid oxide fuel cells.

These applications require a good control of the process during the synthesis of these materials, sometime used as coatings. The methods conventionally used to produce these films, such as sol-gel or PVD, have disadvantages in terms of thickness control, homogeneity and conformity on parts presenting complex geometry. Thus, the production of these thin films by CVD can overcome these disadvantages to obtain coatings with controlled composition and desired crystalline phase, in order to have homogeneous and conformal thin films, by avoiding, for example, the shading phenomena linked to PVD processes oncomplex shaped parts.

Since the crystallized phases of these materials are formed at relatively high temperatures (>1000°C), the most suitable gaseous precursors for the deposition of RESiO are halogen-containing reagents, especially $SiCl_4$ and $RECl_3$, because of their thermal stability. While $SiCl_4$ is liquid at room temperature, rare earth chlorides are solid up to more than 700 °C, complicating their transport to the reaction zone and the control of their flow. The control of the composition, and therefore of the crystalline phase of the produced coating is difficult.

The case of yttrium silicates is studied here. After setting up an in-situ weighing system, the evaporation of YCl_3 could be studied over a pressure/temperature range matching with the CVD deposition conditions that were previously determined by a thermodynamic approach. In this way, the flow rate of chlorinated precursors could be controlled up to 1150 °C in order to lead to the formation of yttrium silicate coatings on alumina substrates. The obtained coatings were characterized using different techniques: Raman spectroscopy, X-ray diffraction, EDS and SEM.

2:00pm **B2-2-MoA-2 Doped Alumina Coatings**, ***Zhenyu Liu (zhenyu.liu@kennametal.com)***, Latrobe, USA

In order to enhance the performance of the conventional alumina coating and meet the needs for high performance and high-speed cutting applications, the definite demands in the improvement of thermal resistance and wear resistance are necessary. Therefore, it is the technique need to develop novel CVD alternative alumina coatings with novel structures or coating architectures. By using doping elements, such as Ti, Zr and/or other group IV elements, the doped alumina with excellent wear resistance and tool life can be achieved.

The doping process will create not only novel grain crystalline structures but also alternative coating structures. We have developed different doping procedures including Ti, Zr, Hf-doping and the co-doping. The previous research showed that dopant such as Ti can modify the surface energy of formed oxide crystalline planes. One good support on this hypothesis and practice is that the Ti-doped CeO_2 particles showing round shape, in contrast to the un-doped CeO_2 having polyhedron crystal structures. the dopant atoms may distribute at single atom level in the oxide metal ion column and enrich at the grain boundary. According to the Goldschmidt's Rules on Thionic substitution, the ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 15%. (Free substitution can occur if ionic size difference less than 15%; Limited substitution can occur if ionic size difference is 15~30%; little or nonsubstitution can occur if ionic size difference is greater than 30%.) In the systematical doped alumina coatings, the ionic radius of Al^{3+} is ~0.675 Å, Ti^{4+} is ~0.745 Å; Zr^{4+} is ~0.80 Å and Hf^{4+} is ~0.79 Å. The ion size differences from the group IV B is less than 15%, then they should be substituted freely by one another.

At the same time, the dopant atoms can segregate and enrich at the grain boundary. The grain boundary engineering can provide enhanced grain interaction and dopant atoms can function as the pinning atoms or provide pinning effect for grain boundary, leading to enhancement of the thermomechanical properties. It is already accepted that the dopants will markedly strengthen the alpha-Al_2O_3 interface against mechanical deformation.

Keywords: CVD, Al_2O_3, thin films, nucleation, crystal growth

2:20pm **B2-2-MoA-3 Stress Control of AlN-based Multilayer Coatings with Amorphous Intermediate Layers**, *V. Tabouret, R. Reboud, A. Crisci,* ***Frederic Mercier (frederic.mercier@grenoble-inp.fr)***, SIMAP, Grenoble-INP, CNRS, France

Aluminium nitride (AlN) possesses attractive properties like piezoelectricity, high thermal conductivity, low thermal expansion coefficient, high temperature stability, chemical barrier capabilities and ability to develop stable alumina scales at high temperature. Stress control of AlN-based coatings is therefore of high importance for emergence of new applications.

We report in this presentation the possibility to tune the stress in AlN-based multilayers by introducing amorphous intermediate layers. AlN-based multilayer coatings are grown by metal-organic chemical vapor deposition (MOCVD) on 300 µm thick silicium (100) wafer at 900°C. Trimethylaluminium, ammonia and propane were used as Al, N and C precursors. Alternative injection of precursors enables the growth of polycrystalline/amorphous multilayers and the control of the stress in the coatings. In situ curvature, ellipsometry and reflectance measurements are performed simultaneously during growth.

Based on in-situ measurements and ex-situ precession electron diffraction techniques, we demonstrate that the growth of virtually stress free AlN is possible with the introduction of amorphous layers in the multilayer structure.

2:40pm **B2-2-MoA-4 Circumventing Thermodynamic Constraints – A Selective Kinetic Growth of Low Thermal Expansion Al_2TiO_5-coatings by Chemical Vapour Deposition**, ***Sebastian Öhman (sebastian.ohman@kemi.uu.se)***, Uppsala University, Angstrom Laboratory, Sweden

Most materials expand upon heating. Yet, a few are known to behave the opposite way around. Almost exclusively, these may be found among multicomponent transition metal oxides sharing a diverse range of properties. However, their potential applications have remained scarce due to the difficulties faced in their synthesis and their general metastable characters, which typically limits their thermal stabilities.

This talk will present a novel chemical vapour deposition method to prepare such multicomponent phases at low temperatures and with increased stabilities. Specifically, I will demonstrate how aluminium titanate (Al_2TiO_5), a renowned low-to-negative thermal expansion material with favourable heat-resistant properties, can be synthesized at much lower temperatures than predicted by thermodynamics. Examinations of the Al-Ti-O system led us to discover new types of structurally related intergrowth phases, having enlarged unit cells, leading to improved thermal stabilities of these materials. The cause and origin of these intergrowth phases will be discussed based on detailed Raman spectroscopic measurements and in-situ TEM analyses studying their crystallization behaviours.

Materials possessing a low-to-negative thermal expansion are an attractive candidate to improve the thermal resistance of multi-layered coating designs used in applications such as microelectronics, optical engineering, energy harvesting and wear resistance. Thus, this talk aims to not only present a method to fabricate materials for these specific purposes, but also to open the potential of fabricating new multicomponent oxide coatings within other material systems.

3:00pm **B2-2-MoA-5 Atomic Layer Deposition of BN Based on Polymer Derived Ceramics Route: Fabrication of Functional and Protective Coating**, ***Catherine Marichy (catherine.marichy@univ-lyon1.fr)**, W. Hao, A. Hossain, C. Journet,* University Lyon, France **INVITED**

The scientific interest for hexagonal boron nitride (h-BN) material, especially as thin film and nano-/hetero-structures, is growing owing to its potential use in various domains such as microelectronic, spatial, lubricant, energy and environment. Atomic Layer Deposition (ALD) is a technique of choice for fabrication of such thin films and complex nanostructured material.(*1*, *2*) Despite some limitations of temperature and crystalline quality, ALD already demonstrates suited to fabricate BN layers that can successfully be integrated into electronic devices.(*3*) Based on polymer derived ceramics chemistry, we developed a two-step ALD process of BN

that permits access to various BN thin films and complex nano-/hetero-structures. It consists of the growth layer by layer of a preceramic BN films, onto various substrates, at low temperature, and then to its densification into pure BN by annealing process.(*4*)

Herein, the potential of the ALD process based on PDCs route for BN thin films will be discussed. Indeed, BN thin films were successfully deposited in a controlled manner on various inorganic and organic substrates/templates. The application of the developed process for fabricating protective coating towards oxidation and functional quality crystalline BN nano/heterostructures will be presented.

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1. *ChemNanoMat*. **3**, 656–663 (2017).

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