## Hard Coatings and Vapor Deposition Technologies
## Room California - Session B2-2

### CVD Coatings and Technologies

**Moderators:** Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

1:50pm **B2-2-2 Highly Efficient Light trapping by Fractal, MOCVD Processed CoO-based Surfaces on Polymers***, E Amin-Chalhoub, O Debieu, D Samelor,* ***Thomas Duguet****, C Vahlas,* CIRIMAT, CNRS - University of Toulouse, France

Low reflective films containing CoO are processed by chemical vapor deposition from direct liquid injected solutions of $Co_2(CO)_8$ in heptane, in the presence of oxygen. The films are deposited on silicon and epoxy resin – carbon fiber composite coupons in a cold wall reactor operated at 5 Torr between 50 °C and 160 °C. Those processed at 50 °C, 125 °C and 160 °C present a cauliflower-type nodular morphology, with distinct nodules grown on a relatively smooth background, with similar microstructure but on a finer scale. XRD and FTIR analysis reveal that low temperature processed films are composed of CoO, while those processed at 125 °C and above also contain the spinel structure Co3O4. All films contain significant concentration of amorphous, aliphatic carbon. The optical reflectivity in the visible region stems from 1 to 14% depending on deposition temperature. The combination of specific microstructural features of the coatings, namely a fractal “cauliflower” morphology and a grainsize distribution more or less covering the near UV and IR wavelength ranges enhance light scattering and gives rise to a low reflectivity. In addition, the columnar morphology results in a density gradient in the vertical direction that we interpret as a refractive index gradient lowering reflectivity further down. The coating formed at 125◦C shows the lowest reflectivity (1 %) in the range 400 – 750 nm and presents an interesting deep black diffuse aspect. It can thus be applied as antireflective coating in startracking instruments used for spacecrafts navigation.

2:10pm **B2-2-3 Deposition Kinetics, Gas Phase Analysis and Film Characterization of Silicon Carbide by Low Pressure Chemical Vapor Deposition using Vinyltrichlorosilane and Hydrogen***,* ***Anthony Desenfant****,* LCTS-University of Bordeaux, France*; G Laduye,* AIR LIQUIDE, Paris-Saclay Research & Development, France*; C Descamps,* Safran Ceramics, France*; G Vignoles, G Chollon,* LCTS-University of Bordeaux, France

SiC/SiC composites are of great interest for high temperature structural applications such as jet engines. The SiC matrix is usually deposited by chemical vapor deposition (or infiltration: CVD/CVI) using a mixture of methyltrichlorosilane (MTS, $CH_3SiCl_3$) and hydrogen. If not handled carefully, this process can lead to silicon co-deposition and inhomogeneous infiltration of the fiber fabrics. In this context, we have studied vinyltrichlorosilane (VTS, $C_2H_3SiCl_3$) as an alternative precursor for SiC. The low-pressure CVD reactor was associated to a microbalance and an FTIR spectrometer to record the deposition rate and the gas concentrations as a function of the deposition temperature, pressure, $\alpha = (P_{VTS}/P_{H2})_{initial}$ and total flow rate. Model porous substrates were also submitted to CVD/CVI, to evaluate the homogeneity of infiltration in a few selected conditions. This approach allowed proposing a basic mechanism for the CVD using $VTS/H_2$ and, besides, identifying proper conditions for the growth of pure and crystalline SiC. The Arrhenius plots of the deposition rate show three distinct kinetic domains. Free carbon is co-deposited within the low-temperature kinetically-controlled regime CRR1, while VTS is only partially decomposed. Such a carbon excess results from the formation of highly reactive carbon-bearing species, e.g. $C_2H_3^{\bullet}$, in contrast with the silicon-bearing species. Changes in the heterogeneous reactions are responsible for a transient regime CRR2 characterized by a particularly high apparent activation energy and a hysteresis phenomenon. The higher temperature CRR3 domain, of lower activation energy, is more favorable to deposit pure SiC. In the gas phase, $H_2$ seems to play a role in the homogeneous decomposition of VTS. In the solid, the replacement of $H_2$ by Ar leads to carbon-rich coatings, as observed in the CRR1 domain. Low deposition temperatures are usually beneficial to the homogeneity of infiltration for the CVI process. The lowest thickness gradient between the surface and the core of porous substrates is indeed observed in the CRR1 domain. A carbon-rich coating is deposited at the entrance of the model channel pore but the composition sharply turns to pure SiC deeper in the channel. The influence of residence time $\tau_r$ and the depletion of the reactive carbon precursors in the gas phase is likely responsible for such a change in the nature of the deposit. By following the VTS concentration as a function of $\tau_r$, the apparent activation energy of the homogeneous decomposition of the precursor could be evaluated at about 290 kJ/mol. A simple homogeneous and heterogeneous mechanism was constructed based on the previous investigations.

2:30pm **B2-2-4 Hydrothermal Corrosion Behaviors of CVD Silicon Carbides and Cr-based Alloy Coated CVI $SiC_f$/SiC Composites***,* ***Jung Ho Shin****, D Kim, H Lee, J Park, J Park, W Kim,* Korea Atomic Energy Research Institute, Republic of Korea

Replacing Zircaloy with ceramic materials having high accident resistance currently used as fuel cladding on pressurized water reactor have been actively studied after the Fukushima Daiichi nuclear accident. It is expected that the ceramic material with a low amount of hydrogen generated by reaction with a coolant during abnormal operation of the reactor and excellent in high temperature mechanical properties can be utilized as a next generation reactor cladding material. Among them, SiCf/SiC composites have attracted much attention due to its excellent corrosion resistance and high temperature strength as well as its high thermal conductivity and low neutron absorption cross section. Additionally, it does not suffer from fretting wear and hydrogen reactions. The SiC has a very good oxidation resistance due to the formation of a SiO2 protective coating in a high temperature gas environment, but mass reduction of the SiC is occurred by the dissolution of oxide layers of SiO2 / Si(OH)4 in a high temperature hydrochemical environment. Microstructural change and defects occurred during the SiCf/SiC synthesis process affect neutron irradiation deformation and corrosion behavior.

For improving these problems, corrosion resistant coating on cladding is one of the candidate technologies to improve the corrosion resistance of SiCf/SiC composites cladding in the PWR environment. By applying coating technology to SiCf/SiC composistes cladding, it is easy to obtain corrosion resistance without a change in the base materials. Among the surface coating methods, arc ion plating (AIP) is a coating technology to improve the adhesion owing to good throwing power, and a dense deposit. Owing to these advantages, AIP has been widely used to efficiently form protective coatings on cutting tools, dies, bearings, etc. Thus, considering the advantages of AIP, we attempted to improve the corrosion resistance of SiCf/SiC using AIP. For this purpose, we coated Cr-Al alloy on SiCf/SiC composites claddings and their corrosion behavior in the simulated PWR primary water condition.

2:50pm **B2-2-5 Temperature Driven Microstructural Evolution of Nano–lamellar CVD fcc–$Ti_{1-x}Al_xN$***,* ***Michael Tkadletz****, C Hofer,* Montanuniversität Leoben, Austria*; C Wüstefeld,* Technische Universität Bergakademie Freiberg, Germany*; N Schalk,* Montanuniversität Leoben, Austria*; M Motylenko,* Technische Universität Bergakademie Freiberg, Germany*; D Rafaja,* Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Straße 5, 09599 Freiberg, Germany*; C Giacobbe, C Dejoie,* ESRF, France*; H Holzschuh, W Bürgin,* SuCoTec AG, Switzerland*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; C Mitterer,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria

In recent years, nano-lamellar face centered cubic (fcc-) $Ti_{1-x}Al_xN$ coatings with x as high as ~0.8 to ~0.9 deposited by thermal chemical vapor deposition (CVD) have been investigated extensively. However, detailed information about microstructural evolution, decomposition and fcc-wurtzitic (w) transformation at elevated temperatures is still missing. Thus, within the present work, the temperature-induced microstructural changes were studied up to temperatures of 1300 °C for a nano-lamellar fcc-$Ti_{0.2}Al_{0.8}N$ coating that was deposited using thermal CVD at ~850 °C. *In situ* high-temperature X-ray powder diffraction and differential scanning calorimetry experiments were employed to follow the phase evolution at elevated temperatures. Scanning and transmission electron microscopy, carried out *ex situ* for six different microstructural states after isothermal annealing, revealed the distribution of individual phases, morphology of the phase regions and the orientation relationship of fcc-TiN clusters embedded in the w-AlN matrix. Complementary atom probe tomography investigations provided 3D information about the distribution of Ti and Al and about the formation of clusters after annealing. In the as-deposited state, the coating is characterized by columnar, relatively large fcc grains exhibiting a nano-lamellar microstructure. Initial decomposition of supersaturated fcc-$Ti_{1-x}Al_xN$ and transformation of Al-rich fcc-(Al,Ti)N to w-(Al,Ti)N were detected at temperatures of ~850-1000 °C. Up to ~1200 °C, intact nano-lamellar fcc areas were still observed, but they already co-existed with fully decomposed and transformed areas. The results indicate a wavefront-like decomposition/transformation within and across individual grains that constantly reduce the fcc fraction with increasing temperature.

3:10pm **B2-2-6 Dense, Uniform, Transparent $SIO_2/TIO_2$ Coatings Derived from a Single Precursor Source of Tetrabutyl Titanate Modified Perhydropolysilazane***, **Zongbo Zhang,*** Institute of Chemistry, Chinese Academy of Science, China*; D Wang,* University of Chinese Academy of Sciences, China*; Y Luo, C Xu,* Institute of Chemistry, Chinese Academy of Sciences, China

$SiO_2/TiO_2$ thin or multilayers of $SiO_2$ and $TiO_2$ coatings have being widely investigated and applied in the fields of optical waveguiding, antireflection coatings, thermal protection systems, self-cleaning coatings, and semiconductor devices, for their excellent optical, photocatalytic, superhydrophilic, electrical, and mechanical properties. Various methods have been adopted to prepare $SiO_2/TiO_2$ coatings, such as electron-beam evaporation, chemical vapor deposition (CVD), and sol-gel process. Among these methods, the sol-gel method is simple and inexpensive, especially suitable for preparation of coatings on components with complex surface or big dimensions. However, due to the faster hydrolysis rate of Ti precursor, co-hydrolysis of alkoxylsilane and tetra-alkyl orthotitanate usually achieve inhomogeneous dispersion of $SiO_2$ and $TiO_2$ sol, which results in aggregates, cavities, rough surface in the formed $SiO_2$-$TiO_2$ coating.

In this work, dense, uniform, transparent, robust $SiO_2/TiO_2$ composite coatings have been successfully prepared by hydrolysis and subsequent thermal treatment of tetrabutyl titanate-modified perhydropolysilazane. The composition analysis revealed that Ti element was uniformly distributed in the composite coatings. The anatase TiO2 formed initially in the coating when the heat-treatment temperature reached 700oC. The as-prepared coatings have their thickness in range of 100 to 142 nm, and transmittance over 90% in the visible region. The refractive index, surface hardness, and elastic modulus of coatings enhanced continuously with the increasing pyrolytic temperature. Besides, the obtained coating possesses excellent hydrophilicity with contact angle below 40o and low roughness with Sa below 3.5nm.

3:30pm **B2-2-7 Emerging Photoluminescence in Chemical Vapor Deposition Grown $MoSe_2$/*h*-BN Van der Waals Heterostructure***, **Pramoda K. Nayak,*** Indian Institute of Technology Madras, India*; S Ahn, C Hyun, K Ma, H Shin,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Atomically thin transition metal dichalcogenides (TMDCs) with chemical formula $MX_2$ (M = W, Mo and so on, and X = S, Se, or Te) have attracted considerable interest today owing to their sizable band gap in a technologically interesting range1–3 eV [1], which paves the way to consider these materials for new generation field–effect transistors, sensors and optoelectronic devices. In parallel, hexagonal boron nitride (*h*-BN) have also gained a great deal of attention in the last few years with the emergence of two-dimensional atomic crystals and its unique electronic properties including wide band gap, low dielectric constant, high thermal conductivity and chemical inertness [2]. Van der Waals heterostructures made up of TMDs and *h*-BN are supposed to exhibit improved materials properties which are different from that of individual counterparts [3]. Mechanical transfer process is the most preferred way to prepare TMDCs/*h*-BN HS, which includes a deposition of polymers and a solution-based washing process [4], that degrades the quality of sample. Therefore, it is very necessary to develop a simple, fast, and scalable direct growth process to avoid any material deterioration that arises during wet-chemical assisted transfer processes.

In this work, we report direct growth of $MoSe_2$ onto high-quality multilayer *h*-BN using chemical vapor deposition. Interestingly, we observed emerging photoluminescence in $MoSe_2$/*h*-BN HS, *i.e.* the PL intensity of monolayer $MoSe_2$ increases by one order of magnitude with reduced FWHM of 45 meV, implying high crystallinity of $MoSe_2$ while prepared on *h*-BN substrate. This is attributed due to the good interlayer coupling, cleaner and sharper interfaces, smaller lattice strain, and lower doping of the underlying *h*-BN substrate [5]. Our work allows fabrication of a variety of TMDCs/*h*-BN heterostructures and paves new direction to consider these materials for next-generation optoelectronics devices including solar cells, LEDs, Laser diodes and so on.

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[3] L. Fu, Y. Sun, N. Wu, R. G. Mendes, L. Chen, Z. Xu, T. Zhang, M. H. Rümmeli, B. Rellinghaus, D. Pohl, L. Zhuang, L. Fu, *ACS Nano* 10, 2063−2070 (2016).

[4] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, *et al. ACS Nano* 7, 7931–7936 (2013).

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3:50pm **B2-2-8 Innovative Concepts for Advanced CVD Carbide Coatings Grown by Direct Liquid Injection of Metalorganic Precursors***, **Francis Maury,*** CIRIMAT, CNRS - University of Toulouse, France*; A Michau,* CEA Saclay, France*; G Boisselier,* CIRIMAT, France*; F Schuster,* CEA Saclay, France

DLI-MOCVD is an emerging CVD process that combines the use of metalorganic precursors (MO) and direct liquid injection (DLI) of the reactive sources. The main advantages are a significant reduction of the deposition temperatures and the feeding of the reactor by high vapor flow rates. Even if the process can operate at atmospheric pressure, *e.g.* for continuous scrolling treatment, it is under moderately reduced pressures (0.1-5 kPa) that application prospects are greatest due to the diversity of coatings that can be deposited for surface engineering.

Initially DLI technology has been developed and has grown rapidly for the deposition of functional oxide thin films for optical and electronic devices. In that case, oxygen-containing precursors can be selected due to their good volatility, stability and solubility in organic solvents. A solution of precursor is injected and $O_2$ flow rate is frequently added to prevent the film contamination by carbon originating both from the solvent and the precursor since it can be consumed by combustion in the reactor. Oxidation of the film is not a problem since it is an oxide that is deposited.

The challenge of depositing non-oxide coatings as carbides is more complicated because oxygen must be excluded from the process, including from the solvent and the precursor. Then the control of C incorporation in the coating is tricky to deposit the desired phase. The knowledge of the chemistry implemented is a key factor.

Recently, we have developed DLI-MOCVD processes for depositing non-oxide coatings. For instance bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V…) are an important family of CVD precursors for deposition of carbides, nitrides and even the metal. Other new DLI-MOCVD processes were developed for SiC and HfC coatings.

Based on the deposits of $CrC_x$, SiC and HfC, we will highlight and discuss innovative concepts specific to these DLI-MOCVD processes. This includes *(i)* related surfactant effect induced by the solvent to produce smooth surfaces (SiC), *(ii)* positive effects of nanostructuration for hard metallurgical coatings as CrC/CrN multilayers and refractory nanostructured SiC/HfC coatings for high temperature environments, *(iii)* uniform and high conformal coverage coatings (CrC) on 3D pieces for corrosion protection, *(iv)* infiltration efficiency of SiC/HfC multilayer coatings for advanced ceramics, *(v)* self-healing of SiC cracks during the growth of SiC/HfC and *(vi)* deposition of mixed carbides (CrSiC).

4:10pm **B2-2-9 Computational Fluid Dynamics (CFD) Simulation of CVD Process for $(Ti,Si)_x(C,N)_y$ Coating***, **Lianchang Qiu,*** Central South University, China*; S Wang,* Shijiazhuang Tiedao University, China*; Y Du, Z Zhong,* Central South University, China*; H Shi,* Ganzhou Achteck Tool Technology Co., Ltd., China*; L Albir,* Layyous Consulting Ltd., Israel

In the present work, the CVD process for $(Ti,Si)_x(C,N)_y$ coating in the vertical hot-wall reactor was studied through the Computational Fluid Dynamics (CFD) simulation method. By means of ANSYS Fluent software, the reactor model was established and meshed. The CVD process of $(Ti,Si)_x(C,N)_y$ coating from $TiCl_4$-$SiCl_4$-$CH_3CN$-$NH_3$-$H_2$ gas mixture was investigated under different deposition conditions. The thermal and hydrodynamic characteristics inside the reactor were simulated. The influence of concentration of gas species on the growth rate of $(Ti,Si)_x(C,N)_y$ coating deposited on specimens, which were located at different position of the reactor, was predicted. The computational predictions of the growth rate were in reasonable agreement with the experimental measurements. The CFD method is of great importance to optimize the process parameters and provide theoretical guidance for improving the coating uniformity in thermal CVD process.

4:30pm **B2-2-10 Tribological Evaluation and Behavior of DLC Coatings on Steel in PE-CVD System with $TiO_2$ Over Layer using ALD Technique***, **Marco A. Ramirez R.**,* Univap, Brazil*; E Saito,* Federal University of São Paulo, Brazil*; N Fukumasu,* University of São Paulo, Brazil

Diamond-Like Carbon (DLC) coatings have attracted significant attention due to low friction, high hardness and high wear resistance. These films meet conditions that can be used in some mechanical applications in aerospace, medical and automotive industries. The major disadvantage of these coatings is a low adhesion on metallic substrates, caused by elevated compression residual stresses after deposition. Some plasma conventional methods require a high consumption of energy that are used to grow DLC films, resulting in a high level of temperature and pressure during the deposition, which affects the adhesion of the film to the substrate. DLC coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD system, in a very low temperature and pressure (about 87° C and 0.1 Pa) which allowed lower level of collisions and a higher plasma density. Methane gas was used as a precursor. In order to overcome low adhesion of DLC films on steel substrate, a thin amorphous silicon inter-layer was deposited at the interface, and to the last process was to deposit a thin TiO2 film over DLC using ALD Technique. Resulting coatings were observed with SEM and Raman spectroscopy to analyze atomic arrangement. The total residual stress was evaluated by the curvature method. The tribological behavior (friction and wear) was analyzed by lubricated reciprocating wear tests at room temperature. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and methane as a precursor gas to grow DLC films on metallic substrates may represent a new alternative to improve the mechanical behavior in some applications.

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