

## Hard Coatings and Vapor Deposition Technologies

### Room Golden West - Session B2-2

#### CVD Coatings and Technologies

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

8:00am **B2-2-1 Investigation of Ti-based Hard CVD Coatings on Various Metals Sited as Alternate Binder Phase for WC-Co Cutting Tools**, *Linus von Fieandt*, Uppsala University, Angstrom Laboratory, Sweden; *E Lindahl*, Sandvik Coromant R&D Materials and Processes, Sweden; *T Larsson*, SECO Tools, Sweden; *M Boman*, Uppsala University, Angstrom Laboratory, Sweden

Titanium based CVD coatings such as TiN, TiC and Ti(C,N) have been successfully applied as wear resistant coatings on WC-Co cutting tools for almost six decades. Recent research activities for WC based tools aims towards replacement of the Co binder phase, being a suspected carcinogenic. Other metals e.g. Ni and Fe are therefore suggested as possible candidates to replace Co as binder phase.

It is expected that CVD Ti based coatings grown on WC tools with e.g. Fe or Ni as the binder phase will show different nucleation and texture development compared to a conventional WC/Co substrate. The difference in nucleation and initial growth is believed to be attributed to the catalytic properties and reactivity of the binder phase. As such, it is fair to assume that the growth process of the coating needs to be altered in order to facilitate a growth of a controlled morphology and orientation.

Another aspect to be addressed is the coating adhesion. Adhesion is promoted by a low chemical reactivity and a limited diffusion between the binder phase and the coating. Salt like reaction products and brittle intermediate phases are examples of reaction products that can cause poor adhesion.

In this study Ti – based coatings were deposited on various metallic substrates such as; Fe, Ni, Co and Cr using a hot wall CVD equipment. Nucleation, orientation evolution and composition of the deposited layers were investigated. It was found that deposition on pure Ni resulted in a sponge like porous morphology. Deposition on Cr yielded a bimodal morphology with standing platelet crystallites. The coated Fe substrate showed presence of Fe in the deposited coating, which is believed to be caused by substrate corrosion. The conclusions from the experimental results have been supported by thermodynamic calculations.

8:20am **B2-2-2 Hot Filament CVD Diamond Coatings on Cutting Tools for Hard to Machine Materials**, *Michael Woda*, *W Puetz*, *M Frank*, *B Mesic*, *W Koelker*, *C Schiffers*, *O Lemmer*, CemeCon AG, Germany

Low-pressure thin film CVD diamond synthesis using either microwave or hot filament excitation is a well suited deposition technique for pure sp<sup>3</sup> bonded polycrystalline diamond coatings with a large number of various applications on an industrial scale. Most prominent, hot filament CVD diamond coated tools with complex geometries are typically applied at cutting of a certain class of hard to machine materials. Various case studies addressing deposition technology, coating properties and tool performance on some of these materials including graphite, glass-epoxy substances for printed circuit boards (PCB), silicon containing aluminum alloys (with Si larger ≈ 9%), carbon fiber reinforced plastics (CFRP), sintered ceramics or cemented carbides are presented in the scope of this presentation.

8:40am **B2-2-3 Nanocluster Assisted Mesoplasma Epitaxial Bridging**, *R Yamada*, The University of Tokyo, Japan; *S Wu*, Chinese Academy of Sciences, China; *Makoto Kambara*, The University of Tokyo, Japan

Silicon epitaxial films can be deposited by mesoplasma CVD at rates faster by one order of magnitude than the conventional thermal CVD. In this process, Si source gas is first decomposed completely in the mesoplasma and Si nanoclusters form during rapid condensation as actual deposition precursors just before arriving on the film growth surface [1,2]. Owing to the nanoclusters' unique loosely-bound structure, Si nanoclusters are plausibly deposited on a film with high sticking probability to lead to high deposition rate, while maintaining epitaxial film formation as a result of spontaneous and instantaneous rearrangement of constituent Si atoms upon impingement on substrate. Fast rate epitaxy is also observed covering the SiO<sub>2</sub> mask on Si wafer, suggesting that nanoclusters can also be the growth precursors for lateral epitaxial overgrowth (LEO), i.e. the lateral extension of the epitaxial film. This allow us to anticipate that Si substrate with concave grooves with certain appropriate width could be covered by

the epitaxial film that overgrows epitaxially from the adjacent Si region. In this work, we have first employed molecular dynamic (MD) simulation to evaluate the feasibility of the epitaxial film coverage over the nano-sized trench by the cluster assisted mesoplasma CVD for the potential epitaxial bridging. Secondly, Si epitaxial film depositions were also attempted on the Si wafers with porous surface under the typical epitaxial condition.

In brief, in the MD simulation, Si cluster that forms during rapid condensation of high temperature Si vapors is injected from the top at random position and impinges on the nanosized trench with a 100% sticking. It is seen that the Si clusters form the projecting edge from each trench wall and eventually these edges meet and create continuous film, leaving an open space underneath, as expected generally from the coverage phenomena of the trench with high-sticking species. It is however interesting that the film atomic structure preserves the epitaxial relationship from the side single crystal trench wall, indicating the possibility of epitaxial bridging and thus the feasibility of epitaxy over nothing (EON). In addition, smooth epitaxial films are actually deposited on the Si substrate having porous structure that is created by anodic etching, which could be an experimental evidence of feasibility of nanoclusters assisted fast rate epitaxial bridging.

9:00am **B2-2-4 Low Pressure Chemical Vapor Deposition of hex-BN: Relationship between Gas Phase Chemistry and Coating Microstructure**, *P Carminati*, LCTS-CNRS, France; *T Buffeteau*, *N Daugey*, ISM-CNRS, France; *G Chollon*, LCTS-CNRS, France; *F Rebillat*, LCTS-University of Bordeaux, France; *Sylvain Jacques*, LCTS-CNRS, France

In the last few years, BN has become the most promising alternative to pyrocarbon as an interphase material in non-oxide ceramic matrix composites (CMCs) for the next generation of aircraft engine parts. Indeed, the use of BN interphases should improve the mechanical properties and lifetime of SiC-based CMCs under oxidative environment at high temperature. Such BN coatings are often deposited by low pressure chemical vapor deposition (LPCVD) from BCl<sub>3</sub>-NH<sub>3</sub> gas system. But in this case, an insufficient degree of crystallization can make the obtained boron nitride too unstable to environment. Furthermore, little is known about the deposition mechanisms and their impact on the BN microstructure.

In the present work, the effects of deposition temperature and total flow rate on the microstructure of BN coatings deposited from BCl<sub>3</sub>-NH<sub>3</sub>-H<sub>2</sub> gas mixtures at low pressure have been studied. From X-ray diffraction measurements and transmission electron microscopy observations, the coatings appear heterogeneous, i.e. made of a mixture of poorly and highly crystallized domains on a very local scale. The structural homogeneity, as well as the degree of crystallization depends on the deposition chemistry (diluent gas, depletion of gaseous species...). For two given sets of deposition parameters, a comparison with BCl<sub>3</sub>-NH<sub>3</sub>-Ar system was made and the examined coatings exhibit a higher degree of crystallization and a better structural homogeneity than those deposited with H<sub>2</sub> as the diluent gas.

Ex-situ Fourier transform infrared (FTIR) measurements have been carried out on the residual gas mixture at the outlet of the LPCVD reactor in order to detect the species leading to poorly or highly organized BN. The measurements were coupled with ab initio vibrational mode calculations and they allowed the detection and identification of an effective gaseous precursor for highly crystallized BN ex-BCl<sub>3</sub> deposition. The concentration evolutions of the species into the residual gas mixture were also studied as a function of the deposition temperature and total gas flow rate. The NH<sub>3</sub>-free system with hydrogen has also been studied by FTIR and results have shown the formation of BHCl<sub>2</sub>, even at temperatures lower than BN deposition temperatures. This species seems to be an intermediate molecule that reacts further with NH<sub>3</sub> to also form BN. It is thus suspected of being the source of poorly crystallized domains into BN coatings deposited from BCl<sub>3</sub>-NH<sub>3</sub>-H<sub>2</sub> gas mixtures. Finally, assumptions have been put forward to identify the main reaction paths leading to BN.

9:20am **B2-2-5 High-speed Structural Control for Functionalization of Various Oxide Films**, *Akihiko Ito*, Yokohama National University, Japan

INVITED

We have demonstrated that an intense laser field enhances chemical vapor deposition (CVD) process and the developed process achieves not only a **high-speed deposition** but also a **significant orientation growth** in various kinds of ceramic coatings. In addition, the developed coating technology produces **unique nanostructures**, which exhibit outstanding properties. For example, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> are traditional engineering ceramics, but they are still highly valued as practical materials. Functionalization of their

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films with the control of orientation and microstructure is of great interest in both of academic and industrial aspects.

This talk will introduce you to recent topics on high-speed structural control for functionalization of various oxide films with CVD technology, including orientation control of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> films, feather-like structures in  $\beta$ -Al<sub>2</sub>TiO<sub>5</sub> films, nanodendrite formation in Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanocomposite films, superstructure in Ba  $\beta$ -alumina films, high-speed epitaxial growth of transparent CeO<sub>2</sub> thick films, H<sub>2</sub> generation in NaTaO<sub>3</sub> photocatalytic films, and development of Yb-Si-O environmental barrier coatings for SiC/SiC composite in a gas turbine engine.

This work was supported in part by KAKENHI, Japan Society for the Promotion of Science, and Cross-ministerial Strategic Innovation Promotion Program (SIP), "Structural Materials for Innovation, SM<sup>4</sup>I (Funding agency: JST)".

10:00am **B2-2-7 Protective Coatings Enabled by Atomic Layer Deposition Processing**, *Christopher Oldham, J Daubert, G Parsons*, NC State University, USA

Thin film materials for corrosion mitigation is an ongoing area of research and development. Recently several groups have explored using atomic layer deposition (ALD) as a process to form highly conformal protective coatings for metal surfaces. ALD offers unique advantages for depositing uniform coatings in high aspect ratio designs. For corrosion protection applications ALD has been used to protect metal surfaces using common metal oxides materials such as alumina and titania. However, for protection in aqueous environments some ALD coatings etch or dissolve. Other issues with poor nucleation on metal surfaces leads to coatings with high porosity that can compromise the underlying metal surface in corrosive environments. In this presentation we will discuss results on protecting copper and other metals with metal oxide and multi-layer structures deposited by ALD. Results from the surface morphology and electrochemical performance will be presented along with a discussion of using ALD coatings to protect metallic surfaces with challenging coating geometries.

10:20am **B2-2-8 Chromium Carbide Growth at Low Temperature by a High Efficient DLI-MOCVD Process in Effluent Recycling Mode**, *A Michau, Francis Maury*, CIRIMAT, France; *F Schuster*, CEA Saclay, France; *R Boichot, M Pons*, SIMaP, University of Grenoble Alpes, CNRS, France; *E Monsifrot*, DEPHIS, France

For a better control of production cost of manufactured objects that comprise CVD coatings, the improvement of the economic productivity of deposition processes is a challenge. The increasing use of metalorganic precursors is a way to improve the economy of the process because this greatly lowers the deposition temperatures leading to substantial energy savings. When expensive molecular precursors as for precious metals are used the by-products are collected at the exit of the CVD reactor then the leading recyclers and traders develop in parallel complex effluent treatments to refine and reused the collected precursors after removing trace contaminants. This approach is also applied in high volume CVD production facilities. For instance a hydrogen recycle system was proposed for CVD of poly-Si. Also in the growth of Si for solar cells the exhaust gases (H<sub>2</sub>, HCl, chlorosilanes) were collected, separated and recycled. Generally these strategies reduce the production cost but they did not act directly on the CVD process.

To develop large-scale CVD processes using expensive reactants direct recycling of precursor become necessary to achieve a high conversion yield. However direct recycling of effluent using metalorganic precursors was not reported because the quality of the layers strongly depends on the metal source and these compounds undergo complex decomposition mechanisms producing many unstable metal-containing by-products.

The bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V, Nb, Ta) are an important family of CVD precursors for low temperature deposition of carbides, nitrides and even the metal. A greater knowledge of the growth mechanism, a modeling approach and the use of direct liquid injection (DLI) to feed the MOCVD reactor has led us to study the effect of direct recycling of effluents on the quality of chromium carbide coatings using bis(ethylbenzene)chromium(0). The results are compared with those obtained using a fresh solution of precursor. Interestingly, both coatings are amorphous in the temperature range 400-550°C; they exhibit a smooth surface morphology, a dense structure, the same chemical composition (close to Cr<sub>7</sub>C<sub>3</sub>) and a high hardness (23-29 GPa). The main criteria for the selection of MOCVD precursors enabling a successful direct recycling are discussed. It was demonstrated that direct recycling of effluents for instance in a recycle loop is an efficient route to

improve the economy of DLI-MOCVD which makes this process very competitive for the deposition of this important class of carbide protective materials.

10:40am **B2-2-9 Growth and Characterization of SiO<sub>x</sub> Thin Film Deposited by Plasma Enhanced CVD on a Magnesium Alloy**, *Hyunju Jeong, J Cho*, POSCO (Pohang Iron and Steel Company), Republic of Korea

Magnesium alloys have good properties such as low density and high thermal conductivity, but their applications are still limited due to their poor surface quality and corrosion resistance. Even though many studies have been suggested to characterize their surface properties and protect the surface using a variety of techniques, it is necessary to furthermore undertake investigations in order to apply them into various industrial applications, resulting in the improvement of surface properties.

In some industrial application, it is required to employ coating techniques which fabricate transparent coating layers which also act as barrier coating layer against gas and vapor permeation. Chemical vapor deposition (CVD) is known as one of promising coating techniques to form good quality thin films such as passivation films in various industrial areas. Most of all, low temperature processes have advantages of cost reduction, productivity and substrate stability. It is well known that plasma enhanced chemical vapor deposition (PECVD) is less dependent on substrate temperature than conventional CVD, leading to good quality films at relatively low temperature below 300°C.

In the present work, SiO<sub>x</sub> films as transparent and passivation layers were fabricated on the surface of a magnesium alloy using a PECVD technique. Particularly, magnesium and magnesium alloys have material properties such as high surface activity and high thermal conductivity. Such characteristics possibly have an influence on growth of films as well as interface of the films and substrates during PECVD. Therefore, we undertook an investigation to characterize growth and characterize the interface of SiO<sub>x</sub> films and a magnesium alloy. FETEM results displayed thin films grown at the interface of a SiO<sub>x</sub> film and magnesium alloy at substrate temperature of 50 and 300 °C where the thin films tended to be grown as deposition time. XPS analysis revealed that an outer layer close to SiO<sub>x</sub> films was mainly composed of SiO<sub>2</sub> and Mg(OH)<sub>2</sub> whereas an inner layer close to magnesium substrates consisted of Mg(OH)<sub>2</sub> and MgO.

The structures on the surface were evaluated using field emission scanning electron microscopy (FESEM). The cross sectional compositions and structures were examined by field emission transmission electron microscopy (FETEM), scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS). The detail compositions at the interface of films and AZ31 magnesium alloy were discussed using X-ray photoelectron spectroscopy (XPS) measurements.

Keywords: thin films; SiO<sub>x</sub>; PECVD ; Magnesium alloys

11:00am **B2-2-10 Electrochemical Behavior of Graphene Coatings Deposited on Copper Metal by Electrophoretic Deposition and Chemical Vapor Deposition**, *Mohsin Ali Raza, A Ali, F Ali Ghuari, A Aslam, K Yaqoob, A Wasay*, University of the Punjab, Pakistan; *M Raffi*, National Institute of Lasers and Optronics, Pakistan

Graphene gains utmost importance for electronics, composites, sensors and biological applications due to its remarkable properties. The attributes such as two dimensional morphology, chemical inertness, high specific surface area and aspect ratio make graphene a promising candidate for anticorrosive coatings. Graphene has ability to retard electrochemical reactions occurring at metal-electrolyte interfaces by acting as a barrier to aggressive ions. This work aims to compare electrochemical performance of graphene coatings deposited on copper metal (Cu) by electrophoretic deposition (EPD) and chemical vapor deposition (CVD) technique. In the CVD process, graphene coatings were deposited on Cu by passing vapors of sodium ethoxide and argon gas (carrier gas) through a quartz tube at a temperature of 900 °C. In the EPD process, graphene was deposited on Cu, made as anode, from a suspension of graphene oxide and water. The EPD deposition process partially reduced graphene oxide and further reduction was achieved by heating coated samples at 200 °C or by treating coatings with hydrazine solution. The coatings were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and Raman spectroscopy. FTIR analysis revealed that graphene coatings produced by EPD had more oxygen bearing functional groups compared to coatings deposited by CVD. CVD-based graphene coatings had higher adhesion to the substrate than that of EPD-based coatings. AFM images showed that thickness of coatings increased as a function of deposition time. The electrochemical behavior of coatings was studied using tafel analysis and

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electrochemical impedance spectroscopy techniques in 3.5% NaCl solution. The CVD-based graphene coatings performed better than that of EPD coatings and reduced corrosion rate of Cu. The CVD coatings remained intact even after aggressive corrosion testings, while EPD based coatings showed some damage. The comparative study of the electrochemical behavior of graphene coatings clearly demonstrates that graphene coatings deposited by CVD process using sodium ethoxide as precursor are superior to coatings deposited by EPD process using graphite oxide as precursor.

11:20am **B2-2-11 Characterization of Coated Silane Compounds on Aisi 304 Stainless Steel Using Plasma-Oxide Vapour as Adhesion**, *Damilare Baruwa*, University of Johannesburg, South Africa; *P Oladijo*, Botswana International University of Science and Technology, Botswana; *J Chinn*, Integrated Surface Technologies, Inc., USA; *N Maledi*, University of the Witwatersrand, South Africa; *E Akinlabi*, University of Johannesburg, South Africa

Quest for safe, low cost and reliable coating has led to the alternative development of various chemical compounds of silane in order to mitigate corrosion process and reduce the risk of carcinogenic compounds that have been previously employed in hexavalent chromium-based coating materials. Silane is a hydrophobic and hydrophilic chemical compound, but with contact angle above  $110^\circ$  is hydrophobic. The present study was conducted to determine the influence of silane coating on AISI 304 stainless steel. In this study, three different saline-based coatings of composition [Tris(trimethylsiloxy)silyethyl]dimethylchlorosilane (Alkyl); Tridecafloro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) and Henicocyl-1,1,2,2-tetrahydrododecyltrichlorosilane (FDDTS) were deposited on 304 stainless steel. The surface of the substrate was grit-blasted by plasma oxide (vapour) adhesion by using nano-composite structures with a hybrid Atomic Layer Deposition (ALD) and Chemical Vapour Deposition (CVD) process. This investigation present results on microstructure (Optical microscopy, SEM/EDX), mechanical test (EMCO Hardness Tester, ultimate tensile strength, yield strength), chemical phase content (XRD), porosity and the electrochemical corrosion behavior of different silanes coating on AISI 304 stainless steel. The results showed that the coating characterization and their corrosion behavior were different to that of AISI 304 stainless steel which was addressed in the study.

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