New Horizons in Coatings and Thin Films
Room San Diego - Session F4-1

Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

8:00am **F4-1-1 Self-healing Thermal Barrier Coating System for Prolonged Lifetime*, Willem Sloof,*** Delft University of Technology, Netherlands**INVITED**

Thermal barrier coatings (TBCs) are applied on aircraft and industrial gas turbine engines protecting the operating components from demanding high temperature environments. However, the thermal mismatch leads to generation of stresses in the TBCs resulting in micro-cracks that grow and coalesce, leading to ultimate failure of the coating. A new, unique self-healing thermal barrier coating for turbines and other thermally loaded structures has been developed in orderto realize a significant extension of the lifetime of critical high-temperature components..

The concept is based on novel Al_2O_3 coated $MoSi_2$ particles embedded in the TBC layer, typically consisting of yttria partially stabilized zirconia (YPSZ) [1]. Upon high-temperature exposure in an oxidising environment the embedded $MoSi_2$ particles react to form a viscous silica (SiO_2), which fills the cracks and re-establishes adherence in the TBC. Subsequently the SiO_2 reacts with the matrix forming zircon ($ZrSiO_4$), which is a load bearing and solid crystalline ceramic phase. This new concept involves the creation of an inert, oxygen impenetrable, shell of alumina (Al_2O_3) around the actual healing agent, which prevents premature triggering of the healing reaction. With this approach, the healing mechanism will become active only when a crack penetrates the alumina shell.

The $MoSi_2$ particles are alloyed with boron to promote the kinetics of the healing reaction and filling of crack gap with amorphous silica [2]. For manufacturing the self-healing TBC by atmospheric plasma spraying, encapsulation by selective oxidation of aluminium, added to the healing particles, proved to be successful. The core of the encapsulated and embedded healing particles remained intact when exposed to high temperatures in air for long times.

In furnace cycle tests, mimicking TBCs in applications, the crack damage evolution due to mismatch in thermal expansion is determined. The lifetime of the self-healing TBC in the furnace cycle tests compared to a similar TBC but without healing particles, was prolonged and the scatter in the lifetime data reduced making the self-healing TBC more reliable.

[1] W.G. Sloof, S.R. Turteltaub, A.L. Carabat, Z. Derelioglu, S.A. Ponnusami and G.M. Song. *Crack healing in yttria stabilized zirconia thermal barrier coatings*. In: Self-healing materials - pioneering research in the Netherlands, S. van der Zwaag & E. Brinkman Eds., IOS Press, Amsterdam, 2015, pp. 217-225.

[2] Z. Derelioglu, A.L. Carabat, G.M. Song, S.V.D. Zwaag, W.G. Sloof. On the use of B-alloyed MoSi2 particles as crack healing agents in yttria stabilized zirconia thermal barrier coatings, J Eur Ceram Soc 35 (2015) 4507-4511.

8:40am **F4-1-3 TiO_2 Thin Films Deposited onto PET by High Power Impulse Magnetron Sputtering for Photocatalytic Degradation of Carbendazim***, R Marcelino,* Universidade Federal de Minas Gerais, UFMG, Brazil*; M Ratova, B Delfour-Peyrethon,* Manchester Metropolitan University, UK*; C Amorim,* Universidade Federal de Minas Gerais, UFMG, Brazil*; **Peter Kelly**,* Manchester Metropolitan University, UK

Photocatalysis has been widely studied for the removal of contaminants of emerging concern from water. The use of the catalyst in a powdered form results in high surface area, but hinders the catalyst recovery. An alternative approach is to deposit the photocatalyst onto a flexible substrate material that can conform to the shape of a reactor vessel. Titania (TiO_2) in the anatase phase is the most widely used photocatalyst, but when deposited by conventional magnetron sputtering, the coating usually requires elevated temperatures or post-deposition annealing in order to form the desired crystalline structure. This precludes the use of thermally sensitive substrates. However, deposition in HiPIMS (high power impulse magnetron sputtering) mode allows the deposition of anatase titania in a single stage process directly onto polymeric substrates. This paper, therefore, presents data on the performance of photocatalytic thin films of titania deposited onto polyethylene terephthalate (PET) supports via HiPIMS. Photocatalytic activity of the coated film was assessed by the degradation of the photostable fungicide carbendazim (CBZ) in aqueous solution, in the presence of a photosensitizing agent, reaching 35% of CBZ removal under UV-A and visible radiation. The reusability of the coatings was implied by negligible drop in activity after 5 cycles. The titania coatings have been characterized by SEM, XRD and UV-vis spectroscopy.

9:00am **F4-1-4 Thermal Stability of Structure and Enhanced Properties of Zr-Ta-O Films with Low and High Ta Content***, **Petr Zeman**, S Zuzjakova, J Vlček, J Rezek, R Čerstvý, J Houska, S Haviar,* University of West Bohemia, Czech Republic

Development of novel multicomponent ceramic oxide systems is the promising way how to extend application potential of binary oxides. Zirconia is one of the most studied oxide ceramic materials because of its excellent chemical inertness and good mechanical, electrical, optical and thermal properties. Tantalum pentoxide used as thin-film material exhibits interesting electrical and optical properties. The limit for an application of these oxides is the stability of their structure and properties at elevated temperatures.

The present study focuses on investigation of the thermal stability of the structure and optical and mechanical properties of Zr-Ta-O films with a low and high Ta content. Two ternary Zr-Ta-O films ($Zr_{25}Ta_5O_{70}$ and $Zr_5Ta_{25}O_{70}$) and two binary films (ZrO_2 and Ta_2O_5) were prepared by reactive high-power impulse magnetron sputtering of a single Zr-Ta target (with a varying Ta fraction in the target erosion area) in argon-oxygen gas mixtures using a pulsed reactive gas flow control. The films were deposited either without any external substrate heating or at 400°C onto Si substrates at a floating potential. In the as-deposited state, the structure, microstructure, mechanical and optical properties of the films were analyzed and their thermal stability in air in a temperature range of 700°C – 1300°C investigated.

We found that highly optically transparent Zr-Ta-O films exhibit a higher hardness, a higher refractive index and an enhanced thermal stability of the as-deposited structure and optical and mechanical properties than the corresponding binary oxides. The $Zr_{25}Ta_5O_{70}$ film is a single-phase material with a nanocrystalline structure corresponding to the ternary $TaZr_{2.75}O_8$ phase. This as-deposited phase is stable up to a maximum temperature investigated (1300°C) and the film retains its hardness of 19 GPa and refractive index of 2.25 (measured at 550 nm) even after annealing to 1000°C in air. The $Zr_5Ta_{25}O_{70}$ film exhibits an amorphous structure in the as-deposited state with its thermal stability up to 800°C, which is by about 100°C more than in the case of the Ta_2O_5 film. At higher temperatures a crystallization of a coarse-grained β-Ta_2O_5 phase occurs. The thermal stability of mechanical and optical properties will be discussed and presented in more detail.

9:20am **F4-1-5 Electrophysical Properties of Nanoparticle-Added PEO Coatings on Aluminium***, **Noratiqah Yaakop**, B Mingo, L Qiang, Z Wang, A Yerokhin, A Matthews,* University of Manchester, UK

Oxide ceramic coatings produced by Plasma Electrolytic Oxidation (PEO) in electrolytes with nanoparticle additions have been gaining increasing attention. Many electrical and electronic applications such as capacitors, resistors and integrated circuits would benefit from dielectric surface layers produced by green and facile PEO technology. The PEO coatings produced with incorporation of nanoparticles directly from electrolyte are known to be denser, however the influence of nanoparticle additions on electrophysical properties of such coatings requires further investigation.

The PEO coatings have been produced on AA6082 alloy samples using a pulsed bipolar current mode with 1-3 kHz frequency. The composition of the dilute alkaline electrolyte and the concentration of alpha alumina nanoparticles additions were varied from 10 to 30 g/l. Since incorporation of nanoparticles allowed coating porosity to be reduced, thin yet dense PEO coatings with thickness ranging from 10 to 30 micron have been produced in relatively short treatment times, varied from 5 to 15 min.

A Mott-Schottky analysis was performed on the coatings to determine the concentration charge carriers and the flat band potential. For that, electrochemical impedance spectroscopy (EIS) was conducted at increasing potentials from 0 to 1.3 V vs. OCP with step size of 100 mV. The capacitance of the coatings was calculated by fitting the experimental data to an equivalent circuit and a linear relationship between the inversed squared capacitance and applied voltage was found. The dielectric strength of the studied materials was evaluated in the metal-oxide metal configuration by applying an increasing DC voltage until the coating breakdown is achieved. Morphology of the coatings was studied by scanning electron microscopy (SEM) and phase composition of the coatings was analysed by X-ray diffraction. Correlations were sought between characteristics of surface morphology, phase composition and electrophysical properties of the studied coatings.

The results indicate that the electrophysical properties of PEO coatings are comparable and in some cases even better compared to epoxy-based materials used, up to now, for insulated metal substrates. Additionally, these coatings present higher thermal stability and lifetime which makes them potential candidates for electronic applications.

9:40am **F4-1-6 Titania Films Deposited by Constant Current High Power Impulse Magnetron Sputtering**, ***Arutiun P. Ehiasarian,*** *D Loch,* Sheffield Hallam University, UK; *A Heisig, J Neidhardt,* Von Ardenne Anlagen Technik, Germany

TiOx films were produced by reactive High Power Impulse Magnetron Sputtering (HIPIMS) of a pair of metallic targets in an Ar-Oxygen atmosphere. During the HIPIMS process a fast rise and a constant current was maintained during the pulse by regulating the voltage. This resulted in the elimination of stability issues associated with runaway currents and target poisoning for oxygen flows ranging from 10 to 50% of the total gas flow. Time-resolved optical emission spectroscopy revealed that the plasma discharge developed through stages of gas ionisation, gas rarefaction and metal sputtering, the latter associated with cooling of the electron temperature. Evidence is presented of metal ionisation and atomic oxygen sputtering from the target at low pressure and produced in the gas phase at high partial pressure. Films were deposited without intentional heating or substrate biasing and had good transparency. The thickness uniformity was < 2% across a 100x100 mm area. The refractive index increased continuously as the oxygen flow reduced from 45 to 13% reaching a maximum value of 2.55 at a wavelength of 550 nm compared to 2.47 for bipolar pulsed sputtered films. The extinction coefficient in the HIPIMS coatings was of the order of 0.003, similar to bipolar pulsed sputtered films. The films were metallic (non-transparent) at 10% Oxygen flow. The films comprised a mixture of rutile and anatase phase with HIPIMS deposition producing higher fractions of rutile compared to bipolar pulsed DC operation. The hardness of the films and its relation to process conditions are discussed.

10:00am **F4-1-7 Study on Silicon Carbide Based Metal Oxide Semiconductor Capacitor with Magnetron Sputtered ZrO_2 High-k Gate Dielectric**, *S Mourya, J Jaiswal, G Malik, B Kumar,* ***Ramesh Chandra,*** Indian Institute Of Technology Roorkee, India

A silicon carbide (SiC) based two terminal metal oxide semiconductor (MOS) capacitor with magnetron sputtered zirconium oxide (ZrO_2) as a high-k dielectric material using titanium (Ti) gate has been synthesized at room temperature. The structural, morphological and compositional analysis of the dielectric layer has been carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of MOS capacitor were studied at room temperature by applying the dc bias gate voltage swept from –3V to 3V for both, high and low-frequency operation on a probe station. The thermal stability of the MOS capacitor is of critical importance for use in the fabrication of electronics for deployment in extreme environments. Hence, the effects of post-deposition annealing (PDA) temperatures (200-1000 ºC) on the electrical properties of MOS capacitor have been investigated. MOS characteristics of Ti/ZrO_2/SiC/Ti capacitor were correlated with structural and morphological properties of an insulating dielectric layer at different PDA temperatures. It has been observed that a synergetic contribution of lowest effective oxide charge, semiconductor-oxide interface-trap density and total interface-trap density improve the electric breakdown field of MOS capacitor for PDA samples.

10:20am **F4-1-8 On the Importance of the Energy of Negative Ions in Achieving Uniform and High-quality Magnetron Sputtered AZO Films**, ***Fanping Meng,*** Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences,, China

Spatial distribution of highly energetic negative ions inherent in magnetron sputtering of oxides has long made low temperature deposition unsuitable for high quality films uniform over relatively large areas. Here we examine the distributions of both structure and physical properties of magnetron sputtered Al-doped ZnO (AZO) films deposited at low temperatures (≤393 K) in which the bombardment from the negative oxygen ions was systematically studied by changing the discharge voltage (i.e., ion energy) and the substrate position (i.e., ion flux). The film structure was characterized by X-ray diffraction, Raman spectroscopy, and transmission electron microscopy; and the electrical and optical properties were obtained by a Hall system and Spectroscopic Ellipsometry. We found (i) that uniform yet high quality AZO films ($<4x10^{-4}$ Ω cm) can be obtained only when the energy of the negative ions was set below a threshold; (ii) that the ion flux exerted an ever-decreasing effect on the structural uniformity as the ion energy was reduced; and (iii) that a set of structural criteria, incorporating crystallite quality (orientations, size, lattice spacing) and point defects, were derived for low resistivity AZO films. The benefit of lowering the ion energy is then explained in terms of the favorable competition between radiation-induced defect generation and the subsequent dynamic annealing. These findings may pave a way for large-area coating of high quality AZO films at low temperatures.

11:20am **F4-1-11 Combinatorial Thin Film Materials Science: Limitations and Opportunities for Combining Experiments and DFT Based Theory**, ***Jochen M. Schneider,*** RWTH Aachen University, Germany **INVITED**

The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings, energy conversion materials as well as of thin film metallic glasses. Besides elastic properties and phase stability also the interaction of the coating with the ambient can be described based on quantum mechanics. In the talk predictions of the interaction of coated tool surfaces with gases contained in the atmosphere as well as materials to be formed are discussed. Hard coatings used for forming operations of Al and Polymers are investigated and experimental data characterizing these interactions will be discussed. Furthermore, the implications of the presence of point defect for the thermal stability of TiAlN [1] will be analyzed and hybridization implications for the damage tolerance of thin film metallic glasses will be presented [2]. Limitations and opportunities of combining modern electronic structure calculations with combinatorial thin film synthesis und spatially resolved characterization techniques will be discussed.

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