Thin Films
Room Naupaka Salon 1-3 - Session TF-TuP
Thin Films Poster Session I

Moderator: Darrell G. Schlom, Cornell University

TF-TuP-1 Oxidation Behavior of Sputtered $NiFe_2$ Coating on Ferritic Stainless Steel for SOFC Interconnect Application*, **Shujiang Geng**, F Wang,* Corrosion and Protection Division, Shenyang National Laboratory for Materials Science, Northeastern University

Ferrtic stainless steels are confronted with several problems during operation in SOFC cathode working condition such as the spallation of the oxide scale and cathode Cr-poisoning, leading to significantly degradation of the cell performance. To solve these problems, NiFe2 alloy coating has been deposited on SUS 430 ferritic stainless steel via magnetron sputtering method. Electrically conductive $NiFe_2O_4$ spinel coatings were thermally developed on the steels from the sputtered $NiFe_2$ coatings in air at 800^{o}C. Initial oxidation behaviors of $NiFe_2$ coated bare and pre-oxidized steels were investigated for understanding the conversion process from the alloy coating to spinel. The phase structure and composition of coated steels after oxidation were characterized with XRD and SEM/EDS.

The oxidation kinetics analysis of the first 60min exposure demonstrated rapid mass gains were observed during the beginning 5-10 min for the coated bare and pre-oxidized steels, followed with slightly increase. The XRD and SEM/EDS results indicated Fe was preferentially oxidized resulting in un-reacted Ni residue in the coatings during the rapid mass gains stages. Scale formed on the coated bare steel presented multilayered structure, primarily consisting of a top Fe_2O_3 layer followed with $NiFe_2O_4$ layer and NiO layer. During the first 10 min, un-reacted Ni region beneath the NiO layer was decreasing with time. Cr-rich oxide was detected at the interface of scale/steel after 30min exposure. Similar scale structure was observed on the coated pre-oxidized steel except Cr-rich layer at scale/steel interface consistently. Compared with the coated bare steel, the bigger defect gap between columnar-grains in $NiFe_2$ coating on pre-oxidized steel serving as channel for oxygen inward diffusion will presumably provide higher oxygen capacity in coating, which accelerated Ni consumption during oxidation. Chromia layer formed after pre-oxidation treatment acted as a barrier to block Cr outwards diffusion into the alloy coating at the beginning of oxidation. Scales on both coated steels were well-bonded to steel substrate with a few tiny pores distributing discretely. The oxidation mechanisms were discussed.

TF-TuP-2 Effects of Bias Voltage on the Structure and Corrosion Properties of Thick Cr Coatings Deposited Using Cathodic Arc ion Plating*, **Jung-Hwan Park**, Y Jung, D Park, H Kim, B Choi, Y Lee, J Yang,* Korea Atomic Energy Research Institute

After the Fukushima Daiichi nuclear accident, the major issue of nuclear researchers has been an improvement in the oxidation resistance under beyond-design accident conditions. Therefore, accident tolerant fuel (ATF) has been widely studied, which has high-temperature oxidation resistance. For the development of ATF claddings, several advanced cladding materials that have high-temperature oxidation resistance have been proposed, including advanced stainless steels, Mo alloys, and SiC/SiCf composites. However, they require changes in the engineering design of the reactor cores. An alternative approach to improving safety is to fabricate a cladding with a protective coating. A protective coating that has a high oxidation resistance also improves the corrosion performance during normal operation. Several coating materials have previously been suggested, including SiC, FeCrAl, TiN, TiAlN and Cr. Among the candidate materials for protective coating, Chromium coatings are well known for their high hardness, good corrosion, and wear resistance. In our previous work, Cr coating deposited on a zircaloy-4 cladding by cathodic arc ion plating was investigated to evaluate the corrosion protection of zircaloy-4 cladding in a high-temperature steam environment. Compared to pristine Zircaloy-4, Zircaloy-4 with a Cr layer exhibited superior oxidation resistance. However, an oxygen-stabilized alpha zirconium (α-Zr(O)) layer, which was formed through oxygen diffusion, was observed after a high-temperature steam oxidation test.

In this study, we tried to optimize the ion plating conditions to reduce the inward oxygen diffusion. Cr coatings were deposited on a Zircaloy-4 tube using arc ion plating at various substrate bias voltages. The effects of the substrate bias voltage on the corrosion behavior of arc ion plated Cr films has been investigated. We also investigated the relationships among the substrate bias voltage, physical properties, and corrosion resistance for Cr coated zircaloy-4. The internal stress was measured using an iso-inclination method with an x-ray diffractrometer at room temperature. A high-temperature steam oxidation test at 1473 K was executed.

TF-TuP-3 Graphite Tribofilm Extracted from Base Oil by Self-Oxidizing Coating: A Highway for Friction and Wear Reduction*, **Lina Yang**,* State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China., China*; K Zhang,* State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China

Tailoring sliding interface is a vital pathway to minimize friction and wear, commonly, either fluid layers or solid tribofilms have been employed. Herein, the lubricating effects from both ones are combined via in situ formation of graphite tribofilm extracted from PAO base oil (without additives) when introduced catalytic TiN coating enabled by solute Ag atoms (super-hard nature). In this way, superior tribological properties with ultralow friction coefficient at 0.075 and wear rate at 2.28×10^{-11} mm^3/Nm can be obtained. Better yet, the incorporation of solute Ag atoms into TiN structure could induce a charge depletion state and active surface self-oxidation to a special Ag_2O/TiO_2 composite, as demonstrated by electron localization function (ELF) and XPS. Different from traditional metal catalysts, such metallic oxides from solid solution structure are suggested to dominant this catalyst and extraction action. Besides, the direct transfer of part of electrons from the unstable charge structure to oil molecules further ensures the catalytic effect. This study highlights the crucial role of solid solution coating in catalyzing and extracting tribofilms from lubricating oil, which would be a new insight towards a more efficient lubricating system.

TF-TuP-4 Solute Ag Atom Incorporated into TaN with Excellent Tribological Property and Robust Antibacterial Activity*, **Ping Ren**, M Wen,* State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China

Nowadays, designing transition metal nitrides (TMN)-based films deposited on Ti-6Al-4V substrates with enhanced wear-resistance, anti-bacteria and a reduced friction represents urgent challenge for various application including bistoury scalpel, medical catheter, door handle and kitchen utensils et al. Generally, incorporating higher content (> 10 at.%) of antibacterial metallic phase (i.e. Cu, Ag) into TMN matrix to form the TMN/metal nanocomposite film has been considered as an effective approach to achieve improved toughness and antibacterial activity. However, in this system, hardness and wear rate are highly sensitive to soft metal content and can be significantly worsened. Herein, we provide a new strategy to introduce few solute Ag atoms (~ 3.08 at.% Ag) into TaN lattice to form a Ta-Ag-N solid solution structure, simultaneously achieving superhard (~ 40 GPa) yet high toughness, and improved wear-resistance, coupled with remarkable decrease in friction relative to Ag-free TaN film and TaN/Ag nanocomposition film with the same Ag content. In addition, the solid solution Ta-Ag-N film exhibits the excellent antimicrobial activity on Escherichia coli tested by measuring the diameters of the bacteriostasis circles. Obviously, introduction of few solute Ag atoms into TMN may open a new window to improve the comprehensive properties including hardness, toughness, friction, wear-resistance and anti-bacterial.

TF-TuP-5 Influence of Ag Content on the Tribological Properties of MoNbN-Ag Coatings at Elevated Temperature*, K Zhang,* State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, People's Republic of China*; **Xuan Dai**,* State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, China*; M Wen,* State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China, China*; W Zheng,* tate Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China

In recent years, with the increasingly fierce and vigorous development of aviation technology, aerospace engine, as the "crown jewel of the aviation industry", has been constantly improving its requirements of technology and performance. Because the aerospace engines always work in high temperature environment, it is necessary for materials to have reliable tribological performance at high temperature. However, high temperature lubrication is still a considerable challenge for the tribology field, and it results that the damage and failure of motor components are always caused by high temperature friction. Here, a reduced friction coefficient from 25 to 800 ℃ was achieved successfully in MoNbN-Ag coating with tailoring Ag content. The deposited MoNbN coating is a ternary fcc-solid solution, and the transformation from solute Ag atoms to precipitate metal Ag can be realized through the increasing of Ag content. The reduced friction coefficient can be ascribed to silver, molybdenum and niobium reacted with oxygen at elevated temperatures and create lubricious phases molybdenum oxide, niobium oxide ,silver molybdate and silver niobite film on the coating. Amusing, compared with Ag in the form of precipitation in MoNbN coating, when silver exists in the form of solid solution, it has a lower friction coefficient at 25-450 ℃ and a similar friction coefficient at 450-800 ℃. In which, it's attributed to the contribution: solute Ag can activate easier self-oxidation forming Ag_2O+ MoO_3/Nb_2O_5 on the surface, which is beneficial for formation of $Ag_2Mo_4O_{13}$/$AgNbO_3$ during sliding at medium and low temperatures, thereby reducing friction.

TF-TuP-6 High rate Reactive Sputter-deposition of WO_3 Films by using Two Different Deposition Methods, *Yoji Yasuda*, *Y Hoshi*, Tokyo Polytechnic University, Japan

Tungsten oxide (WO_3) is well known as a functional material with excellent gasochromic, electrochromic, and photocatalytic properties. Nano-structured WO_3 films prepared by glancing angle sputter deposition and high-rate gas flow sputtering were reported by Horprathum et al. and Oka et al., respectively. We have already reported that high-rate deposition of WO_3 films at a deposition rate (R_D) of more than 100 nm/min can be achieved by pulsed dc planar magnetron sputtering (PMS). However, poor gasochromic film was obtained near the center area of the substrate. This was due to bombardment by high energy negative oxygen ions that are sputtered from a target surface to the substrate surface during sputter-deposition. This ion bombardment is expected to be completely suppressed if the facing-target type low damage sputtering system (FTS) used for the deposition process.

In this study, we deposited WO_3 films using two different sputtering methods (a PMS and an FTS system), and compared the structure and properties of the resulting films. Typical sputtering conditions are presented in the poster session. R_D of more than 120 nm/min was easily realized with an increase in the sputtering voltage above 700 V. A typical WO_3 film obtained by PMS exhibited inhomogeneous gasochromic properties that depended on the location on the substrate, and films with excellent gasochromic properties were only obtained at the corner of the substrate. It was also found that the nonuniformity of the films can be improved by altering the angle of incidence of the particles on the substrate and relaxing the impact.

In contrast, uniform films were easily obtained by FTS. Details will be presented in the poster session.

TF-TuP-7 Initial Growth of Pentacene Thin Film on Si(001) Substrate, *Takayuki Suzuki*, *K Yagyu, H Tochihara,* Fukuoka University, Japan

Initial growth process of the pentacene molecules on the clean Si(001)-2×1 substrate were investigated by Scanning Tunneling Microscopy (STM) at room temperature (RT). The pentacene molecules were deposited onto the clean Si(001) surface held at RT, using a quartz crucible. We found that the wetting layer forms first by increasing the amount of the deposited pentacene molecules before starting the formation of the first layer, which is not crystalized, but disorder, where the molecules adsorb flatly. It does not have any ordered domain structure. The first pentacene layer that is crystalized with the standing-up pentacene molecules grows on the disordered wetting layer by increasing the deposited amount of the molecules more. The first layer consists of three domains at least, which have different crystal structures from each other: the 'α', the 'β' and the 'γ' domains. Among them, the 'β' domain has a new pentacene crystal structure that can form only on the first layer. The first layer does not have a dendritic shape at least at a field of view of 2 μm. Second pentacene layer starts to form on top of the first layer by increasing the deposited amount more again, before the first layer completely covers the substrate surface. In contrast, the second layer has only single domain. The all other crystal structures found in the present study except for that of the 'β' domain, are similar to those of the four polymorphs reported previously [1]. Moreover, we investigated electronic properties of the various pentacene layers by the I-V measurements. The pentacene layers are semiconducting with a gap of about 4 eV from -1 eV to +3 eV.

Reference

[1] M. Kitamura, Y. Arakawa, J. Phys.: Condens. Matter 20, 184011 (2008), and references therein.

TF-TuP-8 Thermal Stability of Atomic Layer Deposition Precursors, *Kyuyoung Heo*, *J Son, G Jung,* Korea Research Institute of Chemical Technology, Republic of Korea; *W Lee,* Korea Research Institute of Chemical Technology, Republic of Korea, Republic of Korea

The development of high-k dielectric precursors for advanced semiconductor applications requires molecular engineering and chemical tailoring to obtain specific physical properties and performance capabilities. Some high-k precursors such as organometallic precursors for atomic layer deposition (ALD) that have metal atoms bound to cyclopentadienyl, are stored at a sufficiently high temperature due to their low volatility and consumed through continuous deposition for a commercial semiconductor process. In this case, thermal degradation slowly occurs due to storage at a high temperature for a long time, which causes deterioration of physical properties and reliability of the thin film. However, a technique for assessing the reliability of precursor has been undeveloped and thus causing the development of new precursors to be delayed. In this study, we have developed a reliability evaluation method for cyclopentadienyl tris(dimethylamino) zirconium [$CpZr(NMe_2)_3$] through accelerated thermal degradation test under severe environmental conditions in a short period of time. To evaluate the lifetime of precursor, we have investigated the thermal stability and degradation mechanism of precursor by using analysis of NMR and mass and viscosity measurements.

TF-TuP-9 Growth Behavior and Film Properties of Titanium Dioxide by Plasma-Enhanced Atomic Layer Deposition with Discrete Feeding Method, *Heungseop Song*, *D Shin, J Jeong, H Park, D Ko,* Yonsei University, Korea, Republic of Korea

Titanium dioxide (TiO_2) has emerged as an attractive dielectric material for electronic devices such as memory and thin film transistors due to its high dielectric constant and high thermal stability or its role as an important constituent of multi-metal oxide systems. TiO_2 thin films can be fabricated in many ways, such as physical vapor deposition, chemical vapor deposition and spin coating. Among these growth methods, plasma-enhanced atomic layer deposition (PE-ALD) technology becomes one of the most promising methods for nanoscale thin film deposition because of its advantage of conformal growth, precise control of the film thickness and relatively low substrate temperature. However, most PE-ALD TiO_2 processes show a low growth-per-cycle (GPC) of less than 1.0 Å, making them difficult for mass production. T. Park et al. reported the steric hindrance caused by the physical size and proximity of the neighboring parts of the precursor (or partially decomposed) molecule during precursor feeding time and introduced a "discrete feeding method" (DFM) of the metal precursor as a solution for improved GPC of HfO_2 film [1]. In this presentation, we report the growth behavior of TiO_2 film with the DFM-applied and the conventional ALD growing method, using tetrakis-dimethylamido-titanium [$Ti(NMe_2)_4$], as a Ti precursor. Our work focused on improving both physical and electrical properties of the film as well as increasing its growth rate through DFM application. In our experiments, TiO_2 films were deposited on Si (100) substrates at 250 °C. Spectroscopic ellipsometry (alpha-SE model, J. A. Woollam Co. Ltd.) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc., U.K) were examined to compare GPC. As a result, the GPC of the DFM group was increased by 18% compared to that of the conventional method group and the GPC difference from the ellipsometry measurement results of the two groups was also in agreement with the XPS analysis. In addition, we performed a wet etch rate test using 25: 1 HF chemical to compare the physical properties of the thin films and confirmed that the DFM group had a wet etch rate close to 6% of the wet etch rate for the conventional group. This confirms that the denser film was formed when DFM was applied, which was also consistent with the finding of the difference in Ti density observed through Rutherford backscattering spectrometry analysis. We expect that these differences in physical film properties would affect dry etch selectivity and consequently result in better dry etch selectivity compared to SiO_2 that has been most widely used in the semiconductor industry.

[1] T. Park et al., Chem. Mater. 2011, 23, 1654–1658.

TF-TuP-10 Properties of nm Scale Tungsten Thin Film Deposited using Inductively Coupled Plasma Assisted Sputtering*, **Soojung Lee**, T Kim, B Jeong, C Song, J Byun, J Kim, Y Ji, G Yeom,* Sungkyunkwan University, Republic of Korea

As the device width is reduced under 10 nm due to the high integration of semiconductor devices, resistivity of metallization line is significantly increased due to the decrease of the device width. Copper (Cu) is the most commonly used for metallization owing to the low resistivity and high conductivity. However, Cu metallization is known to show the limitation for the nm thickness due to the size effect linked to the long electron mean free path (EMFP) of 39nm. Also, the reliability of Cu is degraded as device operating temperatures and current densities are increased with each technology node. Since W has a smaller EMFP of 19nm, it is expected to reduce the size effect as it goes to nm dimension. Furthermore, W has a very high melting temperature of 3673K, there is a possibility to replace Cu for future metallization material for the metal thickness lower than tens of nm. In this study, ICP assisted sputtering of W has been investigated for lower resistivity of nm scale W film. An internal-type coil antenna has been used for a high ionization, and a DC sputter system has been used for the deposited W thin film. When the characteristics of W thin film deposited with and without ICP assistance were investigated, the decrease of the W thin film resistivity was decreased and, regardless of substrate heating, the deposition rate was increased due to the increase of plasma density. By using high density plasma, we could get dense structure of W thin film at low temperature. Using the XRD, the decrease of β peak which is A-15 structure and the increase of α peak which is bcc structure at both room temperature and 673K were observed with ICP-assisted sputtering. It means ICP assistance influence the decrease of the W thin film resistivity. In addition, analyzing with XPS, the O content in the W thin film which has great influence on the resistivity of W thin film was decreased with increasing the ICP power. As a result, the feasibility of tungsten deposited by ICP assisted sputtering as a next-generation metal interconnect material was investigated.

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TF-TuP-11 A New High Wear-resistant Conductive Coating Based on Transition Metal Nitrides with Solid Solution Structure*, **Yuankai Li**, C Hu,* State Key Laboratory of Superhard Materials, Key Laboratory of Automobile Materials of MOE, and School of Materials Science and Engineering, China

High wear-resistant conductive coatings have recently attracted increasing interest owing to their technological importance in the fields of high-speed railways, artificial joints and electrode materials. However, wear-resistance and conductivity of materials are a dilemma from the perspective of structures and chemical bonds. Thus, developing ideal wear-resistant conductive coatings remains a significant challenge. Here, we propose a novel strategy to design wear-resistant conductive coatings: a transition metal nitride is selected as a base, and its wear-resistance and electrical conductivity are simultaneously improved by doping transition metals or noble metals to form a solid solution structure. The new strategy is demonstrated to be practically feasible and effective by two experiments: doping tantalum and silver into hafnium nitride films. Doping with tantalum and silver can improve wear-resistance and conductivity of hafnium nitride films due to the formation of solid solution structures. The conductivity and wear-resistance of the silver precipitated Hf-Ag-N supersaturated solid solution are higher than those of the Hf-Ta-N solid solution, which is attributed to not only the solid solution strengthening effect but also the effects of precipitate silver including the precipitation strengthening, self-lubrication and additional conductivity enhancement. Combining a series of experiments with first-principle calculations and Drude-Lorentz fitting, we have proved that the formation of solid solution structures can achieve both wear-resistance and conductivity enhancement, apart from well-known strength enhancement. This work provides new insights in designing hard, wear-resistance yet high-conductivity coatings.

TF-TuP-13 Tribo-mechanical and Tribo -corrosion Properties of Thin-on-thick Duplex PVD/HVOF Coatings*, **Jolanta Klemberg-Sapieha**, F Pougoum, J Qian, L Martinu,* Polytechnique Montréal, Canada*; Z Zhou, K Li,* City University of Hong Kong*; R Schulz,* Institut de recherche d'Hydro-Québec

The tribo-mechanical, corrosion and, in general, multifunctional performance of metallic substrates can be significantly enhanced by applying a thin-on-thick duplex coating architecture. Specifically, in a very promising system consisting of a High Velocity Oxy-Fuel (HVOF) coating followed by a Physical Vapor Deposition (PVD) coating, the hard thick HVOF layer provides the load carrying capacity of the soft substrate, while the top dense thin PVD film improves the wear and corrosion resistance . In the present work, pure Fe_3Al coatings and composite Fe_3Al:BN coatings (~300 µm), with a hardness between 4.3 and 12.8 GPa, were prepared on SS304 substrates by HVOF. The top thin PVD layer of diamond like carbon (DLC, 1~2 µm) has been prepared by pulsed DC magnetron sputtering. The tribo-mechanical and tribo -corrosion properties of the DLC/SS304, DLC/Fe_3Al/SS304 and DLC/Fe_3Al:BN / SS304 coating systems were then compared. Application of the DLC layer on top of the HVOF coating allowed one to decrease the friction coefficient from 0.7 to <0.1, and to significantly enhance the wear resistance. Particularly, the DLC/Fe_3Al:BN system exhibits the lowest wear rate of 8×10^{-8} $mm^3/N^{-1}\cdot m^{-1}$. The corrosion resistance of the DLC/Fe_3Al system was increased by 3 orders of magnitude. The wear, corrosion, and tribo -corrosion mechanisms are discussed in detail.

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