Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G1

Advances in Industrial PVD, CVD and PCVD Processes and Equipment

G1-1INVITEDTALK:DepositionofFunctionalNano-CoatingsUsingAtmosphericPressurePlasmas,DaphnePappas(daphne.pappas@plasmatreat.com),A. Aref,A. Sy,PlasmatreatUSA,USAINVITED

Plasma surface engineering has been employed for decades for the development of advanced materials and has offered a plethora of technological solutions. As an example, any microchip used in a computer, tablet or cell phone device, at some point during its production was subjected to a plasma etch or deposition process that took place in a vacuum environment. Over the last decade, plasma processing of materials has expanded, including the development of functional nanocoatings under atmospheric pressure and room temperature conditions. The motivation for this was the need for equipment and processes that could be incorporated in industrial production lines capable of producing large area inline coatings in a cost efficient way, negating the need for vacuum systems. In this talk, an overview of atmospheric pressure plasma jet processes for: i) the activation and cleaning of surfaces and ii) the deposition of polymer functional coatings will be presented. The surface cleaning step is important for surfaces that have residual contaminants or for materials that have low surface energy. This pre-treatment can be instrumental in improving the bonding to adhesives or coatings that are applied on the activated surfaces. Also, results from the deposition of polymer coatings with unique functionality will be presented. The coatings that were developed had a thickness that ranged from 50nm to 690 nm and can serve as anti-corrosion, water repellent, adhesion promoting or biocompatible surfaces. Due to these properties, they are applicable in several industries, including aerospace, automotive, biomedical and microelectronics.

G1-3 Parametric Analysis of the Selective GTAW Remelting Process forWC-10Co-4CrCoatingbyHVOF,HortenciaSantos(hortencia.noronha@gmail.com),UniversidadeFederal do Pampa, Brazil;N. Mayhassen,InstitutoTecnológico de Aeronáutica, Brazil;A. Miranda, H.SVOBODA,Universidad deBuenosAires,Argentina;A.UniversidadeFederal do Pampa, Brazil

Thermal sprayed coatings containing tungsten carbide (WC) are widely used in different industrial applications due to its high hardness, high temperature and wear resistance. As sprayed coatings containing WC usually require a second stage of remelting, after application, to enhance the final properties, which can be made using different heat sources like laser, electric arc, oxi-gas flame or a furnace. Aspects of coating quality like adherence, dilution and level of defects are strongly affected by the heat source and procedure employed. Nevertheless, there is a lack of systematic studies related to these aspects. The objective of this work was to analyze different parameters using GTAW to produce the remelting of WC-Co thermal sprayed coatings obtained by High Velocity Oxi-Fuel (HVOF) process. Samples of carbon steel were coated by HVOF using a WC-Co powder obtaining a coating of 100 microns thickness with a hardness of 1250 HV. Then, the coated samples were remelted using GTAW processes. In each case, the effect of different parameters like power, travel speed and patterns were evaluated. On the refused samples microstructural characterization, microhardness profiles and electrochemical corrosion test were done. There were obtained procedures to remelt the WC-Co coatings with low dilution. The processes produced coatings with hardness values between 1600 and 1800 HV. The resistance to corrosion was similar than the as spray condition. Nevertheless, the integrity of the interphase was strongly improved in both cases.

Acknowledgments

The authors want to acknowledge to RIJEZA-Brasil for providing the coated material and to INTI-Argentina and ITA-Brasil for the wear tests.

G1-4 HIPIMS –Ready on Industrial Scale for Modern Production, Philipp Immich (pimmich@hauzer.nl), G. Negrea, D. Doerwald, R. Jacobs, M. Eerden, R. Ganesan, L. Tegelaers, IHI Hauzer Techno Coating B.V., Netherlands

Since HIPIMS enter the coating scene a lot of investigations on this topic had been carried out. Discovering new properties, different material behavior compared to convention sputtered coatings and better performance in cutting, forming and tribology applications. Most of the investigations were done on small scale deposition units. But bringing this technology to industry, larger units are needed and also process upscaling is needed.

Today real production of coated parts require not only good coating properties also production related topics like reliability, easy maintenance, cost per part and flexibility of the coating unit itself plays an important role.

In this regard different HIPIMS coatings from AlCrN-based, AlTiN-based and hydrogen free DLC such as ta-C systems were deposited on industrial scale units for tribology and tool applications. The applied coatings were investigated concerning mechanical film properties like hardness, Young's Modulus, chemical properties like composition and phase formation. To verify the performance of the coating machine and the deposited coatings, industrial tests in automotive and tool applications are carried out. The obtained results shown, that the HIPIMS technology is ready for serial production in a modern production environment.

G1-5 Carbon coating on Three-dimensional Anodically Oxidized Titanium Foam with Hierarchical Nanostructure for Capacitive Deionization Electrode, J. Huang, Ping-Yen Hsieh (pyhsieh@fcu.edu.tw), J. He, Feng Chia University, Taiwan

Capacitive deionization (CDI) is one of the most promising technique for water treatment and purification. To meet the demand for pursuing high efficiency of desalination, the key component, CDI electrode, requires high chemical stability, high specific surface area, high water wetting ability, and suitable porous structure for ion electrosorption. As opposed to the conventional carbon nanomaterials for CDI electrode, a new design concept is proposed by using facile nanostructure engineering on titanium foam through anodically oxidization and hydrothermal treatment, followed by high-temperature glucose carbonization to develop a carbon film coated titanium dioxide nanostructured porous electrode (CTPE). Further, the feasibility of using such novel electrode for CDI performance was evaluated. The experimental results show that successful preparation of a carbon film coated titanium dioxide nanostructure on titanium foam can be facilitated to obtain CTPE. With the carbon film served to passivate surface and provide low impedance interface, it enhances ion transmission capacity and improves electrochemical stability. By taking the synergistic effect of abovementioned characteristics, the efficiency of salt electrosorption/desorption performance was enhanced significantly based on the cyclic voltammetry results. Finally, under an optimal CDI cell operation condition, the CTPE can reduce sodium chloride water solution with its conductivity from 748 µS/cm to 627 µS/cm, corresponding to the adsorption NaCl amount of 0.54 mg/cm³. Overall, the proposed CTPE can be considered a promising material for CDI application.

G1-6 Digital Twin PVD Coater Matsight - State-of-the-Art and Future Outlook, Adam Obrusnik (obrusnik@plasmasolve.com), P. Zikan, M. Kubecka, PlasmaSolve s.r.o., Czechia

In most fields of industry, CAE (computer-aided engineering) is the go-to tool for designing a new system or a process. Recent scientific advancements and the evolution of high-performance computing also enabled predictive simulation of industrial PVD processes, substantially reducing the effort invested to trial-and-error. As a provider of industrial PVD CAE, we report on the development of MatSight - a user-friendly "digital twin" software that will enable in-house user-friendly CAE of PVD systems and processes. We discuss the numerical strategies and physical assumptions which enable the underlying simulation. The presentation aims to provide relevant use cases and success stories for PVD CAE but it also aims to discuss the challenges encountered during the development limitations PVD simulation. and present of

G1-7 Oxygen-Controlled Crystal Structures and Properties of SnO₂ Infrared Transparent Conducting Films, Liangge Xu (xuliangge@aliyun.com), L. Yang, Harbin Institute of Technology, China; J. Zhu, Key Laboratory of Micro-systems and Micro-structures Manufacturing, China

Tin oxide (SnO₂) has been widely explored for various applications due to its excellent n-type semiconductor properties, low resistance, and high optical transparency in the visible range. However, few studies on the preparation of SnO₂ films using high power pulsed magnetron sputtering have been reported. Oxygen content is a critical parameter in the practice of SnO₂ thin films by high-power pulsed magnetron sputtering. the average free range of Sn atoms is usually much smaller than O atoms. SnO₂ films deposited in a pure Ar atmosphere are likely to be oxygen-deficient and form O vacancies. and such oxygen vacancies will cause lattice distortion, which will affect the mobility of charge carriers in the SnO₂ film. Therefore, oxygen is the main factor affecting the electrical conductivity of SnO₂ films.

In this paper, the reaction mode of high-power pulsed reactive magnetron sputtering at different oxygen partial pressures and the crystal structure and infrared transparent conductive properties of SnO₂ films prepared at 600°C were investigated. The crystal structures and properties of infrared transparent SnO₂ films deposited by high-power pulsed magnetron sputtering at different oxygen partial pressures from 10 to 24 sccm were investigated. For the SnO₂ films deposited with 10~14 sccm oxygen partial pressure, the reaction mode is dominated by the metallic mode, and the polar unsaturated (101) plane is the preferred orientation of the film crystals. For SnO₂ films deposited with oxygen partial pressures of 16 to 18 sccm, the reaction mode is dominated by the transition mode, and the (110) plane shows a preferred orientation. In the deposition process with oxygen partial pressure greater than 18 sccm, the reaction proceeds in the poisoning mode. As the oxygen partial pressure increases, the carrier concentration decreases to 2.335×1015 cm-3; the mobility increases to ~15 cm²/Vs, and the IR transmittance at 4 μ m increases. At the same time, the electrical properties of the prepared SnO₂ films deteriorate due to the oversupply of O₂, with resistivity up to $5.029 \times 10^2 \Omega \cdot cm^2$.

G1-8 INVITED TALK: New Developments in Magnetron Sputtering Devices, D. Monaghan, Victor Bellido-Gonzalez (victor@gencoa.com), T. Sgrilli, R.

Brown, J. Brindley, B. Daniel, Gencoa Ltd, UK INVITED Magnetron sputtering is a mature and well establish PVD deposition technique. Since the introduction of commercial planar magnetrons in the 1970s there are few vacuum coating sectors that haven't been touched by successful implementations of this deposition technique. In the 1970s the semiconductor industry was revolutinonized by the introduction of planar magnetron sputtering as an alternative to evaporation and diode sputtering. Nearly forty years later, still magnetron sputtering is at the heart of many of the manufacturing processes from small to large area, with different degrees of functionality, from decorative, to energy, transport, architectural, automotive, aerospace, display, photovoltaic, thermal solar, electronics, etc.

Different sectors have typically required adaptation of the basic concepts of magnetron sputtering for the specific functionality and purpose. There has been a need for a continuous development of sources and process solutions. Among those, the need for better controls, and better monitoring. This presentation will give an overview of magnetron sputtering with its main breakthroughs, the current status of the technology in important for some relevant PVD coating sectors and will look at the current and future challenges ahead.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G2

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications

G2-1 INVITED TALK: Enhancing TiAl Oxidation Resistance at High Temperature: A Challenge for the Aerospace Industry, *Marjorie Cavarroc (marjorie.cavarroc@safrangroup.com)*, Safran Tech, France INVITED The 21st century is one of major importance for the aerospace industry because of the important increase in flight demands from the Asian market. Evaluated at 3.8 billion in 2016 by the International Air Transport Association (IATA), the number of airplane passengers is predicted to double by 2037. To supply to the rising demand, to mitigate operation costs, and to reduce the environmental impact of such air traffic, aircraft designs are pushed to technological limits. This is particularly true for the engines, whose efficiency is dictated by their thrust-to- weight ratio. Judicious weight reduction combined with the elevation of engines' operating temperatures will therefore improve their efficiency.

In this context, titanium aluminides (TiAI) attract immense interest because of their low weight and their high specific strength at high temperature compared to conventional titanium or nickel alloys. This allows for the manufacture of lighter blades and the reduction of the mass of other components.

TiAl are intermetallic compounds. Their ordered structure and strong atomic bonds give them good mechanical properties and good oxidation resistance. These properties are almost of the same order of magnitude as the ones of Nickel-based alloys. They also have a lower density than Nickel based alloys (3.9 to be compared to 8.3), that could allow a significant weight reduction of the engines. However, intermetallic compounds are known to be brittle and to have low toughness.

Presently, TiAl is used for application parts exposed to temperatures lower than 750°C. Above this temperature, mechanical properties are severely reduced. The range of temperature at which severe oxidation appears is between 750 °C and 850 °C, depending on the alloy.

The oxygen embrittlement and the ductility loss of TiAl alloys are commonly considered as a subsurface effect due to the uptake of oxygen into the $\alpha 2$ phase. The γ phase has a low oxygen uptake, can act as a barrier against oxygen and has better mechanical properties than the $\alpha 2$ phase.

Up to now the most promising approach to protect γ -TiAl-based alloys against environmental degradation at temperatures as high as 1000 °C is surface engineering. By decoupling bulk and surface properties, it allows the protection of various types of materials against environmental degradation without impacting their carefully designed composition.

A large study, including PVD, PECVD and electrochemical deposition, was performed in order to find a way to protect efficiently TiAl at high temperature. A review of this study will be presented and performances of the different coatings will be compared.

G2-3 Electrolytic Plasma Polishing as Post-Treatment for Additively Manufactured Stainless Steel, Nicolas Laugel (nicolas.laugel@manchester.ac.uk), A. Matthews, A. Yerokhin, The University of Manchester, UK

The Additive Manufacturing (AM) of metals promises disruptive changes in a host of manufacturing industries. While the field has been advancing at a rapid pace over the past years, resulting surface states remain a particularly unyielding obstacle to a wide range of applications. Powder particle sizes in the tens of micrometres impose similarly sized features on AM surfaces, with obvious negative impacts on mechanical performance or dimensional precision.

Electrolytic plasma polishing (EPPo) is a finishing method used for the polishing, cleaning, deburring, smoothing of metals and alloys. In contrast with other finishing techniques requiring careful control of directionality, such as mechanical polishing or laser-based methods, EPPo natively effects the surface as a whole. Among other geometry-independent approaches, such as electropolishing or chemical etching, EPPo stands out with its benign water-based electrolytes, low material removal for a given target surface state, and treatment times in the minutes. With these characteristics, the method complements AM particularly well, with few or no constraints put on piece design as well as ease of application for industrial actors who do not necessarily have experience in hazardous chemical handling and waste management.

The work presented here focuses on two complementary approaches for in-depth characterization, of the process itself and of the resulting surfaces respectively, with the ultimate goal of streamlining the optimization of EPPo on an application-by-application basis. In situ analysis of the process could enable the automated fine-tuning of parameters through direct feedback. To help realize this, comprehensive analyses in the frequency domain of the electrochemical cell current response were conducted and shown to give real-time information on the balance between the different reactions and physico-chemical phenomena at play. Additionally, plasma light emission and gas evolution were analyzed to inform interpretation and the role of the different process parameters.

Extensive ex situ analysis of the surfaces was performed in terms of morphology and composition. Very superficial dealloying (~10nm) could be demonstrated in the case of Ni-Cr steels which, along with the overall

roughness decrease, is believed to drive moderate improvements in corrosion resistance and microhardness. Surface profilometry over macroscopic areas was used to determine the strength of the smoothing effect as a function of the lateral size of features, a metric particularly pertinent to the finishing of AM pieces and their large-scale surface roughness.

G2-4 PEO Coatings for Adhesive Bonded AA6060 Components, *Dominic Shore (dominic.shore@manchester.ac.uk)*, The University of Manchester, UK; J. Avelar-Batista Wilson, BCW Manufacturing Group Ltd, UK; A. *Matthews, A. Yerokhin,* The University of Manchester, UK

Adhesive bonded aluminium components have become increasingly important to the automotive industry, where lightweight structures are imperative to performance and vehicle efficiency. Since the mid-20th century, conventional anodizing processes have been applied to aluminium components subject to adhesive bonding, to increase bond durability and corrosion resistance. However, conventional anodizing generally uses strongly acidic electrolytes which have a significant environmental impact. Anodizing procedures are generally multi-stage processes which can be resource intensive and time consuming. This study looks into application of Plasma Electrolytic Oxidation (PEO) as an alternative to conventional anodizing techniques for the preparation of aluminium parts for bonded structures. PEO is a promising emerging coating technique for the production of oxide coatings with excellent tribological performance and corrosion resistance. It offers an alternative route for the production of well adhered oxide coatings where weak alkaline electrolytes can be utilised in place of the highly acidic electrolytes associated with conventional anodizing processes. PEO has the further potential to reduce the number of additional treatments prior to and after the anodizing stage, offering scope for savings in resources and time.

In this investigation, experiments were carried out to produce PEO coatings on the alloy AA6060-T6 using different electrolyte compositions and power/polarity regimes, to develop coatings with differing characteristics for comparison. Detailed analyses of the microstructure, chemical and phase composition of these coatings was carried out using methods including SEM, EDS, GDOES and XRD. The adhesive strength of coatings was assessed using mechanical tests including tensile lap-shear testing. Analysis of the fracture behaviour and the ultimate strength of the adhesive joints was considered along with the observed physical/compositional characteristics of the different coatings to determine the suitability of PEO coatings for bonding applications and to achieve an understanding of the important parameters influencing the joint strength when bonding PEO coated AA6060-T6. The coatings were further investigated using electrochemical techniques such as EIS and subjected to accelerated corrosion testing along with investigations into the abrasive wear of the coatings to determine their overall suitability for automotive applications. It is intended that the findings of this study will be of interest for potential industrial applications and will also contribute to the general understanding of the mechanical properties of PEO coatings.

G2-5 Cobalt-based Thin Films as Electrocatalysts for Water Recombination Applications, *Clara Linder (clara.linder@liu.se)*, Linköping University, IFM, Nanostructured Materials, Sweden; *S. Gangaprasad Rao, A. Le Febvrier*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *S. Munktell*, Swerim AB, Sweden; *P. Eklund*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *E. Björk*, Linköping University, IFM, Nanostructured Materials, Sweden

Catalysts and electrocatalysts are crucial for energy production and storage solutions. Water recombination is one important reaction for these applications, but due to sluggish kinetics, an electrocatalyst is required. Cobalt oxides have presented good performances for the oxygen reduction reaction (ORR) [1], and in some cases as good as noble metal-based catalysts [2]. To develop cost efficient systems and functionalized surfaces, the catalysts can be synthesized as nanomaterials or thin films.

In this work, cobalt thin films were deposited on low alloyed steel using magnetron sputtering. The thickness of the film was estimated to 200 nm with cross-section scanning electron microscopy (SEM) analysis. Co-films were then electrochemically oxidized at room temperature in an alkaline solution. The final material was a multi-layered mix of cobalt oxides, one of them being Co₃O₄ identified with X-Ray Diffraction (XRD). The catalytic performances of the oxidized films were evaluated in 1M KOH electrolyte saturated with oxygen. Cathodic currents in 10-50 mA/cm² range, corresponding to ORR activity, were measured with linear scan voltammetry. Different characterization techniques (SEM, XRD and X-ray

photoelectron spectroscopy) were used to define the material properties of the thin films and its catalytic activity.

This work has shown that thin films can be used as electrocatalysts, after electrochemical modification, efficiently for oxygen reduction reaction for energy production and storage solutions.

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Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G3

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

G3-1 Enhancing the Performance of Rake and Flank Surface Textured Ceramic Tool Filled With Solid Lubricants, Sathiya Narayanan Nagarajan (sathyasairam89@gmail.com), S. Venkata Sai Prabhu, S. G, A. G, S. N, Sastra Deemed University, India

Non-hazardous, toxic-free, allergic-free and less cost-orientated methods are expected by the industries and the industrial workers for the better working-environment. In this work, an effort is made to achieve this expectation by integrating the concept of surface texturing and extended self-lubrication for machining grey cast iron materials. Cross-chevron and line textures were fabricated on the tool's rake and flank faces using Nd: YAG laser texturing machine. An untextured ceramic tool (UT), crosschevron and line textured tool (TT) and solid lubricants (MoS2 and Graphite) and SAE 40 oil mixed chemical solutions filled textured tool (STL) are considered for machining under dry conditions. The particles' average size was observed to be 1400 nm and 1590 nm for MoS₂ and graphite solid lubricants, whereas the polydispersity index (PdI) found to be 0.903 and 0.977 respectively. The solid lubricants' PdI values indicated that the particle samples were larger in size distribution and polydisperse. The experimental results observed with the reduced main cutting force, feed force, average friction co-efficient for semi-solid lubricant filled texture tool than other considered tools.

G3-2 Characterization of Different AlCrN PVD Coatings Deposited into H13 Steel for Lube-free Aluminum Die Casting Application, Nelson Delfino de Campos Neto (ndelfino@mymail.mines.edu), A. Korenyi-Both, S. Midson, M. Kaufman, Colorado School of Mines, USA

In the high-pressure die casting process, organic lubricants are sprayed onto the die surface prior to each shot to prevent the liquid aluminum from soldering and sticking to the steel die. The organic-based lubricants act as a parting agent, but also produce several undesirable outcomes including: i) reducing the quality of the castings by increasing the amount of entrapped gasses, ii) increasing production costs, and iii) producing effluents that must be treated and discarded. However, portions of the die that become extremely hot, such as small core pins, are difficult to lubricate, and so PVD coatings are often applied to these areas to assist in minimizing soldering. Ideal PVD coatings for die casting applications must exhibit excellent adhesion to the die substrate, have good mechanical and tribological properties, high oxidation resistance, and exhibit chemical inertness to and/or be non-wetting by liquid aluminum.

Recent research at the Colorado School of Mines examined whether PVD coatings could be used to minimize or eliminate the use of conventional organic lubricants during die casting, and a test was developed to quantitatively measure the adhesion strength of aluminum die casting alloys solidified against PVD coated steel substrates. Three PVD coatings (AlCrN, AlTiN and CrWN) were identified where the aluminum die casting alloy exhibited zero adhesion strength to coated substrates. To evaluate the performance in a commercial die casting environment, an entire H13 steel die was PVD coated with AlCrN, and the testing demonstrated that the PVD coating enabled a reduction in the required amount of conventional lubricant spray by around 85%.

To further reduce or eliminate the use of conventional lubricants, coatings with improved non-wetting behavior need to be identified. In the present study, three different AlCrN-based PVD coatings have been examined, and characterization techniques have been used to determine their structure,

mechanical properties, wear resistance and adhesion resistance to molten aluminum alloys. This study has demonstrated that small differences in the AlCrN coating can led to appreciably improved performance.

G3-3 12 μm in PVD with HiPIMS, *Christoph Schiffers (christoph.schiffers@cemecon.de), T. Leyendecker, W. Kölker,* CemeCon AG, Germany

Higher coating thickness gives higher wear volume. Today's standard in tool coatings is 3-4 μm . More than 6 μm is for traditional coating technologies not a viable option due to excessive intrinsic stress. No real improvement are the usual work arounds such as bond coats and multilayers with soft intermediate layers. The process gets slower and more prone to failures. A dense morphology with low compressive stress is needed.

HiPIMS is a good candidate since it is known for a dense structure without any droplets resulting in toughness and hardness at the same time. The real innovative leap is stress management by synchronising the HiPIMS pulses on the cathodes with the substrate bias. This paper will introduce the concept of selective ion biasing. Plasma analytics reveal that the flux arriving at the substrate per HiPIMS pulse is composed of the wanted metal ions coming from the target and other ion portions which highly influence the intrinsic stress of the growing film. Selective ion biasing is a fully new tool and allows to precisely select certain ion portions out of the pulse while suppressing unwanted species. Now the coating developer can actively tune the intrinsic stress of the film by setting the synchronisation parameters.

Full control on the process and the growing film – that's the quantum leap of selective ion biasing. And this for different HiPIMS frequencies and pulse data for each and every cathode – tailored for the respective target material.

A case study of FerroCon[®]Quadro as a 12 μ m PVD coating illustrates how HiPIMS moves the frontiers of the possible in tool coatings. Applications such as the milling of crank shafts, railway tracks and heavy duty turning show the enormous performance benefit of very thick PVD coatings for cutting tools. 12 μ m PVD work, in HiPIMS.

G3-4 Cross-sectional Characterization of Microstructural, Phase and Elemental Changes during High-Temperature Oxidation of AlCrSiN Coatings, Nikolaus Jäger (nikolaus.jaeger@unileoben.ac.at), Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria; S. Spor, voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany; M. Meindlhumer, Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Austria; H. Hruby, F. Nahif, voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany; C. Mitterer, Montanuniversität Leoben, Austria; J. Keckes, Erich Schmid Institute for Materials Science, Austrian Academy of Sciences, Leoben, Austria; R. Daniel, Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Austria

Increasing demands in machining and forming industry towards advanced applications such as dry cutting or high-speed machining stimulate the development of coatings with enhanced properties to protect the surface of tools and workpieces under extreme conditions. Besides substantial requirements on the mechanical properties, also thermal stability and oxidation resistance play a key role in high-temperature applications.

In this work, the high-temperature oxidation of AlCr(Si)N coatings with 0, 2.5 and 5 at.% Si-content was studied. Differential scanning calorimetry together with thermogravimetric analysis and ex-situ X-ray diffraction revealed a shift of the on-set temperature for oxidation from 1100°C for AlCrN to 1260 °C for both Si-containing coatings and a much slower oxidation progress for the latter due to their nanocomposite microstructure. In addition to these conventional characterization methods, an AlCrSiN coating with 5 at.% Si was partially oxidized at 1400 °C for 1 h and studied along its cross-section to investigate microstructural and elemental changes during high-temperature oxidation.

X-ray nano-diffraction of the sample cross-section revealed the formed phases, residual strain state and structural variations across the coating thickness: (i) A dense oxide layer at the surface comprising mainly of Al2O3 and Cr2O3 protected the coating from further oxidation. (ii) Below this oxide layer, a fine-grained transition zone with incomplete oxidation was found. (iii) The bottom half of the coating was not oxidized and consisted only hexagonal AlN.

A detailed TEM analysis allowed for a better understanding of the microstructural and elemental changes during oxidation and revealed: (i) a separation of the oxide layer into an Al-rich and a Cr-rich part, (ii) a strong outwards diffusion of Cr into the oxide layer and (iii) a pronounced separation of the not oxidized part of the coating into Al-rich and a Si-rich grains.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G4

Pre-/Post-Treatment and Duplex Technology

G4-1 INVITED TALK: Comprehensive Characterization of Surface Modification Mechanisms in Boron Nitride Films Prepared by a Reactive Plasma-assisted Coating Technique, Koji Eriguchi (eriguchi.koji.8e@kyotou.ac.jp), Kyoto University, Japan; M. Noma, SHINKO SEIKI CO., LTD, Japan; M. Yamashita, Hyogo Prefectural Institute of Technology, Japan; K. Urabe, Kyoto University, Japan; S. Hasegawa, Osaka University, Japan INVITED Boron nitride (BN) films are of great importance in a wide variety of engineering fields such as machinery, electronic devices, and space applications [1-4]. Various process technologies have been developed to form stable BN films. Recently, we proposed a reactive plasma-assisted coating (RePAC) system [5] to fabricate high-hardness (cubic) BN stack structures on a Si substrate and investigated the surface modification under various plasma exposures [6]. In this study, we performed comprehensive characterization of the BN films on crystalline Si substrates using various analysis techniques, i.e., indentation and electrical tests in combination with a molecular dynamics (MD) simulation. The (µm-thick) BN films prepared by the RePAC system exhibited characteristic electron tunneling behaviors governed by the Frenkel-Poole effects [7][8] in response to process conditions (e.g. the energy of incident Ar ions). The relationship between the electrical dielectric constant determined by capacitance-voltage test and the Knoop hardness was clarified for various process conditions. An inductively-coupled Ar plasma reactor where the energy and flux of incident ions were controlled was used to investigate the surface modification mechanisms of the BN films. The formation of a surface plasma-damaged layer (a few nm thick) was identified by a nanoindentation technique [9]. The energy dependence of the sputtering yield of the BN films was compared with that of SiO2 films, indicating that the BN film is one of the promising candidates for the usage in harsh environments such as a long-time plasma exposure. The MD simulations predicted the formation and reconstruction of the *sp*³-bonded BN phase in the hexagonal background under the irradiation of ions, showing a good agreement with the experimental findings. The comprehensive characterization as performed in this study should be employed for future BN process designs.

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G4-3 Notable Difference between Rapid-Thermal and Microwave Annealing on Ge pMOSFETs, *Fu-Yang Chu (xxmoon666@gmail.com), K. Chang-Liao,* National Tsing Hua University, Taiwan; *D. Ruan,* National Tsing Hua University, China; *S. Yi,* National Tsing Hua University, Taiwan

Effects of rapid-thermal-annealing (RTA) and microwave annealing (MWA) on GeOx interfacial layer (IL) and HfO_2 gate dielectric in Ge pMOSFET are studied in this work. High gate leakage and low hole mobility may be

induced by diffusion of GeOx during RTA thermal process. The electrical characteristics, such as high hole mobility of ~510 cm2/V-s, low EOT of ~0.7 nm, and very low gate leakage density (JG) of ~10-4 A/cm₂ at VG=VFB+ 1 V

in Ge pMOSFET, can be simultaneously achieved by the efficient annealing effects of MWA on hydrogen plasma (H*) treated GeOx IL, thanks to the suppression of GeOx out-diffusion. The notable different between RTA and

MWA can be attributed to good annealing effect on gate stack with low thermal budget of MWA.

G4-4 Characterization of Tungsten-doped InZnO Thin Films with Plasma Treatment for Conductive-bridge RAM Applications, *Chih-Chieh Hsu (cchsu.06g@g2.nctu.edu.tw),* National Chiao Tung Universiy, Taiwan; P. Liu, K. Gan, D. Ruan, Y. Chiu, S. Sze, National Chiao Tung University, Taiwan In this study, the impact of plasma treatment on InWZnO (IWZO) CBRAM was reported.In order to improve the characteristics of IWZO CBRAM device, we use oxygen remote plasma to surface-treat the IWZO layer. Oxygen plasma can slightly suppress oxygen vacancies in IWZO. The set voltage of the device becomes more uniform and smaller, which is beneficial for low power operation. The a-IWZO CBRAM shows the excellent memory performance, such as high switching endurance (up to3 ' 10³ cycles) and overshoot current decrease. Without high temperature is used in the process, which would be suitable for memory in flexible substrates.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G5

Hybrid Systems, Processes and Coatings

G5-1 INVITED TALK: Frontiers of Surface Engineering for Ultra-low Friction and Wear, Ali Erdemir (erdemir8184@gmail.com), Texas A&M University, USA INVITED

In recent years, great strides have been made in the design and synthesis of new materials and coatings (such as atomically thin graphene, MoS₂, HBN, etc. and diamondlike carbons) affording friction coefficients as low as 0.001. When considering the fact that friction and wear related energy losses account for nearly a quarter of the global energy output at these days, the further development and uses of such materials will help in achieving a sustainable energy future that is also environmentally sensible. In this presentation, a comprehensive overview of what makes and breaks super-low friction in such materials is provided in relation to the many intrinsic and extrinsic factors acting on them and on sliding interfaces. In light of the recent analytical, experimental, and computational advances, an attempt will also be made to elucidate those underlying mechanisms that are most responsible for such ultra-low friction and wear behaviors. Several case studies involving monolithic and hybrid coating systems providing super-low friction and wear are also presented as the most exciting developments in tribological field. Overall, these and other novel approaches are leading the way for the design and production of next generation tribological systems that can dramatically increase efficiency, reduce carbon emission, as well as improve reliability in future moving mechanical systems.

G5-3 From On-line Sensor Validation to in-situ Monitoring of Layer Growth: Coatings around Fiber-Bragg-Gratings, Uwe Beck (uwe.beck@bam.de), A. Mitzkus, M. Sahre, T. Lange, M. Weise, M. Bartholmai, V. Schukar, F. Basedau, D. Hofmann, E. Köppe, BAM Berlin, Germany

The lack of *on-line* validation procedures for structure-embedded fiberoptical strain sensors, in particular fiber-Bragg-gratings (FBG), resulted in limited applications in structural health monitoring (SHM). Degradation under service conditions and ageing as a result of climatic influences or delamination under load were unsolved validation issues. This could be overcome by means of an auto-diagnosis procedure based on FBG-sensors coated by electrochemical deposition (ECD) with a magnetostrictive NiFecoating on top of an adhesive Cu/Cr adhesive layer deposited by physical vapour deposition (PVD) around the FBG strain sensor. This allows at any time under service a validation of sensor functionality, stability, and reliability. For this purpose, a magnetic strain-proportional reference field is introduced. The optical read-out is realized by the measurement of the Bragg-wavelength shift. The ratio of resulting strain and exciting magnetic reference field should be constant given that the sensor is in proper function [1, 2, 3]. In principle, the magnetostrictive coating around the FBG should also work as on-line magnetic field sensor and other applications in material science. One of these applications is the *in-situ* monitoring of ECD processes as the deposition of the ECD NiFe-layer on the FBG revealed. Challenges are the monitoring of temperature, deposition stages/thickness, and resulting mechanical stress under given plating conditions. Monitoring problems can be solved by applying a pre-coated FBG to the electrolytic process as the shift of the Bragg wavelength is affected by both the temperature of the electrolyte near the substrate and the stress formation in the growing layer. The experimental FBG set-up and the guantitative determination of temperature- and stress-related strain are described for a nickel-iron electrolyte. The in-situ measurement of Bragg wavelength shifts of a precoated FBG during electrochemical deposition allows a detailed analysis of stress states due to changes in the growth morphology of the layer. The separation of mechanical and thermal contributions to this shift provides information on the individual deposition processes in terms of a process fingerprint [4].

[1, 2, 3] DFG projects SCHU 2707/2-1, BA 5015/1-1, BE 3206/2-1.

[4] A. Mitzkus, M. Sahre, F. Basedau, D. Hofmann, and U. Beck; Journal of The ECS, 166 (6) B312-B315 (2019)

G5-4 Characterization of the Combination of Microwave and Laser Ablation Plasmas, Enrique Camps (enrique.camps@inin.gob.mx), E. Campos-Gonzalez, Instituto Nacional de Investigaciones Nucleares, Mexico The main aim of the present work is to report on the study of the combination of continuous plasma, formed by a microwave electron cyclotron resonance (ECR) discharge and pulsed plasma of laser ablation which allow studying the formation of materials in the form of thin films making use of the relatively high densities of the microwave discharge and the wide range of ion energies produced in the pulsed laser ablation plasmas. With this arrangement it is possible to deposit thin films of materials that in the usual microwave discharge require the use of pollutant and corrosive substances, as the required element is obtained from a pure solid target. Moreover, as the laser ablation process is carried out in plasma as the background gas, instead of a neutral gas, the presence of contaminants, such as oxygen can be significantly reduced. For the purpose of the present paper a nitrogen microwave ECR discharge was combined with the plasma created during the ablation of an aluminum target, in order to deposit AIN thin films. Plasma parameters were measured by a Langmuir probe, and the chemical species contained in the plasma were analyzed by optical emission spectroscopy (OES).

G5-6 Thermal Stability of Passivated Oxygen Vacancy in Indium Gallium Zinc Oxide with Supercritical Fluid Cosolvent Oxidation, Post Annealing or Oxygen Plasma Treatment, *Chia-Yu Lin (mandylin21107@gmail.com)*, *P. Liu*, National Chiao Tung University, Taiwan; *D. Ruan*, National Chiao Tung University, China; *Y. Chiu, K. Gan, C. Hsu*, National Chiao Tung University, Taiwan; *S. Sze*, National Chiao Tung University, USA

In this report, the thermal stability of oxygen vacancy in indium gallium zinc oxide (IGZO), which was passivated by supercritical fluid (SCF) cosolvent oxidation, post annealing or oxygen plasma treatment, has been investigated in detail. With X-ray photoelectron spectroscopy (XPS) analysis, it can be found out that the oxygen vacancy passivated by SCF treatment exhibits better thermal stability than other oxidation treatment. Besides, the IGZO treated with different treatment has been used as the channel material for thin thin-film transistor device. Similar with the XPS result, the device with SCF treatment shows excellent reliability and uniformity even within high temperature ambient.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session G6

Application-Driven Cooperations between Industry and Research Institutions

G6-1 Hard Protective Coatings Inside Narrow Tubes and Cavities in Aircraft Engine Components, J. Crespo Villegas, A. Kilicaslan, O. Zabeida, E. Bousser, Polytechnique Montreal, Canada; Jolanta-Ewa Klemberg-Sapieha (jsapieha@polymtl.ca), Polytechnique Montrtreal, Canada; L. Martinu, Polytechnique Montreal, Canada

There is an ever-growing interest in the use of functional coatings to protect surfaces of materials and workpieces against harsh environments such as corrosion, abrasion or solid particle erosion (SPE), making surface

engineering solutions a very attractive balance between performance and cost. Numerous vapor-based fabrication techniques have been developed, namely PVD, CVD, and PECVD, that can be used to achieve the high hardness and high wear resistance while being compatible with substrate materials such as metals, and different substrate shapes. This is increasingly important in the case of inner surfaces of tubular components, such as parts of aircraft engines, oil pipelines, mining components, and numerous others.

In the present work, we study a novel Non-Line-Of-Sight (NLOS) technique to coat the inner parts of non-linear surfaces and cavities with hard, wearand erosion-resistant coatings possessing high SPE resistance, a hardness significantly higher than the hardness of the particles impacting the surface, as well as a large thickness (more than 8 μ m).

Specifically, we review, study and demonstrate the fabrication process of hard SPE-resistant TiN protective coatings on the inner surfaces of narrow tubes using an NLOS approach yielding a uniform film thickness and properties along the tube axis (better than 20%). The deposition process indicates the importance of applying pulsed-DC PECVD when uniform hard TiN films are prepared at low-frequency in the kHz range. The TiN films (about 12 μ m thick), exhibit high hardness and relatively low Young's modulus (25 and 225 GPa, respectively), corresponding to the (111) preferred crystallographic orientation. We show that the SPE resistance on the inner surface decreased by a factor of more than 15 compared to the bare substrate and that the process is well suited for the protection of aerospace, manufacturing, 3D printed and other critical components with a complex shape of inner surfaces.

G6-2 Prediction of Loss of Barrier Properties in Cracked Thin Coatings on Polymer Substrates Subjected to Tensile Strain, *Marcus Vinícius Tavares da Costa (marcus.tavares@angstrom.uu.se), E. Gamstedt,* Uppsala University, Angstrom Laboratory, Sweden

The layered structure of carton containers for food and beverage packaging is one of the most widely used products in our daily life which allows the transportations while keeping the food protected. This design has been around for decades, but more sustainable solutions are needed to replace aluminium barrier layers with thinner and more environmentally friendly coatings. Recent developments in thin film deposition over large areas of polymer substrate have sparked the interest of food packaging producers in thin brittle coatings of nanometre thick of various compositions in the package structure. Such coatings can be impermeable and therefore enhance the barrier properties of the packages as a whole [1]. However, when these coatings are implemented in the manufacture process, cracking in the coating is almost inevitable since the package materials are deformed in the converting process, and hence the barrier properties are impaired. A mechanism-based model to predict the loss of barrier properties during deformation in the manufacturing process could potentially serve as a tool in developing improved packaging.

In this presentation, we will tackle this question by showing how the fracture behaviour of coatings on polymers substrates is affected by uniaxial tensile deformation, and subsequently how a key barrier property for beverage packaging, namely the oxygen transmission rate (OTR), is affected by the fractured coating. This is done quantitatively by numerical modelling. The modelling is dependent on reliable experimental characterization published previously [2, 3]. The specimens for this study case were produced by roll-to-roll atomic layer deposition of metal oxides, with thickness values between 4 and 20 nanometers on poly(ethylene terephthalate) substrate films. The advantages and disadvantages of the model will be addressed, as well as its accuracy.

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G6-3 PALMS - Plasma Additive Layer Manufacture Smoothing, Tomasz Brzezinka (tomasz.brzezinka@wallworkht.com), J. Housden, A. Fox, Wallwork Cambridge Ltd, UK; N. Laugel, A. Matthews, A. Yerokhin, The University of Manchester, UK

Additive manufacturing (AM) offers unprecedented design freedom and the possibility to produce lightweight optimised components that are impossible to make with traditional techniques. Despite the significant progress made in AM, the surface roughness of parts produced by this method remains a significant hindrance to more wide-spread industrial use. The aerospace and medical industries, where the surface finish of components is highly critical, are particularly attentive to the issue. We have developed PALMS (Plasma Additive Laver Manufacture Smoothing). an innovative cost-effective macro-polishing solution based on electrolytic plasma technology. The use of electrolytic plasma polishing, with its fast and uniform material removal, makes for a particularly effective method of finishing components. The method is moreover largely unaffected by complex geometries, a key advantage for an AM finishing method. AM parts are treated in less than 90 minutes with highly reproducible resulting surface states, leaving a uniform, smooth micro-finish (R_a<0.1µm), and considerably improved aesthetics and mechanical performance.

This collaboration, involving multiple industrial partners within the framework of the PALMS project and coordinated by Wallwork with academic support from the University of Manchester, recently led to a published account of some of the development achieved (Yang et al. Additive Manufacturing 2020, vol. 34 p. 101204). Strategies for successful PALMS application to further case studies, such as hot stamping tools or AM demonstrators will be discussed here, and the resulting surface performance presented.

Surface Engineering - Applied Research and Industrial Applications

Room On Demand - Session GP

Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-1 Corrosion Induced Diffusion Pathways in Thin Film Materials Investigated by Atom Probe Tomography, Oliver Hudak (oliver.hudak@tuwien.ac.at), CDL-SEC, TU Wien, Austria; E. Aschauer, TU Wien, CDL-SEC, Austria; V. Dalbauer, FAU Erlangen, Germany; L. Shang, O. Hunold, M. Arndt, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; P. Polcik, Plansee Composite Materials GmbH, Germany; P. Felfer, FAU Erlangen, Germany; H. Riedl, TU Wien, CDL-SEC, Austria

Corrosion processes are common phenomena in fields of engineering and there is nearly never an instance, where a material is totally inert to its environment and its corrosive nature. Therefore, corrosion and corrosion-resistance are essential variables that play a pivotal role in the development of protective coatings. Ingenuity of next generation PVD coatings has given rise to a wide range of material concepts set out to withstand all kinds of corrosive attacks (e.g. NaCl, HCl, SO₃ and O₂). While their performance is mostly assessed on descriptors such as mass change, impairment of mechanical properties, or variance in electrochemical surface potential, little work has been dedicated to understand corrosion driven diffusion pathways, specifically on an atomic scale.

This study showcases a systematic approach on highlighting preferred diffusion pathways of corrosive media in arc-PVD thin films. For investigating the effect of grain size, droplet formation and crystallinity on the overall diffusion mechanism, a novel marker architecture was developed. Eliciting chemical and structural changes upon arrival of the diffused media, this marker system facilitates improved application of high-resolution analytical methods, such as APT and TEM, to help identify preferential diffusion paths.

GP-2 Engineered Phase Differences between HiPIMS Power and Substrate Bias for Improved Mechanical Properties of Titanium Nitrides, *Ying-Xiang Lin (qw36100@gmail.com)*, *W. Wu*, Da-Yeh University, Taiwan

In order to enhance the hardness, density, and adhesion of the deposited film, a substrate bias was normally applied during the deposition to attract ions to the substrate to increase the bombardment of the Ar⁺ on the film. However, an excessively ion bombardment also causes an extremely high compressive residual stress of the film and leads to peel off. Therefore, adjusting the substrate bias voltage to obtain a proper ion impact to the film is an important factor in the process. High-power pulsed magnetron

sputtering (HiPIMS) is an advanced technology of conventional magnetron sputtering. The plasma density of HiPIMS is three levels higher than conventional magnetron sputtering due to its high ionization rate. Therefore, a high amount charged particles are generated in the HiPIMS process. Applying a DC bias voltage in HiPIMS process helps these charged particles reach the substrate, but a high amount charged particles also cause the bias fail instantaneously. Meanwhile, two group high-energy ions of gas and target were observed when the pulse is turned on and off, respectively. Therefore, adjusting the phase differences between HiPIMS power and substrate bias becomes critical in a HiPIMS deposition process. However, the effect of applying synchronized and phase different bias on the film deposition has not been detail discussed.

Ti films have high mechanical strength and excellent corrosion resistance and are often used as an interface layer for TiN deposition to enhance adhesion. In this study, different phase difference bias of HiPIMS deposited Ti and TiN layer was individually investigated. A DC substrate bias was also used for comparison. The plasma composition in front of the target and substrate was individually analyzed by optical emission spectroscopy (OES), and it was found that Ti²⁺ and Ar⁺ increased significantly at the substrate after applying DC bias and pulsed bias. According to the XRD, SEM and AFM results, the grain size and surface roughness of Ti and TiN decreased when a synchronous pulse bias was applied. Finally, the corrosion resistance of Ti/TiN was analyzed to determine the best substrate bias condition for HiPIMS process.

Keywords: HiPIMS, TiN/Ti, Phase difference pulse bias, Substrate bias

GP-3 Thermally Spayed Coatings with Integrated Sensor Systems for Tribological Load Surfaces, Annett Dorner-Reisel (a.dorner-reisel@hssm.de), Schmalkalden University of Applied Sciences, Germany; W. Ahmad Akhtar, J. Seeger, G. Reisel, Oerlikon Metco WOKA GmbH Barchfeld, Germany

Monitoring systems for load, damage, temperature, fatigue assessment during operating of machines, wind turbines or transportation systems are of great interest. The main focus of the present research is the development of a strain and stress sensing reliable sensor, that signals overloading and general behaviour and its protection during operating, what would give a long durability of the smart property. In addition to the sensors sensitivity against stress and strains, it needs to be adequate protected. Therefore, films and coatings are selected and proven.

These thin films and coatings were deposited on piezo-sensor systems. The aims are:

(a) protection of the piezo-sensor during embedding process

(b) protection of the sensor during tribological loading during practical application of the metallic components

(c) receiving proper electric signals from embedded sensors

Thermally sprayed WC-NiCr and Cr3C2-NiCr coatings with approximately 250 µm thickness were deposited on steel substrates. Flat piezoelectric sensors were embedded. Tribological behaviour of thermally sprayed coatings without and with sensor embedding was tested. The Palmqvist fracture toughness was measured and data are correlated to the wear behaviour and the electric signals from the coatings.

GP-4 Performance Enhancement of pGe MOS device with Pre- and Post-Deposition Microwave Annealing Treatment, Yu-Hsuan Chien (teresa.chien888@gmail.com), National Tsing Hua University, Taiwan; K. Chang-Liao, D. Ruan, S. Yi, National Tsing Hua University, Taiwan; F. Chu, National Tsing Hua University, Taiwan

Recently, germanium (Ge) based metal-oxide-semiconductor (MOS) device with high-k gate insulator has been widely investigated for its higher electron and hole mobility than silicon, and easier integration with traditional technology than III–V materials. Beside, microwave annealing process was proposed to improve electrical characteristics for its lower thermal budget compared with the traditional annealing process. In this work, complete microwave annealing treatments have been applied on the pGe MOS device, instead of the traditional thermal process. As a result, the device with both pre- and post- deposition microwave annealing exhibits better electrical performance than other samples.

GP-5 Design of Surface Layers with Phase Change with Novel Properties, Rahul Basu (ra4499@gmail.com), VTU Kundana, Bangalore, India

A model for a phase change layer with thermal and mass transport is formulated/ Variable diffusivity and surface conditions are embedded in the model. Subsequently boundary lengths for mass and thermal penetration are evaluated by special techniques. Diffusivities which ares normally assumed constant, are allowed to vary as transformations progress. Solutions for specific variable diffusivities are computed where penetration lengths are evaluated. An integral method is applied along with perturbation expansions,to evaluate the boundary layer thickness. Applications are postulated for self healing paints, roofing material, radar absorbing/deflecting coatings and other possible consumer and military spinoffs.

GP-6 Effect of Cu Content and Melting Temperature on the Oxide Film Formation and the Quality of Molten 6000-Series Aluminum Alloys, H. Jang, P. Youn, H. Kang, G. Lee, J. Park, E. Kim, J. Jeon, Sunmi Shin (smshin@kitech.re.kr), Korea Institute of Industrial Technology (KITECH), Republic of Korea

In recent years, the interest of high strength aluminum alloys is growing due to the demand for the light-weight vehicles to meet the strengthened environmental regulations. Heat treatable 6000-series aluminum alloys (Al-Mg-Si alloys) are the typical high-strength aluminum alloys and are widely used as a panel material because of its thermosetting property, which increases the strength when baked finish. The inclusions formed during casting can affect the precipitate formation in the post heat treatment process and impede the work hardening ability of nano-precipitates of Al-Mg-Si alloys. The inclusion formation during casting is affected by the alloying elements, the liquid state oxidation of the alloy surface, and the casting process conditions. In order to reduce the internal defects and improve the mechanical properties of high-Cu-containing Al-Mg-Si alloys, the effect of Cu content on the oxide film formation on the surface of the molten alloys need to be clarified and the quality of molten alloys should be precisely controlled. In this study, the oxide film on the surface of molten Al-Mg-Si-Cu allovs was characterized by electron microscopy and DSC-TGA and the effect of Cu content and the melting temperature on the oxide film formation energy was estimated by thermodynamic calculations. In relation to the characteristics of the oxide film, the melt quality of Al-Mg-Si-Cu alloys was discussed.

GP-7 TiO2-Silicon Nanowire Arrays for Inorganic Solar Cell Applications, Ai-Huei Chiou (ahchiou@nfu.edu.tw), National Formosa University, Taiwan Large-area ordered single crystal SiNW arrays on p-type (100) silicon wafer without the use of a template were prepared in a silver nitrate and hydrofluoric acid (HF/AgNO₃) solution at 50oC. The result showed that highly dominant peak at 69° is belong to (004) silicon plane which can be explained equally by preferential etching along [100] directions. The linear relationship of SiNW arrays could be adjusted by controlling the etching time. Besides, the result showed that SiNWs gave the best anti reflective properties (3.07% in the broad visible band) and well-aligned properties with 45 minutes. A n-TiO₂/p-SiNW heterojunction has been fabricated by RF magnetron sputter. The crystal structure of TiO₂ layer reveal its anatase and rutile both structured hybrid. A n-type TiO2 thin films were deposited sputtering on the p-SiNW arrays having hydrophilicity features. In this study, a rare inorganic-inorganic heterojunction solar cells using titanium dioxide and silicon nanowires was fabricated. The present results indicated that the power conversion efficiency (PCE) of n- TiO₂/p-SiNWs better than n- TiO₂/p-Si inorganic-inorganic heterojunction solar cells. The inorganicinorganic heterojunction solar cells used itanium dioxide and silicon nanowires, in which the Voc is of 0.139V, Jsc is of 94.81 mA/cm2 and, the FF is of 21.3% and efficiency is of $2.81 \times 10^{-3\%}$. Key words: silicon nanowires (SiNWs), Electroless Metal Deposition (EMD), inorganic solar cell

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