

# Thursday Afternoon Poster Sessions, April 26, 2018

## Fundamentals and Technology of Multifunctional Materials and Devices

Room Grand Hall - Session CP

### Symposium C Poster Session

#### CP-2 Effect of Nitrogen Content on Structure and Properties of MoN<sub>x</sub> Coatings, *Jian Wang*, University of New South Wales, Australia

Molybdenum nitride (MoN<sub>x</sub>) coatings were deposited onto AISI M2 tool steel substrates (hardened to HRC 60) by closed field unbalanced magnetron sputtering ion plating (CFUMSIP) and controlled by means of a closed-loop optical emission monitor (OEM), which was used to control the nitrogen content. The structure of the coatings was investigated by X-ray photoelectron spectrometry (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The analysis showed that increased nitrogen content led to a transformation from bcc Mo phase to fcc Mo<sub>2</sub>N phase and then to fcc MoN phase as the OEM level was decreased. The mechanical and tribological properties were evaluated by nano-indentation, wear and scratch testing. During the wear test, the Mo<sub>2</sub>N exhibited the lowest coefficient of friction. Further, during the scratch test, the Mo coating failed at the lowest load. This presentation will relate the processing conditions to the structure and hence mechanical behavior of these coatings.

#### CP-3 Stress Metrology for G6 and Larger Flat Panel Displays, *Wojtek Walecki*, Frontier Semiconductor, USA; *W Hung*, Frontier Semiconductor, USA, United States of America; *D Kim*, Sejong University, Korea

We report novel photo-elastic method for measurement of the stress in polyimide (PI) based flat panel displays (FPD) and flexible displays (FD) structures. Method is based on measurement of the change of the state of polarization of the light undergoing reflection (or transmission) in the structures containing PI layer(s). Commonly used FPD and FD contain layers of 5 μm or thicker PI layers. PI has stress optic coefficient of about 3.4E-10 Pa<sup>-1</sup> [1], which is almost 100 times larger than glass [2]. This allows easily measurement of stress with sensitivity of the order of 5 MPa and less. We present apparatus for local stress measurements having lateral resolution of 3 cm, and stress resolution of 5 MPa. Presented tool gives promise to become capable of measuring glass panels of the size 1.5 m x 1.85 m does not contained any moving parts. Our tool can be combined with more traditional stress induced deflection based stress measurement [3]. We discuss also methods of numerical analysis of optical data, including stress separation algorithm optimized for this problem, and practical problems related to analysis of the data.

[1] Noe, Susan Cunningham. *A prism coupling study of optical anisotropy in polyimide including moisture, stress, and thickness effects*. Diss. Massachusetts Institute of Technology, 1992.

[2] Sun, Lan, and Samad Edlou. "Low birefringence lens design for polarization sensitive optical systems." *Proc. SPIE*. Vol. 6289. 2006.

[3] Walecki, Wojtek *J Stress Metrology for Flat Panel Displays G6 and Bigger*. Abstract submitted to Photonics West 2018 SPIE OPTO (PW180).

#### CP-4 Hydrogen Barrier Properties of Diamond-like Carbon Coatings, *Motonori Tamura*, University of Electro-Communications, Japan

The hydrogen barrier properties of the coatings of diamond-like carbon (DLC) were evaluated. Using plasma chemical vapor deposition and sputtering, DLC coatings were deposited on Type 316L stainless steels. The hydrogen permeation rate was reduced to 1/1000 or lower by the DLC coatings. The DLC coatings with high hydrogen content had high hydrogen barrier function. For hydrogen diffusion in coatings, the movement of atoms through hydrogen trap sites such as pores in coatings, and crystal defects such as dislocations, is important. The DLC coatings are amorphous, and there are both sp<sup>3</sup> and sp<sup>2</sup> bonds, and excess hydrogen could be found in the interstitial space and the hydrogen trap sites. In the DLC coatings with high hydrogen content, these hydrogen trap sites are likely already filled with hydrogen atoms, and the movement of new hydrogen atoms could be limited.

CP-5 Effect of N<sub>2</sub> Flow Rate on the Properties of TiN film on Si Substrate for Thermal Detector Application, *Yi-Ching Huang*, *K Lin*, *Y Lai*, National Nano Device Laboratories, National Applied Research Laboratories, Taiwan  
Titanium nitride (TiN) is a suitable material for the mirror film of thermal detector due to its high IR reflectivity property. TiN thin films have been deposited on p-type Si (100) substrate with different nitrogen flow rate by

magnetron sputtering system. Increasing the N<sub>2</sub> flow rate played a significant factor in controlling the properties of TiN films. In the study, the surface performance, phase, element ratio, and the optical and electrical properties of the TiN films will be characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectrometer (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and current-voltage (I-V) measurement. The results indicated that the TiN film with 40 sccm N<sub>2</sub> flow rate had high reflection (88%) in the IR range and exhibited the lower sheet resistance and high I<sub>on</sub>/I<sub>off</sub> ratio.

#### CP-6 Graded Multilayer Thin Film of BaTiO<sub>3</sub>/PVDF with High Energy Storage Density, *XiaoHui Wang*, Tsinghua University, China

Organic-inorganic 0-3 nanocomposites, which combine the potentially high dielectric strength of the organic matrix and the high dielectric permittivity of the inorganic filler, are extensively studied as energy-storage dielectrics in high-performance capacitors. To obtain high dielectric constants, a large volume fraction of the inorganic component is necessary, but this will frequently deteriorate the dielectric (breakdown) strength and thus limit the energy density value of the overall nanocomposite. In this study, a graded multilayer BaTiO<sub>3</sub>/poly(vinylidene fluoride) thin film structure is presented as a means to achieve both a higher breakdown strength and a superior energy-storage capability. Key to the process is the sequential deposition of uniform dispersions of the single component source, which generate a blended PVDF-BTO-PVDF structure prior to full evaporation of solvent, and thermal treatment of the dielectric. The result is a 2-2 like sandwich structure with partial 0-3 character, seamless interfaces between layers and a concentration gradient of the BTO. The central layer designed to provide the high electric displacement, is composed of high volume fraction 6-10 nm BTO nanocrystals produced by a TEG-sol method. The outer layers of the structure are predominantly PVDF, with a significantly lower volume fraction of BTO, taking advantage of the higher dielectric strength for pure PVDF at the electrode-nanocomposite interface. The film is mechanically flexible, and can be removed from the substrate, with total thicknesses in the range 1.2 – 1.5 μm. Parallel plate capacitance devices exhibit highly improved dielectric performances, compared to reported values for BTO-PVDF 0-3 nanocomposites, with low-frequency permittivity values of 20-25, a maximal discharged energy density of 19.4 J/cm<sup>3</sup> and dielectric breakdown strengths of up to 495 kV/mm.

#### CP-7 Synthesis of Bi<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> Nano Structured Thin Films for Photocatalytic Applications, *M Calheiros*, *F Correia*, *J Marques*, *Carlos Tavares*, University of Minho, Portugal

The increasing scarcity of potable water has served as motivation for the development of decontamination processes. Photocatalytic degradation is one of the most viable processes compared with conventional ones. This process uses the UV radiation effect to produce hydroxyl radicals, with the assistance of a photocatalyst. The most commonly used catalyst is TiO<sub>2</sub> semiconductor, characterized by its low toxicity and high chemical stability. This work aims to synthesize Bi<sub>2</sub>O<sub>3</sub> thin films with fibrous morphology for subsequent functionalization with a top TiO<sub>2</sub> thin film. A Hastelloy B3 thin film was used as an interface layer between the glass substrate and the Bi seed layer in order to promote some interfacial roughness and improve film adhesion. The growth of Bi<sub>2</sub>O<sub>3</sub> thin films was performed by magnetron sputtering and adapted to abide the vapor-liquid-solid (VLS) mechanism, mainly concerning its 3D growth morphology and its high roughness templates. Subsequently, the TiO<sub>2</sub> photocatalytic thin films were deposited onto the Bi<sub>2</sub>O<sub>3</sub> thin films. SEM observations revealed a pine-tree morphology for the Bi<sub>2</sub>O<sub>3</sub> nano structures, with an enhanced surface area. The photocatalytic efficiency assessment was performed by conducting an assay using methylene blue dye as the pollutant and a solar radiation simulator. The tests show that the thin films of Bi<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> are more efficient at degrading the pollutant when compared with the TiO<sub>2</sub> thin films.

#### CP-8 Improvement of Mechanical Properties in 3D Printed Ceramic Core, *Hye-Yeong Park*, *B Kim*, *G Cho*, *E Kim*, *Y Jung*, Changwon National University, Republic of Korea; *J Zhang*, Indiana University Purdue University Indianapolis, USA

Ceramic core employed in a precision casting process is typically not recyclable, which reduces productivity and increases production cost. Therefore, a new fabrication process for ceramic core combined with 3D printing process and organic-inorganic binder conversion process was proposed in our previous study. However, the core made of coarse mullite bead (average particle size: 250 μm) did not develop sufficient green and firing strengths due to the porosity and pore size. Therefore, to improve the mechanical properties, especially the strength, the packing density of

# Thursday Afternoon Poster Sessions, April 26, 2018

ceramic core was increased, through mixing fine mullite powder (average particle size: 16 $\mu$ m) and zircon flour (average particle size: 43 $\mu$ m) with coarse mullite bead. Green bodies with the two types of poly vinyl alcohol (PVA), which have the same molecular structure with a large difference in their boiling points were 3D printed. Then the samples were heat-treated at 250°C to evaporate the PVA with a lower boiling point. The heat-treated core samples were dipped into the inorganic precursor, and dried and heat-treated at 1000°C for the organic-inorganic conversion process. Through the combination of starting powders, the compact density of the sample was increased and the pore size was reduced, resulting in an increase in the inorganic binder coating efficiency and an improvement in the glassification conversion efficiency. The study demonstrates the feasibility of fabrication of ceramic core with excellent strength through 3D printing process.

**CP-9 Enhanced Efficiency of Perovskite Solar Cells with Ferroelectricity,** T Nguyen, S Shin, S Kim, H Choi, **ChungWung Bark**, Gachon University, Republic of Korea

Perovskite solar cells (PSCs), which emerged as tremendously attractive devices in thin-film photovoltaic technology to utilize renewable energy sources, have been improved with the unprecedented breakthrough in recent years. Ferroelectric materials with a vast array of intriguing electrical properties have been applied in photo-related devices; however, there was rarely that these materials appeared in solar cell device configuration. In this work, mesostructured TiO<sub>2</sub> combined lanthanum bismuth titanate (BLT) nanoparticles in a combination with perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> light absorber is capable of maximizing the absorbed visible light. Interestingly, the robust spontaneous electrical polarization of these ferroelectrics under applying positive bias voltage promotes the desirable separation of photoexcited carriers and drives the charge transportation that contributes to high-efficiency PSCs. Application of uniform nano-sized BLT powders through high-energy ball milling process and perovskite layer fabricated by two-step solution deposition technique will pave the way for fabricating hybrid organic-inorganic perovskite solar cell with high solar energy conversion in the coming years.

**CP-10 Improvement in Hygroscopicity of Inorganic Binder through Dual Coating Process,** Hyun-Hee Choi, H Lee, G Cho, E Kim, Y Jung, Changwon National University, Republic of Korea; J Zhang, Indiana University-Purdue University Indianapolis, USA

In a conventional sand casting process, the mold is manufactured by mixing ceramic materials and organic binders, which is widely used in foundry industry due to the simple manufacturing process and low production cost. However, it is difficult to form complicated products since the organic binders are decomposed and the defects in the mold are generated during casting at high temperatures. In order to solve these problems, organic-inorganic binder conversion process has been proposed. One issue in the process is that, when stored at room temperature for a long time before heat treatment, the mold strength is reduced and/or the mold is fractured, which is caused by the hygroscopicity of the water-soluble inorganic binder. Therefore, in this study, a dual coating process was proposed and applied to reduce the hygroscopicity of the inorganic binder in preparing the casting mold. The prepared sample was dipped into a solution of inorganic binder precursor (TEOS: SiO<sub>2</sub> precursor and NaOMe: Na<sub>2</sub>O precursor), and then dipped into a solution of water-insoluble organic binder after a drying process. Finally the sample was heat-treated at 1000 °C to generate a glass phase by organic-inorganic conversion process. The contact angle of the sample with the water-insoluble organic binder was increased, while it was impossible to measure the contact angle in the conventional sample. It was confirmed that the green and firing strengths were maintained by the water-insoluble organic binder coating layer. The effects of the holding time and humidity at room temperature on the strength and microstructure of the mold were investigated, in terms of organic binder species employed in the dual coating process.

**CP-11 Synthetic Parameter Influence on Morphological and Electrochemical Properties of Porous NiO Thin Films Prepared by Chemical Bath Deposition,** Jung-Hoon Yu, H Yang, R Jeong, J Lee, D Kim, K Hwang, H Seo, S Nam, J Boo, Sungkyunkwan University, Republic of Korea  
Chemical bath deposition (CBD) is an advantageous thin film deposition technique for depositing compound semiconductors at low temperature. In this paper, nickel oxide (NiO) thin films were prepared by CBD method under aqueous solution containing nickel sulfate, potassium persulfate, and ammonia water at room temperature. Prepared NiO thin film has porous structure with two dimensionally networked nanoflake arrays. In this process, concentration of ammonia water and nickel sulfate significantly affect on morphological features. Increase of ammonia

concentration cause the growth kinetics until 30 ml of ammonia. Over 30 ml, however, it tended to not only decrease the thickness of films but also change the growth direction of flakes. In addition, lower concentration of nickel sulfate form a thicker NiO thin film but high concentration forms a lower thickness. This phenomenon is derived from Oswald ripening between crystal growth and aggregation at the CBD process. Each prepared NiO thin films were characterized by electrochromic measurement to apply on electrochromic window. Optimized NiO thin film shows good electrochromic performance with fast switching speed (11.0 s and 7.5 s), high optical modulation ( $T_{bleaching}$ : 80% and  $T_{coloring}$ : 17 %) and high cycling durability (over 5000 cycle).

**CP-12 Characteristics of Perovskite Solar Cells Fabricated by using Lead Free Perovskite,** S Shin, C Bark, **HyungWook Choi**, Gachon University, Republic of Korea

Lead halide perovskite is an excellent candidate for use as a light harvester in solar cells. The perovskite structure (CH<sub>3</sub>NH<sub>3</sub>)PbX<sub>3</sub> (X = halogen) consists of organic components at cuboctahedral sites and inorganic components at octahedral sites, and perovskites exhibit the chemical properties of the organic component. Solid-state hybrid organic-inorganic solar cells often employ a layered structure of nanoparticulate titania, an organometal halide perovskite, and a spiro-MeOTAD hole transport material (HTM). One concern, however, is the potential toxicity of lead, an important component of conventional perovskite solar cells. Currently, the most likely substitute is a tin, and it is a Group 14 metal, similar to lead. In this paper, we develop a new type of perovskite photoresist for non-toxic perovskite solar cell applications. This is also a non-toxic material for solar cells compared to conventional materials used for perovskite solar cells. The perovskite precursor solution was prepared by dissolving CH<sub>3</sub>NH<sub>3</sub>I and SnI<sub>2</sub> in N-dimethylformamide (DMF). The application of the perovskite layer produced by the sequential deposition technique through the perovskite produced by using the tin is likely to replace the Pb-based perovskite, which is a safety and commercialization of the perovskite solar cell Improve technological progress.

**CP-14 The Influence of Disordered Grain Boundaries on Carrier Transport in Degenerated Polycrystalline AZO Thin Films Deposited by Magnetron Sputtering,** Hiroki Tokunaga, T Miyata, T Minami, Kanazawa Institute of Technology, Japan

The influence of disordered grain boundary on carrier transport is investigated for degenerated polycrystalline Al-doped ZnO (AZO) thin films prepared using two magnetron sputtering deposition (MSD) apparatuses. The AZO thin films with an Al content of 3 at.% and a thickness of 500 nm were prepared on glass substrates at a substrate temperature of room temperature (RT) in a pure Ar gas atmosphere at a pressure of 0.6 Pa using a dc and an r.f. (13.56 MHz) power supply applied either separately or in combination; dc-MSD and rf-MSD or rf+dc-MSD. When the electrical properties were evaluated by the van der Pauw method, the obtained mobility ( $\mu^{Hall}$ ) and carrier concentration ( $n^{Hall}$ ) in polycrystalline AZO thin films prepared by MSD methods exhibited the location dependences (distributions) on the substrate surface, when moved from the location corresponding to the center on the target surface to one corresponding to the erosion area on the target. The location dependences of  $\mu^{Hall}$  and  $n^{Hall}$  were also controlled by rf+dc-MSDs carried out with varying superimposed r.f. power. However, we found that the  $\mu^{Hall}$ - $n^{Hall}$  relationship resulting from those location dependences always exhibited a positive slope. In addition, we found that the main scattering mechanism, which limits the mobility of AZO thin films is attributed to grain boundary scattering caused by the reflection of electrons from the potential barrier at the grain boundary between crystallites. The obtained  $\mu^{Hall}$ - $n^{Hall}$  relationships with a positive slope in degenerated AZO thin films prepared by various MSDs always exhibited fair agreement with those calculated using Mayadas and Shatzkes (MS) theory. However, the significance and reliability of reflectivity used as a fitting parameter in the semi-classical MS theory seem questionable. Munoz's group recently reported that the increase in the resistivity of a metallic specimen must be estimated under the effect of electron scattering from disordered grain boundaries based upon Kubo formalism. Disordered grain boundaries were represented by a one-dimensional periodic array of Dirac delta functions separated by a distance producing a Krönig-Penney (KP) potential. They used Green's function built from the wave functions, which are solutions of the KP potential. In quantum theory, the positively sloped  $\mu^{Hall}$ - $n^{Hall}$  relationship in degenerated semiconductors such as AZO thin films is attributed to Anderson localization, induced by electron grain boundary scattering from disordered successive grains.

# Thursday Afternoon Poster Sessions, April 26, 2018

1) C. Munoz et al., Appl. Surf. Sci. **329** (2015) 184. & Appl. Phys. Rev. **4** (2017) 011102.

**CP-15 Physical and Electrochromic Behavior of the ZnWO<sub>4</sub> Active Layer synthesized by Co-sputtering Technique for the Energy Harvesting Devices**, G Malik, S Mourya, J Jaiswal, Ramesh Chandra, Indian Institute of Technology Roorkee, India

This article presents a detailed investigation on a zinc tungstate (ZnWO<sub>4</sub>) active layer, prepared by reactive DC magnetron co-sputtering using standard Zn and W targets, on a transparent conducting glass ITO (indium doped tin oxide) substrate at various temperatures. The ITO substrate is used as a working electrode and ZnWO<sub>4</sub> active layer serve the purpose of a mixed conductor, which is a source of ions and electrons for the electrochromic devices. The physical properties of the fabricated active layer are investigated by x-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), and UV-Vis-NIR spectrophotometry. The quality and the elemental distribution of the active layer are confirmed using X-ray photoelectron spectroscopy (XPS). To determine the optical behavior, Variable angle spectroscopic ellipsometry (VASE) is deployed to calculate the optical constants ( $n$  and  $k$ ). Finally, the electrochemical performance of the active layer was analyzed by cycle voltammetry technique (CV). XRD diffractogram professed that the films are polycrystalline in nature with a monoclinic structure having P2/c space group. SEM micrographs and the cyclic voltammogram of the active layer revealed the surface modification and temperature dependent electrochromic response. This work is an attempt towards the "green nanotechnology" with energy harvesting for human comfort and financial benefits.

**CP-16 The Influence on Electrical Characteristics of Amorphous Indium Tungsten Oxide Thin Film Transistors with Multi-Stacked Active Layer Structure**, Kai-Jhih Gan, P Liu, D Ruan, Y Chiu, M Yu, T Chien, Y Chen, P Kuo, S Sze, National Chiao Tung University, Taiwan

A novel amorphous indium-tungsten-oxide thin film transistor with a multi-stacked active layer is well discussed in this work. A multi-layer channel is proposed to effectively enhance the carrier mobility and device stability, simultaneously. A top capping oxygen-rich a-IWO thin film is used for suppressing the plasma damage to channel layer during backchannel passivation layer deposition process or the oxygen desorption from channel layer by the backchannel passivation material. In addition, a bottom buffer oxygen-rich a-IWO thin film is deposited to avoid the oxygen vacancy formation during the following thermal process. On the other hand, a 1-nm thick WO<sub>3</sub> layer is inserted between the high-k gate insulator and the multi-stacked active layer, which plays important roles as interfacial layer for improving the interface quality and reducing the surface roughness. Besides, a HfO<sub>2</sub> dielectrics film is chosen as gate insulator for realizing low-voltage operation. In this research, the sample with multi-stacked active layer exhibits a high On/Off current ratio of  $\sim 1 \times 10^7$  for low gate leakage current, attributing to the bottom oxygen-rich thin film. Then, a high field-effect mobility of  $\sim 21 \text{ cm}^2/\text{V}\cdot\text{s}$  is achieved by a low surface roughness. Due to the good interface quality, the subthreshold swing is about 0.1 V/decade. This multi-stacked active layer structure exhibits its potential application for the future high-resolution and large-size display manufacture.

**CP-17 Assessment of Structural and Magnetic Properties of Cobalt-Iron-Nickel Thick Films on Copper Formed by Electroforming**, Scooter D. Johnson, C Joye, H Newman, N Nepal, A Kozen, S Shin, Naval Research Laboratory, USA

Co-Fe-Ni alloys form a family of soft magnetic material with a large magnetic saturation ( $\sim 20 \text{ kG}$ ) and very low coercive field ( $< 10 \text{ Oe}$ ) that can play an important role in developing micro electromechanical systems and other novel device structures. For example, integration of magnetic structures into vacuum electronic traveling wave amplifier circuits may dramatically reduce the bulk magnetic material needed in these devices, thereby producing favorable scaling opportunities in larger systems. Vacuum electronic devices have been made using ultraviolet lithography and electroforming (UV-LIGA) to form bulk copper structures. Magnetic components to aid in directing the electron beam passing through the electromagnetic circuit are traditionally machined, brazed together and drilled out to accept the copper circuit structure. To explore the integration of magnetic materials into these circuits by additive manufacturing, we explore tuning the elemental and structural composition of the electroformed Co-Ni-Fe magnetic films. The resulting films were assessed using x-ray photoemission, x-ray diffraction, scanning

electron microscopy, vibrating sample magnetometry, and ferromagnetic resonance techniques.

Samples were formed using a sulfate electrolyte bath consisting primarily of cobalt sulfate, nickel sulfate and iron sulfate with several additives to act as a buffer, improve adhesion, and reduce stress. The pH was varied from 2.8 to 3.2, and the galvanic methods were varied. The plating was carried out in a nitrogen glovebox to exclude oxygen in the atmosphere. The effects of hydrogen annealing are also studied, since vacuum electronic devices are often hydrogen brazed at temperatures up to 1050 deg C.

Film thickness was estimated to be about 100  $\mu\text{m}$ . VSM results on initial samples suggest that the films have a good magnetic saturation value of about 19 kG with a small coercive field of about 50 Oe. The anisotropy field was estimated using a Stoner-Wohlfarth fit and suggests a high degree of magnetic anisotropy perpendicular to the film surface. XPS results indicate that the sample compositions vary in Ni and Fe content. Additional Co and Ni increases the magnetic saturation value while the coercive field remains unchanged.

**CP-18 Sputter-deposited Nanostructured Metal-Oxide Films for Hydrogen Gas Sensing**, S Haviar, Jiří Čapek, N Kumal, Š Batková, M Fialová, R Čerstvý, University of West Bohemia, Czech Republic; T Duchoň, F Dvořák, Charles University, Czech Republic

We present the study of nanostructured metal-oxide films prepared using a gas aggregation cluster source. The main advantage of the use of the cluster source is the possibility to prepare films with a high reactive area without the need for the use of wet techniques (often used for preparing nanostructured sensors). The films with the desired stoichiometry can be prepared directly without the need for subsequent thermal and/or chemical treatment.

Mixtures of tungsten oxide (WO<sub>3</sub>) and cupric oxide (CuO) were deposited by cluster source and/or by conventional reactive dc sputter deposition. Sputtering conditions were tuned to vary the chemical composition and structure of the prepared films. The prepared films were characterized by means of X-ray diffraction, scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The elemental composition was determined by energy and wave dispersive spectroscopy. The oxidation state of metals was studied by X-Ray Photoemission Spectrometry. Subsequently, the films were examined for their sensorial response when assembled into a hydrogen gas sensor. Noble-metal catalysts (Pd, Pt) deposited by dc magnetron sputtering were used to support the response and to lower the working temperature.

The layers were tested for response to a time-varied hydrogen concentration in synthetic air at various temperatures. The response sensitivity and the response time were evaluated. It is shown that optimization of the structure and composition results in enhanced sensorial properties.

**CP-19 A Library of Broadband Reference Dielectric Functions, Valence Band Spectra and Raman Spectra of Epitaxial Conductive Nitride Films Grown on MgO**, S Kassavetis, T Zorba, J Arvanitidis, D Christofilos, Aristotle University of Thessaloniki, Greece; G Abadias, Université de Poitiers, France; D Gall, Rensselaer Polytechnic Institute, USA; Panos Patsalas, Aristotle University of Thessaloniki, Greece

Conductive nitrides, such as TiN, ZrN, and TaN have emerged as significant alternative materials for photonics and plasmonics, due to the combination of their electronic conductivity with their thermal and mechanical stability and refractory character. One of the major drawbacks for the implementation of these materials in plasmonics and photonics is their excessive electronic losses, which are usually originating from the small grain size of the grown films due to their high melting point. Therefore, their refractory character is both a blessing (in terms of stability) and a curse (in terms of grain size). This drawback might be overcome by growing nanostructures of the finest crystalline quality that can be achieved by epitaxial growth. Epitaxial or pseudo-epitaxial growth of most conductive transition metal nitrides can be achieved on MgO along all the principal orientations, or on c-cut sapphire, respectively. Therefore, for the design of photonic and plasmonic devices, it is of utmost importance to know the optical response and the electron density of states of epitaxial transition metal nitrides on MgO. In this work, we provide a library of: i) the dielectric function spectra of epitaxial transition metal nitrides (TiN, ZrN, NbN, TaN, MoN, WN) in the broad range 0.193-125  $\mu\text{m}$  (6.5-0.00992 eV), which were extracted by combining spectroscopic ellipsometry and FTIR reflectance/transmittance measurements, ii) the Raman spectra and the stability of these films upon exposure to intense laser beams, and iii) the experimental electron density of states of the valence band based on X-ray

# Thursday Afternoon Poster Sessions, April 26, 2018

photoelectron spectra. In particular, the dielectric function spectra and Raman spectra of this library may also be used as references for in-situ and real-time monitoring of film growth by ellipsometry or Raman spectroscopy.

**CP-21 Electrical Properties of Molybdenum Doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Thin Films,** *J Galindo, Anil Krishna Battu, R Chintalapalle*, University of Texas at El Paso, USA

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>), which is a stable oxide of Ga, has been attracting the scientific and research community in view of its interesting physical, chemical and electrical properties.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin films find numerous applications in high temperature sensors, photovoltaics, optoelectronics, and anti-reflection coatings. The structural and electrical properties  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin films are quite important for their integration into optoelectronics, photovoltaics and sensors. Recently, we proposed an approach to obtain tunable structural and electronic properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin films using refractory metal incorporation. In this work, we performed a comprehensive study of the electrical properties of molybdenum (Mo) doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (GMO) thin films. The results indicate that the resistivity, sheet resistance, conductivity, charge carrier concentration, and mobility are dependent on the microstructure, chemistry and Mo-content. Most importantly, the variable Mo content from 0 to 12 at% found to influence the electrical properties and allow us to obtain GMO films with a wide range of electrical properties. The results and implications for utilizing GMO films in electronic and optoelectronic devices will be discussed.

**CP-22 Electron Beam Deposition and Characterization of Transparent WO<sub>3</sub>/Al/WO<sub>3</sub> Multilayer Thin Films,** *A Leyva, K Makeswaran, Ramana Chintalapalle*, University of Texas at El Paso, USA **INVITED**

The ever-increasing demand for sustainable energy calls upon practices for efficient energy utilization, management, and harvesting. Smart windows, which can control the throughput of visible light and solar radiation in buildings can contribute to the energy efficiency and cost savings. In this work, an attempt is made to fabricate the multilayered D/M/D architecture using WO<sub>3</sub> (D) and Al (M). The effect of Al thickness [Al(t)] on the performance of WO<sub>3</sub>/Al/WO<sub>3</sub> multilayered films fabricated by electron-beam deposition onto silicon and glass substrates has been evaluated. Efforts were made to understand the effect of Al(t) on the structure, morphology, mechanical durability and optical behavior of the D/M/D multilayered films. The optical, electrical and mechanical responses suggest possible integration of these WO<sub>3</sub>/Al/WO<sub>3</sub> films for smart window applications with enhanced performance.

**CP-24 Numerical Ellipsometry: Extension of Concepts of n-k Plane Solutions from Isotropic to Anisotropic Films,** *Frank Urban, D Barton*, Florida International University, USA

Ellipsometry is an optical technique for determining properties of laminar reflecting (or transmitting) structures from the measurement of light polarization state change resulting from the light-sample interaction. In all but the simplest of cases, the measurements must be followed by data processing in which the measured data is compared to an appropriate mathematical model of the sample derived from Maxwell's equations and measurement conditions. Thus a key common problem is determining how many and which measurements to make. A single ellipsometer measurement consists of a single complex data point and therefore usually more than one measurement is required. Previously we have addressed these problems using Complex Analysis in the n-k plane for homogeneous isotropic films. One of the key findings was that certain angles and wavelengths are useful and others are not. The purpose of the work here is to extend that analysis to anisotropic films. These films have a greater number of unknowns and consequently require more measurements. The central question remains, how many measurements are needed and which specific measurements will provide sufficiently independent equations considering the unknowns. It can be that additional measurements vary to such a small degree that they are not useful considering measurement error tolerance. The work to be presented will show how to identify useful measurements based upon the anticipated sample configuration. The approach avoids making unnecessary measurements which can actually reduce rather than increase the solution accuracy.

**CP-25 Piezophotocatalytic and Piezoelectric Performance of Titanium Zinc Nitride Nanorod,** *Hsin-Yi Lee, K Chang*, National Cheng Kung University (NCKU), Taiwan

Flexible strain sensors have many applications such as structural health monitoring, mechanical testing, and pulse power suppliers. Piezotronic strain sensors, which consist of a metal–semiconductor– metal interface,

are well-suited for these applications due to their high sensitivity and fast response times. Zinc oxide (ZnO) nanowires (NWs) are a popular material for use in piezotronic strain sensors.[3] However, Zinc oxide has relatively high work function, so we can enhance its field electron emission with titanium nitride (TiN) coating, which has good electrical conductivity and relatively low work function.[1][4][5] Therefore, TiN thin film makes it potential in ideal field emitters. In our research, we want to develop the new material which has piezo-related properties and low work function simultaneously.

In this work, piezophotocatalytic and piezoelectric performance of Titanium Zinc Nitride Nanorod thin films deposited by RF magnetron sputtering were described. TiN and ZnN have centrosymmetric structure. However, thin film capacitors fabricated by sputtering Zn doped TiN nanorods from Zinc and Titanium targets in N<sub>2</sub> ambient has non-centrosymmetric structure, because electric polarization and relative permittivity measurements yield distinct ferroelectric properties.

Based on various measurements including piezopotential, piezotronic, piezophototronic, and piezophotocatalytic analyses obtained by characterization tools, (i.e. X-ray diffraction, X-ray photoelectron spectroscopy, Raman scattering, Scanning electron microscope, Transmission electron microscopy, Secondary-ion mass spectrometry, UV-Vis, and I-V methods) we found that the base pressure of vacuum chamber, the chamber pressure and temperature, the sputtering power, and gas flow significantly influenced this material's crystallinity, morphology (i.e. surface roughness), structure properties (i.e. crystallite size), electrical properties (i.e. refractive index), optical, and mechanical properties. In addition, we use combinatorial methodology to fabricate the material [6], which has significant piezoelectric properties in the specific concentration of Zinc, for use as a piezoelectric sensor.

Keywords: Titanium Zinc Nitride, Zinc doped, nanocolumn, morphology control, composition spread, combinatorial magnetron sputtering, piezotronic / piezophototronic effects, photocatalysis / piezophotocatalysis.

**CP-26 Well-alignment ZnSnO<sub>3</sub> by Epitaxially Oriented PVDF and Synergistic Piezo-related Performance of the ZnSnO<sub>3</sub>/PVDF Nanocomposites,** *Chen-Hui Chou, K Chang*, National Cheng Kung University (NCKU), Taiwan

According to previous researches, two-step hydrothermal method was used to deposit ZnSnO<sub>3</sub> on the different kinds of substrate and control their alignment with different conditions such as substrate, temperature, surfactant, and others.<sup>[1,2]</sup> In this research, a novel way was proposed to fabricate ZnSnO<sub>3</sub>/polymer nanocomposites by simple hydrothermal and polymer epitaxy method. This research emphasized on improving the alignment of ZnSnO<sub>3</sub> nanorods<sup>[3,4]</sup> by polymer epitaxy<sup>[5]</sup> such as PVDF and its synergistic piezo-related performance of the ZnSnO<sub>3</sub>/PVDF nanocomposites.<sup>[6]</sup> PVDF was used to control the alignment of the fabricated ZnSnO<sub>3</sub> nanorods and enhance its piezo-related performance including piezopotential, piezotronic, piezophototronic, and piezophotocatalytic analyses.

XRD and SEM were used to characterize the ZnSnO<sub>3</sub>/PVDF nanocomposites. The results from the XRD confirmed the presence of ZnSnO<sub>3</sub>. SEM analysis showed the morphologies and alignments of the ZnSnO<sub>3</sub> nanorods and PVDF. These nanocomposites exhibited average piezopotentials. Piezotronic analysis was also conducted on ZnSnO<sub>3</sub>/PVDF nanocomposites, exhibiting high current density when the ZnSnO<sub>3</sub> are well-aligned. When under UV light illumination, the output current density obtained were several times higher for ZnSnO<sub>3</sub>/PVDF. These confirmed the alignment control and synergistic piezophototronic property of the material.

In a piezophotocatalytic experiment, the decomposition of methylene blue (MB) was also investigated. The ZnSnO<sub>3</sub>/PVDF nanocomposites exhibited better degradation property than pure ZnSnO<sub>3</sub>. All the promising enhancement was attributed to the well-aligned ZnSnO<sub>3</sub>, which reduced the recombination of photogenerated electron–hole pairs and enhanced the mobility of these pairs resulting from the energy band distortion caused by applied stresses. Finally, we can use this nanocomposites or this epitaxially fabricating method to other materials on various electronic applications, such as multifunctional electronic-skin.<sup>[7]</sup>

Keywords: ZnSnO<sub>3</sub>/PVDF nanocomposites, epitaxy, ZnSnO<sub>3</sub> nanorods, piezophotocatalysis, electronic-skin

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# Thursday Afternoon Poster Sessions, April 26, 2018

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## CP-27 Challenges and Limitations for the Optical Characterization of Sub-micron Temperature Fields in Plasmonic Metamaterials, Juan Antonio Zapien, City University of Hong Kong, Hong Kong

Surface plasmons at metal-dielectric interfaces can efficiently confine and amplify electromagnetic (EM) energy in deep sub-wavelength volumes. Concomitant with the large EM field enhancement, Joule heating occurs which severely limits performance for applications such as miniaturized optical circuits. However, the same effect provides a great opportunity to remotely control temperature distributions in the micro- to nano- scale. These highly localized thermal fields have applications to research in catalysis, heat-assisted magnetic recording, phononic circuitry, and photothermal medical therapy among others. A fundamental step to advance the emerging applications of thermoplasmonics is the capability to provide fast, quantitative, contactless experimental determination of the resulting temperature distributions.<sup>[i]</sup>

Spectroscopic ellipsometry (SE) is a phase sensitivity and self-referenced technique expected to have tremendous impact for contactless, marker-free, optical characterization at the nano-scale.<sup>[ii]</sup> However, numerical, fully-vectorial SE data analysis is required for non-layered samples with characteristic lateral dimensions (L) between  $l/10$  and  $10(l)$ . To date, two systematic approaches seem favorable and will be reviewed; namely, the rigorous coupled-wave analysis (RCWA) method which was highly successful to study optical critical dimension (OCD) of 1D gratings by the semiconductor industry,<sup>[iii]</sup> and, more recently, the Finite-Difference Time-Domain that is being systematically investigated by our group.<sup>[iv]</sup>

In this presentation we will provide an assessment of the expected capabilities of SE to provide quantitative optical characterization in plasmonic metamaterials including changes in refractive index and thermal expansion effects based on the known instrumentation and computational limitations currently available.

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## CP-28 The Modification of Refractive Index by using Solid State Diffusion, Hung-Pin Chen, W Cho, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan; C Lee, National Central University, Taiwan; Y Lin, National Tsing Hua University, Taiwan; W Chen, Instrument Technology Research Center, Taiwan

The optical coatings with excellence performance would be achieved more easily when the materials chosen have relatively adjustable refractive index. In this study,  $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$  structures were fabricated using electron beam evaporation and 800°C post-annealing treatments were carried out. According to the inter-diffusion, the ZnO layer became a high refractive index material with porous structure and the  $\text{ZnAl}_2\text{O}_4$  spinel was formed as low refractive index material and the refractive index contrast of the multilayer was increased. In the  $\text{Al}_2\text{O}_3/\text{ZnO}/\text{Al}_2\text{O}_3$  structure, the porous ZnO layer with an average porosity of 19.78% was successfully prepared and the refractive index was from 2 reduced to 1.357 by 800°C post-annealing process due to solid state diffusion mechanism.

## CP-29 Effect of Silicon Content on the Structural, Optical and Electrical Characteristics of SiO<sub>x</sub> Films Prepared by Sputtering, Karim Monfil Leyva, A Salazar Valdez, Benemérita Universidad Autónoma de Puebla, Mexico; A Morales Sánchez, Centro de Investigación en Materiales Avanzados SC, Mexico; J Luna López, M Domínguez Jiménez, A Muñoz Zurita, Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. The non-stoichiometric Silicon dioxide ( $\text{SiO}_x$ ) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters.  $\text{SiO}_x$  can be deposited by several physical vapor deposition techniques but Sputtering technique particularly allows a great control on film thickness.  $\text{SiO}_x$  films can be obtained by simultaneous co-sputtering of Si and fused quartz ( $\text{SiO}_2$ ) targets. The Si content in the  $\text{SiO}_x$  layers can be modified by a variation on RF-power applied to Si (Psi) target and keeping constant the RF-power applied to  $\text{SiO}_2$  target.

In this work, we studied the effect of the increase of silicon content on the optical, structural and electrical properties of thin  $\text{SiO}_x$  films obtained by Sputtering. The Psi was changed between 10 and 50 W. All the films were annealed at 1100 °C in  $\text{N}_2$  for 3 hours. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from all the  $\text{SiO}_x$  films to confirm a change on stoichiometry. Absorbance spectra of  $\text{SiO}_x$  films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our  $\text{SiO}_x$  films. X-ray photoelectron spectroscopy (XPS) measurements in depth profile revealed that Si content was increased from 3.5 to 10.7% in the  $\text{SiO}_x$  films. AFM images were obtained to calculate and relate the surface roughness according to Si content.  $\text{SiO}_x$  films showed a wide photoluminescence (PL) at room temperature (RT) between 575 nm to 875 nm. The PL intensity and peak position also showed a dependence on Silicon content and the possible presence of defects.

An Indium-Zinc Oxide (IZO) gate, optically semitransparent in the visible range, was deposited onto the  $\text{SiO}_x$  films surface. Also, Aluminum backside contact was added by Sputtering. Current-voltage (I-V) measurements of IZO/ $\text{SiO}_x$ /Si devices were obtained. A high conduction regime was measured even for low gate voltages. Electroluminescent (EL) emission was observed with the naked eye as discrete shining points on the surface of the devices. The intensity of the shining points showed a dependence on the Si content of  $\text{SiO}_x$  films. The EL emission was related to the recombination of charge moving through conductive paths within the  $\text{SiO}_x$  film.

## CP-30 Optical Properties of the TiO<sub>2</sub> Films Grown by Atomic Layer Deposition using Tetrakis(Dimethylamino)Titanium and H<sub>2</sub>O, Wen-Hao Cho, P Huang, C Chen, Y Yu, C Yang, C Kei, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Titanium dioxide ( $\text{TiO}_2$ ) is a promising material due to its attractive physical and chemical properties. Atomic layer deposition (ALD) is one of the deposition methods for  $\text{TiO}_2$  and could provide films with excellent conformality. The  $\text{TiCl}_4$  precursor has been widely used with  $\text{H}_2\text{O}$  to deposit  $\text{TiO}_2$  films in ALD process. However, the reaction by-product HCl are corrosive. In this study,  $\text{TiO}_2$  films were grown on silicon substrates and glass by ALD using  $\text{H}_2\text{O}$  and tetrakis(dimethylamino)titanium (TDMAT) instead of  $\text{TiCl}_4$  to avoid the damage from reaction by-product. The thickness of  $\text{TiO}_2$  films at different substrate temperature were measured by ellipsometer and the highest growth rates per cycle (GPC) was 0.6649 Å at 100°C. The X-ray diffraction showed that the  $\text{TiO}_2$  films were anatase phase. The transmittance (T) and reflectance (R) were measured and the absorption was obtained from 1-T-R. From absorption spectrum, we found that the  $\text{TiO}_2$  films had slight absorption in visible light range. This should be caused by the residual carbon and nitrogen in the films. Furthermore, the  $\text{TiO}_2$  film had lowest absorption at 100°C. The composition analyses were also carried out.

## CP-31 Fractal Analysis of Titanium Nitride Films with Different Morphologies and Evaluation for the Direct Methanol Fuel Cell Applications, Kai-Ling Chuang, M Tsai, Y Tsai, F Lu, National Chung Hsing University, Taiwan

TiN is an important coating material with many technological applications because of its high hardness and chemical stability, as well as low resistivity. With various surface morphologies, conductive TiN films are expected to take part in many more applications. In our previous work,

# Thursday Afternoon Poster Sessions, April 26, 2018

granular and pyramidal morphologies TiN films could be tailored by merely adjusting the gas flow ratio, leading to changes in the texture coefficients. The objective of this work is to further analyze morphologies of the TiN films by estimating fractal dimensions of the films. The TiN films with different morphologies were then employed for the supporting electrodes on direct methanol fuel cells. Pyramidal and granular TiN films were produced with N<sub>2</sub>, air, and simulated-air as the reactive gas during magnetron sputtering. With the TiN films turning from granular to pyramidal morphology, the value of fractal dimension decreased from 1.95 to around 1.63 for those three reactive gases. The development of the morphologies was associated with the texture of the films that changed from rather random orientation to a mainly (111) preferred orientation. From the test of methanol oxidation, the TiN electrodes with different morphologies showed promising current densities responses, compared to traditional metal and carbon supports.

## **CP-32 Growth Kinetics Behavior and Morphology of Multicomponent Coating on Zirconium Hydride during Oxidizing Atmosphere, G Yan, Jiandong Zhang, L Wang, S Bai, GRINM company, China**

Zirconium hydride, as essential structural materials within the nuclear reactors, has the problem of hydrogen loss, which reduces the neutron moderating efficiency and service life. To prevent or slow down the hydrogen loss in moderator from zirconium hydride, multicomponent coatings (MC) for preventing hydrogen escaping were formed on zirconium hydride by in-situ oxidation method in oxidizing atmosphere decomposed by carbamide. Growth kinetics and morphology of in-situ oxidation MC on zirconium hydride were studied using x-ray diffraction (XRD), scanning electron microscope (SEM), auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy(XPS), focusing on kinetics of growth kinetics and morphology of the coating. As a result, it shows growth kinetics followed a parabolic law with respect to in-situ MC duration. XRD shows the phase structure of coating consists mainly of ZrN and ZrO<sub>2</sub>, including tetragonal zirconia (*t*-ZrO<sub>2</sub>) and monoclinic zirconia (*m*-ZrO<sub>2</sub>). SEM depicts coatings were accumulated and combined densely with substrate. AES indicates that the coating is mainly composed of carbon, nitrogen, oxygen and zirconium, which show that the atomic concentration of carbon and nitrogen decreased continuously, while, oxygen and zirconium increased with sputter time increasing. XPS investigates the chemical binding states in the coatings were Zr-O、Zr-C、Zr-N-O、Zr-N bonds. Under the test of simulated working condition, the MC reduce the hydrogen loss effectively, compared with other single oxide/nitride coatings.

## Author Index

### Bold page numbers indicate presenter

— A —

Abadias, G: CP-19, 3  
Arvanitidis, J: CP-19, 3  
— B —  
Bai, S: CP-32, 6  
Bark, C: CP-12, 2; CP-9, 2  
Barton, D: CP-24, 4  
Batková, Š: CP-18, 3  
Battu, A: CP-21, 4  
Boo, J: CP-11, 2  
— C —  
Calheiros, M: CP-7, 1  
Čapek, J: CP-18, 3  
Čerstvý, R: CP-18, 3  
Chandra, R: CP-15, 3  
Chang, K: CP-25, 4; CP-26, 4  
Chen, C: CP-30, 5  
Chen, H: CP-28, 5  
Chen, W: CP-28, 5  
Chen, Y: CP-16, 3  
Chien, T: CP-16, 3  
Chintalapalle, R: CP-21, 4; CP-22, 4  
Chiu, Y: CP-16, 3  
Cho, G: CP-10, 2; CP-8, 1  
Cho, W: CP-28, 5; CP-30, 5  
Choi, H: CP-10, 2; CP-12, 2; CP-9, 2  
Chou, C: CP-26, 4  
Christofilos, D: CP-19, 3  
Chuang, K: CP-31, 5  
Correia, F: CP-7, 1  
— D —  
Domínguez Jiménez, M: CP-29, 5  
Duchoň, T: CP-18, 3  
Dvořák, F: CP-18, 3  
— F —  
Fialová, M: CP-18, 3  
— G —  
Galindo, J: CP-21, 4  
Gall, D: CP-19, 3  
Gan, K: CP-16, 3

— H —

Haviar, S: CP-18, 3  
Huang, P: CP-30, 5  
Huang, Y: CP-5, 1  
Hung, W: CP-3, 1  
Hwang, K: CP-11, 2  
— J —  
Jaiswal, J: CP-15, 3  
Jeong, R: CP-11, 2  
Johnson, S: CP-17, 3  
Joye, C: CP-17, 3  
Jung, Y: CP-10, 2; CP-8, 1  
— K —  
Kassavetis, S: CP-19, 3  
Kei, C: CP-30, 5  
Kim, B: CP-8, 1  
Kim, D: CP-11, 2; CP-3, 1  
Kim, E: CP-10, 2; CP-8, 1  
Kim, S: CP-9, 2  
Kozen, A: CP-17, 3  
Kumal, N: CP-18, 3  
Kuo, P: CP-16, 3  
— L —  
Lai, Y: CP-5, 1  
Lee, C: CP-28, 5  
Lee, H: CP-10, 2; CP-25, 4  
Lee, J: CP-11, 2  
Leyva, A: CP-22, 4  
Lin, K: CP-5, 1  
Lin, Y: CP-28, 5  
Liu, P: CP-16, 3  
Lu, F: CP-31, 5  
Luna López, J: CP-29, 5  
— M —  
Makeswaran, K: CP-22, 4  
Malik, G: CP-15, 3  
Marques, J: CP-7, 1  
Minami, T: CP-14, 2  
Miyata, T: CP-14, 2  
Monfil Leyva, K: CP-29, 5  
Morales Sánchez, A: CP-29, 5

Mourya, S: CP-15, 3  
Muñoz Zurita, A: CP-29, 5  
— N —  
Nam, S: CP-11, 2  
Nepal, N: CP-17, 3  
Newman, H: CP-17, 3  
Nguyen, T: CP-9, 2  
— P —  
Park, H: CP-8, 1  
Patsalas, P: CP-19, 3  
— R —  
Ruan, D: CP-16, 3  
— S —  
Salazar Valdez, A: CP-29, 5  
Seo, H: CP-11, 2  
Shin, S: CP-12, 2; CP-17, 3; CP-9, 2  
Sze, S: CP-16, 3  
— T —  
Tamura, M: CP-4, 1  
Tavares, A: CP-7, 1  
Tokunaga, H: CP-14, 2  
Tsai, M: CP-31, 5  
Tsai, Y: CP-31, 5  
— U —  
Urban, F: CP-24, 4  
— W —  
Walecki, W: CP-3, 1  
Wang, J: CP-2, 1  
Wang, L: CP-32, 6  
Wang, X: CP-6, 1  
— Y —  
Yan, G: CP-32, 6  
Yang, C: CP-30, 5  
Yang, H: CP-11, 2  
Yu, J: CP-11, 2  
Yu, M: CP-16, 3  
Yu, Y: CP-30, 5  
— Z —  
Zapien, J: CP-27, 5  
Zhang, J: CP-10, 2; CP-32, 6; CP-8, 1  
Zorba, T: CP-19, 3