

## Thin Films

Room: Mauka - Session TF-WeP

## Thin Films Poster Session

**TF-WeP1 Inductively Coupled Ar-Based Plasma Etching of Palladium for Low Damage in Underlying GaN Semiconductor, Yong-Yeon Kim, J.K. Kim, J.M. Lee, Sunchon National University, Republic of Korea**

The etch characteristics of Pd for the fabrication of blue laser and light emitting diodes were investigated by using inductively coupled Ar-based plasma for low damage in underlayer. Up to date, the etch characteristics of Pd was not fully understood, because the suitable gas to form a volatile etch-product was not known due to the chemical inertness of Pd. Furthermore, the control of gas mixture for the low damage in underlying GaN semiconductor is more preferable in order to fabricate high quality optical devices. Therefore, it is important to selection of gas mixture in plasma. Furthermore, it was found that the photoresist was eroded when the ICP source power was increased above 100 W, when the Ar plasma were used as active etchant.

When the 50 sccm of Ar was used as etchant gas, the highest etch rate of 60 nm/min was achieved at source and table power of 50 W and 200 W, respectively. The etched sidewall was observed to be most anisotropic, where the angle was about 88 degree. When the additional gas, such as Cl<sub>2</sub> and CHF<sub>3</sub>, was added in the Ar plasma, different effect on the etch characteristics were observed, especially for the sidewall angle. On the other hand, when the Ar gas was used, the carrier concentration of the underlying GaN was decreased by two orders of magnitude due to the etch-damage. However, the addition of Cl<sub>2</sub> and CHF<sub>3</sub> by 20 %, respectively, the carrier concentration of the etched GaN surface was increased to the value of as-grown sample, maybe due to suppression of the etch-damage. In this presentation, more detailed results about etch-characteristics of Pd will be reported.

**TF-WeP2 Effect of Copper Layer Thickness on the Thermal Performance of LED Ceramic Package Substrate, HyunMin Cho, S. Jang, S. Ha, KETI, Republic of Korea**

LED (Light Emitting Diode) has been one of the promising technology for the energy saving. Now, conventional lamps such as incandescent and fluorescent lamps are rapidly being replaced by LED lamps. By the progress of LED technologies, the efficiency and reliability of LED devices have been dramatically increased compared to decade ago. Also, the power of LED lightings have been increased. To maintain LED performance, it is very important to manage heat from the LED chip. To deal with high power LED chip over 3 W or COB (Chip on Board) type arrayed LED chips over 10 W, ceramic substrate such as aluminum nitride has been adopted instead of plastic or aluminum oxide substrate because of its high thermal conductivity in the range of 170~250 W/m.K. For the metal circuit pattern on the substrate, mainly copper is used for the high thermal and electrical conduction. We investigated the effect of metal layer thickness on the thermal performance of high power LED package. First we simulated the junction temperature of LED package according to copper layer thickness. The decrease of LED junction temperature was occurred with the increase of metal layer thickness. But, the effect was reduced with higher thickness. We also manufactured LED packages with various copper layer thicknesses and tested thermal performance by thermal transient measurement and compared with the simulation data. With this results, we could optimize the copper layer thickness of the LED package substrate.

**TF-WeP3 Characteristics of Al, Ag, and Cu Metal Mesh Prepared by Photolithography for Touch Screen Panels, M.J. Kim, Pungkeun Song, S.H. Cho, Pusan National University, Republic of Korea**  
Pusan National University, Republic of Korea

**TF-WeP4 Improved Initial Growth Behavior of Atomic Layer Deposited SrTiO<sub>3</sub> Films with [Sr(demamp)(tmhd)]<sub>2</sub> as Sr-precursor, Woongkyu Lee, W. Jeon, Y.W. Yoo, C.H. An, M.J. Chung, Seoul National University, Republic of Korea, T.-M. Chung, B.K. Park, S.M. George, C.G. Kim, Korea Research Institute of Chemical Technology, C.S. Hwang, Seoul National University, Republic of Korea**

Strontium titanate (SrTiO<sub>3</sub>, STO) has been attracting a great deal of attention as the capacitor dielectric material for DRAM with design rule < 20 nm due to its much higher dielectric constant ( $k > 100$ ) compared with those of presently adopted dielectrics based on ZrO<sub>2</sub> ( $k \sim 30 - 40$ ). Because of the severe three-dimensional geometry of DRAM capacitors, atomic layer deposition (ALD), which provides the ultimate step coverage, is

indispensable. The conformality of film is generally induced by self-limited growth mechanism of the ALD. However, in previous studies, non-ideal excess growth was observed during the early stage of STO deposition on Ru electrode, the most promising electrode material. The excessive growth was more dominant for the incorporation of Sr into the film compared with Ti. This was mainly attributed to the reduction of in-situ oxidized Ru substrate during the O<sub>3</sub> pulses in the previous ALD steps.<sup>[1, 2]</sup> Such adverse effect was further aggravated by the high growth temperature (370 °C), which was adopted for the in-situ crystallization of the STO film. Also, the weak chemical bonding between the cyclopentadienyl (Cp)-based ligands and Sr ions in the conventional Cp-based Sr-precursor induced such problem.

In this study, therefore, [Sr(demamp)(tmhd)]<sub>2</sub>, developed by Korea Research Institute of Chemical Technology,<sup>[3]</sup> which is supposed to have a chemical properties in medium of the Cp-based Sr-precursor and tmhd-based homoleptic Sr-precursor, was adopted as the new Sr-precursor and attempted ALD process of STO film. A high density (250 g/m<sup>3</sup>) O<sub>3</sub> was employed as the oxygen source for SrO deposition and sputtered Ru was used as the substrate with its temperature of 370 °C. Ti(Me<sub>5</sub>Cp)(OMe)<sub>3</sub> was employed as the Ti-precursor which is also reacted with O<sub>3</sub>. With this novel heteroleptic Sr-precursor, good ALD-specific saturation growth behaviors were observed with respect to the precursor injection, Ar purge, O<sub>3</sub> injection, and Ar purge step times. Most importantly, the unwanted overgrowth of Sr element in initial stage of film growth decreased substantially, and the linear growth behavior of both Sr and Ti were achieved. Meanwhile, the growth rate was decreased to 0.50 Å/cycle, which was lower than the previous case with Cp-based Sr-precursor (1.23 Å/cycle) but assisted to have a denser as-deposited film. With more ideal-like ALD process, the deposited film showed excellent film properties including high purity, high crystallinity, high electrical properties, and excellent step coverage.

[1] S. W. Lee, et al., Chem. Mater. 23, 2227, 2011.

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[3] S. M. George, et al., Eur. J. Inorg. Chem. 2014, 2002, 2014.

**TF-WeP5 Nanoscale Wrinkle Structures on Polydimethylsiloxane using Ion-Beam Bombardment, JuHwan Lee, H.-G. Park, H.-C. Jeong, Y.H. Jung, D.-S. Seo, Yonsei University, Republic of Korea**

Research on topological wrinkle structures at the nano- or micrometer scale is continuously growing because of the development of robust techniques for controlled patterning of polymer and the emergence of novel applications that benefit from the wrinkle structures. The wrinkle structures can be applied to various systems such as stretchable electronics, microlens arrays, microelectromechanical devices, tunable surface adhesion, friction and robotics. To produce a wrinkle structure on this scale, photolithographic, printing, embossing or writing techniques have traditionally been used. However, these methods have relatively high costs and limited throughput when producing customized features. Therefore, alternative spontaneous wrinkle structure fabrication methods have attracted considerable attention in recent decades. These methods, including plasma activation, UV/ozone treatment, laser excitation, and ion-beam (IB) treatment, use surface reformation on the polymer layer, which minimizes the combination of the bending energy of the outer layer and the stretching energy of the inner layer. Among the various alternative methods, IB bombardment has excellent penetrability with high-energy Ar<sup>+</sup> ions, which leads to stable and reliable wrinkle structure fabrication. Recently, we have shown that irradiation of Ar<sup>+</sup> ions on the surface of a polydimethylsiloxane (PDMS) substrate results in the formation of a stiff skin on the substrate, which has a chemical composition resembling amorphous silica. Since the stiff skin deformation is constrained by the PDMS substrate, the skin experiences in-plane compressive strain upon ion beam irradiation and buckles to accommodate the induced mismatch strain between the skin and the polymeric substrate.

Here, we demonstrated the formation of a wrinkle structure on the surface of PDMS through IB bombardment. We fabricated various sizes of wrinkle structures as a function of IB irradiation time and confirmed the formation of these structures using a variety of AFM analyses.

**TF-WeP6 Molecular Arrangements and Electronic States of Well-Defined K-Doped Coronene and Picene Monolayers, Masahiro Yano, M. Endo, R. Shimizu, Y. Hasegawa, Y. Yamada, M. Sasaki, University of Tsukuba, Japan**

In this paper, we demonstrate that K-doped coronene and picene monolayers form well-defined structures and they are model systems suitable to clarify the mechanism of electronic and structural modifications of aromatic hydrocarbon crystals due to alkali doping. It can be a basis to

control the electronic properties of organic materials by foreign metal-doping.

Modification of the electronic properties of organic materials by doping with foreign metals is one of the key technologies used in next-generation organic electronics. In general, microscopic structural information is essential for understanding the underlying mechanisms. However quite few number of investigations have addressed the microscopic structural features with respect to doping, mainly due to difficulties in the measurement of inhomogeneous samples. Therefore, basic investigation into the microscopic structural nature of metal-doped organic systems utilizing well-defined models is necessary.

In the present study, we have investigated molecular-scale structure and electronic state of K-doped coronene and picene monolayer. For the substrate, we employ inert surfaces, such as Au(111) and highly oriented pyrolytic graphite (HOPG), to minimize the effect of the substrate on the reaction between K and molecules.

After the coronene and picene monolayers were prepared on Au(111) or HOPG using vacuum deposition, K was deposited on the monolayer from alkali dispensers.

The structures were observed by means of scanning tunneling microscope (STM). STM images show significant structural changes of coronene and picene monolayers upon K deposition. Both the K-doped monolayers exhibit well-defined herringbone-like molecular arrangement. In this phase, while the surface reconstruction of Au(111) is still visible, individual K atoms are not observed. We speculate that K atoms intercalate between molecular planes and directly interact with the molecules.

The electronic states were investigated by means of photoemission spectroscopy on a HOPG substrate. In both the monolayers, with increasing doping, a new state appears more clearly just below the Fermi level. The formation of this state is very sensitive to the molecular arrangement [1].

Moreover, it should be noted that a very similar photoemission spectrum has been reported in K-doped thick picene film on HOPG [1]. This similarity ensures the perspective that the well-defined K-doped monolayer can be a model for the doped aromatic hydrocarbons crystals.

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[1] H. Okazaki *et al.*, *Phys. Rev. B* **88**, 245414 (2013).

**TF-WeP7 Failure Behaviors of Stretchable Electrodes Based on Metal Nanostructure Percolation Networks**, *Guh-Hwan Lim, H. Sim, B. Lim*, Sungkyunkwan University, Korea, Republic of Korea

Metallic nanostructures such as nanowires and nanosheets are promising candidates for the fabrication of highly conductive electrodes, but the practical application of metal nanostructure-based electrodes in stretchable electronics is often limited by significant performance degradation associated with poor mechanical stability of a nanowire or nanosheet percolation network against repeated deformation. We studied failure behaviors of stretchable electrodes made of Ag nanowires or Au nanosheets deposited on various elastomeric substrates such as PDMS and Ecoflex during stretching cycles, and suggested a way of improving stretchability and stability of these metal nanostructure-based stretchable electrodes.

**TF-WeP8 Properties of Photo-Induced Hybrid Channel Thin-Film Transistors Via Solution Process**, *YoonHo Jung, H.-G. Park, H.-C. Jeong, D.-S. Seo*, Yonsei University, Republic of Korea

Oxide thin-film transistors (TFTs) have been actively studied to this day and suggest the promising technique with carbon nanotube, nanowire, nanoparticle, or small molecules. Oxide TFTs are made of metals that have sufficiently large ns orbitals to overlap with each other. Thus, they can transport charge carriers without being sensitive to the crystalline structure. An advantage of these devices is that they can be conductive even when the material is in an amorphous phase. With this technique, solution processing is a useful method for generating amorphous oxide TFTs. In addition to its low manufacturing cost, easy deposition, and simple procedure, this method is important because of its outstanding synthesis capacity. With this method, each material can be simply mixed, and uniform films can be formed to achieve multi-component systems. Thus, this property is essential for making oxide films that consist of more than two materials.

Among a variety of solution-processed oxide TFTs, InGaZnO TFTs are the most widely used materials. In InGaZnO TFTs, Ga suppresses carriers and suppression of carriers is achieved by increasing the number of oxygen vacancies. Oxidization of the material is highly related to an electronegativity and a lower electronegativity increases the tendency to be oxidized. In this study, we chose yttrium because the electronegativity of Y is 1.2 which is much lower than that for Ga. Therefore, more oxidization occurs in the channel lattice, which leads to additional suppressing oxygen vacancies.

Azobenzene is a small organic molecule that has been frequently used for organic TFTs. Furthermore, the photo-induced isomerization of azobenzene is an interesting property. In each phase, which is trans- or cis-phase, the molecular structure is different. Normally, the molecule remains in the trans-phase because of higher stability. When exposed to an appropriate light source, azobenzene changes into the cis-phase.

Herein, we investigated solution-processed amorphous InYZnO with azobenzene channel TFTs. The effects on the electrical and structural characteristics of TFT channels due to the photo-induced isomerization of azobenzene were analyzed using a field effect-scanning electron microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), and electric characteristic analysis.

**TF-WeP9 Uniform Alignment of Liquid Crystal Molecules on Solution-Based Oxide Films**, *Hae-Chang Jeong, H.-G. Park, D.-S. Seo*, Yonsei University, Republic of Korea

Liquid crystal displays (LCD) are useful and important device because it is closely related in our daily life, such as mobile display, portable devices, TV and so on. The uniform LC orientation on the alignment film is very important to obtain high quality display. The conventional method, rubbing on the polyimide layer, has some drawback such as generation of debris and accumulation of electrostatic charge. To resolve the shortcomings of LC alignment, alternatives have been investigated for a long time but it is difficult to apply to a commercial purpose. We investigate the solution process using tin-oxide as an alignment layer. In this process we can obtain alignment layer of self-alignment properties. LC molecules are well aligned in higher annealing temperature process along to the filling direction. Because fully oxidized films keep strong van der Waals force between LC molecules and solution-based oxide films. At higher annealing temperature, a tin oxide alignment layer has uniform and increasing nano-crystalline. The average transmittance of oxide alignment layer at higher annealing temperature has 81.21%. This transparency is similar to those of conventional LC alignment materials. The electro-optical properties of solution-based oxide films can be obtained by electrically controlled birefringence (ECB). At higher annealing temperature, the threshold voltage is 1.408V and this result is better performance to conventional method and material. Because process of solution-based oxide films allows for uniform alignment as well as high performance property, it is very simple and useful method.

**TF-WeP10 Fabrication of SiC based AFM Cantilever for NSOM Application**, *S.-H. Nam, K.-H. Hwang, J.H. Yu, Jinsu Lee, J.-H. Boo*, Sungkyunkwan University, Republic of Korea

Silicon carbide thin films were deposited on Si(100) substrates by metal-organic chemical vapor deposition(MOCVD) in high vacuum condition at  $2.0 \times 10^{-7}$  Torr using 1,3-disilabutane as a single source precursor which contains silicon and carbide in 1:1 ratio at various temperature in the range of 700 ~ 1000 °C. The XPS result shows that the SiC thin film grown at 950 °C which have carbon rich for silicon and carbon at 1:1.2 ratio. XRD result shows that the SiC thin film grown at 900 °C which appeared at  $2\theta = 41.6^\circ$  for SiC (200) reflection at a large intensity and a single shape diffraction peak. SEM images result show that the SiC thin film grown at 900 °C which has influence on the small grain size and single crystallinity. AFM images result show that the SiC thin film has smooth surface at RMS = 20nm. In this paper, we fabricated the small aperture for the better performance such as less noise, higher resonant frequencies and fast imaging. We will apply that silicon carbide thin film has smooth surface on NSOM application.

**TF-WeP11 Reliability and Life Time Flexible OLED Device Fabricated on ITO/Ag NW/ITO Thin Film on PES Substrate**, *WooJin Yeon, Y.T. Oh, K.H. Kim, E.S. Kim, DongChan. Shin*, Chosun University, Republic of Korea

We demonstrate OLED device on ITO/Ag NW/ITO thin film on PES substrate and investigate degradation of life time. Transparent conducting layers are fabricated in three type of ITO, ITO/Ag thin film (TF)/ITO, and ITO/Ag nano wire (NW)/ITO. The total thickness of TCO layers is set to be 150 nm. Single ITO thin film shows the highest transparency of 97%, ITO/Ag NW/ITO 90%, and ITO/Ag TF/ITO is the lowest of 81%. Sheet resistance of ITO/Ag NW/ITO is reduced to be 12.74  $\Omega/\square$  compared to single ITO TF of 32.42  $\Omega/\square$ . Figure of merit of Ag nano wire inserted TCO shows the best value. According to bending test, Single ITO thin film layer shows abrupt failure on just one time bending, resistance of ITO/Ag TF/ITO increases 130% at 60 times bending, but ITO/Ag NW/ITO shows only 26% increase. Double layered simple OLED device of NPB and Alq<sub>3</sub> is fabricated and resultant device properties will be discussed.

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**TF-WeP12 A Study of the Mechanical Properties of Trench Type Cu/Mo Thin Films for Flexible Copper Interconnect, JongHyun Seo,** Korea Aerospace University, Republic of Korea, *H.-S. Kim,* Korea Aerospace University, *HH. Choe, J.-H. Jeon, J.H. Yoon,* Korea Aerospace University, Republic of Korea

In this work, the adhesion properties sputtered molybdenum (Mo) thin films as a copper (Cu) diffusion barrier layer on polymer substrates were examined using micro-scratch tests. We fabricated trench type copper interconnect rather than typical metal inlaying type.

There was made a comparison of the mechanical properties between a new trench copper layer and a traditional metal inlay type copper interconnect by means of photolithography technique followed by wet patterning. The metal / polymer interface were examined by using the auger electron spectroscopy. Cu/Mo trench typed films have 50% higher values of adhesion forces than that of Cu/Mo inlay type. A physical modeling is proposed, on average volume stress analysis to explain an improvement in the mechanical stability of the buried Cu interconnects in the flexible substrate.

**TF-WeP14 Computational Simulation Study on Structure Change of Si-DLC Films, Takeshi Tsuruda, H. Murabayashi, Y. Wang, Y. Kobayashi, T. Kuwahara, S. Bai, Y. Higuchi, N. Ozawa, K. Adachi,** Tohoku University, Japan, *J.M. Martin,* Ecole Centrale de Lyon, France, *M. Kubo,* Tohoku University, Japan

Diamond-like carbon (DLC) consisting of  $sp^2$  carbon ( $Csp^2$ ) and  $sp^3$  carbon ( $Csp^3$ ) has low friction property. Therefore, DLC is used as solid lubricant in the sliding parts of machinery to decrease energy loss by friction. It was suggested that the low friction property of DLC is caused by formation of a graphene layer on the surface [1]. Moreover, Si-doped DLC (Si-DLC) films show excellent tribological property because of formation of  $Csp^2$  on the surface [2]. Therefore, transformation from  $Csp^3$  to  $Csp^2$  on the DLC surface is important for the low friction. For further decrease in the friction of the DLC films, we need to clarify the mechanism of the transformation from  $Csp^3$  to  $Csp^2$  at atomic scale. In this study, to elucidate the transition mechanism from  $Csp^3$  to  $Csp^2$  on the DLC films by Si-doping, we develop our tight-binding quantum molecular dynamics simulator [3].

First, to reproduce van der Waals interaction and transformation for  $Csp^2$  and  $Csp^3$ , we add Lennard-Jones and trigonometric functional potential to our simulator. Next, to confirm the accuracy of our developed simulator, we perform compression simulation of a-graphite layers under a pressure. Here, the bottom layer is fixed and load pressure is applied to the top layer. From 1 to 15 GPa, the structure change is not observed for 50 ps. At a pressure of 16 GPa,  $Csp^3$ - $Csp^3$  bonds continuously increase when graphite layers become close. Then, the six-membered rings of diamond structure are generated from graphite layers. This indicates the transformation from  $Csp^2$  to  $Csp^3$ . In the experiment, the structure change from graphene to diamond takes place at 17 GPa [4]. Thus, the simulation result is in good agreement with the experimental result. Thus, our developed program succeeds to reveal the transformation from  $Csp^3$  to  $Csp^2$ .

Next, to investigate how Si-doping influences on the surface structure of the DLC films, we perform relaxation calculation for Si-doped diamond(111) surface with 3.225 % Si content. At 48.9 ps, the chemical bond between the C atom bound with the doped Si atom and C atom of the lower layer is dissociated. Furthermore, we observe generation of the  $Csp^2$  atoms after the dissociation. This indicates that the Si-doping induces the transformation from  $Csp^3$  to  $Csp^2$  and generation of graphene-like structure on the surface. Thus, we propose that Si-DLC films show low friction because Si-doping generates  $Csp^2$  on the surface of the DLC films.

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[4] L. Wendy, et al., *Science*, **302**, 425 (2003).

**TF-WeP15 Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Chemical Reaction of Molybdenum Dithiocarbamate on DLC surface, Hiroki Murabayashi, T. Tsuruda, Y. Wang, Y. Kobayashi, S. Bai, Y. Higuchi, N. Ozawa, K. Adachi,** Tohoku University, Japan, *J.M. Martin,* Ecole Centrale de Lyon, France, *M. Kubo,* Tohoku University, Japan

In recent years, diamond-like carbon (DLC) is expected as a solid lubricant material for engines because of its excellent friction properties such as low friction and high wear resistance. DLC films are lubricated with oil in the engine. Furthermore, molybdenum dithiocarbamate (MoDTC) is used as friction modifier in oil. DLC coating with oil and MoDTC solution showed a low friction coefficient [1]. Moreover, the low friction of the DLC films with MoDTC was enhanced by a chemical reaction during friction, since the friction coefficient gradually decreased with increasing friction time. Understanding of the low friction mechanism of DLC with MoDTC is strongly required to decrease in the friction of the DLC films. Then, our purpose is to reveal the chemical reactions between the MoDTC and DLC films by our tight-binding quantum chemical molecular dynamics code [2].

To investigate chemical reaction between MoDTC and DLC film during friction, we perform the friction simulation of MoDTC sandwiched by the DLC surfaces. At first, we compress linkage isomer of MoDTC (LI-MoTC) by the DLC surfaces. Here, we use LI-MoDTC because it is isomerized in oil phase [3]. We apply a pressure of 1 GPa to the upper DLC film. After the compression, the C atom of the DLC surface binds with the S atom of LI-MoDTC and the C-S bond is generated between the DLC surface and LI-MoDTC. Next, to perform the friction simulation of DLC films with LI-MoDTC, we apply a pressure of 1 GPa to the DLC film and forcibly slide it with 100 m/s. The S-Mo bond in the adsorbed LI-MoDTC is elongated from 2.52 Å to 3.76 Å and the S-Mo bond is dissociated during the sliding. To reveal chemical reaction during the S-Mo bond dissociation in detail, we investigate electron transfer between LI-MoDTC and the DLC surface during the compression. The charge of S atom of LI-MoDTC changes from +0.45 to +0.82 before and after the generation of C-S bond. This indicates that electrons transfer from the sulfur atom of LI-MoDTC to the DLC films. We think that S-Mo bond is weakened due to the electron transfer between LI-MoDTC and DLC film. Thus, we suggest that the electron transfer from LI-MoDTC to DLC films during the LI-MoDTC adsorption on the DLC surface weakens the S-Mo bond and the mechanical force dissociates the weakened S-Mo bond during the friction.

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[3] T. Onodera, M. Kubo et al., *Tribology Online*, **3**, 80-85 (2008).

**TF-WeP20 Lifetime Calculation of Encapsulated Organic Device Under Specific Weather Conditions, Namsu Kim,** Korea Electronics Technology Institute (KETI), Republic of Korea, *D. Kim,* Korea Electronics Technology Institute (KETI), *K. Hwang,* University of California at San Diego, *S. Graham,* Georgia Institute of Technology, *S. Kim,* Korea Electronics Technology Institute (KETI)

One of primary technical obstacles toward commercialization in organic device is the achievement of reliable long lifetimes. The low work function materials and transparent conductive oxides used to form electrical contacts to the active layers are generally reactive and susceptible to water vapor and oxygen. Thus, developing thin-film encapsulation technologies protecting organic electronic devices from water vapor and oxygen is critical. In addition, variable environment of photovoltaic modules makes it difficult in predicting lifetime of them.

In this study, the lifetime of encapsulated organic device under specific weather condition was predicted based on total amount of permeated water permeated through barrier layers. Previous study presented the relation between the overall barrier performance and the shelf lifetime of encapsulated organic solar cells experimentally. Based on previous study, the total permeated water vapor through identical barrier layer under continuously varying environment can be calculated and compared to experimental data. For analytical calculation, diffusion and solubility coefficients were experimentally determined using quartz crystal microbalance as well as water vapor permeation instrument.

**TF-WeP22 Spin Valve Junctions Based on Fe<sub>3</sub>Si/FeSi<sub>2</sub>/Fe<sub>3</sub>Si Trilayered Films, Tsuyoshi Yoshitake,** Kyushu University, Japan, *K. Sakai,* Kurume National College of Technology, Japan, *Y. Asai, K. Ishibashi, Y. Noda,* Kyushu University, Japan, *K. Takeda,* Fukuoka Institute of Technology

Since the discovery of GMR and TMR effects, spin-dependent carrier transport has received attention from physical and engineering viewpoints. Whereas GMR and TMR films generally employ nonmagnetic metal and insulator spacers, we have studied Fe<sub>3</sub>Si/FeSi<sub>2</sub> artificial lattices, in which FeSi<sub>2</sub> is semiconducting and its employment as spacers is

specific to our research. The combination of Fe<sub>3</sub>Si and FeSi<sub>2</sub> has the following merits: (i) a magnetoresistance effect in the CPP structures is easily detectable since the electrical conductivity of FeSi<sub>2</sub> spacer layers is distinctively larger than that of Fe<sub>3</sub>Si layers; (ii) a spin injection efficiency might be higher than that in TMR films; (iii) the epitaxial growth of Fe<sub>3</sub>Si layers on Si(111) substrates is successively kept up to the top Fe<sub>3</sub>Si layer across FeSi<sub>2</sub> spacer layers, which is beneficial to the coherent transportation of spin-polarized electrons; (iv) Fe<sub>3</sub>Si is feasible for a practical use since it has a high Curie temperature of 840 K and a large saturation magnetization, which is half of that of Fe.

A spin valve is one of the most important principle for spin-dependent carrier transport, and the formation of parallel or antiparallel alignments of ferromagnetic layer magnetizations should be realized and controlled in devices with spin valves. Previously, we have prepared Fe<sub>3</sub>Si/FeSi<sub>2</sub> artificial films, wherein interlayer coupling was induced between Fe<sub>3</sub>Si layers across FeSi<sub>2</sub> spacers and the formation of parallel and antiparallel alignments of ferromagnetic layer magnetizations was induced owing to the interlayer coupling [1,2]. The parallel or antiparallel alignments of layer magnetizations can be realized in multilayered films comprising ferromagnetic layers with different coercive forces, and it needs not the precise control of the spacer thickness. In this work, Fe<sub>3</sub>Si/FeSi<sub>2</sub>/Fe<sub>3</sub>Si trilayered films were prepared and the magnetic properties as spin valves were investigated.

An Fe<sub>3</sub>Si(7000 Å)/FeSi<sub>2</sub>(7.5 Å)/Fe<sub>3</sub>Si(1000 Å) artificial film was fabricated by facing-targets direct current sputtering with using a mask method. The magnetization curve was measured using a VSM. The shape of the magnetization curve clearly exhibited the formation of parallel and antiparallel alignments with the magnetic field. This should originate from a difference in the coercive force between the top and bottom FeSi<sub>2</sub> layers. The electrical properties accompanied by the change in the magnetization alignment will be presented at the conference.

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**TF-WeP23 Application of Double-Lorentzian Line-Shape in XPS Analysis of Metallic Zn and ZnO Thin Films., Gabriela Molar-Velazquez, G. Gomez-Sosa, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico**

There are several line-shapes widely employed in XPS spectra analysis, such as Gaussian, Lorentzian, Voigt, Doniach-Sunjjic, among others. In the case of transition metals, the high asymmetry present in the main core levels peaks might lead to misinterpretation as considering artificial peaks during fitting. Some of this problems could be avoided by employing the double-Lorentzian line-shape. In this study, analysis of XPS spectra of Zn and ZnO films (including the early oxidation stages at room temperature) were performed using double-Lorentzian line-shape. The chemical composition of ZnO samples were calculated and different peaks for the metallic Zn 2p, Zn 3p, Zn 3s and Zn 3d core levels were identified.

**TF-WeP25 Double-Lorentzian Line Shape in XPS Analysis of Metallic Nickel, Chromium, Cobalt and Their Oxide Films, Gustavo Gomez-Sosa, J.A. Torres-Ochoa, M. Bravo-Sanchez, J.H. Mata-Salazar, D. Cabrera-German, J. Ibarra-Nuno, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico**

The current methods for quantitative analysis of X-ray photoelectron spectroscopy (XPS) data are clearly insufficient for closely reproducing the high asymmetry and strong background signal of the core level peaks of transition metals and their oxides. Using the double-Lorentzian asymmetric line-shape [1] and the active background approach [2], it is possible to obtain close fits to these core levels. The samples were prepared by metal sublimation on Si (100) wafers. The asymmetry factor found from the analysis was 1.83 for Ni 2p, 2.84 for Cr 2p and 2.9 for Co 2p. Previously unreported shake-up satellites were identified at 0.45, 1.1 and 1.9 eV away from the main peak in the metallic films of the Cr 2p, Co 2p and Ni 2p core levels, respectively. The evolution of the oxidation of metals was also studied by exposing metallic films to UHP oxygen in a range from 4 L to 400 GL. Further oxidation was obtained using a tubular oven with UHP oxygen with positive pressure. The final thickness of oxide films ranged from 2 to 3 nm. The composition was calculated employing the MultiLayer Model. The close agreement with the expected values (1:1 for nickel oxide, NiO; 2:3 for chromium oxide, Cr<sub>2</sub>O<sub>3</sub>; and 1:1 for cobalt oxide, CoO) validates the peak areas obtained with the double-Lorentzian line-shape.

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**TF-WeP26 Improved Adhesion of Diamond-Like Carbon Films by r.f. Plasma CVD Process with Cylindrical Electrode, Keisuke Shiba, Tokyo Denki University, Japan, Y. Ohgoe, Tokyo Denki University, M. Hiratsuka, Nanotec Corporation, K. Ozeki, Ibaraki University, K. Hirakuri, K. Sato, Tokyo Denki University, Japan**

Diamond like carbon (DLC) film has been widely used because of its good properties such as good biocompatibility, anti-corrosion, high hardness, and high wear resistance. Therefore, DLC film has been applied to practical uses in medical and industrial fields. However, lack of film adhesion onto metallic materials has limited DLC coating applications. In order to improve adhesion strength of DLC film onto a substrate, intermediate layer such as Si layer has been introduced between the DLC layer and the substrate.

In this study, DLC films were deposited on stainless steel substrate by using r.f. plasma chemical vapor deposition (r.f. plasma CVD) without intermediate layer. To improve adhesion of DLC film onto metallic materials, the cylindrical electrode around a sample was installed on the cathode side electrode (Fig. 1, 2). Cylindrical electrode was selected for the height of 5, 10, and 20 mm, respectively. DLC film was deposited under the following condition ( CH<sub>4</sub> gas pressure: 10 Pa, r.f. electrical power: 200 W, film thickness: 200 nm).

The adhesion of the DLC films was measured by using a scratch test. The characteristics of the DLC films were investigated using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS).

In the scratch test, the critical load of the film with 10mm-cylinder height showed 8.5 N, as compared with the film without the cylinder (4.6 N) (Fig. 3). Additionally, the Raman spectrum of the film on the stainless steel substrate showed peaks at approximately 1550 cm<sup>-1</sup> and 1350 cm<sup>-1</sup>, referred to the G-band and D-band, respectively.

These results showed that the films were a typical DLC film and the DLC film was completely deposited with strong adhesion between the films and substrates by using only r.f. plasma CVD technique. This technique affects to DLC film adhesion property onto metallic materials under r.f. plasma CVD process.

**TF-WeP28 Inductively Coupled Plasma Reactive Ion Etching of CoFeB Thin Films Using a CH<sub>3</sub>COOH/Ar Gas Mixture, Adrian Garay, S.M. Hwang, J.H. Choi, C.W. Chung, Inha University, Korea**

Magnetic random access memory (MRAM) holds the promise of replacing traditional memory devices such as DRAM, SRAM and flash memory. The MRAM device compared to its counterparts (DRAM, SRAM, flash memory, etc.), offers higher density, faster access time, unlimited read/write endurance and non-volatility. MRAM devices are mainly composed of a magnetic tunnel junction (MTJ) stack and CMOS.

In order to achieve high storage densities in MRAM devices, the pattern transfer in magnetic layers that comprise the MTJ stacks is a critical step. In the early stage of research, a wide range of etching gases such as HBr, Cl<sub>2</sub> etc has been employed for the ICPRIE of CoFeB thin films. In general, when using halogen gases, the etch rates are extremely high; but the sidewall redeposition and corrosion problems are common. Recently, an effort to improve the etching characteristics of magnetic layers, while at the same time reducing post-etching treatment, non-corrosive etching gases such as CO/NH<sub>3</sub>, CH<sub>3</sub>OH, CH<sub>4</sub> have been researched. The use of this etching gases mixed with Ar gas had to prove to yield a redeposition-free anisotropic etch profile despite the low etch rates compared to halogen gas mixtures.

In this paper the inductively coupled plasma etching characteristics of TiN hard masked CoFeB thin films was studied by using a CH<sub>3</sub>COOH/Ar gas mixture. A CH<sub>3</sub>COOH solution was introduced into the chamber using a specially designed feeding system. The etch rates were obtained using a surface profilometer (Tencor P-1) and etch profiles were observed by using a field emission scanning electron microscopy (FESEM-HITACHI 4300SE). The surface chemistry and etch mechanism were analyzed by using optical emission spectroscopy (OES-Ocean Optics Maya 2000 Pro) and X-ray photoelectron spectroscopy (XPS).

**TF-WeP29 Electronic Transmission of Two, Three and Four Magneto-Electrostatic Barriers on Graphene: An Approach to Diode, Transistor and Thyristor.**, R.A. Reyes Villagrana, Jesús Madrigal Melchor, J.R. Suárez López, I. Rodríguez Vargas, Universidad Autónoma de Zacatecas, México

In 1904, J.A. Fleming patented the first thermionic diode. Then in 1947, J. Barden, W. H. Brattain, and W. B. Shockley invented the bipolar transistor. Later in 1958, J. S. Kilby and R. Noyce developed the first integrated circuit. Since then it has researched, developed and implemented analog electronics. Both the diode and bipolar transistor structures have pn and pnp or npn respectively. However, there is another device having a pnpn structure, known as the *thyristor*. This device has different applications, but its main function is to control high power systems. This paper presents a study on the transport properties of Dirac electrons through a structure of two, three and four magneto-electrostatic barriers on a sheet of graphene, an approach to the structures of a diode, transistor and thyristor is presented. The calculation of pn, pnp, and pnpn structures was conducted using the transfer matrix method and the formalism of linear Landauer-Büttiker scheme. The results show that at normal incidence, with increasing two, three and four barriers increases the number of oscillations in the transmission bands. Furthermore, increasing the value of the thickness ratio of the barrier / well width, the transmission bands are shifted toward the blue and decrease transmission windows. Increasing the electrostatic potential decreases the size of the transmission bands. The effect of the magnetic field causes the transmission spectra increase the width of the central maximum band, and reduces the width of the bands of transmission side. Also, the increase of the magnetic field produces peaks in the transmission bands that arise in this type of structure, number of peaks in the transmission bands, corresponding to the number of wells in the structure. The conductance shows oscillations, which has an explanation by the bound states. Exists interest from the authors continue to explore further the benefits presented graphene in the development of new devices.

**TF-WeP32 Influence of Deposition Conditions on the Structural and Optical Properties of nc-Si/SiO<sub>2</sub> Films in SiO<sub>x</sub> Matrix using HW-CVD.** Ateeq Dutt, Matsumoto, Centro de Investigación y de Estudios Avanzados del IPN, Mexico, Santana-Rodríguez, Universidad Nacional Autónoma de México, Mexico, Santoyo Salazar, Godavarthi, Centro de Investigación y de Estudios Avanzados del IPN, Mexico

We have find the influence of deposition time and chamber pressure on the morphology and optical properties of the nanocrystalline silicon (nc-Si) and related composite particles embedded in the amorphous silicon oxide (a-SiO<sub>x</sub>) matrix using hot wire chemical vapor deposition (HW-CVD). Catalyst material Tungsten (W) was employed for the decomposition of source gases in the reaction chamber. Differences in the crystalline nature of the film deposited on crystalline-Silicon and glass substrates have been explained before also as a function of filament temperature [1]. In this studies using X-Ray diffraction (XRD) and Raman spectroscopy phase differences has been explained with respect to time of deposition and deposition pressure. XRD results demonstrate the presence of crystalline particles related to silicon composites in the amorphous matrix. Fourier transform infrared spectroscopy has been used to study the various surface species present in the film. The as-deposited samples grown at low substrate temperature of about 200°C, has shown photoluminescence spectra in almost all of the visible range (white emission). Photoluminescence has been found to be in correlation with the size of nc-Si particles and/or the defects present in the thin film. This low temperature deposited material could open gateways in future for further device fabrication based on the Si thin film technology.

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**TF-WeP34 Chemically Enhanced Raman Scattering of Rhodamine 6 G Molecule Adhere to Graphene, MoS<sub>2</sub> and WSe<sub>2</sub>: Efficiency Variation determined by Pressure and Charge Transfer.** Hyunmin Kim, Daegu Gyeongbuk Institute of Science and Technology, Korea, Y. Lee, Sungkyunkwan University, Korea, S.M. Jeong, Daegu Gyeongbuk Institute of Science and Technology, Korea, J.H. Cho, Sungkyunkwan University, Korea, J.-H. Ahn, Yonsei University, Korea

Recently, graphene enhanced Raman scattering (GERS) is very popular as a method to extract chemical information from dye molecules due to its excellent quenching effect on otherwise superfluous fluorescent backgrounds. Here, we introduce a new method to enhance Raman signals of a graphene-rhodamine 6G (R6G)-graphene sandwich structure by creating a magnet-induced static pressure to maximize the chemical contact of the R6G molecules with graphene. The increase in pressure in the graphene-R6G-graphene sandwich geometry plays a crucial role in enhancing the Raman signal by approximately up to 30 times in comparison

to that acquired from a R6G/graphene layered film. In addition, we found that the pressure-induced enhancement effects in the planar vibrational motion of the R6G (1200–1500 cm<sup>-1</sup>) were more recognizable than the low wavenumber region and were almost comparable to the surface-enhanced Raman scattering signals observed from the spontaneously formed “folded” pseudo  $\pi$ -bonded graphene-R6G-graphene sandwich structures. The enhancement effect diminished with an increase in the number of graphene layers (on the bottom side), clearly discernible upon imaging the graphene/glass sandwiched structures placed on top of exfoliated multilayered graphene coated with R6G. We also studied the surface enhanced Raman scattering of R6G using 2-dimensional hexagonal honeycomb layers such as MoS<sub>2</sub>, WSe<sub>2</sub> systems to compare with graphene. Thick (~10 nm) physisorbed adsorptions of R6G onto MoS<sub>2</sub> and WSe<sub>2</sub> nanosheets were made with soaking ~ 100 M level of aqueous R6G solution, allowing us to implement a photocurrent measurement and subsequently correlate it with Raman spectroscopy. The fluorescence quenching factor of R6G molecules coated on MoS<sub>2</sub> and WSe<sub>2</sub> systems was measured by approximately 100 times higher than that of solution-state R6G molecules. All results were quantitatively correlated with the amount of charge transfers obtained from phototransistor measurement, strongly suggesting that the Raman enhancement factor of molecules coated to hexagonal atomic layered systems can be predicted by photocurrent measurements. We also investigated the thickness dependence of MoS<sub>2</sub> and WSe<sub>2</sub> layers on the enhanced Raman signals of adsorbed R6G, showing that the enhancement effect of MoS<sub>2</sub> systems was maximized in the single layered nanosheets, demonstrating almost a linear-scale tailoring of Raman signals with the increase of the numbers of layers, while that of WSe<sub>2</sub> still remained substantial until the double layered nanosheets followed by a drastic decrease above them.

**TF-WeP36 Negative Thermal Expansion of Polystyrene Ultrathin Films Supported on Si Substrates revealed by X-Ray Reflectivity: Quench Rate Dependence.** Kazuki Nishimori, S. Nakahara, K. Sekiya, Kwansai Gakuin University, Japan, Y. Chunming, Shanghai Institute of Applied Physics, China, I. Takahashi, Kwansai Gakuin University, Japan

Understanding of ultrathin functional polymers is important for various fields of nanotechnology. However, physical property of polymeric thin films with thicknesses comparable to the size of molecules is significantly different from that of bulk due to the confinement effect and heterogeneity peculiar to thin films sandwiched between air and solid substrate. As one of the deepest and most interesting unsolved problems, origin of negative thermal expansion (NTE) often observed in ultrathin glassy polymer films has attracted considerable attention. In the present study, we find key factors for the emergence of NTE with polystyrene (PS) ultrathin films quenched from the rubbery state with different cooling rates. Samples are mono-dispersive atactic PS with molecular weight Mw = 955,000 and glass transition temperature of 375 K. Thin films around 6 nm thick were formed by spin-coating technique on Si (100) substrates. Prior to the rapid cooling, thin PS films were annealed at 405 K for 12 hours in a low vacuum. From 405 K, the films were cooled to the liquid nitrogen temperature with different cooling rates and heated to room temperature in vacuum. Thermal expansivity was evaluated with X-ray reflectivity (XR) measured isothermally from room temperature to 405 K, which affords us precise temperature dependence of thickness, average electron density and root mean square of surface roughness. Relaxation in glassy state is also obtained through temporal variation in thickness at a certain temperature that can be monitored by XR. A strong correlation between cooling-rate-dependent-NTE and relaxation behavior at room temperature is revealed in this study.

**TF-WeP37 Large-Scale Laser Scribing of Complex Motifs.** Goran Rasic, North Carolina Central University

Micro- and nanolithography techniques are a key factor in pushing the limits of science and technology. This is especially true in the semiconductor industry which has made remarkable progress over the last 20 years. With the technology focus moving to progressively smaller scale, numerous lithography methods of manufacturing complex micro- and nanostructures (such as photo, nanoimprint, e-beam, soft and focused ion beam) have been developed. However, most of these techniques have limitations in the form of material choices, speed, cost and/or pattern shape/size. Clearly a fast, low-cost and versatile method of producing high quality surface nanostructures is needed. Here, an approach that offers low-cost, fast manufacturing of complex patterns over large scale is presented. By utilizing existing and well known technology such as the optical disc drive and combining it with tools used in photolithography a novel manufacturing technique is made available. The method proposed can be used to directly scribe the desired pattern on the light sensitive material or create a master to be used for transferring a pattern to the appropriate material. In all cases the procedure is similar. First, the desired motif is drawn on a computer using any drawing program. Second, a label enabled

media such as lightscribe or labelflash DVD is coated with the material to be inscribed (e.g. photoresist to create a master). The disc is then inserted in the appropriate labeling disc drive and the pre-drawn image is engraved in material/photoresist. If necessary the disc can be treated post-scribing to create the structures; e.g. develop the photoresist. Finally, the surface of the material is engraved with the predetermined pattern. The method described here represents an affordable, fast and versatile way of manufacturing complex micro- and nanostructures without some of the design, throughput and material limitations faced by costlier techniques, making state of the art research more affordable and accessible.

**TF-WeP38 Probing Ni(111)-graphene interface using Raman spectroscopy,** *Guanjun Cheng, I. Calizo, A.R. Hight-Walker*, National Institute of Standards and Technology

Theoretical simulations have shown that due to the hybridization of Ni d-electrons with the  $\pi$ -orbitals of graphene, graphene phonon dispersion is significantly altered and there is no Raman signal from graphene on Ni(111) due to the suppression of the Kohn anomaly (Nano Lett, 2010, 10, 4335-4340). In this work, we deposit Ni thin film by thermal evaporation onto mechanically exfoliated graphene, few-layer graphene (FLG), and graphite, and probe the Ni-graphene interface using Raman spectroscopy. When the sample is annealed in forming gas, Ni(111) thin film is produced on graphene, FLG, and graphite. We observe the disappearance of Raman signals from graphene underneath Ni(111) using a low power excitation laser and the re-appearance of Raman signals from graphene with a higher power excitation laser. This work provide direct experimental evidence for the strong interactions between Ni(111) and graphene.

**TF-WeP40 High Temperature Self-Lubricant Coatings with Release of a Lubricious Agent for Machining Applications,** *F. Fernandes*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK, *Albano Cavaleiro*, University of Coimbra, Portugal

Binary TiN and ternary (TiX)N hard coatings, with X = Cr, Al, Si, Cr, etc, are well established in commercial tribological applications due to their high oxidation resistance and high hardness. Such coatings have been used to protect the surface of milling and machining tools; however, their friction coefficient revealed to be fairly high, at high temperature. This is a key point during machining of low thermal conductivity materials such as Ti-alloys. Liquid lubricants and oils have been used to reduce the friction and temperature between the sliding contacts; however, they frequently volatilize at high temperature, leading frequently to the failure of the cutting tools and, consequently, to increasing machine down times. To face these problems, solid lubricant coatings have been developed in the last decades to reduce the friction coefficient. The approach has been combining the intrinsic properties of binary and ternary coatings with elements that give lubricious properties, as it is the case of V. Such element forms thin reaction films of V-O on the surface of coatings with interesting properties at high temperature. Thus, the main goal of this work was to study the effect of V content on the oxidation and tribological properties of TiSi(V)N coatings deposited by DC reactive magnetron sputtering. Comparison of these results with those achieved for TiN, and TiSiN coatings prepared as references is also provided. The oxidation resistance of films was characterized by thermo gravimetric analysis and the tribological properties evaluated in pin-on-disc wear equipment, using as counterparts Al<sub>2</sub>O<sub>3</sub> and HSS balls. V additions increased the oxidation rate and decreased the friction coefficient and volume loss of coatings. SEM and Raman analysis showed that V<sub>2</sub>O<sub>5</sub> phase is the responsible for this tribological performance. TiSiN displayed the lowest wear resistance among all the tested coatings.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Adachi, K.: TF-WeP14, 3; TF-WeP15, 3  
Ahn, J.-H.: TF-WeP34, 5  
An, C.H.: TF-WeP4, 1  
Asai, Y.: TF-WeP22, 3

## — B —

Bai, S.: TF-WeP14, 3; TF-WeP15, 3  
Boo, J.-H.: TF-WeP10, 2  
Bravo-Sanchez, M.: TF-WeP25, 4

## — C —

Cabrera-German, D.: TF-WeP25, 4  
Calizo, I.: TF-WeP38, 6  
Cavaleiro, A.: TF-WeP40, 6  
Cheng, G.: TF-WeP38, 6  
Cho, H.: TF-WeP2, 1  
Cho, J.H.: TF-WeP34, 5  
Cho, S.H.: TF-WeP3, 1  
Choe, H.H.: TF-WeP12, 3  
Choi, J.H.: TF-WeP28, 4  
Chung, C.W.: TF-WeP28, 4  
Chung, M.J.: TF-WeP4, 1  
Chung, T.-M.: TF-WeP4, 1  
Chunming, Y.: TF-WeP36, 5

## — D —

Dutt, A.: TF-WeP32, 5

## — E —

Endo, M.: TF-WeP6, 1

## — F —

Fernandes, F.: TF-WeP40, 6

## — G —

Garay, A.: TF-WeP28, 4  
George, S.M.: TF-WeP4, 1  
Godavarthi: TF-WeP32, 5  
Gomez-Sosa, G.: TF-WeP23, 4; TF-WeP25, 4  
Graham, S.: TF-WeP20, 3

## — H —

Ha, S.: TF-WeP2, 1  
Hasegawa, Y.: TF-WeP6, 1  
Herrera-Gomez, A.: TF-WeP23, 4; TF-WeP25, 4  
Hight-Walker, A.R.: TF-WeP38, 6  
Higuchi, Y.: TF-WeP14, 3; TF-WeP15, 3  
Hirakuri, K.: TF-WeP26, 4  
Hiratsuka, M.: TF-WeP26, 4  
Hwang, C.S.: TF-WeP4, 1  
Hwang, K.: TF-WeP20, 3  
Hwang, K.-H.: TF-WeP10, 2

Hwang, S.M.: TF-WeP28, 4

## — I —

Ibarra-Nuno, J.: TF-WeP25, 4  
Ishibashi, K.: TF-WeP22, 3

## — J —

Jang, S.: TF-WeP2, 1  
Jeon, J.-H.: TF-WeP12, 3  
Jeon, W.: TF-WeP4, 1  
Jeong, H.-C.: TF-WeP5, 1; TF-WeP8, 2; TF-WeP9, 2  
Jeong, S.M.: TF-WeP34, 5  
Jung, Y.H.: TF-WeP5, 1; TF-WeP8, 2

## — K —

Kim, C.G.: TF-WeP4, 1  
Kim, D.: TF-WeP20, 3  
Kim, E.S.: TF-WeP11, 2  
Kim, H.: TF-WeP34, 5  
Kim, H.-S.: TF-WeP12, 3  
Kim, J.K.: TF-WeP1, 1  
Kim, K.H.: TF-WeP11, 2  
Kim, M.J.: TF-WeP3, 1  
Kim, N.: TF-WeP20, 3  
Kim, S.: TF-WeP20, 3  
Kim, Y.Y.: TF-WeP1, 1  
Kobayashi, Y.: TF-WeP14, 3; TF-WeP15, 3  
Kubo, M.: TF-WeP14, 3; TF-WeP15, 3  
Kuwahara, T.: TF-WeP14, 3

## — L —

Lee, J.H.: TF-WeP5, 1  
Lee, J.M.: TF-WeP1, 1  
Lee, J.S.: TF-WeP10, 2  
Lee, W.: TF-WeP4, 1  
Lee, Y.: TF-WeP34, 5  
Lim, B.: TF-WeP7, 2  
Lim, G.-H.: TF-WeP7, 2

## — M —

Madrigal Melchor, J.: TF-WeP29, 5  
Martin, J.M.: TF-WeP14, 3; TF-WeP15, 3  
Mata-Salazar, J.H.: TF-WeP25, 4  
Matsumoto: TF-WeP32, 5  
Molar-Velazquez, G.: TF-WeP23, 4  
Murabayashi, H.: TF-WeP14, 3; TF-WeP15, 3

## — N —

Nakahara, S.: TF-WeP36, 5  
Nam, S.-H.: TF-WeP10, 2  
Nishimori, K.: TF-WeP36, 5  
Noda, Y.: TF-WeP22, 3

## — O —

Oh, Y.T.: TF-WeP11, 2  
Ohgoe, Y.: TF-WeP26, 4  
Ozawa, N.: TF-WeP14, 3; TF-WeP15, 3  
Ozeki, K.: TF-WeP26, 4

## — P —

Park, B.K.: TF-WeP4, 1  
Park, H.-G.: TF-WeP5, 1; TF-WeP8, 2; TF-WeP9, 2  
Polcar, T.: TF-WeP40, 6

## — R —

Rasic, G.: TF-WeP37, 5  
Reyes Villagrana, R.A.: TF-WeP29, 5  
Rodríguez Vargas, I.: TF-WeP29, 5

## — S —

Sakai, K.: TF-WeP22, 3  
Santana-Rodríguez: TF-WeP32, 5  
Santoyo Salazar: TF-WeP32, 5  
Sasaki, M.: TF-WeP6, 1  
Sato, K.: TF-WeP26, 4  
Sekiya, K.: TF-WeP36, 5  
Seo, D.-S.: TF-WeP5, 1; TF-WeP8, 2; TF-WeP9, 2  
Seo, J.H.: TF-WeP12, 3  
Shiba, K.: TF-WeP26, 4  
Shimizu, R.: TF-WeP6, 1  
Shin, DongChan.: TF-WeP11, 2  
Sim, H.: TF-WeP7, 2  
Song, P.K.: TF-WeP3, 1  
Suárez López, J.R.: TF-WeP29, 5

## — T —

Takahashi, I.: TF-WeP36, 5  
Takeda, K.: TF-WeP22, 3  
Torres-Ochoa, J.A.: TF-WeP25, 4  
Tsuruda, T.: TF-WeP14, 3; TF-WeP15, 3

## — W —

Wang, Y.: TF-WeP14, 3; TF-WeP15, 3

## — Y —

Yamada, Y.: TF-WeP6, 1  
Yano, M.: TF-WeP6, 1  
Yeon, W.J.: TF-WeP11, 2  
Yoo, Y.W.: TF-WeP4, 1  
Yoon, J.H.: TF-WeP12, 3  
Yoshitake, T.: TF-WeP22, 3  
Yu, J.H.: TF-WeP10, 2