Tuesday Afternoon Poster Sessions, December 13, 2016

Nanomaterials
Room Mauka - Session NM-TuP

Nanomaterials Poster Session

NM-TuP1 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces, *Victor Petrov,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The possibility of existence of such VSLs was predicted theoretically (V.A.Petrov, 1977) [1,2]; simultaneously and independently they were realized (T.Cole et al.1977) [3]. At the present time, all these VSLs are developed only in 2D systems.

In this work we suggest a new method of development of the VSL in the quantum wires (QWR).where superlattice effects should be maximal. The special feature of this method is the combination of the main properties of the VSL - the separation in the system by some way of the long translation period A - with the possibility of developing this situation in the QWR on semiconductor low - index surfaces. It is easy to see that this situation is possible when the axis of the QWR which lies on the low - index surface will be oriented at the necessary angles to the basic translation vectors along the surface. In this case the translation symmetry of the QWR will be determined by its orientation on the crystal surface since the possibility of a free motion only along the axis of the wire selects in the initial two - dimensional translation group along the surface a one - dimensional translation subgroup along the wire with the basic period A. Thus, in the one-dimensional VSL the period A is selected by the orientation of the wire on the surface. For example, if the QWR is realized in the MOS system with the use of a narrow gate (V.A.Petrov 1978)[4] then the orientation of the wire will be determined simply by the appropriate orientation of the gate.

The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of minigaps in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a superlattice energetic spectrum of the particle. Illustrative estimates of the magnitude of the minigaps for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

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NM-TuP2 Influence of Electron Interference Effects on Reflection of Electron Waves From Potential Barrier in 2D Semiconductor Nanostructures, *Andrey Nikitin, V.A. Petrov,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

The influence of the interference of electron waves in the case of their reflection from potential barrier on the spatial distribution of the density of quantum-mechanical current $ej_x(x,z)$ (e − electron charge) in 2D semiconductor nanostructure which is represented by rectangular narrow ($x < 0, QW_1$) and wide ($x > 0$, QW_2) quantum wells (QWs) sequentially oriented along the direction of the propagation of electron wave has been studied theoretically. It is supposed that the wave falls from the narrow QW_1 on the semi-infinite potential barrier V_0 in height in the wide QW_2, the energy of the falling wave being less than V_0. Differing widths of QW_1 and QW_2 provide the non-orthogonality of wave functions of particles in these regions and the corresponding existence of electron interferential effects in this kind of nanostructure. In particular cases these effects lead to the appearance of spatially inhomogeneous distributions $ej_x^{(1)}(x,z)$ in QW_1 and $ej_x^{(2)}(x,z)$ in QW_2. It has been analytically demonstrated that in case of an electron wave falling along the first (lower) quantum-dimensional subband in QW_1 and its kinetic energy E_x being less than the energy positions of all the other subbands in QW_1 (*i.e.,* the undamped propagation of the wave reflected from the barrier with real quasi-momentum is possible only along

this lower subband) $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ are equal to zero. However, if a particle has such an energy that the refection of the wave with real quasi-momenta is possible along more than one (lower) subband, then the situation completely changes due to the interference of the reflected waves. In this case the interference leads to an existence of a complicatedly oscillating spatially inhomogeneous distribution $ej_x^{(1)}(x,z)$, and under the barrier in QW_2 it provides the appearance of exponentially damped at $x \to \infty$ and possessing a coordinate dependence of leakage $ej_x^{(2)}(x,z)$ under the barrier. Besides, three regions of the symmetric along z axis propagation $ej_x^{(2)}(x,z)$ are formed under the barrier. They are the central one, in which the current is directed in axis x positive direction, and two side regions in which the current is directed in negative direction. The presence of the regions of that kind provides the charge flow from under the barrier. The numerical calculations of $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ have also been made taking into account 31 subbands. It should be noted that these kinds of effects have a general nature and exist in 1D and 2D nanostructures with arbitrary profiles of QWs and barriers.

NM-TuP3 Understanding Ligand-Surface Passivation of Cation-Rich Colloidal Quantum Dots: First-Principles Study, *J.-H. Ko, D. Yoo, Yong-Hyun Kim,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Colloidal quantum dots (CQDs) are attractive nanomaterials for optoelectronic and photovoltaic applications because they are useful for mass production and easy to tune optical and electronic properties by controlling the size of CQDs. Generally, stable CQDs with good ligand-surface passivation are essential for such CQD applications. Yet, microscopic understanding how CQD surfaces are stabilized with passivating ligands is not clear in the colloidal environment. In this study, we performed first-principles density-functional theory (DFT) calculations for understanding ligand-surface passivation of cation-rich surfaces of IV-VI, II-VI, and III-V CQDs. Calculation results indicate that while non-polar surfaces of CQDs are self-passivated, polar surfaces of cation-rich CQDs, i.e. (100) and (111) for zinc blende semiconductors, have reactive surface dangling electrons that should be properly coordinated with passivating anionic ligands. We will discuss how such polar surfaces of CQDs could be stabilized by organic and inorganic ligands based on electron counting rule and coordination chemistry.

NM-TuP4 Ar Plasma Treated Transparent Silver Nanowire Electrodes for Flexible Quantum Dot Light-Emitting Diodes, *J-W. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; Jiwan Kim,* Kyonggi University, Republic of Korea

A smooth, ultra-flexible, and transparent electrode was developed from Ag nanowires (AgNWs) embedded in a colorless polyimide (cPI) by utilizing an inverted film-processing method. The resulting AgNW-cPI composite electrode is highly transparent and has an ultra-smooth surface with a low sheet resistance. The thickness of this conductive composite film was reduced to less than 100um with extreme flexibility. This film exhibited mechanical durability up to a bending radius of 5 mm. Green quantum dots light-emitting diodes (QLEDs) were fabricated using these composites as bottom electrodes (anodes). Hole-injection in QLEDs was poor, because AgNWs were largely buried beneath the composite's surface. Thus, we used a simple plasma treatment to remove the thin cPI layer overlaying the nanowires without introducing other conductive materials. As a result, we were able to finely control the flexible QLEDs electrical/optical properties using the enlarged conductive pathways. The fabricated flexible devices showed only slight performance degradation after a repeated bending test.

NM-TuP5 High-throughput Synthesis of Emissive Glass Microcomponents via Contact Flow Lithography, *Jiseok Lee,* Ulsan National Institute of Science and Technology, Republic of Korea

We report a high-throughput synthesis of emissive microcomponents with rare-earth-doped upconverting nanocrystals (UCNs) using a contact flow lithography. Upconverting nanocrystals were synthesized using hydrothermal reaction and used as anti-Stokes emitters that absorb near-infrared (NIR) light and emit in visible spectrum. We utilized contact flow lithography for massive production of nonspherical composite microcomponents. Emissive composite microcomponents with a variety of shapes was synthesized and corresponding glass microcomponents were obtained through polymer burn-off. The synthesized particles with UCNs are stable at high temperature and have great potential to use as anti-counterfeiting platform.

NM-TuP6 Effect of Redox-Induced Conformational Changes in Charge Transport Characteristics of a Ferrocene-Alkanethiolate Molecular Device: Temperature-Dependent Transition Voltage Spectroscopy Analysis, *Hyunhak Jeong, Y. Jang, D. Kim, W.-T. Hwang, J.-W. Kim, T. Lee,* Seoul National University, Republic of Korea

The ultimate aim of molecular electronics is to overcome the limit of the conventional silicon based solid-state electronics by utilizing either single molecules or a bundle of molecules as an active electronic device component. For example, Nijhuis et al. recently reported a robust molecular diode using ferrocene-alkanethiolate self-assembled monolayers (SAMs) and eutectic Ga and In (EGaIn) electrodes.[1] They demonstrated a large rectification ratio of up to ~1000 and reported that the strong asymmetric electrical characteristics could be interpreted by hopping assisted tunneling transport arising from the ferrocene-alkanethiolates and the electrodes.

Similar to these studies, we have also examined the possibility of the electronic device application by fabricating a large number of molecular devices based on ferrocene-alkanethiolate (denoted as FcC) SAMs using a conventional solid-state device fabrication technique both on rigid and flexible substrates.[2] Specifically, we observed a distinctive temperature dependence on the electrical characteristics; that is, the current density decreased as the temperature increased in a certain temperature range when a sufficient voltage was applied with a certain voltage polarity. This behavior was in contrast to the usually expected thermally activated charge transport in the molecular device junction or other device junctions in which, most times, the current density increases as the temperature increases. In that study,[2] we suggested the unusual thermal characteristics are probably due to the redox-induced conformational changes of the FcC in the molecular junctions. While the analysis was quite reasonable and consistent with the experimental results, further evidence was needed to support our suggested explanation. We also performed temperature-dependent transition voltage spectroscopy (TVS) analysis based on a multibarrier tunneling model, which supports the occurrence of the proposed redox-induced conformational changes in the FcC molecular junctions.[3]

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NM-TuP7 High Elastic Modulus, High Extensibility Nanorods Constructed of pH-Responsive Cyclic Peptide Polymer, *Kenan Fears, M. Kolel-Veetil, D. Barlow, N. Bernstein, C. So, K. Wahl,* US Naval Research Laboratory, USA

Due to their ability to self-assemble into supramolecular nanorods in solution, cyclic β -tripeptides (CBTPs) have been used as molecular scaffolds that predictably display functional groups along the axis of the assembly. To enhance the mechanical strength and processability of such nanostructures, we synthesized a linear polymer of amide-bonded CBTP subunits using previous computational analysis on the conformational stability and tunability as guidance. Two amino acids in each subunit (β -HLys or β -HGlu) form "hinges" with neighboring subunits, and electrostatic repulsions between the third, β -HOrn, forced the polymer to adopt a disordered conformation when protonated. When deprotonated, atomic force microscopy revealed rigid nanorods exhibiting an elastic moduli (51.3 GPa) stiffer than any report peptide-based material. The hinges also allow the nanorods to elongate under tension which should impart the polymer with high extensibility and resilience. Nanorods were decorated with Au nanoparticles to demonstrate the ease in functionalizing the polymer, greatly expanding its potential applications beyond a structural material. The solubility and structural control achieved by combining covalent bonds, non-covalent bonds, and electrostatic interactions suggest the polymer may not only exhibit excellent processability but also mimic toughness and elasticity found in nature.

NM-TuP8 Growth and Optical Properties of Catalyst-free Ga(In)N Nanorods with Different Top Shapes, *Moon-Deock Kim, B.-G. Park, J.-W. Hwang,* Chungnam National University, Republic of Korea; *W.-C. Yang, D.-Y. Kim, K.-B. Chung,* Dongguk university, Republic of Korea

In this work, we have investigated the kinetic process and adatoms mechanism of four different top shapes of catalyst-free Ga(In)N nanorods (NRs) namely flat, taper, hammer, and mushroom structures were grown in holes of a patterned Si (111) substrate by plasma-assisted molecular beam epitaxy. Arrays of nano-holes with diameter of 80 nm on the Si substrate were obtained by using of self-assembled silica nanospheres as a nano-hole mask. The silica nanospheres coated on the Si substrate and then spread using a spin-coating method. A 10 nm-Ti deposited after dry etching to sizes control and then removed silica nanospheres by chemical etching. Different top shapes of Ga(In)N were obtained by varying the growth conditions namely growth temperature and N2 plasma power, and the morphology evolution was explained based on the interrelation between sidewall diffusion and direct impingement during the NRs growth. GaN NRs grown at the growth temperature (T_g) and *Ga* flux of 650 °C and 5×10^{-7} Torr, respectively, were used as the buffer for the subsequent growth of GaN NRs with different top shapes. GaN NRs with flat top (Fig. 1(a)) was obtained without altering the growth conditions that was used for the buffer growth. When the T_g was increased gradually from 590 °C to 650 °C under *Ga* flux of 1×10^{-7} Torr, we obtained GaN NRs with top tapered shape (Fig. 1(b)). On the other hand, hammer shaped GaN NRs (Fig. 1(c)) were obtained when the T_g was reduced gradually to 570 °C, while keeping the Ga flux 1×10^{-7} Torr during the growth of GaN NRs. Furthermore, mushroom shaped Ga(In)N nanostructure (Fig. 1(d)) on top of GaN NRs were obtained when introducing *In* flux of 1×10^{-7} Torr at T_g ~ 350 °C under the same Ga flux. The variations in the shape of GaN NRs are explained by the interrelation of sidewall diffusion and the supersaturation of adatoms at the top surface [1, 2]. Photoluminescence measurements revealed higher light emission for tapered GaN when compared to non-tapered structure. APSYS simulations were further conducted to theoretically confirm the observed experimental results. We believe that our results can provide crucial information for the shape controlled growth of GaN NRs with diverse nanostructures and promising approach for the realization of high brightness LEDs.

Fig. 1 SEM images of GaN NRs with different top shape (a) flat, (b) tapered, (c) hammer and of GaInN with (d) mushroom

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NM-TuP9 Semi-green Synthesis and Characterization of Superparamagnetic Fe_3O_4-MNPs with Aqueous Extracts from C. Verum and Natural Extract from V. Planifolia, *A.L. Ramírez-Núñez,* Doctoral Program in Nanosciences and Nanotechnology CINVESTAV-IPN, Mexico; *Jaime Santoyo-Salazar,* Nanosciences and nanotechnology, CINVESTAV-IPN, México; *L.F. Jiménez-García,* Faculty of Sciences, UNAM, México; *G. Goya Rossetti,* Instituto de Nanociencia de Aragón, Spain

Recently biosynthetic methods employing either biological entities or plant extracts have emerged as an easy, fast and economical alternative to chemical and physical síntesis procedures for the production of safer nanomaterials for human use. An eco-friendly semi-green method was used in order to obtain magnetite magnetic nanoparticles (Fe_3O_4-MNPs). Besides the know effect of polyphenols as therapeutical agents in cancer diseases, biomolecules from aqueous extracts can act as capping and reducing agents wich effectively replace toxic chemical reductans. Plant extracts with a rich mixture of active biological phytochemicals (i.e. polyphenol compounds, tannins, saponnins, flavonoids) control and shape the growing nanoparticles. Superparamagnetic properties have been studied extensively due to their potential use in hyperthermia in cancer treatment. The green synthesis of Fe_3O_4-MNPs with aqueous extracts represent a major advantage in the synthesis of superparamagnetic materials for biomedical usage, due to their diminished toxicity to biological organisms and more efficient drug delivery carriers for specific cancer diseases. In order to explore the diversity of biomolecules in the obtention of Fe_3O_4-MNPs, in this work an aqueous extract from *Cinnamomun verum* and *Vanilla planifolia* (natural pods and synthetic extract) were used during the synthesis of magnetite.

The Fe_3O_4 MNPs obtained were identified by XRD (PDF-19-0629) corresponding to an inverse spatial group *Fd3m* (227) inverse spinel FCC structure, a= 8.355 Å in synthetic vanilla and a=8.362 Å in vanilla pods extract (*V. planifolia),* and a=8.366 Å in *C. verum*. IR peaks at 576 cm^{-1} correspond to Fe-O bonding formation; vibrational peaks at 576-1641 and 3415 cm^{-1} suggest phenol molecules involved in bio-reduction process. XRD and HRTEM diffraction patterns overlap with the corresponding Fe_3O_4 peaks (220),(311),(400),(511),(440). The *d* spacing 2.4 Å in *V. planifolia* and 2.7 Å in *C. verum* match the main diffraction plane 35° (311). The particle size calculated by Scherrer´s equation by Scherrer´s equation *(t=Kl/b cos Θ)* in *V. planifolia* was 12 nm and 14 nm in *C. verum*. AFM-MFM data show a monodomain arrangement of 2-3 nm in *V. planifolia* and 5-6 nm in *C.*

verum. VSM data indicate that magnetization increases rather using *C. verum* extract (64.89 emu/g) than *V. planifolia* (46.6 emu/g). The SPA values suggest that vanilla pods extract has an advantageous performance during Fe3O4-MNPs synthesis due to their increased heating capability (64.51 W/g). The bio-synthesis of Fe_3O_4 MNPs obtained by aqueous plant extracts are commensurable to those obtained by a chemical method with a better performance than synthetic extract.

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NM-TuP10 Nanostructure Surface Design for Increased Photovoltaic Responses in Ethanol Photochemical Fuel Cells, K. Hirakawa, D. Rodriguez, K. Anderson, **Yong Gan,** California State Polytechic University Pomona, USA

Electro-spun Titanium nanofibers can be applied to the surface of photoanode to create a multi-catalyst anode. The electrospinning process is considered in this study and found that it is as one of the simplest ways to create nanofibers with varying diameters ranging from 50 to 500 nm. When combined with a polyvinylpyrrolidone (PVP) composite, titanium oxide creates a nanofiber with high surface area while containing the intrinsic semiconductor properties of . The effects of using silicon nanowires (SiNW) on the surface of doped silicon as a substrate was also studied in this work. SiNWs create a porous surface feature due to the electrodeposited silver on silicon. Silver has a plasmonic effect which allows free electrons to oscillate on the surface of the metal when exposed to light. This plasmonic effect allows Silver to be used as a photocatalyst. Silicon can also be easily etched which creates another photocatalyst . The porous SiNWs enhances the phonon scattering about the interfaces of the nanowires due to its high anti reflectivity causing higher absorption. The functionality of a PEC cell is driven by many factors. nanotubes are the primary interest in this research. The purpose of this work is to determine the effects of type of the surface modified nanostructured photocatalyst anode, the ethanol concentration levels, on the response time of the photoelectrochemical (PEC) reaction when exposed to UV light source. Over a short period of UV irradiation exposure, the response time influences how much the potential difference changes between the anode and cathode. Creating multi-catalyst anodes using doping techniques, electrospinning applications, and electrodeposition methods change the photocatalytic properties. Varying the concentration of the fuel by lowering the energy density present in the electrolyte also effects the response time of the photoanode. By inspecting the various response times, the efficient photoanode in this study is identified.

NM-TuP11 Microfluidic Capacitive Sensors Using Ionic Liquid Electrodes and CNT/PDMS Composites for Multimodal Sensing Applications, **SunGeun Yoon,** S.M. Lee, Chung Ang University, Republic of Korea

There are many studies of demonstrating capactive sensors for various purposes such as detecting pressure, body motions, and temperature variation. However, its perfoming principle is mainly dependent on physical and geometrical changes of dielectric layers. In this study, we developed a new class of microfluidic capacitive sensors with utilizing ionic liquid serving as electrodes and CNT/PDMS composites (CPCs) as a dielectric layer. The working principle of our microfluidic sensors was investigated with geometrical changes of microfluidic channel and variations of electric double layer (EDL) capacitance. Our microfluidic capacitive sensors showed detection of localized pressure, lateral pressure movement, and even temperature variations with high sensitivity. By using multimodal capability, the microfluidic capacitive sensor was successfully performed as a keypad and applied to a bottle and human skin. This microfluidic capacitive sensors could offer great opportunity of development for future stretchable and flexible electronic devices such as wearable electronics, soft robotics, electronic skin, and human healthcare systems.

NM-TuP18 Adsorption and Thermal Processes of NO with Silicene on ZrB₂/Si(111), **Jun Yoshinobu,** ISSP, Univ. of Tokyo, Japan; K. Mukai, H. Ueda, S. Yoshimoto, C. Lee, T. Ozaki, Univ. of Tokyo, Japan; A. Fleurence, Y. Yamada-Takamura, Japan Advanced Institute of Science and Technology, Japan

We investigated the adsorption and thermal processes of NO with silicene on ZrB₂/Si(111) using synchrotron radiation X-ray photoelectron spectroscopy (XPS) and density-functional theory (DFT) calculations. NO is dissociatively adsorbed on the silicene surface at 300 K. The substitutional adsorption of a nitrogen atom to a silicon site in the silicene honeycomb predominantly occurs. An oxygen atom is most probably inserted between two Si atoms of the silicone honeycomb. With increasing NO exposure, the honeycomb structure of silicene is destroyed and three dimensional silicon oxinitride may be formed. By heating above 900 K, the oxide species start to desorb from the surface most probably as SiO species. After heating to 1053 K, no oxygen is observed by XPS; nitrogen species remain on the surface. At the same time, the bare silicene domains are restored. The substitutional nitridation of silicene including $Si_3 \equiv N$ species may provide a two-dimensional SiN honeycomb sheet on the surface.

NM-TuP19 Cellulose Nanowhiskers Topography & Young's Modulus Imaging Using Atomic Force Microscopy, B. Kim, **Gerald Pascual**, P.. Kondapani, K. Lee, Park Systems Corporation

Carbon nanotubes (CNTs) are a popular sample for various nanotechnology studies. However, they are very difficult to synthesize en masse. As a result, researchers have started looking at alternatives with similar properties. One of the candidates to replace CNTs in some nanocomposite materials is cellulose nanowhiskers (CNWs), structures that can be readily produced from plant sources. To determine the feasibility of substituting CNWs for CNTs, it is important to verify the two materials have similar morphologies and nanomechanical properties. One must first establish a baseline for comparison by accurately characterizing CNW properties at nanoscale . To this end, three CNW samples were examined using an atomic force microscope (AFM) with non-contact AFM mode and an AFM-based fast nanomechanical mode. The target properties for evaluation were the samples' topography to determine the nanowhiskers' size and shape and their Young's modulus values. The ensuing AFM measurements yielded topography data showing the nanowhiskers ranging from 100 to 1000 nm in length and 1 to 3 nm in width. Nanomechanical property data acquired with the AFM in fast nanomechanical mode demonstrated the CNW samples had a modulus value of approximately 180 GPa . Not only do these measurements establish a baseline CNW to CNT comparison for topography and a specific nanomechanical property, but they also demonstrate the viability of AFM as an effective tool for dimensional nanometrology and quantitative property measurements of novel nanocomposite components.

NM-TuP20 Dynamics of Carbon Monoxide Adsorbed on Tungsten (310) Surface of Cold Field Electron Emitters, **Soichiro Matsunaga**, Y. Suwa, K. Kasuya, S. Katagiri, Hitachi Ltd, Japan

We investigated a tungsten (310) surface, which has been widely used as electron emitting surface of cold field emitters (CFE). The intensity of electron beams emitted from a CFE rapidly decreases even under an ultra-high vacuum (UHV) environment of 10^{-8} Pa [1]. There has been a recent report that a stable operation region with high current angular density appeared by operating a CFE under an extreme-high vacuum (XHV), from 10^{-9} to 10^{-10} Pa[2]. That study revealed that the decreasing of the emitted beam is caused by residual hydrogen gas in CFE gun chambers, and they used a non-evaporative getter (NEG) to evacuate the hydrogen gas from the gun chamber. In the stable operation region of a NEG-evacuated CFE, we have observed unexpected increasing and step-wise shifting of the beam current.

In order to understand the mechanisms behind the unexpected beam fluctuations, we performed electron emission experiments and computational simulation of the emission surface. Results showed that the step-wise fluctuation is related to the adsorption of a single carbon monoxide (CO) molecule onto the W(310) surface. We performed a first principle calculation of the CO-adsorbed W(310) surface in order to understand the mechanism behind the step-wise fluctuation. To study the site of electron emission on the single-CO-molecule-adsorbed surface, we developed a calculation method to evaluate the heterogeneous potential barrier height of the surface under strong electric fields. On the basis of these experimental and calculation results, we propose that the adsorption

and diffusion of a single CO molecule on W(310) surface cause the step-wise fluctuations of the current.

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Author Index

Bold page numbers indicate presenter

— A —
Anderson, K.: NM-TuP10, 3
— B —
Barlow, D.: NM-TuP7, 2
Bernstein, N.: NM-TuP7, 2
— C —
Chung, K.-B.: NM-TuP8, 2
— F —
Fears, K.: NM-TuP7, **2**
Fleurence, A.: NM-TuP18, 3
— G —
Gan, Y.: NM-TuP10, **3**
Goya Rossetti, G.: NM-TuP9, 2
— H —
Hirakawa, K.: NM-TuP10, 3
Hwang, J.-W.: NM-TuP8, 2
Hwang, W.-T.: NM-TuP6, 2
— J —
Jang, Y.: NM-TuP6, 2
Jeong, H.: NM-TuP6, **2**
Jiménez-García, L.F.: NM-TuP9, 2
— K —
Kasuya, K.: NM-TuP20, 3
Katagiri, S.: NM-TuP20, 3

Kim, B.: NM-TuP19, 3
Kim, D.: NM-TuP6, 2
Kim, D.-Y.: NM-TuP8, 2
Kim, J.: NM-TuP4, **1**
Kim, J.-W.: NM-TuP6, 2
Kim, J-W.: NM-TuP4, 1
Kim, M.-D.: NM-TuP8, **2**
Kim, Y.-H.: NM-TuP3, **1**
Ko, J.-H.: NM-TuP3, 1
Kolel-Veetil, M.: NM-TuP7, 2
Kondapani, P..: NM-TuP19, 3
— L —
Lee, C.: NM-TuP18, 3
Lee, J.: NM-TuP5, **1**
Lee, K.: NM-TuP19, 3
Lee, S.M.: NM-TuP11, 3
Lee, T.: NM-TuP6, 2
— M —
Matsunaga, S.: NM-TuP20, **3**
Mukai, K.: NM-TuP18, 3
— N —
Nikitin, A.V.: NM-TuP2, **1**
— O —
Ozaki, T.: NM-TuP18, 3

— P —
Park, B.-G.: NM-TuP8, 2
Pascual, G.: NM-TuP19, **3**
Petrov, V.A.: NM-TuP1, **1**; NM-TuP2, 1
— R —
Ramírez-Núñez, A.L.: NM-TuP9, 2
Rodriguez, D.: NM-TuP10, 3
— S —
Santoyo-Salazar, J.: NM-TuP9, **2**
So, C.: NM-TuP7, 2
Suwa, Y.: NM-TuP20, 3
— U —
Ueda, H.: NM-TuP18, 3
— W —
Wahl, K.: NM-TuP7, 2
— Y —
Yamada-Takamura, Y.: NM-TuP18, 3
Yang, W.-C.: NM-TuP8, 2
Yoo, D.: NM-TuP3, 1
Yoon, S.G.: NM-TuP11, **3**
Yoshimoto, S.: NM-TuP18, 3
Yoshinobu, J.: NM-TuP18, **3**