

## Thin Films

Room: Makai - Session TF-MoM

### Self-Organized and Nanostructured Thin Films

**Moderator:** Shixuan Du, Institute of Physics, Chinese Academy of Sciences

8:40am **TF-MoM1 Growth Kinetics, Structure, and Properties of 2D Layered Materials**, *Suneel Kodambaka*, University of California, Los Angeles **INVITED**

Two-dimensional (2D) layered materials owing to a wide range of properties (e.g., graphene is metallic, h-BN is insulating, and MoS<sub>2</sub> is semiconducting) have attracted immense attention over the past decade for a variety of optoelectronic and nanoelectronic applications. Recent efforts have focused on vertical integration of 2D layers of dissimilar materials (e.g., graphene/h-BN and graphene/MoS<sub>2</sub>). In these heterostructures, due to relatively weak van der Waals interactions, orientational registry between the layers is not expected and is often difficult to control. This talk will focus on the effect of interlayer orientation on the electronic structure of the resulting heterostructures. Using a combination of *in situ* low-energy electron microscopy (LEEM) and density functional theory (DFT) calculations, we investigated the electronic properties of graphene/Pd(111). From the LEEM images we determined the graphene growth kinetics and measured graphene work function as a function of orientation and layer thickness. Recently, we extended our DFT calculations to study the electronic structures of h-BN/Ni(111) and graphene/MoS<sub>2</sub> heterostructured layers. We found that hBN can chemisorb or physisorb on Ni(111), with metallic or insulating properties, respectively and these properties are not altered when graphene is placed atop hBN. For graphene on MoS<sub>2</sub>, we found that rotating graphene layer by 30° with respect to MoS<sub>2</sub> changes the MoS<sub>2</sub> band gap from 1.68 eV direct to 1.56 eV indirect. We attribute the observed orientation-dependent bandgap to the variation in the S-S interplanar distance with the MoS<sub>2</sub>-graphene interlayer orientation.

9:20am **TF-MoM3 Deposition and Tribomechanical Properties of Hf-B-C Thin Films**, *Elham Mohimi, T. Ozkan, S. Babar, P.J. Sempstrott*, University of Illinois at Urbana-Champaign, USA, *A.A. Polycarpou*, Texas A&M University, *G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign, USA

The tribomechanical properties of thin film coatings can be enhanced by alloying to afford a multicomponent nanostructure. Our group previously reported the conformal growth and favorable mechanical properties of HfB<sub>2</sub> and Hf-B-N hard coatings by chemical vapor deposition (CVD) at low substrate temperature. Here, we alloy C into HfB<sub>2</sub> in order to reduce the friction coefficient and enhance the hardness. A useful analogue is C-alloyed TiB<sub>2</sub>, which exhibits super hardness and good thermal stability. However, there have been no previous studies of Hf-B-C alloys.

Hf-B-C nanocomposite coatings are deposited by CVD onto Si or stainless steel discs using the precursor hafnium borohydride, Hf(BH<sub>4</sub>)<sub>4</sub>, with a co-flow of dimethylbutene (DMB), (CH<sub>3</sub>)<sub>3</sub>CCCH=CH<sub>2</sub>, as the carbon source. Depositions are performed in a high vacuum chamber with base pressure of 10<sup>-8</sup> Torr, hafnium borohydride pressure 0.1-0.5 mTorr and DMB pressure 0.05-0.4 mTorr at substrate temperatures of 250-600°C. DMB also acts as growth inhibitor – it reduces the film growth rate by a factor of 2-6 compared to growth using the precursor alone, an effect which enhances conformality. For higher temperature growth, DMB increases the film density and decreases the surface roughness. XPS analysis indicates a mixture of HfB<sub>2</sub>, HfCx and B4C phases, however, this is uncertain due to the small shifts between different bonding states.

As-deposited films are XRD amorphous with hardness values of 9-26 Gpa and reduced modulus of 99-208 Gpa. Upon annealing at 700°C for 3 hours under inert gas atmosphere, the films transform to a partially nanocrystalline structure, which increases the hardness to 17-34 Gpa and the elastic modulus to 158-248 Gpa. The tribological properties of Hf-B-C films are superior to those of HfB<sub>2</sub> films. This is attributed to graphitic attachment of carbon atoms on contacting surfaces as evidenced by EDS analysis of the wear scar surface. Summarizing, this system affords conformal growth at low growth temperatures, suitable for the fabrication of complex structures such as MEMS.

9:40am **TF-MoM4 Effect of Chemical Reaction on Low Friction of Diamond-Like Carbon in Water Lubrication : A Theoretical Study**, *Shandan Bai, Y. Niiyama, Y. Kobayashi, Y. Higuchi, N. Ozawa, K. Adachi, S. Mori, K. Kurihara, M. Kubo*, Tohoku University, Japan

[Introduction] Diamond-Like Carbon (DLC) coatings have low friction and anti-wear tribological performances. Furthermore, water lubrication improves the friction properties of DLC films and reduces the emission of CO<sub>2</sub>. The friction coefficient of the DLC films drastically changes under water lubrication, since some tribo-chemical reactions occur during the sliding. However, tribo-chemical reactions are difficult to be revealed only by experimental analyses in details. The computational technique is efficient method to investigate the low friction mechanism [1]. In this study, we reveal the tribo-chemical reaction between DLC film and water using the computational method on an atomic scale.

[Method] To clarify the tribo-chemical reactions of DLC films under water lubrication, we use our tight-binding quantum chemical molecular dynamics (TB-QCMD) method [2]. We construct the sliding simulation model consisting of 80 water molecules and two DLC substrates. The thickness of water is approximately 1.0 nm. The friction simulation is performed for 100,000 steps with the time step of 0.1 fs. We apply contact pressures of 0.5 and 5 GPa on the top layer of upper substrate of DLC films, while it is forcibly slid with a horizontal velocity of 10 m/s. The simulation temperature is set at 300 K, achieved by velocity scaling method.

[Results and Discussion] We perform our TB-QCMD calculations to investigate the low friction properties of DLC in water lubrication. Under a contact pressure of 0.5 GPa, one C-OH bond is generated on the DLC surface at 0.045 ps during the sliding, because of the dissociation of a water molecule. Furthermore, at 3.655 ps, we observe another C-OH bond generation on the surface. The result indicates that OH terminates the DLC surface under a contact pressure of 0.5 GPa. Under a contact pressure of 5 GPa, generation of a C-OH bond is observed on the surface at 1.380 ps. Furthermore, at 3.880 ps, it is very interesting to see the generation of C-O-C on the DLC surface, which is a different chemical reaction with that under pressure of 0.5 GPa. The friction coefficients are 0.81 and 0.05 under contact pressures of 0.5 and 5 GPa, respectively. Those results indicate that the friction coefficient decreases with increasing a contact pressure. We think that the chemical reaction leads to the structure change on the DLC surface and the low friction properties of DLC in water lubrication under high contact pressures.

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10:20am **TF-MoM6 Growth of Large-Area 2D Transition Metal Dichalcogenides**, *Lain-Jong Li*, King Abdullah University of Science and Technology, Saudi Arabia **INVITED**

The direct-gap property of the semiconducting transition metal dichalcogenide (TMD) monolayers is attractive for optoelectronics and energy harvesting. Here I would like to discuss the synthetic approaches to obtain crystalline and sub-mm sized MoS<sub>2</sub>, WSe<sub>2</sub> and WS<sub>2</sub> monolayers directly on arbitrary substrates using vapor phase reaction between metal oxides and S or Se powders.<sup>1-2</sup> These layer materials can be transferred to desired substrates, making them suitable building blocks for constructing multilayer stacking structures. By using micro-beam X-ray photoelectron spectroscopy, we report the determination of band offsets in TMD heterostructures.<sup>3</sup> These physical quantities are fundamentally important for novel devices based on heterostructures formed between dissimilar TMDs. Some possible applications based on TMD heterostructures will be discussed.

#### References

<sup>1</sup> Huang, J. K. et al. Large-Area Synthesis of Highly Crystalline WSe<sub>2</sub> Monolayers and Device Applications. *Acs Nano* 8, 923 (2014).

<sup>2</sup> Lee, Y. H. et al. Synthesis of Large-Area MoS<sub>2</sub> Atomic Layers with Chemical Vapor Deposition. *Advanced Materials* 24, 2320 (2012).

<sup>3</sup> M.-H. Chiu et al. Determination of band alignment in transition metal dichalcogenides heterojunctions. arXiv:1406.5137

11:00am **TF-MoM8 Influence of Testing Conditions on the Tribological Behaviour of C(N)-WS<sub>2</sub> Self Lubricating Thin Films**, *Albano Cavaleiro, M. Evaristo*, University of Coimbra, Portugal, *T. Polcar*, University of Southampton, UK

Transition metal dichalcogenides (TMD) have a layered structure and weak inter-layer bonding allowing to display very low friction coefficient when a tangential force is applied. Being sliding contact a surface phenomenon, these materials have been largely studied in the form of thin coatings.

Whenever conditions exist for establishing stronger bonds between the layers, the friction coefficient can significantly increase. This is the reason why the industrial applicability of these coatings is still very limited due to the deficient tribological behavior in humid atmospheres, for which strong bonds can be formed through oxygen. In order to overcome this problem different approaches were followed based on alloying TMD with different elements. Among these elements, our group has developed a deep study on the addition of carbon and nitrogen. We have proved, as it was already known, that the friction coefficient could increase from the range [0.005 – 0.05] up to [0.05 – 0.3] when the coatings were tested in dry or in humid conditions, respectively.

The aim of this talk is to present a systematic study concerning the influence of humidity in the tribological behavior of TMD+C coatings. We deposited W-S-C coatings with increasing C content up to 60 at.% with two S/W ratios, close to 1.4 and 1.0. These coatings were tested by pin-on-disk in different humidity range from RH=20% up to RH=95%. Contrarily to what we have observed in previous studies, we could not find any case where the friction coefficient went down lower than 0.1. Furthermore, there was no clear trend on the effect of either the humidity or the S/W ratio on the friction coefficient. The detailed analysis of the sliding surfaces allowed to conclude that, in all tests, orientation of WS<sub>2</sub> crystals in the top sliding contact could not be achieved. The comparison with previous deposited W-S-C coatings allowed to conclude that the different tribological behavior could be attributed to a different nanostructure arrangement in the as-deposited conditions.

# Monday Afternoon, December 8, 2014

## Thin Films

Room: Lehua - Session TF+NM-MoE

## Nanostructures, Graphene, and Magnetism

**Moderator:** Stephen Muhl, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

5:40pm **TF+NM-MoE1 Low-Dimensional Electronic System on Metal-Adsorbed Germanium Surfaces**, *Kan Nakatsuji*, Tokyo Institute of Technology, Japan **INVITED**

The electronic properties of metallic nano-materials attract much interests not only because of their potential application to novel electronic devices but fundamental low-dimensional physics point of view. One of the ways to fabricate nano-materials is to deposit small amount of metal atoms on crystalline semiconductor surfaces. In the present study, we have investigated atomic and electronic structures of gold adsorbed Ge(001) and Ge(111) surfaces which exhibit one- and two-dimensional atomic structure, respectively, by scanning tunneling microscopy (STM), angle-resolved photoelectron spectroscopy (ARPES) and density functional calculations.

The Au-adsorbed Ge(001) surface has periodic arrangement of one-dimensional (1D) chain structure and a metallic surface state. This metallic state has been reported to be strictly 1D showing Tomonaga-Luttinger liquid (TLL) behavior[1]. In the present study, its band shape was precisely investigated using a single-domain surface prepared on a vicinal substrate. Our ARPES results clearly revealed that the band has anisotropic two-dimensional (2D) shape in contrast to the previous report. The band dispersion is steeper in the direction perpendicular to the chain contrary to the intuitive expectation from 1D structure[2]. Our STM study revealed that the top of the 1D chain shows 8 times periodicity on average along the chain with a lot of defects[3]. This rather high density of defects may cause the reduction of density of states at the Fermi level which was previously interpreted as a TLL behavior.

The Au-adsorbed Ge(111) surface exhibits  $\sqrt{3}\times\sqrt{3}$  periodicity. Two metallic surface states,  $S_1$  and  $S_2$ , were observed around  $\Gamma$ , which is consistent with the calculated band structure of the CHCT model. 2D electronic system is confirmed by a rounded hexagonal Fermi surface of  $S_1$  band[4] which has contributions from surface Au and Ge atoms.  $S_2$  is originated only from the Ge atoms. These surface bands split into spin-polarized bands owing to the strong spin-orbit interaction[5]. The modification of the electron filling of the  $S_1$  band by additional Au atoms will be also discussed[6].

The author thanks Y. Motomura, R. Niikura and Prof. F. Komori in Institute for Solid State Physics, University of Tokyo for their close collaboration, and Y. Oda and Prof. A. Ishii in Tottori University for their collaboration in theoretical part of this work.

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6:20pm **TF+NM-MoE3 Effective Mass of a Two-Dimensional  $\sqrt{3}\times\sqrt{3}$  Ga Single Atomic Layer on Si(111)**, *Michael Schnedler*, Forschungszentrum Jülich GmbH, Germany, *Y. Jiang*, Peking University, China, *K.H. Wu*, Institute of Physics, Chinese Academy of Sciences, China, *E.G. Wang*, Peking University, China, *R.E. Dunin-Borkowski*, *P. Ebert*, Forschungszentrum Jülich GmbH, Germany

The transport of charge carriers in semiconductor nanostructures is particularly important for nanoscale devices. In a semi classical approach, the transport of charge carriers is to a large degree governed by the effective masses of electrons and holes, which are reasonably well known for most bulk materials. However, with ongoing miniaturization of semiconductor devices and the trend towards the use of nanostructures, the increasing surface to volume ratio reduces the relative fraction of bulk material. Hence, transport in semiconductor nanostructures is to a large degree determined by surface and/or interface effects, where little is known about the effective masses.

The effective masses of surface states can be derived from angle-resolved photoemission spectroscopy (ARPES), but it is hardly applicable on individual nanostructures. In contrast scanning tunneling spectroscopy (STS) is ideally suited for probing the local density of states of an individual nanostructure, but it is a very difficult task to quantitatively

measure the involved  $k$  vectors and hence the dispersion relation and the effective mass.

Therefore, we illustrate here a methodology applicable to individual semiconducting nanostructures for extracting effective masses of a two dimensional  $\sqrt{3}\times\sqrt{3}$  Ga single atomic layer on Si(111) directly from scanning tunneling spectra. The methodology is based on calculating the tunnel current using its dependence on the effective density of states mass and a parabolic band approximation followed by fitting to the measured tunneling spectra. An effective mass of  $m_{\text{eff}}=0.59 \pm 0.06$  is obtained for the empty surface state, in good agreement with a band structure calculation and inverse photo electron spectroscopy data.

6:40pm **TF+NM-MoE4  $\alpha'$ , $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> Interstitial Compound as a New Candidate for Rare Earth Free Permanent Magnet - From Thin Film to Bulk**, *M. Takahashi*, *Masahiro Tobise*, Tohoku University, Japan **INVITED**

After surprising first report ( $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> phase exhibited a giant saturation magnetization in 1972 as a thin film form [1]), many researches challenged to realize single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>. At 1993, present author et al. established the method in thin film to attain a relatively high volume fraction of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> using a reactive sputtering [2]. Precisely determined value of  $M_s$  of  $\approx 240$  emu/g ( $\approx 2.2$  T) even though relatively small value compared to initially reported one and value of  $K_u$  ( $\approx 10^7$  erg/cm<sup>3</sup>) are very attractive as rare earth free permanent magnet material [3]. But as it was very difficult to form metastable  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> single phase even in the thin film, it had been believed that the synthesis of a single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> in bulk form was almost impossible. In 2013, our group established the synthesis procedure of single-phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> nanoparticle for the first time, and reported  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> exhibit  $M_s$  of  $\approx 234$  emu/g and  $K_u$  of  $\approx 10^7$  erg/cm<sup>3</sup> [4]. This nanoparticle powder could be synthesized starting from the reduction of Fe-oxides and following nitriding with ammonia gas at temperatures around 145 °C under the very low moisture and oxygen contents less than 1 ppm through the all process. Mössbauer spectra also revealed that the perfect formation of the single phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub>. In order to improve coercivity through the evaluation of magnetic interaction and the quality of  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> crystalline, the anisotropy field  $H_i^{\text{pfc}}$  and switching field  $H_p$  are determined by rotational hysteresis loss analysis using randomly oriented nanoparticles assembly. Coercivity of nanoparticle assembly consisting of single-phase  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> formed around 145 °C exceeds 2000 Oe. Normalized coercive force  $H_c/H_i^{\text{pfc}}$  and normalized switching field  $H_p/H_i^{\text{pfc}}$  are about 0.16 and 0.3, respectively. Coercivity has been improved by surface treatment and reached 3200 Oe at present. Detail on the relationship between these magnetic properties and reversal mechanism is discussed.

## References

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7:40pm **TF+NM-MoE7 Interfaces between Transferred, CVD-Grown Graphene and MoS<sub>2</sub> Probed with STM and ARPES**, *H. Coy-Diaz*, Department of Physics, University of South Florida, Tampa, FL 33620, USA, *J. Avila*, *M.C. Asensio*, 2. Synchrotron Soleil, Orme des Merisiers - Saint Aubin, BP 48 - 91192 - GIF SUR YVETTE Cedex, France, *Matthias Batzill*, Department of Physics, University of South Florida, Tampa, FL 33620, USA

Heterostructures made of different van der Waals materials are of increasing interest because of potential applications in energy harvesting and combination of spin- and valley-tronics. However, the interface properties of these materials are not yet well characterized. One challenge for their characterization is the preparation of large-area high quality materials that enable employment of surface characterization techniques such as scanning probe microscopy and photoemission spectroscopy. Here we demonstrate the transfer of CVD-grown graphene to bulk MoS<sub>2</sub> substrates and report the first STM and ARPES studies of such a system. As expected for weakly interacting materials STM studies only exhibit a very weak moire-superstructure and (nano) ARPES measurements show that the Dirac cone of graphene is maintained. However, (nano) ARPES also shows the formation of band-gaps in the pi-band of graphene where the out-of-plane molecular orbitals of MoS<sub>2</sub> intersect with the electronic-states of graphene. This modification of the electronic structure of graphene in the

graphene/MoS<sub>2</sub> heterostructure is contrary to expectations of simple van-der Waals stacked materials. The high quality of the samples will enable further studies of the spin state of the graphene and MoS<sub>2</sub> substrate as well as enable preparation of other heterostructure materials and thus will give a detailed description of the interaction in these heterostructure systems.

8:00pm **TF+NM-MoE8 Universality of Seebeck Coefficients in Graphene/h-BN Nano-Composites**, *Yosuke Ayako, A. Akaishi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Thermoelectric materials have attracted much attention because of their promising applications in power generation. Recently, we have shown that the superlattices consisting of zigzag graphene nanoribbons (GNRs) and BN nanoribbons (BNNRs) have giant Seebeck coefficients [1]. Such giant Seebeck coefficients of the superlattice models stem from the so-called pudding-mold band with a finite energy gap [2]. Although such types of superlattices have great fascination with thermoelectricity, the experimental synthesis of these two-dimensional structures may be an extremely-challenging task.

In the present study, we suggest more easy-to-make, practical one-dimensional structures possessing the pudding-mold band. We propose the graphene/h-BN hybrid nanoribbons with zigzag edges (hereafter referred to as "nano-composites"), in which both edges of GNRs are terminated with BNNRs. In this study, we specify the models using integer  $n$  and  $m$ , which are the numbers of dimer lines of GNRs and BNNRs, respectively. The Seebeck coefficients of nano-composites have been evaluated on the basis of the Boltzmann transport theory. Electronic band structures have been calculated using the first-principles calculations within the framework of the density functional theory. We have also employed the armchair nano-composites for comparison.

We have shown that the pudding-mold bands have been confirmed for the zigzag nano-composites, but not for the armchair ones. The Seebeck coefficients for the zigzag nano-composites decrease monotonically with increasing  $n$ . Their maximum values become higher than those for graphene and GNRs, though not to the extent of the superlattices [1]. On the other hand, the Seebeck coefficients for the armchair nano-composites do not become higher compared with those for the pristine armchair GNRs, since the mechanism of the enhancement based on the pudding-mold band does not work for these composites. Here, we should not overlook that the Seebeck coefficients for the armchair nano-composites show the oscillatory-decreasing behavior with increasing  $n$ , and their dependence on  $n$  can be classified into three categories of  $3n$ ,  $3n+1$ , and  $3n+2$ , being analogous to the electronic structure of the zigzag carbon nanotubes [3]. Nevertheless, the Seebeck coefficients shows the universal dependence on the band gaps: the maximal, absolute Seebeck coefficient depends only on the bandgap irrespective of the structural category of nano-composites.

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8:20pm **TF+NM-MoE9 Reduction of Oxygen on Nitrogen-Doped Graphene**, *Akihide Ichikawa, A. Akaishi, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee *et al.* have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e<sup>-</sup>) that is reduced to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and the direct four-electron pathway (4e<sup>-</sup>) that reduces to water (H<sub>2</sub>O). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V (2e<sup>-</sup>) and 1.23V (4e<sup>-</sup>), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH\*, OH\*, and O\* (where "\*" refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Norskov *et al.* [4]. We have taken account of effects of electrode potential,  $\Phi$  of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the 2e<sup>-</sup> and 4e<sup>-</sup> reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH\* (the 2e<sup>-</sup> pathway), and the formation of OOH\* (the 4e<sup>-</sup> pathway) are confirmed to be the rate-limiting steps, respectively. The effects of electric field and water environment will also be discussed in the presentation.

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## Thin Films

### Room: Makai - Session TF-MoE

## Electronics and Displays on Flexible and Hard Substrates

**Moderator:** Lain-Jong Li, King Abdullah University of Science and Technology

5:40pm **TF-MoE1 Organic Thin Film Transistors: Materials, Device Interfaces and Performances**, *Yunqi Liu*, Institute of Chemistry, CAS, China **INVITED**

Organic/polymer thin-film transistors (O/P TFTs) are of great interest for practical applications in active-matrix displays, radiofrequency identification tags, biosensors, and integrated circuits owing to their advantages of low cost, light weight, and mechanical flexibility. In this presentation, I will report a few results on O/P TFTs from my research group,<sup>[1-10]</sup> including materials, device interfaces and performances.

References

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6:20pm **TF-MoE3 Investigation of Strain Sensors Based on Thin Graphite Wires**, *Takanari Saito, M. Matayoshi, J. Shirakashi*, Tokyo University of Agriculture & Technology, Japan

Among the flexible electronic devices, the strain sensors have attracted a great deal of interest due to its wide range of utility in real life, for example, the detection of human motion, monitoring personal health and therapeutics. Previously, we have reported that thin graphite wires are simply and easily fabricated from pyrolytic graphite sheet (PGS) [1] which is commercially available from Panasonic Corporation and have potential applications in

microheaters [2]. In this report, we focus on the thin graphite wires fabricated on sticky tapes as flexible devices and investigate the electrical properties of the thin graphite wires for strain sensors.

The experimental procedures are as follows. First, graphite wires with the length of 45 mm and the width of 1 mm were cut off from PGS. Then, we prepared thin graphite wires with thickness down to about 3  $\mu\text{m}$  using mechanical exfoliation. The electrical properties of the thin graphite wires were studied by applying a tensile bending stress with the radius of curvature from 5 to 25 mm. When applying tensile strains by bending the graphite wires, resistance of the graphite wires could show increasing response. The relative change in resistance ( $\Delta R/R_0$ ) under a bending radius of 5 mm was 48 %, where  $R_0$  is the resistance under zero strain;  $R$  is the resistance under strain; and  $\Delta R=R-R_0$ . It has been proposed that resistance of graphite-based strain sensors under the bending stress changes due to variations in length and cross-sectional area as well as the distance between conductive particles [3]. Hence, the resistance changes of our thin graphite wires are caused by similar mechanism. Therefore, it is suggested that thin graphite wires simply and easily fabricated from PGS can be used as strain sensors.

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6:40pm **TF-MoE4 Photovoltaic Devices, Sensor and Electrostatic Self-Assembly Based on Conjugated Polymers**, *Chang-Lyoul Lee*, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology (GIST), Republic of Korea, *N.C. Greenham*, Cavendish Laboratory, University of Cambridge, UK, *S.-H. Han*, Mokpo National Maritime University, Republic of Korea, *W.-E. Lee*, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology (GIST), Republic of Korea, *G. Kwak*, Kyungpook National University, Republic of Korea **INVITED**

**In this talk, I will introduce two topics. One is polymer photovoltaic devices and the other is sensor for detecting biomolecules (or heavy metal ions) and patterning application of conjugated polyelectrolyte through *in-situ* electrostatic self-assembly.**

The roll of triplet states in photovoltaic devices (PV) is less studied than in PLEDs. Recent studies show that utilization of triplet excitons in conjugated polymer improves PV device performance. The triplet exciton dynamics of conjugated polymer in phosphorescent dye blended polymer PV device was investigated by photo-induced absorption (PIA) spectroscopy. From the low temperature PIA experiments of phosphorescent dye blended conjugated polymer films, the origin of the enhancement of triplet exciton population of conjugated polymer was revealed. And also, the PIA and PV response studies of phosphorescent dye blended conjugated polymer : fullerene bulk heterojunction PV device as well as phosphorescent dye blended conjugated polymer : fullerene bilayer PV device reveal the photo-physical interaction among the conjugated polymer, phosphorescent dye and fullerene and effects of triplet excitons to the PV device performance. (*Adv. Funct. Mater.*, **20**, 2945, 2010).

The second section of this talk is sensor and patterning application of conjugated polyelectrolyte (CPE). Conjugated polyelectrolyte (CPE) with new signal transduction mechanism, based on sulfonated poly(diphenylacetylene), was developed. The CPE showed relatively weak FL emission in water due to a highly dense stack degree of side phenyl rings, while the stack structure was consistently relaxed by being combined with proteins, showing a great PL amplification. Consequently, the CPE was highly responsive to even a little amount of proteins because each of numerous side phenyl rings act as FL probes. (*Chem. Commun.*, **49**, 9857, 2013).

A new method for patterning conjugated polymer (CP) by *in-situ* electrostatic self-assembly (ESA) of conjugated polyelectrolyte (CPE) with surfactants in a film was reported. The *in-situ* ESA was simply realized by contacting the film to appropriate surfactant solutions. The contacting parts on the CPE film have completely different solubility from the non-contacting parts; the polymer chains in the contacted part also undergo supramolecular rearrangement, consequently resulting in dramatic PL emission enhancement. The optical and structural properties of the contacted part were regulated by varying the alkyl tail length of the surfactants employed. Highly resolved CP patterns can be readily obtained through this *in-situ* ESA approach. (*unpublished results*)

7:40pm **TF-MoE7 Substrate Dependant Film Growth Mechanism for the Production of Highly Durable Multi-Layer Plastic Mirrors**, *Colin Hall, K. Zuber, E. Downey, E. Charrault, D. Evans, P. Murphy*, University of South Australia

The use of polymers to replace traditional materials in the automotive, aerospace and other industries is continuing at a high pace. Polymers offer distinct advantages over glass and metals, such as weight, impact strength, and the ability to be formed into complex shapes. To ensure long service life, however, in some applications the polymers must be coated to provide protection from damage due to mechanical abrasion or chemical attack. This coating can also enhance the plastic's functionality, such as changing its optical, electrical or surface properties.

One such example of this is the development of a highly durable plastic mirror through the deposition of a physical vapour deposition (PVD) multi-layer stack.<sup>1,2</sup> The growth of sputtered layers on plastic substrates requires the use of a relatively thick "hardcoating" (some 3 to 8  $\mu\text{m}$  thick). This hardcoating is used in the ophthalmic and automotive industries and is typically a thermal cured organosilicone nanocomposite resin. Subsequently, a silica and chromium PVD multilayer was deposited to form the durable mirror coating. In developing this coating system to meet automotive glass mirror performance, it was found that there were substrate dependant effects on the sputtered layers characteristics. That is, the type of hardcoating had a direct influence on the growth of the sputtered layers. Interestingly, it was found that the mechanical properties of this hardcoating correlated with changes in optical, electrical and mechanical properties of the grown multi-layer stack.

The understanding developed has aided in the successful commercialisation of the plastic mirror, as the spotter mirror in the Ford F250 truck. However, as the plastic/hardcoat/PVD architecture is used extensively elsewhere (ophthalmic and decorative coatings) the phenomenon is of wide interest.

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8:00pm **TF-MoE8 Investigation of Peculiar Spin Electronic States Induced by Spin-Orbit Interaction Using High-Resolution Spin-Resolved Photoemission**, *Taichi Okuda*, Hiroshima University, Japan **INVITED**

Spin-orbit-interaction induced spin polarized surface states such as Rashba spin split states or topological surface states(TSS) are the new class of quantum matter and getting much attention as the key materials for the realization of spintronic devices. Spin polarization reversal in the surface state bands with respect to time reversal symmetry point in these materials expects to suppress backscattering by nonmagnetic impurities and to realize dissipationless spin transport.

In case of Rashba systems, however, the possible back scattering to the spin split pair band having opposite spin polarization hampers the complete suppression of backscattering. In addition, some quasi particle interference pattern of STM measurements show the existence of the scattering path even in the topological insulators. Furthermore, for the real application one should also consider to protect the surface states from the contamination. It has been reported that small amount of gas adsorption can produce the band bending in the topological insulators and changes the property of the TSS dramatically. Thus, in order to use the spin-polarized surface states and realize the spintronic devices one should eliminate these problems.

Here I present some recent results of spin- and angle-resolved photoelectron spectroscopy (SARPES) that show the hints to solve these problems. The first example is a Rashba system on one-dimensional surface states. High-resolution SARPES of Au induced chain structure on vicinal Si(111) surface shows clearly one-dimensional Rashba spin-split states. Interestingly the spin polarization vector is not in-plane but points perpendicular to the surface deviating from the normal Rashba spin-split states. This out-of-plane spin polarization and the one-dimensional band structure will help to reduce the scattering probability of the electron in the system.

Bi film on vicinal Si(111) surface also shows interesting spin structure having out-of-plane spin polarization. Unlike the Bi film on normal Si(111) surface that has (111) orientation, the film on the Si(557) surface shows LEED pattern and surface band structures similar to those of Bi(110) surface. Because of the lower symmetry ( $C_{1h}$ ) of the sample structure not only in-plane but also significant out-of-plane spin polarization has been observed.

As the other examples, the investigation of lead based topological insulator  $\text{PbBi}_4\text{Te}_7$  will be presented. Surface and bulk sensitive SARPES measurement proved the existence of spin-polarized topological surface states protected physically under the quintuple layer. This protected TSS will open the pathway to utilize the spin-split electrons in the future.

8:40pm TF-MoE10 Spin Current at Surfaces of Strong Spin-Orbit Coupling Materials, Shuji Hasegawa, N. Fukui, R. Hobaru, University of Tokyo, Japan, T. Hirahara, Tokyo Institute of Technology, Japan, A. Takayama, University of Tokyo, Japan

Recent studies have shown that the surface states exhibit spin-split and spin helical structures when spin-orbit coupling is strong enough. This is due to break down of space-inversion symmetry at crystal surfaces. Surface Rashba systems and topological insulators (TI) are the typical examples. This causes interesting phenomena relating to flow of spins, such as spin-polarized current [1] and spin current (without charge current) at crystal surfaces and edges of thin atomic layers of such materials. Such spin current may be useful for future spintronics devices because spin current causes no energy dissipation.

“Spin Hall Effect” (SHE) is one of such phenomena, which produces spin current perpendicular to the charge current. Due to bending of electron flow in opposite directions depending on the spin orientation, caused by strong spin-orbit coupling, a flow of spin is produced in the direction perpendicular to the charge current. Its time-reversal process also occurs (inverse SHE) in which the spin current produces charge current, by which we can detect the effects.

By using a H-shaped pattern of thin Bi<sub>2</sub>Se<sub>3</sub> film, one of the topological insulators, we have tried to detect the SHE. The pattern was fabricated in a UHV-FIB (Focused Ion Beam) combined with a four-tip STM and MBE chambers [2]. In order to verify the SHE, we measured the nonlocal voltage drop caused by SHE and inverse SHE. All the processes including the film growth, patterning and measurements were done *in situ* in UHV to protect the surface states with a four-tip STM equipped with FIB [2]. The nonlocal voltage drop obtained was mainly explained by the classical Ohm’s law, with small deviation. The deviation is explained by the SHE. From the data fitting we could deduce the spin-Hall angle and spin relaxation length.

[1] T. Tono, et al., New J. Phys. **15**, 105018 (2013).

[2] N. Fukui et al., e-J. Surf. Sci. Nanotech., submitted.

## Thin Films

Room: Makai - Session TF-TuM

## Interfaces in Multilayers & Nanocomposites

Moderator: Juan Luis Pena Chapa, CINVESTAV-IPN

Unidad Merida, Mexico

8:00am **TF-TuM1 Looking Below the Surface with Photoemission: Standing Waves and Hard X-rays**, Charles Fadley, University of California at Davis, USA **INVITED**

I will present some new directions in soft x-ray photoemission (XPS, SXPS) and hard x-ray photoemission (HXPS, HAXPES, HIKE) [1-5], with illustrative examples of applications to a range of sample types. These involve combined SXPS and HXPS studies of buried layers and interfaces in magnetic and transition-metal oxide multilayers [1], as well as semiconductor junctions [2]; solid-gas or solid-liquid interfaces with high ambient pressures [4,5]; and the use of standing waves from multilayer mirrors to enhance depth contrast in spectroscopy [1,3,4,5].

### References

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, the Army Research Office, under MURI Grant W911-NF-09-1-0398, the Forschungszentrum Julich, Peter Grunberg Institute (PGI-6), and the LABEX-PALM, APTCOM project of Le Triangle de Physique, Paris.

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[5] "Chemical-state resolved concentration profiles with sub-nm accuracy at solid/gas and solid/liquid interfaces using standing-wave ambient-pressure photoemission (SWAPPS)", S. Nemsak et al., submitted.

8:40am **TF-TuM3 ToF-SIMS and XPS Characterization of Plasma Polymerized ppAA/Teflon-like Thin Films Interfaces**, V. Spampinato, EC-JRC-IHCP Ispra (ITALY), Italy, C. Desmet, A. Valsesia, P. Colpo, F. Rossi, EC-JRC-IHCP Ispra (ITALY), **Giacomo Ceccone**, EC-JRC-IHCP Ispra (ITALY), Italy

The availability of the high energy cluster sources open new possibilities in the use of surface analysis techniques such XPS and ToF-SIMS to characterize organic films which are important in different application fields ranging from energy to food and medicine (1, 2). In particular the use of molecular depth profiling allows the investigation of the distribution of molecules within the different layers of organic films and nanostructured materials (3).

Plasma polymerization is a well established method to deposit controlled thin films on different substrates and it is applied in many industrial and research activities (4, 5).

In this work we report the analysis of multilayers plasma polymerized polyacrylic acid (ppAA) and teflon-like (PTFE) films using XPS and ToF-SIMS. In particular, XPS has been used to verify the surface composition of the different polymeric films, whilst ToF-SIMS depth profiles have been obtained by means of Ar<sub>n</sub><sup>+</sup> and Bi<sub>n</sub><sup>+</sup> (n=1 and 3) polyatomic sources. Both single beam and dual beam analysis have been investigated and the different parameters (ion energy, analysis fluence and analysis area) have been studied to evaluate the degree of sample damage (6).

Finally, preliminary data on the use of ToF-SIMS depth profiling technique to identify the presence of nanoparticles at ppAA/PTFE interfaces will be also presented and discussed.

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9:00am **TF-TuM4 A detailed Assessment of Indium Diffusion in InGaAs/high-k/TiN MOS Devices Employing ARXPS**, Alberto Herrera-Gomez, O. Ceballos-Sanchez, CINVESTAV-Unidad Queretaro, Mexico, M. Vazquez-Lepe, Universidad de Guadalajara, T. Duong, R. Arroyave, Texas A&M University, A. Sanchez-Martinez, CINVESTAV-Unidad Queretaro, Mexico, F. Espinosa-Magaña, Cimav-Unidad Chihuahua

The electrical performance of InGaAs-based MOS structures is affected by post deposition annealing. A proper characterization of the structural alterations associated with the degradation of the interface and electrical properties is important for understanding failure mechanisms [1]. While most of the results are focused in the control of interfacial passivation [2], phenomena such as diffusion of atomic species from the substrate has not been as widely examined. The samples employed in this study were TiN/high-k/InGaAs MOS structures with different thermal treatments. X-ray spectroscopy (XPS) studies revealed the appearance of an indium peak induced by annealing. Through a robust methodology based on angle-resolved XPS, it was found that the new peak is related to diffusion of indium through the dielectric into the metallic layer. This is the case when the high-k material is alumina [3], hafnia [4] and zirconia [5]. The transport of gallium is only patent in the case of hafnia and zirconia [4,5]. The structure of the samples was characterized employing the MultiLayer Method [6] and the experimental methodology described in Reference 7. Once the structure (thickness and composition) of the various layers constituting the nanofilms were assessed, it was possible to generate the expected angular behavior of the XPS signal from the indium peak under different scenarios. By employing this "scenarios" approach it was possible to robustly show the diffusion phenomenon and to quantify the amount of transported mass. These results, together with density function theory (DFT) calculations, allowed for the assessment of the activation energy for the diffusion of indium through the high-k dielectrics. It was surprising to find that, for all three dielectrics, the transport activation energy of indium is around 0.8 eV.

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9:20am **TF-TuM5 Electric and Thermoelectric Properties of Molecule-Nanoparticle Composite Structures Influenced by Surrounding Gases**, ShienDer Tzeng, Y.S. Li, K.T. Chiang, I.C. Ni, National Dong Hwa University, Taiwan, Taiwan, Republic of China

Nanocomposite structures formed by the assembly of nanoparticles with functional surface molecules have many interesting properties [1-3]. We found that these surface molecules at the interface between nanoparticles play very important role on the physical properties (e.g., resistance and Seebeck coefficient reported in this work) of the nanocomposite thin film. For instance, shorter length of surface molecules results in shorter interparticle gap distance and thus increases the electric and plasmonic coupling between nanoparticles. Besides, the barrier height could also be tuned by using different kinds of molecules. Furthermore, the interparticle gap distance or the barrier height of charge conduction could also be influenced by their surrounding gases. In this work, we show that Heme modified nanoparticle assembled films could be used for low water vapor

pressure sensing (as shown in Fig. 1). From high vacuum to  $\sim 0.01$  Torr water vapor, the resistance of Heme device could increase 1%. By contrast, 8-mercaptooctanoic acid (MOA) or 6-mercaptohexanoic acid (MHA) modified nanoparticle assembled films need 1 Torr water vapor to cause 1% resistance change. Besides, we found that the response is proportional to  $P^r$ , and the characteristic energy of water adsorbed in the nanocomposite structure could be calculated from the value of  $\gamma$ . Furthermore, the response time of such water vapor sensors could be less than 0.2 sec, much shorter than most known humidity sensors. We also found that the thermoelectric properties of these molecule-nanoparticle composite thin films were very sensitive to surrounding gases (as shown in Fig. 2). For instance, the Seebeck coefficient of MHA-modified gold nanoparticle assembled films was about  $12.5 \mu\text{V/K}$  in high vacuum ( $10^{-5}$  Torr), but became  $120 \mu\text{V/K}$  in 600 Torr  $\text{O}_2$  gas. Such great change in Seebeck coefficient could be explained by the change of density of state contributed by the gas molecules adsorbed on the surface molecules.

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9:40am **TF-TuM6 Laser Lift-Off of Single-Crystal GaAs Thin Films for Low-Cost, High-Performance Photovoltaics, Optics and Electronics, Bruce Clemens**, Stanford University, *G. Hayes*, Stanford University, USA

GaAs and related III-V sphalerite materials offer a wide array of tunable characteristics that lend themselves to many advanced device technologies. However, the cost of GaAs substrates limits their use, specially for photovoltaics. Separating epitaxially-grown layers from a growth substrate can reduce costs, however the current approach, which uses an acid to laterally etch an epitaxial sacrificial layer, is slow and can damage other device layers. Here, we demonstrate laser lift-off as a new approach that is orders of magnitude faster, and that enables more freedom in the selection of other device layers. We grow a structure with a spatially-tuned optical absorption coefficient by growing a small-band-gap, pseudomorphic layer between the GaAs substrate and a GaAs film and device structure. By using InGaAsN with a band gap of 0.9 eV for this layer, we achieve high absorption of 1064 nm (1.17 eV) light from a Nd:YAG nanosecond laser pulse, while GaAs is essentially transparent for this wavelength. Illumination through the back of the GaAs substrate with laser fluences of about  $0.7 \text{ J/cm}^2$  achieves transfer of the GaAs layer to a flexible polymer substrate. Transmission electron microscopy and x-ray diffraction show that the initial InGaAsN layer is coherently strained to match the GaAs substrate, and that the GaAs film is strain-free and free of dislocations, both before and after lift-off. Thermal modeling shows only modest heating outside of the InGaAsN layer, so that the film or device above the InGaAsN layer experiences minimum thermal exposure. Examination of the lift-off interfaces shows evidence of melting and re-solidification. We demonstrate a process using additional InGaP etch layers that allow for quick and easy clean-up of this melted region, resulting in restoration of the original GaAs wafer surface to a condition suitable for re-use. Thus our process can transform the GaAs substrate from a consumable to a manufacturing tool.

10:20am **TF-TuM8 SIMS Depth Profiling and 3D characterization of Organic/Inorganic Surfaces by FIB Crater Wall Imaging and Tomography, N.J. Havercroft**, ION-TOF USA, Inc., *Felix Kollmer*, ION-TOF GmbH, Germany, *R. Moellers*, *D. Rading*, *S. Kayser*, *E. Niehuis*, ION-TOF GmbH

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices is of major importance. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is known to be an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. In the so-called dual beam mode the pulsed analysis beam is combined with a low energy sputter ion beam for the removal of material. This allows depth profiling of multilayers with high depth resolution as well as three-dimensional analysis.

However, the analysis of structures at greater depth ( $> 10 \mu\text{m}$ ) requires long measurement times and the build-up of surface roughness at the crater bottom limits the achievable spatial resolution. Moreover, extremely rough samples, samples with voids, and material that exhibits strong local variations in density or sputter yield are unsuitable for conventional depth profiling. Not only that the initial surface topography is unknown but it is also modified and in many cases even roughened by the sputtering process.

In order to overcome these limitations we used a combined SIMS/FIB setup. Either a Bi cluster beam or a mono-atomic Ga beam is used to FIB mill a crater into the sample. Subsequently, a 2D TOF-SIMS image of the vertical crater wall is acquired. Since the crater wall is hardly affected by the aforementioned roughening problems this approach allows the in-depth distribution of elements to be determined by analyzing a plane perpendicular to the surface at high lateral resolution ( $\Delta l < 50 \text{nm}$ ) [1].

Moreover, by serial slicing of the crater wall followed by intermediate analysis steps this approach can be extended in order to provide the full 3D characterization of the analyzed surface. We will present 2D and 3D data of reference material, multilayer samples and technically relevant real world samples such as fuel cells and battery electrodes. For thin multilayer samples the FIB process can be performed under grazing incidence in order to bevel the surface and hence magnify and accentuate thin layers in the plane of the analyzed crater wall.

However, FIB/SIMS approach fails when analyzing organic surfaces since the molecular structure is almost completely destroyed by the sputtering process. We will discuss methods to maintain the molecular structure under high dose sputtering conditions by performing the FIB milling with massive argon clusters.

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10:40am **TF-TuM9 Growth and Characterization of Heteroepitaxial III-N Semiconductor Films using Atomic Layer Epitaxy, N. Nepal, Virginia Anderson, J.K. Hite, C.R. Eddy, Jr.**, US Naval Research Laboratory

Aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) semiconductors and their corresponding ternary films, such as InGaN, offer attractive properties, with high breakdown fields and widely tunable direct band gaps. Currently, III-nitrides are primarily deposited with molecular beam epitaxy and chemical vapor deposition. The addition of Atomic Layer Epitaxy (ALE) to the possible growth techniques is driven by the need for ever thinner films integrated into complex heterostructures, something that is increasingly difficult to achieve by conventional techniques. Furthering the attraction of ALE is the promise of lower growth temperatures that allow the deposition of a wider range of indium containing ternary films.

Here we report on ALE in a plasma-equipped Ultratech/Cambridge Nanotech atomic layer deposition system to grow AlN, GaN, and InN at temperatures significantly lower than needed for molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD).[1] In growing epitaxial materials, the substrates and corresponding surface preparation procedures are important. The substrates include silicon(111), sapphire, and MOCVD gallium nitride on sapphire, as well as graphene.[2]

For InN on a-plane sapphire, the expected wurtzite hexagonal phase was heteroepitaxially grown for films deposited in the temperature window of 220 to 260 C, well below the typical minimum 450 C temperature used in MOCVD. At an even lower temperature, 183 C, the heteroepitaxial InN on a-plane sapphire was discovered to be cubic phase with a NaCl structure, a phase of InN that had before been unreported.[3] Heteroepitaxial AlN films were grown on GaN/sapphire at a much lower temperature (500 C) than by MOCVD, typically 1100 C or more. Finally, GaN has been included in ALE deposited ternaries in the relatively low temperature window of 250-400 C even as its optimization continues. The ALE grown III-N films have carbon and oxygen contamination that hinders their immediate use in many applications, and improving the film purity is a major focus. In addition, initial deposition of indium ternaries indicates that more stoichiometries are available by ALE than MOCVD.

The possibilities for greater use of III-nitrides are apparent even at the early stages of progress in atomic layer epitaxy. Further characterization during and after deposition of the films should lead to materials suitable for use in high electron mobility transistors, as well as optoelectronic devices.

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11:00am **TF-TuM10 Controlling Charges States at Nanoscale Schottky Contacts, Tae-Hwan Kim**, Pohang University of Science and Technology, Republic of Korea, *H.W. Yeom*, Institute for Basic Science

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized



chemical bonds at metal-semiconductor interfaces have been recognized to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switching in their I-V and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

11:20am **TF-TuM11 Enhancement of Contact Properties of Ytterbium Silicide by Alloying with Molybdenum**, *Sekwon Na, H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

As scale-down of metal-oxide-semiconductor field effect transistors (MOSFETs) continues, the portion of resistance rising from the contact of total resistance has become burdensome. This has fueled a drive to find a new contact material with a low contact resistance. In particular, rare-earth (RE) metal silicides (Er, Yb, etc.) are promising as source/drain contact materials, since they have a very low Schottky barrier height (SBH) on n-type silicon (0.2~0.4eV).

Among several RE silicides, ytterbium silicide deserves much attention due to its some favorable characteristics for low SBH applications. In this study, we embarked full investigation of Yb silicide by thoroughly analyzing how the formation of the epitaxial silicide layer influences electrical properties including sheet resistance and SBHs. Moreover, we alloyed Yb with Mo to improve oxidation resistance of the material at high temperatures.

Ytterbium and molybdenum were deposited on an n-type silicon (001) substrate with a resistivity of 1-10ohm-cm using a radio frequency (rf) magnetron sputtering system. For the Mo-alloyed sample, the composition of Mo was found around 20 at. % from EDS analysis. To remove the native oxide of the silicon substrate, the wafer was dipped in 1% HF solution and then rinsed with deionized water. The films were deposited at room temperature and at a working pressure of 9mTorr in Ar ambient. Subsequently, a tantalum nitride (TaN) capping layer with the thickness of 50nm was deposited. To measure SBH, we fabricated Schottky diodes by forming circular dots (diameter: 50 $\mu$ m) of Yb via lift-off. The samples were annealed using rapid thermal annealing (RTA) at various temperatures (300°C ~800°C) for 1 minute in N<sub>2</sub> ambient. For characterization, we utilized transmission electron microscopy and X-ray diffraction. The electrical characteristics were examined using an HP semiconductor parameter analyzer.

Dynamic microstructural evolution of the Yb/Si contact, in which solid-state amorphization between Yb and Si, nucleation and growth of an epitaxial YbSi<sub>2-x</sub> layer, and disruption of the layer due to oxidation occurred successively with the temperature increasing. However, the microstructures of Mo-alloyed samples annealed at high temperatures show that the Mo-rich region is formed above the epitaxial layer, and it fended off oxygen diffusion. Thus, the epitaxial layer remained up to 800°C. While the epitaxial Yb silicide led to low SBHs, oxidation increased significantly SBHs at high temperatures in Yb/Si samples. Protection of epitaxial layer by Mo-segregated region helped to remain low SBHs over a wide temperature range (600~800°C).

# Tuesday Afternoon Poster Sessions

## Thin Films

Room: Mauka - Session TF-TuP

## Thin Films Poster Session

**TF-TuP3 Novel Techniques and Devices for In-Situ Film Coatings of Long, Small Diameter Tubes or Elliptical and other Surface Contours\***, *Ady Hershcovitch, M. Blaskiewicz, J.M. Brennan*, Brookhaven National Laboratory, *A. Custer, A. Dingus, M. Erickson*, PVI, Oxnard, California 93031, USA, *W. Fischer*, Brookhaven National Laboratory, *N. Jamshidi*, PVI, Oxnard, California 93031, USA, *C.J. Liaw*, Brookhaven National Laboratory, *R. Laping*, PVI, Oxnard, California 93031, USA, *W. Meng*, Brookhaven National Laboratory, *H.J. Poole*, PVI, Oxnard, California 93031, USA, *R. Todd*, Brookhaven National Laboratory

Two devices and techniques that can, via PVD, coat various surface contours or very long small aperture pipes. First 3-axes robotic manipulators controlling separate robotic assemblies resulted in 9-axes of motion combined with conformal shape of the cathodes that can articulate various curved surface contours was developed and successfully used for optically coating aircraft canopies. Second a magnetron mole was developed in order to in-situ coat accelerator tube sections of the Brookhaven National Lab (BNL) relativistic heavy ion collider (RHIC) that have 7.1 cm diameter with access points that are 500 meters apart, for copper coat the RHIC vacuum tube in order to alleviate the problems of unacceptable ohmic heating and of electron clouds. A magnetron with a 50 cm long cathode was designed fabricated and successfully operated to copper coat a whole assembly containing a full-size, stainless steel, cold bore, of the RHIC magnet tubing connected to two types of RHIC bellows, to which two additional pipes made of RHIC tubing were connected. The magnetron is mounted on a carriage with spring loaded wheels that successfully crossed bellows and adjusted for variations in vacuum tube diameter, while keeping the magnetron centered. Electrical power and cooling water were fed through a cable bundle. The umbilical cabling system, which is enclosed in a flexible braided metal sleeve, is driven by a motorized spool. To increase cathode lifetime, movable magnet package was developed, and thickest possible cathode was made, with a rather challenging target to substrate distance of less than 1.5 cm. Optimized process to ensure excellent adhesion was developed. Coating adhesion of 10  $\mu\text{m}$  Cu passed all industrial tests and even exceeded maximum capability of a 12 kg pull test fixture. Details of experimental setup for coating two types of bellows and a full-scale magnet tube sandwiched between them will be presented. Room temperature RF resistivity measurement indicated that 10  $\mu\text{m}$  Cu coated stainless steel RHIC tube has conductivity close to copper tubing. Work is in progress to repeat the RF resistivity measurement at cryogenic temperatures. Plans are to develop techniques for in situ coating of elliptical and other surface contour RF cavities and long beam pipes with thick superconducting films.

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**TF-TuP5 Ultrasound Influence on the Si-SiO<sub>2</sub> System Defects Structure**, *Daniel Kropman*, Tallinn University of Technology, Estonia, *T. Laas*, Tallinn University, Estonia

The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO<sub>2</sub> system by means of electron spin resonance (ESR), selective etching, MOS capacitance technique and secondary ions mass-spectroscopy (SIMS) is presented.[1,2]. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. The influence of the UST on the Si-SiO<sub>2</sub> interface properties depends on the oxide thickness and crystallographic orientation. The density of point defects and absorbed impurities at the Si-SiO<sub>2</sub> interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. UST is widely used in medicine, not only for diagnostic, but for cancer treatment too. UST influence on inorganic and organic materials have common properties. These allow to suggest that UST may be used in biotechnology for materials properties modification.

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**TF-TuP6 Fabrication of Transparent Superhydrophobic Surface by Single, Multi-Step and Gas Mixture Method Using CH<sub>4</sub>/C<sub>4</sub>F<sub>8</sub>/He Atmospheric Pressure Plasma**, *Duksun Han, S.Y. Moon*, Chonbuk National University, Republic of Korea

Superhydrophobic surface was prepared by CH<sub>4</sub>/C<sub>4</sub>F<sub>8</sub>/He atmospheric pressure plasma. Single step and multi-step processes using CH<sub>4</sub> and C<sub>4</sub>F<sub>8</sub> precursors are performed to investigate evolution of a transparency and wettability. In case of the single step process, a surface modification using C<sub>4</sub>F<sub>8</sub> showed high water droplet contact angle (WCA) relative to the CH<sub>4</sub> plasma treatment due to a difference of surface free energy. On the other hand, the contact angle was remarkably increased to 152°, indicating superhydrophobic property, using sequential multi-step CH<sub>4</sub> and C<sub>4</sub>F<sub>8</sub> plasma treatment. Also, a rapid single-step method using a He, CH<sub>4</sub>, and C<sub>4</sub>F<sub>8</sub> mixture plasma was performed. In this case, WCA was gradually increased to 170° and the transparency was decreased when the gas ratio of C<sub>4</sub>F<sub>8</sub> to the total flow rate was increased. The chemical and physical mechanism responsible for hydrophobicity by atmospheric pressure plasma is discussed through the investigation of chemical composition and surface morphology using a FTIR, XPS, SEM and AFM.

**TF-TuP7 Influence of the Transfer and Chemical Treatment of CVD(Chemical Vapor Deposition) Graphene for Flexible Transparent Electrodes**, *Y. Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea, *H. Kim*, Korea Electronics Technology Institute, *WooSeok Yang*, Korea Electronics Technology Institute, Republic of Korea

It has become critically important to develop reliable method to transfer chemical vapor deposited (CVD) graphene from its growth substrate to the target substrate without leaving undesired polymer residues on the graphene surface. Here, we have found that for the two different transfer method – wet transfer using poly(methyl methacrylate) (PMMA) and dry transfer using polydimethylsiloxane (PDMS) as support layer, the amount of polymer residues and other impurities left on the graphene surface varies depending on the solvent used to remove those polymers. The exposure of the graphenes to different organic solvents such as acetone and chloroform resulted in different amount of polymer residues and impurities present on the graphene surface, which impact the electronic structure of the transferred graphene. It was found that the graphene obtained using the dry transfer method and acetone as solvent showed a 2D to G (I<sub>2D</sub>/I<sub>G</sub>) intensity ratio of 4.58 and a 2D peak full width-half maximum (FWHM) of 24.66, which was higher than that using the wet transfer method and chloroform as solvent. These results showed that graphene was less affected by the polymer residues and impurities for the dry transfer method rather than the wet transfer method. In addition, using acetone rather than chloroform as solvent in the dry transfer method led to less contaminated graphene.

**TF-TuP8 A Study on Amorphous InGaZnO Thin Film Transistor with Wet Etched Copper/Molybdenum Alloy Electrode**, *JongHyun Seo, J.-H. Jeon, H.H. Choe, J.H. Yoon*, Korea Aerospace University, Republic of Korea, *H.-S. Kim*, Korea Aerospace University

We fabricated the back channel etch type copper/molybdenum alloy/Indium gallium zinc oxide thin film transistors using only wet patterning in phosphoric acid based copper etchant. Compared with pure molybdenum S/D electrode, New Mo alloy electrodes showed better TFT performances both in mobility and on current. The mobility was increased by 50% and on current increased up to 100% compared to those of pure molybdenum electrodes. Little is known about the effect of S/D electrode material on the electrical properties of amorphous IGZO oxide TFTs.

A modeling based on the reduced elastic strain energy by reduction in biaxial elastic modulus of the Mo alloy film is proposed to explain enhanced electrical properties of Cu/Mo alloy/IGZO TFT. The effects of alloy percentage in the alloy, chemical additives on the electrical properties of back channel etch type Cu/Mo alloy/IGZO oxide TFTs were investigated using surface analysis and electrochemical methods.

**TF-TuP9 Synchrotron Radiation Photoelectron Spectroscopy Study on Surface Oxidation of Ge(100) and Ge(111) at Room Temperature**, *Akitaka Yoshigoe*, Japan Atom Energy Agency, Japan, *R. Okada*, University of Tsukuba, Japan, *Y. Teraoka*, Japan Atomic Energy Agency, Japan, *Y. Yamada*, University of Tsukuba, Japan, *M. Sasaki*, University of Tsukuba, Japan

Germanium (Ge) has been interesting as future substitute channel material for metal-insulator-semiconductor field-effect-transistors (MISFETs) because of its high carrier mobility. Although precise controlling of the surface oxide layer of Ge surfaces is important for fabrication of dielectric/Ge interface in Ge-based devices, fundamental aspects of

oxidation reaction at Ge single crystal surfaces and nature of the oxide monolayer have not yet been well understood. In this presentation, we report the nature of oxides of Ge(100)-2×1 and Ge(111)-c(2×8) surfaces fabricated with pure oxygen gas (O<sub>2</sub>) at 300 K. Surface oxide and its evolution from very initial stages to the maximum oxide coverage were measured by real-time photoelectron spectroscopy using synchrotron radiation. All experiments were conducted with SUREAC2000 at BL23SU in Spring-8. We found the saturation oxide coverage on both surfaces is less than one monolayer. We found that initial sticking coefficient of O<sub>2</sub> was much smaller than that for Si(100). SR-XPS measurements demonstrated that the maximum oxidation number of Ge in saturation region was as small as 2+, which exhibits a strong contrast to the case of Si where 4+ state is spontaneously formed. Our results suggest that native oxides layer with Ge<sup>4+</sup> cannot be formed only with pure O<sub>2</sub> gas. Our findings reveal the significant difference between the nature of surface oxides of Ge and Si and can be useful for a precise control of oxide layer on Ge surfaces.

This research was partially supported by grants-in-aid from the Ministry of Education, Cultures, Sports, Science and Technology, for Exploratory Research, No. 26420289. The synchrotron radiation experiments were performed at the BL23SU of Spring-8 with the approval of JASRI (Proposal No. 2007B3802, 2008A3804, 2008B3804, 2009A3804, 2011A3804, 2011B3802, 2012A3802, 2012B3802, 2013A3802, and 2013B3802).

**TF-TuP10 Effect of Al Doping on Crystallization and Electrical Property of CeO<sub>2</sub> Films Deposited by RF Magnetron Sputtering.** *Keiji Ishibashi*, COMET Inc., Japan, *T. Okazaki, H. Kamata, Y. Notani, K. Hara, T. Osawa, K. Aoki, K. Fujiyama*, Hosei University, Japan, *S.-G. Ri, S. Suzuki*, COMET Inc., Japan, *Y. Yamamoto*, Hosei University, Japan

To suppress crystallization of CeO<sub>2</sub> thin films as a gate stack material in MOS devices, Al was doped in CeO<sub>2</sub> films during radio frequency (RF) magnetron sputtering deposition on p-type Si (100) substrates. Deposition was carried out at room temperature in an Ar atmosphere of 5.3 Pa to a typical thickness of 35 nm using a CeO<sub>2</sub> target on which some Al metal plates were bonded. The composition of the resultant deposited films measured by X-ray photoelectron spectroscopy was Ce<sub>0.28</sub>Al<sub>0.06</sub>O<sub>0.66</sub>, equivalent to (CeO<sub>2</sub>)<sub>0.9</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>0.1</sub> in terms of the molar fraction. The post annealing was performed in air and N<sub>2</sub> in the temperature range from 200 to 600°C. Addition of aluminum oxide with 10% molar fraction into CeO<sub>2</sub> during sputter deposition was effective in suppressing crystallization. The deposited films remained amorphous after annealing up to 500°C from observation of X-ray diffraction and transmission electron diffraction. The interfacial SiO<sub>2</sub> layer was grown after annealing in both ambients of air and N<sub>2</sub>. While after annealing in air the interface consisted of a simple double layer of CeO<sub>2</sub>/SiO<sub>2</sub>/Si, a lower oxide such as Ce<sub>2</sub>O<sub>3</sub> was formed between CeO<sub>2</sub> and SiO<sub>2</sub> in an N<sub>2</sub> annealing ambient. The leakage current measured at the applied electric field of 1 MV/cm (gate voltage=3.5 V) was decreased to as low as the order of 10<sup>-8</sup> and 10<sup>-7</sup> A/cm<sup>2</sup> after annealing at 200°C in air and N<sub>2</sub>, respectively. The C-V hysteresis of the samples annealed in air was broadened with the increase of annealing temperature. Annealing in N<sub>2</sub> reduced C-V hysteresis in contrast to air annealing, but appearance of a kink and gradual slope in the depletion state on its C-V curves suggested the existence of a large amount of shallow states originated from the lower Ce oxide at the interface. The flat band voltage after annealing was shifted toward higher gate voltages due to the fixed negative charge arising from Al oxides. The Al doping in CeO<sub>2</sub> was effective in suppressing crystallization of CeO<sub>2</sub> films, but introduced complicated behavior in I-V and C-V electrical characteristics, while in the non-doped CeO<sub>2</sub> films electrical neutrality of the interfacial lower Ce oxide (Ce<sub>2</sub>O<sub>3</sub>) was maintained and led to relatively simple behavior in electrical characteristics.

**TF-TuP11 Electrical and Crystallization Properties of Al Doped CeO<sub>2</sub> Thin Films Deposited by Reactive RF Sputtering with O<sub>2</sub> Introduction.** *Takashi Osawa, Y. Notani, K. Hara, K. Aoki, K. Fujiyama*, Hosei University, Japan, *K. Ishibashi, S. Suzuki*, COMET Inc., Japan, *Y. Yamamoto*, Hosei University, Japan

Cerium dioxide is one of the materials of interest as a gate stack in metal-oxide-semiconductor (MOS) devices. CeO<sub>2</sub> is likely to crystallize, however, leading to the possible increase of the leakage current. To suppress crystallization of CeO<sub>2</sub> thin films, Al was doped in CeO<sub>2</sub> films during deposition using RF magnetron sputtering using CeO<sub>2</sub> target on which Al plates were bonded with the applied RF power of 50 W at room temperature at a pressure of 5.3 Pa. The deposition was carried out with and without O<sub>2</sub> introduction in order to investigate the influence of oxygen deficiency in the deposited film. The deposition time was adjusted so as to obtain the typical thickness of CeO<sub>2</sub> films of 35 nm since the deposition rate decreased with increasing the O<sub>2</sub> flow rate varying as 0, 2, 5 and 10%. The post annealing was performed in an N<sub>2</sub> atmosphere in the temperature range from 200 to 600 °C.

The electrical properties after annealing were characterized by I-V and C-V measurements using the Hg probe as an electrode. Irrespective of the

amount of O<sub>2</sub> introduction, the leakage current at 3 MV/cm was minimized around 1.0×10<sup>-7</sup> A/cm<sup>2</sup> after annealing at 200 °C. After annealing at 400 °C, the leakage current increased by 3 orders of magnitude. For the sample annealed at 600 °C, the leakage current was recovered to the level of the as-deposited sample. The dielectric constant was increased with increasing amount of introduced O<sub>2</sub>. It tended to increase with increasing annealing temperature, but exceptionally decreased after annealing at 400 °C. The C-V characteristic represented the kink or even the step in the depletion region for sample annealed at 400 °C. The flat band voltage was shifted toward higher gate voltage with increasing annealing temperature, probably due to the fixed negative charge arising from Al oxides. The fact that the C-V hysteresis was broadened with the increase of introduced O<sub>2</sub> implied that the existence of Al oxide in the film enhanced the generation of the interfacial states.

In the X-ray diffraction spectrum, the as-deposited samples represented strong CeO<sub>2</sub> and weak Ce<sub>2</sub>O<sub>3</sub> peaks when the amount of introduced O<sub>2</sub> flow ratio was 0 and 2% while Ce<sub>2</sub>O<sub>3</sub> peaks almost disappeared with the O<sub>2</sub> introduction above 5%. After annealing at 200 – 600 °C the peak other than CeO<sub>2</sub> was not observed. Judging from the electron diffraction image obtained from the fast Fourier transform (FFT) processing of high resolution transmission electron microscope image, CeO<sub>2</sub> crystalline structure appeared to be destroyed due to the transition to another phase after annealing at 400 °C.

**TF-TuP15 Atomically-resolved Orientational Ordering of C60 Molecules on Epitaxial Graphene on Cu(111).** *M. Jung, D. Shin, S.-D. Sohn, S.-Y. Kwon, N. Park*, UNIST, *Hyung-Joon Shin*, UNIST, Republic of Korea

The interaction between molecular adsorbates and graphene is one of the fundamental issues for tailoring the properties of graphene-based molecular devices, because the electronic and structural properties of molecular layers on surfaces are determined by intermolecular and molecule-substrate interactions. Here, we present the atomically resolved experimental measurements of the self-assembled fullerene molecules on single-layer graphene on a Cu(111). Fullerene molecules form a (4 × 4) superstructure on graphene/Cu(111), revealing only single molecular orientation. We can resolve the exact adsorption site and the configuration of fullerene by means of low-temperature scanning tunnelling microscopy (LT-STM) and density functional theory (DFT) calculations. The adsorption orientation can be explained in terms of the competition between intermolecular interaction and molecule-substrate interaction, where strong Coulomb interactions among the fullerenes determine the in-plane orientation of the fullerene. Our results provide important implications for developing carbon-based organic devices using a graphene template in future.

**TF-TuP17 Novel Fabrication of Flexible Graphene-based Chemical Sensors with Heaters using Soft Lithographic Patterning Method.** *Jongsun Lim*, Korea Research Institute of Chemical Technology, Republic of Korea

We have fabricated graphene-based chemical sensors with flexible heaters for the highly-sensitive detection of specific gases. We believe that increasing the temperature of the graphene surface significantly enhanced the electrical signal change of the graphene-based channel, and reduced the recovery time needed to obtain a normal state of equilibrium. In addition, a simple and efficient soft lithographic patterning process was developed via surface

energy modification for advanced, graphene-based flexible devices, such as gas sensors. As a proof of concept, we demonstrated the high sensitivity of NO<sub>2</sub> gas sensors based on graphene nanosheets. These devices were fabricated using a simple soft-lithographic patterning method, where flexible graphene heaters adjacent to the channel of sensing graphene were utilized to control graphene temperature.

**TF-TuP18 Field-induced Confinement and Quantum Transport in Graphene.** *Satoshi Moriyama*, National Institute for Materials Science, Japan, *Y. Morita*, Gunma University, Japan, *E. Watanabe, D. Tsuya*, National Institute for Materials Science, Japan

**Field-induced Confinement and Quantum Transport in Graphene**

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Graphene consists of a single atomic layer of carbon atoms and has provided a new stage for studying low dimensional physics. The corresponding energy dispersion adopts the so-called Dirac cone, which leads to a massless Dirac-particle and relativistic quantum physics in a condensed matter. From the application point of view, the ballistic transport and high mobility in graphene make them possible candidates for future nanodevices, such as integrated quantum-dot (QD) devices. However, confining massless Dirac fermions in graphene is difficult due to Klein tunneling and the zero-band-gap electronic structure. Therefore, although attempts have been made to design graphene QD devices, they often suffer from severe design limitations. They basically consist of small QD islands, which confine electrons geometrically, to which narrow graphene-constrictions are connected. We have also demonstrated double QD devices, which exhibits single-electron transport of two lateral QDs coupled in series [1]. In this case, the device performance has been limited due to detailed constriction and edge orientation. It is crucially important to develop other methods of creating graphene nanostructures and control the constrictions.

In this paper, we report an alternative approach to confine the massless carriers in graphene, in which graphene mesoscopic structures are perfectly isolated and metallic contacts are directly deposited onto them without constrictions. We show an experimental demonstration of a magnetic-field-induced quantum confinement in the graphene device. There are several theoretical scenarios for field-induced confinement of massless Dirac fermions, such as the confinement by inhomogeneous magnetic fields. Here, the confinement in our device is induced by both a uniform magnetic field perpendicular to the graphene sheet and an electrostatic surface-potential formed by the metal/graphene junction. Our experimental results indicate that a quantum confinement–deconfinement transition is controlled by the magnetic field [2].

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#### **TF-TuP19 Enhanced Electrical Properties of Patterned Graphene-Embedded Indium Tin Oxide Transparent Conductive Electrode, Shin Kim, J.K. Kim, J.M. Lee, Sunchon National University, Republic of Korea**

Graphene has attracted a great attention by many researchers in terms of its interesting electrical, optical, and mechanical properties [1]. Furthermore, graphene has showed potential applications such as photovoltaics [2] and optical device [3] as well as transparent electrode[3]. This paper reports the deposition of graphene-embedded indium tin oxide (ITO). Specially, we will show a patterning of graphene which was embedded in ITO will enhance the electrical and optical properties of ITO. ITO films with a thickness of 50 nm were deposited on Corning glass substrate by direct current magnetron sputtering method using an ITO target at room temperature. The graphene samples employed in this work were grown on Cu foils by thermal chemical vapor deposition method. The graphene was transferred to ITO and then patterned with line shape (3um and 12um, respectively) using photoresist. After the dry-etching by using O<sub>2</sub> plasma, ITO was deposited on the patterned graphene again. The sheet resistance and resistivity of the sample were recorded with each fabricating steps. The sheet resistance of ITO film with a thickness of 100 nm showed a 92 ohm/sq. ITO film that the sheet of graphene was embedded in showed a decreased resistance of about 80 ohm/sq. On the other hand, the sheet resistance of ITO films that patterned graphene embedded in was significantly decreased to as low as about 51 and 49 ohm/sq for 3 um and 12 um line shaped graphene embedded ITO, respectively.

In this presentation, we will report the detailed results and mechanism about the enhanced electrical properties of the graphene embedded ITO films.

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#### **TF-TuP20 Evaluation of Diamond-Like Carbon Films that Enable Observation of Living Cells by Electron Microscopy, Tomotaka Kozuki, Hiroshima International University, Japan, N. Nawachi, Hiroshima Prefectural Technology Research Institute**

In conventional scanning electron microscopy (SEM), the specimen to be observed must be placed in a vacuum. Consequently, observation of living cells has been extremely difficult. In recent years, a method has been proposed to solve this problem and enable observation of samples under atmospheric pressure. In this method, observation in air is accomplished by introducing an electron beam into air from an electron gun located in a vacuum by using silicon nitride (SiN) as an electron transmission film that separates the vacuum and air. However, the resolution is not entirely satisfactory. We therefore noted that diamond-like carbon (DLC) films, in

which the primary constituent is carbon, offer both excellent electron transmissivity and sufficient strength to withstand atmospheric pressure.

An electron transmission film that uses DLC was fabricated by forming a DLC film on a silicon (Si) substrate and then etching the Si component from the back side[1]. We compared the electron transmissivity of a DLC film fabricated by this method with commercial SiN. For a 200-nm-thick DLC film, transmission started at an accelerating voltage of 3 keV, with over 95% of electrons being transmitted at 8 keV. For a SiN film of the same thickness, although transmission started at an accelerating voltage of 4 keV, an accelerating voltage of over 15 keV was required in order to reach a transmissivity of 95%. Furthermore, at an accelerating voltage of 12 keV, the transmissivity was approximately 75% for both a 500-nm-thick SiN film and a 1- $\mu$ m-thick DLC film, showing that a DLC film of approximately twice the thickness of a SiN film could achieve electron transmissivity of 75%.

Next, a 1- $\mu$ m-thick DLC film or a 500-nm-thick SiN film was used as the electron transmission film for observation of a metal mesh by SEM. Although the electron transmissivity was virtually the same at the accelerating voltage of 12 keV, the image obtained when using the DLC film was significantly clearer. This is attributed to the DLC consisting of lighter elements, and thus producing less electron scattering in the film. By using these characteristics of DLC electron transmission films, we succeeded in observing yeast under atmospheric pressure at 10,000 $\times$  magnification by SEM.

By using a DLC film as an electron transmission film, we thus succeeded in obtaining clearer images at lower accelerating voltages as compared with existing electron transmission films. Taken together, the results of this study suggest tremendous potential for the use of DLC films in medicine, particular for biopsy.

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#### **TF-TuP21 Chemistry of Active Oxygen in RuO<sub>x</sub> and Its Influence on the Atomic Layer Deposition of TiO<sub>2</sub> Films, Woojin Jeon, W. Lee, C.H. An, M.J. Chung, C.S. Hwang, Seoul National University, Republic of Korea**

Atomic layer deposition (ALD) is a highly intriguing thin-film growth technique with self-regulating and self-terminating properties due to the saturated chemical reactions between the adsorption sites and the chemically adsorbing precursor molecules. In such ALD processes, the substrate plays a crucial role by taking part in the ALD-specific chemical reactions. The surface of the substrate must provide the chemical adsorption sites, which would anchor the incoming metal or non-metal precursors via the ligand exchange reactions. There are other cases, however, where the oxygen ions (or atoms) inside the bottom layer film play the crucial role in the film growth. Typical example is Ru (and RuO<sub>2</sub>), which are the material of choice as the capacitor electrode in futuristic DRAM. Recent reports on the inducing of rutile phase formation in the atomic layer deposition (ALD) of TiO<sub>2</sub> films, which have the highest dielectric constant among the binary dielectric oxides, by adopting Ru or RuO<sub>2</sub> as the bottom electrode invokes an even higher interest in this material. While both Ru and RuO<sub>2</sub> electrode have similar electrical properties, the initial stage of deposition of TiO<sub>2</sub> film by ALD exhibited quite different behavior on each substrate due to their different oxygen contents. In this study, the initial growth behavior of ALD TiO<sub>2</sub> film on Ru and RuO<sub>2</sub> substrate with various oxygen contents has been investigated in a greater detail, which has not been explored previously. Ru, RuO<sub>x</sub> ( $x \sim 1$ ) and RuO<sub>2</sub> films were grown by the cycling pulsed chemical vapor deposition process at a substrate temperature of 230 °C using RuO<sub>4</sub> and H<sub>2</sub>(5%)/N<sub>2</sub>(95%) as the Ru-precursor and reducing agent. The phase control was achieved by controlling the injection time of H<sub>2</sub>(5%)/N<sub>2</sub>(95%) gas for the given RuO<sub>4</sub> injection condition.

It was found that the growth per cycle of TiO<sub>2</sub> at the initial growth stage was drastically increased on RuO<sub>x</sub> (RuO<sub>2</sub>/Ru mixture) compared to Ru and even RuO<sub>2</sub>, although it has been reported that higher oxygen content film (RuO<sub>2</sub>) promotes the initial growth of TiO<sub>2</sub>. This is attributed to the drastic increase in the chemical activity of oxygen in the mixture film of RuO<sub>2</sub>/Ru. The catalytic decomposition of RuO<sub>2</sub> with the help of Ru in the film played the crucial role for the increase in the active oxygen. While RuO<sub>2</sub> and Ru mostly retained their structures during the ALD of TiO<sub>2</sub> or chemical etching using O<sub>3</sub> gas, the RuO<sub>x</sub> film, which was composed of 56% RuO<sub>2</sub> and 44% Ru, drastically changed its phase composition during the ALD of TiO<sub>2</sub> at 250 °C and became almost Ru. Other chemical effects depending on the chemical composition and phase structure were also examined in detail.

**TF-TuP22 Effects of Double Active Layer and Acetic Acid Stabilizer on the Electrical Properties of Solution-processed Zinc Tin Oxide Thin Film Transistor.** *Jihun Shin, S.J. Kim, S.S. Ha, Y.J. Im, C.H. Park, M.S. Yi*, Pusan National University, Republic of Korea

We investigated the effect of double active layer and acetic acid stabilizer for zinc tin oxide thin film transistor (TFTs) fabricated using solution processes.

Double active layer was composed of two layers made by ZTO solution doped with different Sn concentration (Sn 30 atomic % or Sn 60 atomic %). ZTO solutions were synthesized by dissolving zinc acetate dehydrate and tin chloride dehydrate which were dissolved in 2 different stabilizer solutions. AA solution was prepared with 2-methoxyethanol added with acetic acid, where ME solution was prepared with 2-methoxyethanol added with mono-ethanolamine. Thus the AA-ZTO films and ME-ZTO films represent ZTO active layer films formed from AA solution and ME solution, respectively.

The bottom-gate TFTs were fabricated on highly doped n-type silicon wafer which is covered with 200nm SiO<sub>2</sub> layer as a gate insulator. Bottom active layer of ZTO film was deposited on the gate oxide layer by spin-coating the solution at room temperature, drying at 300 °C for 10 min, and the top active layer of ZTO film was made on the bottom ZTO film by same method and then annealing at 500 °C for 60 min. Fig. 1 shows the schematics of the double active layer ZTO TFT.

By adding acetic acid into the stabilizer solution instead of commonly used mono-ethanolamine, electrical performance of ZTO TFTs is enhanced. The XPS and TG-DTA(thermogravimetry differential thermal analysis) data shown in Fig. 2 and 3, have demonstrated that acetic acid plays a role in lowering decomposition temperature and reducing hydroxyl groups in the film.

By using double active layer (bottom layer: Sn 60 at. %, top layer: Sn 30 at. %) in ZTO TFTs, the electrical performance is enhanced. We demonstrated that the bottom active layer supplied electron carriers easily from high Sn concentration, and the top ZTO layer suppressed the leakage current of TFTs because it has relatively lower carrier concentration than the bottom ZTO layer.

The best performances were obtained at Sn concentration of 60 at. % in bottom ZTO layer and 30 at. % in top ZTO layer with the added acetic acid as a stabilizer, where the ZTO TFT exhibited an on/off ratio of  $1.1 \times 10^9$ , a saturation mobility of  $5.04 \text{ cm}^2/\text{V}\cdot\text{s}$ , a subthreshold slope of 0.11 V/decade, and a threshold voltage of 1.6 V. Fig. 4 depicts the transfer curves of the TFTs and the summarized electrical parameters of the ZTO TFTs were shown in Table 1.

**TF-TuP23 Effect of Ge Concentration on Electrical Performance of Ge-doped InZnO thin-film transistor.** *Yongjin Im, J.H. Shin, S.J. Kim, S.S. Ha, C.H. Park, M.S. Yi*, Pusan National University, Republic of Korea

We fabricated amorphous oxide semiconductor thin-film transistors (TFTs) using GeO<sub>2</sub>-doped InZnO (Ge-IZO) thin films as active-channel layers. The Ge-IZO thin films were deposited at room temperature by radio-frequency (RF) magnetron co-sputtering, and then annealed in air for 1 h at 300°C. Some processing parameters such as sputtering oxygen partial pressure [O<sub>2</sub>/(Ar + O<sub>2</sub>)] and sputtering power for GeO<sub>2</sub> target were changed to investigate what was the optimal amount of Ge in the Ge-IZO active layer.

The cross-sectional schematic of Ge-IZO TFT and a FE-SEM image of Ge-IZO thin film studied in this paper are shown in Fig. 1, and the electrical performance of Ge-IZO TFT is compared with IZO TFT in Fig. 2.

A small concentration of Ge added to IZO by co-sputtering with less than 5W of GeO<sub>2</sub> target power enhanced the saturation mobility  $\mu_{\text{sat}}$ . The decrease of  $\mu_{\text{sat}}$  at high power of GeO<sub>2</sub> target in Fig. 2 was caused by the increased disorder in case of the high power of GeO<sub>2</sub> target. Threshold voltages ( $V_{\text{th}}$ ) in Fig. 2 increases with increase in GeO<sub>2</sub> target power until 20W; thereafter, it decreases. This result should be inversely related to the carrier concentration, which indicates that a small concentration of Ge can lead to retention of its strong bonding with oxygen, thereby suppressing the excessive oxygen vacancies. This is the reason why  $V_{\text{th}}$  increases. Higher Ge-concentration can lead to the greater disorder and this explains why  $V_{\text{th}}$  decreases with increase in Ge concentration.

The device performance was better when low concentration of Ge is incorporated to IZO than with pure IZO or high Ge concentration. In order to optimize the electrical properties of Ge-IZO TFTs, we tried to adjust the processing parameters and the best Ge-IZO TFT was obtained at a co-sputtering oxygen partial pressure of 2% and GeO<sub>2</sub> target power of 10 W.

The fabricated Ge-IZO TFT exhibited an on/off ratio of  $3.0 \times 10^7$ , a saturation mobility of  $13.6 \text{ cm}^2/\text{V}\cdot\text{s}$ , a subthreshold swing of 0.98 V/dec, and a threshold voltage of -0.8 V. XPS and XRD analyses of Ge-IZO films were performed to investigate the binding energies of atoms in Ge-IZO films and the crystallinity of the films, and a 90% transmittance of visible

light was achieved, which makes the technology useful for transparent devices.

**TF-TuP24 Active Multiband Terahertz Metamaterial Spatial Filters Based on Vanadium Dioxide Thin Films.** *Han-Cheol Ryu*, Sahmyook University, Republic of Korea, *J.-H. Shin, K.H. Park*, ETRI

This work presents the design, fabrication and terahertz performance of active multiband metamaterial spatial filters based on vanadium dioxide (VO<sub>2</sub>) thin films. VO<sub>2</sub> thin films were deposited on Al<sub>2</sub>O<sub>3</sub> (0001) substrates by the pulsed laser deposition method. Epitaxial relations between VO<sub>2</sub> thin films and Al<sub>2</sub>O<sub>3</sub> (0001) substrates were investigated using X-ray diffraction measurement and transmission electron microscopy observations. The multiband terahertz metamaterial spatial filters, which are artificial electromagnetic structures, can manipulate electromagnetic response at desired frequency bands. They were designed by electromagnetic simulator and fabricated on VO<sub>2</sub> thin films which are phase transition materials due to their insulator-metal transition at a critical temperature. The terahertz characteristics of the fabricated active filters were controlled by electric bias or temperature variation. The tunable frequency responses of the devices were measured by using terahertz time-domain spectroscopy (THz-TDS) system. The measured tunable characteristics of the active terahertz filters based on VO<sub>2</sub> thin films clearly show the possibility for the various tunable terahertz applications such as modulators, filters, and sensors.

**TF-TuP26 Enhancement of SiO<sub>2</sub>/4H-SiC Interface Properties using ALD Oxides and Nitridation.** *Changhyun Kim, S. Lee, H. Lee, H. Kim, H.J. Kang, H.J. Kim*, Seoul National University, Korea, Republic of Korea

4H-SiC is a promising wide band gap material which has excellent properties such as high breakdown voltage, high thermal conductivity, and high saturation drift velocity. These characteristics enable 4H-SiC to be used in difficult environments for Si such as processes require high power, high current, high temperature. It also has an advantage in fabrication process because of its native SiO<sub>2</sub> from thermal oxidation. However, carbon components are inevitably produced during oxidation, causing high SiO<sub>2</sub>/SiC interface state density ( $D_{\text{it}}$ ) and low channel mobility. The nitridation using NO or N<sub>2</sub>O gas is an effective way to lower  $D_{\text{it}}$  and near interface trap density of a SiO<sub>2</sub>/4H-SiC interface.

In this work, we prepared the atomic layer deposited (ALD) SiO<sub>2</sub> with NO post oxidation annealing (POA) to avoid interface oxidation and improve interface properties. We also compared electrical properties of NO POA treated ALD SiO<sub>2</sub> with thermally grown oxides with/without NO POA. The NO POA treated ALD SiO<sub>2</sub> showed much lower  $D_{\text{it}}$  than thermally grown oxides. Also, the metal-oxide-semiconductor (MOS) field effect transistor (FET) with the ALD SiO<sub>2</sub> showed high field effect mobility, especially in the high electric field region.

But these methods could not reach the sufficient passivation of the interface traps due to reoxidation by oxygen source of NO gas. Therefore, we employed thin ALD SiO<sub>2</sub> layer with NH<sub>3</sub> POA for nitridation without reoxidation. Because the NH<sub>3</sub> POA oxide had low breakdown field ( $E_{\text{b}}$ ), we adopted a stacked structure of ALD SiO<sub>2</sub> with NH<sub>3</sub> POA and ALD SiO<sub>2</sub> to exclude oxidation and to improve  $E_{\text{b}}$ , respectively. Inert gas annealing or ozone treatment were used to reduce the defects of upper as-deposited SiO<sub>2</sub>. Oxygen vacancies, a major defect of as-deposited oxide, were effectively reduced by the O<sub>3</sub> treatment. The ALD SiO<sub>2</sub> with NH<sub>3</sub> POA lowered C-V hysteresis and increased the slope of C-V curve, indicating that it reduces the interface defects. It also had low  $D_{\text{it}}$  which might be caused by the suppression of reoxidation. The O<sub>3</sub> treatment increased  $E_{\text{b}}$  effectively, but it did not reach  $E_{\text{b}}$  of thermally grown oxide yet.

In conclusion, ALD oxides with proper nitridation process improved the field effect mobility of MOSFET more effectively than thermal one through decreasing  $D_{\text{it}}$  induced by carbon component at the SiO<sub>2</sub>/4H-SiC interface. The NH<sub>3</sub> POA instead of NO POA showed low  $D_{\text{it}}$  by suppressing of reoxidation, but low  $E_{\text{b}}$  problem remains. The O<sub>3</sub> treated upper ALD SiO<sub>2</sub> increased  $E_{\text{b}}$  maintaining low  $D_{\text{it}}$ .

**TF-TuP27 Molecular Beam Epitaxy and Characterization of Cubic-Phase InN and GaN Films.** *Maximo Lopez-Lopez*, Physics Department, Cinvestav-IPN, Mexico

Group-III nitrides have become one of the most important semiconductor materials in the field of optoelectronic and microelectronic devices. Recently, great interest in III-nitrides with cubic phase has risen due to the absence of built-in electric fields, which can limit the performance of devices. However, the cubic-phase in III-N semiconductors is metastable and can only be grown in a narrow window of conditions. Under non-optimum conditions phase mixing between the metastable cubic (c) and stable hexagonal phases (h) may occur. In this work we present the growth of c-InN films on GaAs(001) substrates using conventional molecular beam epitaxy (MBE) and migration enhanced epitaxy (MEE) techniques. Also, we presented the growth of c-GaN films on GaAs(001) substrates by

conventional MBE, using during the nucleation of c-GaN an As overpressure at different substrate temperatures. In order to promote the formation of c-InN, an InN nucleating layer by alternated deposition of In and N was carried out at a growth temperature ( $T_g$ ) of 380 °C. After the growth of the nucleating layer, c-InN films were grown using one of the two methods: 1) conventional MBE growth, where the growth surface is exposed simultaneously to both elements In and N and, 2) MEE growth, that proceeds by alternated periods of In and N of 5 s each one. Employing these two methods, different samples were prepared by varying  $T_g$  and the flux of In atoms. On the other hand, we found that the use of an As overpressure during the nucleation of c-GaN plays a very important role in the enhancement of crystalline quality and surface morphology of GaN films. We present structural and morphological properties of the films and the dynamics of growth analyzed by reflection high-energy electron diffraction (RHEED). We achieved to grow InN and GaN with cubic phase, as confirmed by RHEED, X-ray diffraction and transmission electron microscopy (TEM). For the growth of c-InN the better structural properties and higher cubic phase purity were obtained by the MEE technique. For the growth of c-GaN, we found that the films nucleated at 600 °C present low roughness and the best crystalline quality with a small incorporation of the hexagonal phase, which was identified by reciprocal space maps (RSM) and TEM.

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**TF-TuP28 Degradation of Phosphorescent Organic Light Emitting Material by UV Exposure for Cathode Sputtering Process, Chan-Jae Lee, Korea Electronics Technology Institute (KETI), Republic of Korea, E.J. Um, M.G. Kwak, Korea Electronics Technology Institute (KETI)**

Organic light emitting diodes (OLEDs) have attracted great attention due to its advantages such as light weight, short response time, low power consumption, wide color gamut, wide viewing angle and high brightness in the area of display and lighting.

OLEDs have two electrodes, anode and cathode. Anode is fabricated by sputter and photolithography process but the cathode is deposited by thermal evaporation method with shadow mask. Thermal evaporation process with large size mother glass is difficult to obtain the uniform and high quality thin film. So to improve size and quality of OLED, various sputtering methods for cathode have been suggested.

Sputtering is a process whereby atoms are ejected from a target material due to bombardment of the target by energetic particles. This process can make the prolonged ion, plasma bombardment of a material and ultra violet (UV) radiation. Generally, organic materials are known as the very weak materials under plasma environment. Especially, bombardment has been pointed out a critical issues as it penetrates into the organic layer and breaks off the bonding of molecules. So, some researchers have suggested a facing target sputtering method that is the two targets are facing and substrate is placed in the vertical direction with two facing targets. So it is possible to reduce the damage of organic layer on the substrate, since the direction of the energetic ions can be changed.

Plasma also creates a cause UV radiation, which its influence against organic material is well known as make the quantum efficiency of organic materials to deteriorate. But in the facing target sputtering method, UV influence against emissive organic material is not known clearly yet.

In this study, we analyzed the degradation of phosphorescent emissive materials by UV exposure for cathode sputtering process. To make the environment of UV exposure, we placed the sample in RF sputtering system. And sample with phosphorescent emissive material, 1,3-Bis(N-carbazolyl)benzene (mCP) and tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>) were placed with different directions and distances from Al target. Farther the distance in the vertical direction of the target, damage is lower by UV. After Al deposition with 100nm thick, PL intensity of organic material by direction deposition is decreased by 70% compared to the sample without Al. But sample that is placed away from the target as much as 1.5 times of the length of the target and in vertical direction to target was reduced by 20% PL intensity. Also we analyzed the critical wavelength of UV radiation against phosphorescent emissive material mCP and Ir(ppy)<sub>3</sub>.

**TF-TuP30 Initial Stage Growth of GaAsSe layers on Sb-terminated Si(110) Surfaces by Metal-Organic Molecular Beam Epitaxy, M. Sato, Y. Suzuki, K. Miyazawa, K. Obara, Katsuhiko Uesugi, Muroran Institute of Technology, Japan**

We report on the heteroepitaxial growth of GaAsSe layers on Si(110) substrates by metal-organic molecular beam epitaxy (MOMBE). The growth process of GaAsSe was characterized by reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and transmission electron microscopy (TEM).

The dilute HF treated Si(110) substrates were thermally cleaned at 550-600°C for 20 min in a flow of the precursor trisdimethylaminoarsenic

(TDMAAs). Atomically flat Si(110) surfaces were successfully fabricated at substrate temperatures as low as 600°C under TDMAAs pressure. After the growth of 10nm-thick GaAsSe layers on TDMAAs-treated substrates, the surfaces were covered with high density dot structures, presumably due to the Stranski-Krastanov (S-K) growth mode. The diameter and density of GaAsSe dots were about 40nm and  $8 \times 10^{10} \text{ cm}^{-2}$ , respectively. As the GaAsSe thickness increases, the formation of giant dots and polycrystalline structures due to coalescence of S-K dots was observed. Then we investigate the influence of V/III flux ratio and the effect of Sb surfactant on the initial growth process of GaAsSe on Si(110) substrates. Polycrystallization of GaAsSe layers has been suppressed using the small V/III ratio of about 2. Furthermore, trisdimethylaminoantimony (TDMASb) treatment of As-terminated Si(110) substrate surfaces at 520°C greatly reduces the three-dimensional island growth due to the surfactant effect of Sb on the Si(110) surface.

**TF-TuP31 Characterization of Diamond-Like Carbon Prepared by High Power Impulse Magnetron Sputtering, Norio Nawachi, West Region Industrial Research Center, Hiroshima Prefectural Technology Research Institute, Japan, K. Itoh, Y. Isagi, West Region Industrial Research Center, Hiroshima Prefectural Technology Research Institute, K. Okamoto, Toyo Advanced Technologies Co., Ltd., Japan, T. Nakatani, Research Institute of Technology, Okayama University of Science, Japan**

Diamond-like carbon (DLC) has been considered as a coating for medical devices due to its biocompatibility. In particular, DLC coatings for dental implant made by titanium base alloy are useful as a means of providing high-hardness and a low-friction coefficient. Usually DLC films are deposited by cathodic arc (CA), plasma-enhanced chemical vapor deposition (PECVD), direct current (DC) or radio-frequency (RF) magnetron sputtering (MS). However, the problem is that DLC films deposited by CA show intrinsic growth defects (droplets). On the other hand, DLC films deposited by DC or RFMS can exhibit smooth surfaces, but adhesion strength of the films is a challenging issue [1, 2]. In recent years, a new magnetron sputtering technology named high power impulse magnetron sputtering (HiPIMS) has emerged. HiPIMS allows production of droplet free highly ionized metal flux generated from a sputter source [3, 4].

In this work, the characteristics of DLC films deposited by HiPIMS have been investigated. DLC films were prepared on silicon (Si) by HiPIMS and DCMS for comparison. Depositions were performed from a graphite target (200mm in diameter) operated at maximum power of 3 kW and at chamber pressure of 0.5 Pa. The same experimental arrangement was used for the DCMS depositions. The DLC films were analyzed by various methods.

In the HiPIMS discharge, the target voltage and peak current were approximately -900V and 200 A, respectively, at a repetition frequency of 1 kHz with a pulse width of 50 μs. The deposition rate in HiPIMS was approximately 50 % lower (23 nm/min) than that in DCMS. Mechanical properties of DLC films prepared by HiPIMS and DCMS will be presented and discussed.

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**TF-TuP32 UHV-STM Study on the Formation of Si(3 3 7)-4x1, Q. Qian, S. Song, Z. Zhang, L. Li, Yong-Zhe Zhu, Department of Physics, Yanbian University, Yanji city, 133000, China**

In the process of one-dimensional metal wire growth on the Si(5 5 12) surface with ultra-high vacuum scanning tunneling microscopy, Si(3 3 7)-4 × 1 structure is discovered. It is found that Si(3 3 7)-4 × 1 is a ultra stable structure with low defect density. It can be expected as a good template for nanostructure growth. However, up to now, there is no routine method to fabricate Si(3 3 7)-4 × 1. Therefore, it is necessary to study the formation reasons of Si(3 3 7)-4 × 1 surface and then fabricate this structure. The possibility is considered in two aspects: Firstly, is it induced only by high temperature annealing? Secondly, is it due to the residual C existed in the UHV-STM chamber? For this purpose, results from four experimental studies are analyzed: One is heating several kinds of Si(5 5 12) vicinal surface at high temperatures, and the others are adsorbing Ge, C<sub>2</sub>H<sub>2</sub>, and O<sub>2</sub> on Si(5 5 12)-2 × 1 surface, respectively. The orientation dependence of this kind of structural phase transition from Si(5 5 12)-2 × 1 to Si(3 3 7)-4 × 1 has been studied as well. To achieve this structural phase transition, an energy barrier needs to be overcome, and a large amount of atoms must be

moved to meet the orientation difference, which is performed by surface melting process via high temperature annealing. This phase transition has the orientation dependence but is not induced by the adsorption of carbon. This research was supported by the National Natural Science Foundation of China (Grant No. 10964014).

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**TF-TuP33 Etch Characteristics of Co<sub>2</sub>MnSi Thin Films in CH<sub>4</sub>/O<sub>2</sub>/Ar Plasmas,** *SuMin Hwang, A. Garay Dixon, J.H. Choi, C.W. Chung*, Inha University

In the semiconductor memory device field, for the next generation it is a big challenge to develop a memory device that has fast speed of read and write, high density of memory storage and non-volatility. Nowadays, Magnetic random access memory (MRAM), one of the possible candidates for non-volatile random access memory (NVRAM), has a received great deal of attention due to its several advantages.

Magnetic random access memory (MRAM) is a hybrid technology between a spintronic device and standard silicon-based microelectronics. Compared to commercial memory devices such as DRAM, SRAM and flash memory, based on charge storage, MRAM devices store data by employing the magnetoresistance effect. MRAM consists of a magnetic tunnel junction (MTJ) stack and a complementary metal-oxide semiconductor (CMOS). MTJ stack is an important part of the MRAM and it is composed of various magnetic materials, metals, and a tunneling barrier layer.

The etching of magnetic materials such as NiFe, NiFeCo, CoFe, CoFeB and FePt using halogen containing gas have been widely researched. However, halogen gases chemistries tend to produce non-volatile etch by products that can cause the corrosion of the magnetic materials after etching. Recently, Co<sub>2</sub>MnSi co-heusler alloy was used as a magnetic material because of high spin polarization and a high Curie temperature (~985K). Furthermore, several researches have reported that the etching of magnetic materials by C, H, O containing gases can produce a vertical etch profile with no post etching redeposition. Therefore, the etch characteristics of Co<sub>2</sub>MnSi thin films using C, H, O containing gas should be developed.

In this study, the etch characteristics of Co<sub>2</sub>MnSi thin films have been investigated in CH<sub>4</sub>/O<sub>2</sub>/Ar gas mixtures using an inductively coupled plasma reactive ion etching (ICPRIE). TiN thin films were applied as a hard mask to enhance the etch selectivity. The etch rates were obtained using surface profilometer and etch profiles were observed by using the field emission scanning electron microscopy (FESEM). The condition of plasma during process was employed by optical emission spectroscopy (OES).

**TF-TuP36 Crystallization of Biodegradable Poly-[(R)-3-Hydroxybutyrate] Ultrathin Films revealed by Surface-sensitive X-ray Diffractions: Effect of Small Amount of Biodegradable Poly(L-lactide)s with Different Molecular Weights,** *Naotaka Torimoto, N. Shimatani, R.R. Kumetha, I. Takahashi*, Kwansai Gakuin University, Japan

Biodegradable polymers synthesized by bacteria are environmental-friendly material. Poly-[(R)-3-hydroxybutyrate] (PHB) is one of the most intensively studied biological polymers and is also used to many applications. We investigated a new confinement effect of biodegradable poly(L-lactide) (PLLA) on crystallization of PHB ultrathin films with surface-sensitive X-ray diffractions in which PLLA with large molecular weight can reduce the crystallinity of PHB thin films effectively, although its mechanism is still not fully-understood. [1] In the present study, we expand our research in a wider range of molecular weight of PLLA as well as that of PHB, since controlling crystallinity, orientation of crystallographic axes with respect to the films surface and surface morphology of PHB thin films should be a key to controlling physical properties including thermal plasticity, brittleness and piezoelectric constant of PHB, that is quite favorable for a wider range of applications. Grazing incident X-ray diffraction (GIXD) and X-ray reflectivity (XR) are used to estimate degree of crystallization, thickness, electron density and surface roughness of polymer blend of PHB and PLLA spin-coated films deposited on silicon 100 wafers isothermally. Molecular weights of PHB were 1,000 and 650,000 g/mol, and those of PLLA were 2,000, 50,000, 100,000 and 300,000 g/mol, respectively for films with typical thicknesses of 30 nm.

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Keywords: biological polymer, polymer blend, crystalline polymer, X-ray surface diffraction, surface and thin films

**TF-TuP37 P3HT-based Multilayer Ultrathin Films Characterized with Surface-Sensitive X-Ray Scatterings –temperature and substrate dependence of crystalline structure-,** *Yusuke Shima, R. Iseiki, J. Takemoto, I. Takahashi*, Kwansai Gakuin University, Japan

Regioregular poly(3-hexylthiophene) (P3HT) has attracted significant interest as one of the promising materials for organic field effect transistors (OFETs) and organic photovoltaics (OPV) to behave a p-type semiconductor with high charge mobility due to its high crystallinity. The organic thin film devices basically consist of conductive polymer films and insulating polymer films. However, maintaining well-defined interface structures is difficult when the temperature of confined system is raised by Joule's heat. Therefore, any information on temperature dependence of interface structure of organic thin films is very important for applications. We study molecular chain orientations, crystallinity and surface morphology of P3HT thin films prepared on several different substrates at high temperatures with grazing incident X-ray diffraction (GI-XD), X-ray reflectivity (XRR), grazing incident wide angle X-ray scattering (GI-WAXS) and atomic force microscopy (AFM). The substrate we have investigated are SiOH, SiO<sub>2</sub>, C surface of SiC(0001) and Si surface of SiC(0001), and poly(4-vinylphenol) (PVPh). We found that substrate greatly affects the crystal growth of P3HT even for films thicker than 25 nm. Keywords: Poly(3-hexylthiophene) (P3HT), X-ray surface scattering, thin film, conductive polymers

**TF-TuP38 Electrical Transport Properties and Photodetection Performances of n-Type NC-FeSi<sub>2</sub>/i-UNCD/a-C/p-Type Si Heterojunction Photodiodes at Low Temperatures,** *Nathaporn Promros, King Mongkut's Institute of Technology Ladkrabang, Thailand, K. Hanada, Kyushu University, Japan, P. Sittimart, King Mongkut's Institute of Technology Ladkrabang, Thailand, M. Takahara, T. Hanada, L. Chen, T. Yoshitake*, Kyushu University, Japan

n-Type nanocrystalline iron disilicide (NC-FeSi<sub>2</sub>)/intrinsic ultrananocrystalline diamond/amorphous carbon composite (i-UNCD/a-C)/p-type Si heterojunctions have been successfully fabricated and their current - voltage characteristics were measured at low temperatures range from 300 down to 60 K. i-UNCD/a-C and n-type NC-FeSi<sub>2</sub> layers were deposited by coaxial arc plasma deposition and pulsed laser deposition, respectively. We investigated their carrier conduction mechanism on the basis of thermionic emission theory and their near infrared photodetection using a 6 mW, 1.31μm laser. The predominant conduction mechanism through the heterojunctions at 300 - 200 K and 200 - 60 K are recombination and tunneling processes, respectively. At 60 K, the ratio between photocurrent and dark current became three orders of magnitudes. The detectivity is  $8.8 \times 10^{11}$  cmHz<sup>1/2</sup>/W at -1 V, which is comparable with the values of existing NIR photodiodes at the same temperature.

**TF-TuP40 The Effects of Plating Applied on Thin Film Process to the Stress Analysis of Silicon Substrate by Simulation,** *Sang-Hoon Lee, C. Park*, Yeungnam University, Republic of Korea

Crystalline silicon is a great, low cost, cheap material and the most widely used for solar cells application. Crystalline silicon solar cells are modules built using crystalline silicon (c-Si), developed from the microelectronics technology industry. Crystalline silicon solar cells have high efficiency. To reduce the cost of manufacturing process, the plating process is analyzed by using the simulation of stress applied on the silicon substrate. In this study, the occurring of metal-silicon interface was modeled to predict the quantitatively of stress affected inside the silicon substrate. We predicted through the changing of simulation what the factors will give a large effect on the value of the results. The stress characteristic factor was found as major factor of the substance to be plated. Mechanical properties of plating materials were changed as density, Young's modulus, and Poisson's ratio. Thermal properties are not considered as parameters because the plating system is became the progress to isothermal process. The density and Poisson's ratio are not expected to give greater effecting on the stress, so Young's modulus is main factor. It was affected sensitivity on the stress of silicon substrate. Controlling the Young's modulus can be adjusted stress in the silicon substrate.

## Thin Films

Room: Makai - Session TF-TuE

### Thin Film Synthesis & Characterization I

Moderator: Ivan Petrov, Linköping University, Sweden,  
University of Illinois at Urbana-Champaign

5:40pm **TF-TuE1 Sputtering Growth of ZnO-based Semiconductors with Band Gap Tunability Over the Entire Visible Spectrum, Naho Itagaki**, Kyushu University, Japan **INVITED**

ZnO is a remarkable multi-functional material with a distinctive property set and a huge range of existing applications. Recently, some research has been directed towards development of ZnO based materials with smaller band gap ( $E_g$ ), which allow light emission/absorption over a broad spectrum from the UV to the visible region. One of the most promising means to narrow the band gap is to alloy ZnO with CdO that has small direct band gap of 2.3 eV. However, there are technological challenges for the growth of high-cadmium-content CdZnO because of the crystal phase segregation between wurtzite ZnO and rocksalt CdO.

In this context, we have developed a new compound, ZnInON (ZION), which is a pseudo-binary alloy of ZnO with InN. Since both ZnO and InN have the same wurtzite crystal structure and different band gaps (ZnO: 3.4 eV; InN: 0.7 eV), the alloy may possess band-gap tunability in a wide range. Here, we first demonstrate the sputtering synthesis of ZION and the band gap tuning by changing the chemical composition ratio. The detailed analysis on the crystal structure as well as the photo-electric properties of this new material are then conducted. Finally, we discuss the advantages of ZION as light-absorbing layers of multi-quantum well (MQW) solar cells, the theoretical efficiency of which exceeds 50%.

From the analyses of wide-range reciprocal space mapping of XRD spectra, we found that ZION has the same crystal structure as wurtzite ZnO and InN. The lattice constant of ZION is in between ZnO and InN, and decreases continuously with decreasing  $[Zn]/([Zn]+[In])$ , which indicate that ZION is a pseudo-binary system of ZnO and InN. The transmittance spectra reveal that the optical absorption edge is shifted continuously toward longer wavelengths with decreasing  $[Zn]/([In]+[Zn])$ . The band gap of ZION films, being determined by Tauc's plot, changes from 3.4 eV to 1.5 eV, which covers entire visible spectrum. The analyses of transmittance spectra indicate that ZION is of direct band gap, and thus it has high absorption coefficient around  $10^5 \text{ cm}^{-1}$ . Furthermore, we found significant advantages of ZION in terms of applications in multi-quantum-well (MQW) solar cells. The lifetime of photo-generated carriers in QWs is increased by a few orders of magnitude when ZION is used as a MQW material instead of conventional GaAs-based materials, owing to the large piezoelectric field (several  $\text{MV}\times\text{cm}^{-1}$ ) that separate electrons and holes. These results indicate that ZION is a promising material that opens new pathways for realizing new generation solar cells with very high efficiency.

6:20pm **TF-TuE3 Improvement of Thermal Stability of p-ZnO:(Al,N) Thin Films by Oxidizing Amorphous Zn<sub>3</sub>N<sub>2</sub>:Al Thin Films, Bingsheng Li**, Harbin Institute of Technology, China

ZnO has attracted much more attention as a potential candidate for more efficient UV-lasers due to its wide band gap of 3.374 eV and a large exciton binding energy of 60 meV. However, the problem associated with the preparation of stable p-type ZnO with high hole density hinders the ZnO-based device application as UV-emitters. Although substantial studies have been focused on this challenging issue, there are, so far, no efficient and practical doping methods to prepare stable p-ZnO with high hole density. The n-type conduction with high electron density ( $10^{21} \text{ cm}^{-3}$ ) have been achieved by doping ZnO with group-III elements (Al, and Ga). On the other hand, although extensive studies have been focused on the p-type doping issue of ZnO, the ZnO-based optoelectronic devices fabricated from p/n junction still suffer from p-type ZnO problem. P-type conduction has been reportedly realized with chemical doping. However, the low hole density and instability in electronic behavior become the bottleneck to improve the ZnO-based device performance.

For improving the thermal stability of p-ZnO, we introduce Al to capture the N by forming Al-N chemical bonds. The bond dissociation energy,  $\Delta H_{298}$ , of Al-N is  $297 \text{ kJ}\cdot\text{mol}^{-1}$ , is much larger than the Zn-N ( $\Delta H_{298} = 160 \text{ kJ}\cdot\text{mol}^{-1}$ ). Theoretical calculations suggested the possible approach to the p-type doping in ZnO with III-V Ga-N co-doping or cluster-doping, which can increase the solubility and stability of N in ZnO. Here, we use Al to stabilize the N-doping, because the corresponding bonds with N and O are stronger for Al than for Ga. For stabilizing N in p-type ZnO, the key issue is

to reduce the compensation of single Al doping due to the formation of only Al-O bands. Another crucial point is to make sure the Al captures more than one N-atoms to form  $\text{AlN}_2$ ,  $\text{AlN}_3$ , and  $\text{AlN}_4$  in ZnO. To realize that, we prepared  $\text{Zn}_3\text{N}_2:\text{Al}$  and convert it to ZnO by an oxidation procedure. For  $\text{Zn}_3\text{N}_2:\text{Al}$ , p-ZnO appears around 600 °C and do not convert back to n-type with further increase of annealing temperature. However, for  $\text{Zn}_3\text{N}_2$ , we did not obtain p-type ZnO. A reasonable explanation is that the Al will stabilize the N during the reaction to form ZnO from  $\text{Zn}_3\text{N}_2$ . Comparing with previous reports, the thermal stability is improved. However, the hole density is still low and needs further improvements. More details about the structural, optical, and electronic properties of the samples will be given in the presentation.

We will optimize the concentration of Al dopant in  $\text{Zn}_3\text{N}_2:\text{Al}$ . The dependence of the hole density in ZnO, oxidized from  $\text{Zn}_3\text{N}_2:\text{Al}$ , on the Al concentration in  $\text{Zn}_3\text{N}_2:\text{Al}$  will be studied.

6:40pm **TF-TuE4 Well-Ordered Monolayers of Alkali-doped Coronene and Picene, Yoichi Yamada, M. Yano, M. Endo, E. Shimizu, Y. Hasegawa, M. Sasaki**, University of Tsukuba, Japan

Although the electronic modifications of the organic thin films by means of the chemical doping have been widely investigated, the structural properties of the doped organic materials have been poorly understood. This is generally due to an inhomogeneity of the doped materials, hindering the detailed understanding of the structure. However, structural information is inevitable for understanding the mechanism of the doping. For the basic investigation on the doping of the organic materials, we utilize well-defined monolayers of organic materials. We model the doping by depositing the dopant onto the monolayer. When the substrate is inert enough, self-organization of the dopants and host materials will be facilitated and well-ordered doped monolayer will be obtained. We focus mainly on so-called "metal-intercalated aromatic superconductors" discovered in 2010 in K-doped picene [1]. Since its discovery, electronic properties of these materials have been investigated by means of the photoemission spectroscopy. However, contradicting results, deviating from a metallic to an insulating ground state, have been obtained. It is speculated that there exists notable variation of the structures in the thin films used in the photoemission studies. The theoretical reports have also reached contradicting results and have suggested that the electronic states are quite sensitive to the molecular arrangements. Therefore it is demanded to realize the well-ordered samples of these materials. Here we demonstrated the fabrication of the well-defined monolayer of the metal-intercalated aromatic superconductors, such as K-doped picene and coronene. These systems enable us the systematic investigations of the relation between structure and electronic properties. It is found that the alkali-doping causes a rearrangement of the host monolayers, based on the scanning tunneling microscopy and the X-ray absorption spectroscopy. Upon the reconstruction, electronic states of the host molecules also change drastically, suggesting the charge transfer from alkali metals to the molecule, revealed by means of the photoelectron spectroscopy. These observations confirm that the well-ordered monolayer, as realized in this study, can properly model the doping process [2,3].

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7:00pm **TF-TuE5 Electrochromic Thin Film Synthesis, Understanding and Performance Enhancement, Yi Ren, S.Y. Chiam, J. Liu**, Institute of Materials Research and Engineering, Singapore

Electrochromic (EC) thin films are important for enabling technologies such as smart windows and non-volatile displays. To date, various organic EC films have been shown to possess high coloration efficiency and many color variety, while inorganic films have demonstrated excellent optical modulation and cycling stability. In addition, flexible EC devices that are retrofittable to existing windows can also be achieved by utilizing organic or porous inorganic films, and this poses new challenges in device integration and performance enhancement. In this presentation, I will first talk about various synthesis methods used by us for EC thin film deposition. Solution-based methods which target for low-cost and large-scale fabrication will be emphasized. Besides chemical bath deposition and electroplating, an innovative dip coating method with better thickness control will be introduced. Materials covered range from inorganic metal oxides (such as nickel, tungsten, molybdenum and tantalum oxide) to organic polymer electrolytes. We found that different synthesis methods result in films with different structure, phase and defect density. These differences in turn significantly affect the electrochromic performance of the material. Therefore, in the second part of the presentation, I will focus



on characterizing and correlating the physical and electrochromic properties of the synthesized films. As an example, layered nickel oxide/hydroxide will be discussed in details. With different synthesis methods and post treatments, we are able to investigate the electrochromic performance of films with different structures (compact, porous and nanostructured), phases ( $\alpha$  and  $\beta$  phase), defect density (amount of  $\text{Ni}^{3+}$  sites) and intercalated species (water and anions). By changing electrolyte, we can also study the role of different ions in causing the color change, in particular,  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{Li}^+$ . Recently, we have successfully identified the causes of the activation and degradation phenomenon observed in oxide material. We have also proved the importance of having existing reaction sites such as defects for improved electrochromic reaction involving  $\text{Li}^+$ . The above knowledge can be extended to other layered material such as tungsten and molybdenum oxides. Last but not least, our ongoing work also focuses on synthesizing and characterizing thin films that can be functioned as solid electrolyte in electrochromic device. Besides the organic polymer electrolyte, we also look at emerging inorganic metal oxide electrolyte such as tantalum oxide. Their synthesis and ion conducting properties play significant role in device integration and performance.

7:40pm **TF-TuE7 Thin Film Synthesis via Nanogrinding**, *Chris Papadopoulos*, University of Victoria, Canada

Thin films composed of nanoscale particles possess unique and varied electrical, optical and mechanical properties, which can be used to create advanced functional materials and nanostructured composites for devices. Such thin films find applications in electronics, optics, photovoltaics, energy storage, biomedicine, etc.

Here we describe a general approach to nanoparticle thin film synthesis based on *colloidal* or *nanogrinding*. Nanogrinding can produce large amounts of nanoscale particles in an appropriate solvent without the use of complex chemical or physical processing. The nanogrinding method typically employs planetary ball milling to grind a starting bulk powder into a nanoscale colloidal suspension suitable for thin film coating. Ball milling uses the rotary motion of a grinding jar containing the sample, grinding beads and a liquid medium, which is arranged eccentrically on a so-called sun wheel. The efficient energy transfer during planetary ball motion leads to nanogrinding being a fast and inexpensive process for the creation of nanostructured thin films. In addition, nanogrinding is very flexible allowing the formation of semiconducting, metallic or insulating particles and films. These unique advantages combine to create a general solution-based processing approach for thin film surface coatings and devices (including non-planar geometries).

Results of nanogrinding trials using high-purity bulk materials (Si, silicides, oxides) and characterization of the nanoparticles and films via electron microscopy, scanning probe methods, Raman spectroscopy and elemental analysis are presented. Zirconia grinding vessels and either zirconia or silicon nitride beads are used in a planetary ball mill to grind readily available high-purity powders initially consisting of ~10-50 micron particles dispersed in solvent. Grinding speeds and times are varied between 200-1000 rpm and 10-500 minutes, respectively. After milling, the resulting colloidal dispersions are optionally filtered and deposited on a substrate for further analysis. As grinding time is increased, the resulting particles and films display good uniformity with sizes below 100 nm. Atomic force microscopy of the particles showed that diameters down to ~2-4 nm could be achieved. Elemental analysis indicates that contamination from the grinding tools is minimal.

Nanogrinding is an efficient route to directly creating nanoparticles suitable for thin film deposition of various materials from solution. By adjusting the grinding parameters, the size and dispersion of the particles can be controlled and their properties optimized for applications, including thin film electronic and optical devices.

8:00pm **TF-TuE8 Effect of Annealing on Current Conduction Mechanism in High-k Dielectric Thin Films Deposited on Silicon Substrates**, *Anil Khairnar, P.A. Deshmukh, V.S. Patil, K.S. Agrawal, A.M. Mahajan*, North Maharashtra University Jalgaon, Maharashtra, India-425001, India

**Abstract:**

The ever increasing demand for functionality and speed for semiconductor applications requires enhanced performance, which is achieved by the continuous miniaturization of CMOS dimensions. However, as we further reduce the device dimension, transistor with conventional structure and material is attaining its fundamental scaling limit. Beyond the 22 nm node fundamental as well as practical constraints will limit the maximum performance achievable by these scaled transistors. The integration of high-k gate dielectric provides a promising solution to continue improving the device performance, as their higher k-value allows a physically thicker layer while aiming the same capacitance and Equivalent Oxide Thickness (EOT). This study primarily focused on studying the electrical properties of high-k

MOS capacitors with metal gate electrodes. In this work, we have deposited  $\text{HfO}_2$  and  $\text{Al}_2\text{O}_3$  thin film deposited on silicon substrate by RF sputtering technique and Plasma enhanced atomic layer deposition system (PEALD) respectively. The deposition of  $\text{HfO}_2$  is confirmed by FTIR measurement. Current density vs voltage characteristics have been studied by I-V measurement further comparative study of current conduction mechanisms is done. In MOS structure due to the charge trapping and interface characteristics of dielectric films causes leakage current in dielectrics. The density of leakage current has been investigated and analyzed, by current-voltage and conduction mechanisms. Among the various conduction mechanisms  $\text{HfO}_2$  and  $\text{Al}_2\text{O}_3$  film on Si follows the Fowler Nordheim (FN) tunneling. The Poole Frenkel (PF) emission, Schottky emission (SE) and Trap assist tunneling (TAT) also studied. The barrier height ( $\phi_b$ ) is calculated of experimental work through Fowler Nordheim tunneling mechanism.

**Keywords** -  $\text{HfO}_2$ ,  $\text{Al}_2\text{O}_3$ , high-k, leakage current density, FN tunneling.

8:20pm **TF-TuE9 Effects of Very High Frequency  $\text{O}_2$  Plasma Reactant on High-k Film Properties Deposited by Atomic Layer Deposition**, *Gilsang Yoo, I.K. Oh, C.W. Lee*, Yonsei University, Republic of Korea, *T.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea, Republic of Korea, *H.B.R. Lee*, Incheon National University, Republic of Korea, *H.J. Kim*, Yonsei University, Republic of Korea

High permittivity (high-k) dielectrics have been explored for an alternative gate insulator to conventional  $\text{SiO}_2$  in the metal oxide semiconductor field effect transistor (MOSFET) technology. Among various high-k deposition techniques, atomic layer deposition (ALD) appears to be one of the suitable methods due to its excellent process controllability for extremely thin high-k films. Plasma-enhanced atomic layer deposition (PE-ALD) using plasma reactant has been spotlighted because of its several benefits over conventional thermal ALD using gas reactant, such as lower process temperature and improved film properties by the reactive radicals of reactants. However, use of plasma reactants negatively influences electrical properties of high-k films in MOSFET since ion bombardment of energetic radicals generates defects in films. Instead of radio frequency (RF) plasma which is usually used for plasma assisted processes, very high frequency (VHF) plasma for chemical vapor deposition (CVD) process was reported. The negative effects of plasma on film properties were reduced in VHF plasma process due to its lower ion kinetic energy and higher plasma density than RF plasma. Therefore, VHF plasma is expected to be a better plasma reactant for PE-ALD than RF plasma in the context of high growth rate and low ion damage. However, there has been no report on PE-ALD using VHF plasma reactant.

For this study,  $\text{Al}_2\text{O}_3$  PE-ALD were developed using Trimethylaluminum (TMA) precursor and  $\text{O}_2$  plasma reactant on Si substrate.  $\text{O}_2$  plasma reactant was generated using two different frequencies, 13.56 MHz and 60 MHz for RF and VHF, respectively. The processes exhibited ALD mode with good self-saturation behavior and linear growth as a function of growth cycles. To investigate the characteristics of plasma density and electron temperature, a Langmuir probe was installed in the chamber. The thickness and density of the films was analyzed by spectroscopic ellipsometry and X-ray reflectivity (XRR), respectively. By using VHF plasma, better film properties were observed compared to RF plasma. The growth rate of VHF plasma (2.7 Å/cycle) was higher than that of RF plasma (2.3 Å/cycle). In addition, the VHF PE-ALD film was denser than RF PE-ALD film (3.26 for VHF and 3.11  $\text{g/cm}^3$  for RF plasma), since ion and radical density generated by VHF is higher than those by RF. The VHF PE-ALD provides improved film qualities, such as low leakage current and low interface trap density, compared to RF PE-ALD grown film. The VHF plasma reactant for PE-ALD has potentials for various applications which require very thin and dense films in nanoscale regime.

# Wednesday Morning, December 10, 2014

## Thin Films

Room: Makai - Session TF-WeM

### Thin Film Synthesis and Characterization II

Moderator: Naho Itagaki, Kyushu University, Japan

8:00am **TF-WeM1 Novel Methods for Fitting the Fe 2p and Sn 3d XPS Data from Metallic and Oxidized Surfaces**, *M. Bravo-Sanchez*, CINVESTAV-Unidad Queretaro, Mexico, *Jorge A. Huerta-Ruelas*, CICATA-Queretaro, Mexico

Fe and Sn oxides are present in many products and industrial processes. Surface analysis with techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in understanding their properties. Most of the core level spectra from metallic and oxidized Fe and Sn surfaces show very large background signals, highly asymmetrical line-shapes, and a series of shake-up satellites that overlaps with the higher binding-energy branch of the peak doublets. For these reason, a proper fit of these spectra has been elusive. This has prevented the quantification, through the analysis of XPS data, of the composition of oxidized surfaces and of the thickness of thin oxide layers. In this work we jointly employed the SVSC background [1] and the double Lorentzian line-shape [2] to closely model the Fe 2p and Sn 3d spectra. With this approach it was possible to resolve previously unreported shake-up satellites and to quantify the thickness and composition of thin oxide films. The validity of the method is strongly suggested from the reproduction of the thickness assessed with transmission electron microscopy. The expected compositions are also reproduced. Examples of oxide films ranging from 2 to 5 nm will be discussed in full. [1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. *Journal of Electron Spectroscopy and Related Phenomena* (in press) DOI 10.1002/sia.5453. [2] A. Herrera-Gomez. "A double Lorentzian shape for asymmetric photoelectron peaks." Internal Report. Cinvestav-Queretaro.(2011). <http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf>

8:20am **TF-WeM2 Microstructure Control in Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-sputtering using Selective Metal-Ion Irradiation**, *Greczynski, Lu, Jensen*, Linköping University, Sweden, *Ivan Petrov, J. Greene*, Linköping University, Sweden, University of Illinois at Urbana-Champaign, *Kölker, Bolz, Schiffers, Lemmer*, CemeCon AG, Germany, *L. Hultman*, Linköping University, Sweden **INVITED**

It was realized early on in the HIPIMS literature<sup>1</sup> that there exist a time separation between the Ar and metal-ion dominated fluxes at the substrate which opens the possibility for selection one of the components for ion-assisted by using a pulsed bias voltage with suitable synchronization. Here, we explore systematically this avenue by using pseudobinary TiN-based model systems TiMeN (i.e. TiAlN, TiSiN, and TiTaN) to carry out experiments in a hybrid configuration with one target powered by HIPIMS, the other operated in DCMS<sup>2,3</sup> mode and probe the effects of (i) metal versus rare-gas ion irradiation as well as (ii) the type of metal ion used (Ti vs Me). We employ a metastable NaCl-structure Ti<sub>0.39</sub>Al<sub>0.61</sub>N as a model system to demonstrate that switching from Ar<sup>+</sup> to Al<sup>+</sup>-dominated bombardment eliminates phase separation, minimizes renucleation during growth, reduces the high concentration of residual point defects, and thus results in dense, single-phase, stress-free films.<sup>4</sup> For metastable alloys, TiAlN and TiSiN, mechanical properties are shown to be determined by the average metal-ion momentum transfer per deposited atom ( $p_d$ ).<sup>5</sup> Irradiation with lighter metal-ion ( $M_e = Al^+$  or  $Si^+$  during Me-HIPIMS/Ti-DCMS) procures fully-dense single-phase cubic Ti<sub>1-x</sub>(Me)<sub>x</sub>N films. In contrast, with higher-mass film constituents such as Ti, ( $p_d$ ). Easily exceeds the threshold necessary for phase segregation which results in precipitation of second w-AlN or Si<sub>3</sub>N<sub>4</sub> phases. With the TiTaN system we show that synchronized pulsed ion bombardment in the hybrid system with the heavy-metal ions (Ta) permits to grow dense, hard, smooth, and stress-free thin films at lowered substrate temperature, with no external heating.<sup>6</sup> Overall, we demonstrate that using synchronous bias to select the metal-rich portion of the ion flux opens new dimension for ion-assisted growth in which momentum can be tuned by selection of the metal ion in the hybrid/cosputtering configuration and stresses can be eliminated/reduced since the metal ion is a component of the film.

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<sup>6</sup>G. Greczynski, J. Lu, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 32 (2014) 041515

9:00am **TF-WeM4 Mechanical and Electrical Properties of ZrB<sub>2</sub> Thin Films**, *Lina Tengdelius*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Sweden, *E. Broitman, F. Eriksson*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, *M. Samuelsson*, Impact Coatings AB, Linköping, *J. Lu, J. Birch*, Department of Physics, Chemistry, and Biology (IFM), Linköping University, *T. Nyberg*, Department of Solid State Electronics, Uppsala University, *H. Högborg*, Department of Physics, Chemistry, and Biology (IFM), Linköping University

Zirconium diboride (ZrB<sub>2</sub>) exhibits a number of favorable properties including high melting point, high hardness, and low resistivity [1,2]. In addition, the compound is chemically inert and shows good wear and corrosion resistance, even at elevated temperatures. These properties make ZrB<sub>2</sub> thin films interesting for applications in demanding environments.

In order to enable reliable evaluation of the mechanical and electrical properties of this material, the films should exhibit well defined properties, including being stoichiometric, show high crystalline ordering, and being free of contaminants. Moreover, the substrate material must be appropriately chosen for the measurements of the functional properties.

The aim of the current study is to investigate and determine the electrical and mechanical properties of ZrB<sub>2</sub> thin films. In order to do so, well defined ZrB<sub>2</sub> thin films, were deposited using direct current magnetron sputtering (DCMS) from a compound source, on Al<sub>2</sub>O<sub>3</sub>(0001) substrates enabling evaluation of said properties.

It was found that epitaxial growth of ZrB<sub>2</sub> films, up to a thickness of 1.2 μm, is possible by DCMS of a ZrB<sub>2</sub> compound target on Al<sub>2</sub>O<sub>3</sub>(0001) substrates, and at a temperature of 900 °C. The obtained ZrB<sub>2</sub> thin films were characterized with regards to mechanical and electrical properties, and the results showed that the films exhibited resistivity values of ~125-200 μΩ cm, and notably high hardness values of up to 50 Gpa, as well as high elastic recovery.

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9:20am **TF-WeM5 Effect of Vacuum Annealing on the Thin Films Of Copper Oxide prepared by Reactive DC Magnetron Sputtering**, *Dhanya S. Murali, M.K. Jain, A. Subrahmanyam*, Indian Institute of Technology Madras, India

Cu<sub>2</sub>O is an interesting p-type semiconductor; it has high optical absorption coefficient in the visible region and reasonably good electrical properties. It finds application in p-n junction based devices such as solar cells and high mobility p-type thin film transistors<sup>1,4</sup>. Among p-type oxides, cuprous oxide (Cu<sub>2</sub>O) in single crystal form<sup>1</sup> is known to have the highest hole mobility ~100 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at room temperature (300 K). Lee *et al.*<sup>3</sup> reported a Hall mobility of 62 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for Cu<sub>2</sub>O thin films at room temperature. Sohn *et al.* performed vacuum annealing of copper oxide (CuO) thin films on Si substrate in order to obtain Cu<sub>2</sub>O thin film which possesses Hall mobility of 47.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and good optical properties<sup>4</sup>.

In the present communication, we report the effect of vacuum annealing (at 623K and 700 K) on polycrystalline copper oxide thin films deposited (at room temperature 300 K) on a borosilicate glass substrate employing reactive DC magnetron sputtering. Argon and oxygen are the sputter and reactive gases respectively. Pure (99.9%) copper is the target. Deposition pressure is 3.5x10<sup>-3</sup> mbar and the target power density is 1.4 Wcm<sup>-2</sup>. The films were characterized by X-ray diffraction, Hall effect (with temperature variation in the range 20 K to 300 K) and Raman spectroscopy (excitation wavelength 532 nm and in the temperature range 77 K to 700 K). Optical band gap is evaluated using UV-Vis spectrometer (400 – 1100 nm). The “as

prepared" films show CuO phase. At an annealing temperature of 623K (in vacuum at  $5 \times 10^{-6}$  mbar), transition to a mixed phase of CuO and  $\text{Cu}_2\text{O}$  is observed. Further annealing at 700 K, CuO transforms completely to a cubic  $\text{Cu}_2\text{O}$  phase. Sohn *et al.*<sup>4</sup> reported similar transition at 773 K (CuO prepared on Si substrate by RF sputtering). The optical direct band gap is observed at 2.06-2.51 eV. The reduction of phase CuO to  $\text{Cu}_2\text{O}$  is observed to enhance the optical transmittance in the visible region<sup>4</sup>. The Hall mobility measurements showed that the vacuum annealed  $\text{Cu}_2\text{O}$  thin films have high Hall mobility ( $51 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) at 300 K room temperature. High temperature (300 K to 700 K) Raman studies were carried out to confirm the phase by keeping the CuO sample on a hot stage in argon atmosphere, the phase change is observed at 723 K.

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9:40am **TF-WeM6 A Study to Reduce Deviations of Sensitivities to Constant CO Gas of Pt Doped  $\text{SnO}_2$  Thin Film Based Micro Gas Sensor**, *Jun-gu Kang*, Sungkyunkwan University, Korea, Republic of Korea, *J.-S. Park*, Korea Electronics Technology Institute (KETI), Republic of Korea, *H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

Gas sensors based on metal oxide semiconductors have been used for detecting low level toxic and explosive gas for a long time, since metal oxide semiconductors enable to make gas sensors operate at low power consumption as well as supply with low price. Recently, researchers have studied nanostructured metal oxide semiconductors to improve sensitivity by enlarging the surface area that react gas directly. However, such gas sensors based on nanomaterials suffer from a large deviation of sensitivities among gas sensors. In the present work, we employed a  $\text{SnO}_2$  thin film, with a well-defined surface area and thus a small deviation in sensitivity, and, in addition, doped it with a noble metal to improve stability. For the fabrication of the micro platform, which consists of a micro heater and sensing electrode on  $\text{SiN}_x$  membrane, we started with a Si substrate(100) by deposition of a low stress  $2 \mu\text{m}$ -thick  $\text{SiN}_x$  film using a low pressure chemical vapor deposition process. After deposition of a tantalum layer, serving as an adhesion layer, a Pt film was deposited as a heating element. The heater layer of Pt on Ta was patterned and etched using a dry etching process with an advanced oxide-etching equipment. An  $1 \mu\text{m}$ -thick insulating layer was produced on the patterned heater layer. A sensing electrode layer of Pt was sputtered and then patterned using a dry etching process. A  $\text{SnO}_2$  thin film, as sensing material, was deposited with RF sputtering on the sensing electrode of a micro platform. And then, Pt doping was done by Pt thin film sputtering, and heat treatment to form Pt islands on  $\text{SnO}_2$  thin film. After finishing the front side process of the wafer, we patterned the back-side of the wafer and etched it in a KOH solution to release the  $\text{SiN}_x$  film as a membrane. In this presentation, sensing properties of fabricated gas sensors to indoor pollutant gases such as CO, HCHO and toluene will be presented. We will also show the possibility to reduce deviations of sensitivities to the constant CO gas concentration among thin film based micro gas sensors.

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10:20am **TF-WeM8 Barium Oxide Glass Targets for Thin Film Dielectric Material**, *C. Stutz*, Air Force Research Laboratory, *G. Kozlowski*, University of Dayton Research Institute, *S. Smith*, University of Dayton Research Institute, *J. Goldstein*, Air Force Research Laboratory, *G. Landis*, University of Dayton Research Institute, *C. Hollbrook*, *John Jones*, Air Force Research Laboratory

Barium-rich, alkali free glasses are expected to be useful for high voltage capacitors due to the high energy storage capacity of Barium, the high resistivity of alkali-free glasses, and the possibility of forming a smooth, glassy surface to minimize the surface electric field intensity. To better understand the structure-property relationships in these glasses, we have synthesized 17 samples of eight different compositions ranging from 22% to 48% mol percent BaO, with a constant ratio of  $\text{SiO}_2$  to  $\text{B}_2\text{O}_3$ . These samples were studied with Raman and showed a narrow intermediate range (29-32% BaO) that was independent of BaO content between the stressed-rigid elastic phase (24-29% BaO) and the flexible elastic phase (32-48% BaO). The samples were fabricated into 2.5 cm diameter targets for a pulsed laser deposition (PLD) thin film process. They were nominally clear and made from a melt that was poured into a mold. However the targets would

break up when exposed to the 248 nm one joule laser and the deposition onto the substrate was negligible. The targets were also annealed at 50 degrees below the glass transition temperature, but this did not help. A new target process was developed that was more involved and instead of pouring the melt into a form it was poured into de-ionized water to be quenched then ground using a mortar and pestle. After grinding the glass was pressed into a pellet and sintered for densification. The new targets were not transparent. Due to the new process the glass targets were able to withstand the 248 nm one joule laser. Also good coverage of the substrate was obtained during PLD growth. We will discuss the characterization of the thin films based on results from atomic force microscopy, x-ray, and Raman spectra. Also impedance spectroscopy will be presented.

10:40am **TF-WeM9 Near Infrared Photodiodes Comprising Iron Disilicides Prepared by Sputtering**, *T. Yoshitake*, Kyushu University, Japan, *M. Shaban*, Aswan University, Egypt, *N. Promros*, King Mongkut's Institute of Technology Ladkrabang, Thailand, *Motoki Takahara*, T.M. Miostafa, Kyushu University, Japan, *R. Baba*, Kysushu University, Japan

Semiconducting iron disilicide ( $\beta\text{-FeSi}_2$ ) is a new candidate applicable to near-infrared photoelectronic devices [1-3], because it possesses features such as a direct optical band gap of 0.85 eV above an indirect gap (0.76 eV) and a large absorption coefficient, which is  $10^5 \text{ cm}^{-1}$  at 1.0 eV[4]. Since  $\beta\text{-FeSi}_2$  can be epitaxially grown on Si, a heterojunction diode comprising a  $\beta\text{-FeSi}_2$  film and singlecrystalline Si substrate is a device that can be briefly formed by employing vapor deposition. For near-infrared light detection in the Si/b- $\text{FeSi}_2$  heterojunction diodes, near-infrared light transmitted through the front-side Si substrate can be absorbed in the depletion region of the back-side  $\beta\text{-FeSi}_2$  film.

In our previous works, we have progresses researches on p-type Si/n-type  $\beta\text{-FeSi}_2$  heterojunction diodes, totally from the epitaxially growth of  $\beta\text{-FeSi}_2$  film on Si(111) by sputtering [5] to the evaluation of p-type Si/n-type  $\beta\text{-FeSi}_2$  heterojunctions as photodetectors [6,7]. It was confirmed that  $\beta\text{-FeSi}_2$  in the heterojunction evidently contributes to the photodetection of near-infrared light from the photoresponse spectrum. In addition, the heterojunction clearly exhibited current due to photogenerated carriers for 1.33  $\mu\text{m}$  light in the *I-V* curves in comparison with that in the dark. The detectivity at temperatures lower than 100 K reach approximately  $2 \times 10^{11} \text{ cmHz}^{1/2}/\text{W}$ , which is comparable with that of existing near infrared photodiodes comprising PbS and InAs at the same temperature. However, the external quantum efficiency is less than 10 % [6,7].

In this presentation, the progress thus far of our research and recent problems that we are facing and should be solved for the next step will be introduced. A serious problem for the heterojunctions is that a barrier due to a band offset appears in the valence band and it prevents from the flow of photogenerated carriers from the n-type  $\beta\text{-FeSi}_2$  layer to the p-type Si layer. The opposite combination, namely n-type Si/p-type  $\beta\text{-FeSi}_2$ , is structurally ideal because of it has no barriers due to the band offset. In order to form p-type  $\beta\text{-FeSi}_2$ , the residual carrier density should be reduced for controlling the conduction type. Carbon doping, which might be effective for a reduction in the carrier density, will be introduced.

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11:00am **TF-WeM10 Epitaxial Growth of Ag/MgO(001) and Ag/Si(111) by Pulsed Laser Deposition for Use as an Alternative to Single Crystal Metallic Substrates**, *Jeff Terry*, *D. Velazquez*, Illinois Institute of Technology

Single crystal metal substrates are often used as platforms for growth. Epitaxial films are potentially cheaper starting points for chemical synthesis single crystal substrates. We report on the epitaxial growth of thin silver films in the crystallographic orientations (001) and (111) using pulsed laser deposition (PLD). The films were deposited on  $\text{MgO}(001)$  and  $\text{Si}(111)$  substrates to a thickness of 40 nm at 150 °C and 170 °C, respectively. For the first 2-4 nm, growth was three-dimensional at which point a gradual transition to two-dimensional growth occurred, as monitored by reflection high-energy electron diffraction (RHEED). Scanning tunneling microscopy (STM) was used to show that the surface roughness was less than 5 Å in  $100 \times 100 \text{ nm}^2$  for either orientation. Photoelectron spectroscopy (PES) was used to probe the chemical state of the films. The positions of the Ag  $3d_{5/2}$  and Auger MNN peaks were used to calculate the Auger parameter to be 726.3 eV, which corresponds to metallic Ag. These films may be

inexpensive replacements for single crystal Ag substrates in certain applications.

11:20am **TF-WeM11 Enhancement of Uniformity and Whiteness of Electrogalvanized Steel Sheet by Deposition of a Transition Metal Thin-Film between Deposited Zinc and Iron Substrate.** *Wonhwi Lee*, POSCO, Republic of Korea

Electrogalvanized steel sheets are widely used in automobiles, building interior decorations and home appliances because of its excellent surface uniformity and formability. Among the wide areas of its applications, barely post-treated electrogalvanized steel sheets used in home appliances are processed no further treatments but to form essential resin coating layers for the functions of anti-fingerprinting or Chromate-free. In this case, it is a key quality to have uniformity and good whiteness of its surface.

However, the electrogalvanized zinc layer with partially oriented and enlarged grains is normally produced due to the epitaxial growth along the iron substrate. The oriented zinc grains on the surface lead to the dispersion of reflecting light that results in lowering whiteness.

In addition, iron oxide scales or oil stains remained on the substrate even after the all pre-treatments of rinsing, degreasing and pickling processes may induce poor uniformity of the galvanized surface.

To solve these problems which are derived from the iron substrate, some manufacturers have created a nickel nano-layer on a substrate. The deposition of the nickel layer on a substrate has brought a galvanized surface not only the uniformity but also the better whiteness. This is because the nickel layer significantly enhances the quality of deposited zinc since the condition of substrate is no longer transferable. Recently, however, its high cost as a raw material and harmful fumes during welding processes have arisen as critical problems to solve.

In this article, we suggest to deposit a thin film of a single or as an alloy of transition metals between the deposited zinc and the iron substrate. The thin layers were made by electrodeposition method and several transition metals were selected for the coating materials. These coating materials were electrodeposited with the coating weights in the range of 10 to 50mg/m<sup>2</sup>. The results show that the better whiteness and uniformity of the galvanized zinc can be achieved by the thin layer which minimizes the influences from the substrate and interrupts coarsening of zinc grains as well. Furthermore, it is a remarkable finding that the zinc grains are randomly oriented on the surface with much smaller sizes.

11:40am **TF-WeM12 Effect of Organic Substrate Materials on Electrical and Mechanical Properties of Cr Thin Film Prepared by DC Magnetron Sputtering.** *H. Park, D. Kim, I. Park, K. Bae*, Pusan National University, *Young-Rae Cho*, Pusan National University, Republic of Korea

Sputtering is one of the most popular physical vapor deposition methods due to their versatility and reproducibility. Effect of organic substrate materials on electrical and mechanical properties of chrome (Cr) thin films was investigated. For the application of wearable or flexible electronic devices, the materials for substrate were selected from flexible organic materials such as leather, cloth (melton), paper and plant. The Cr films were deposited on the several different substrates by DC magnetron sputtering. The thickness of Cr films was varied from several tens to 500 nm. For the explanation of the electrical and mechanical properties, a sheet resistance and fatigue properties in cyclic stress of the samples were characterized. When we deposited Cr film over 400 nm in thickness, the sheet resistance of Cr film on smooth substrates (leather, A4 paper, melton) showed small values. However, the sheet resistance of Cr film on rough substrates (toilet paper, wool) showed very large values. Furthermore, we will try to prepare more wide range of organic substrates such as rubber and plant. Finally, the relationships between their physical properties of samples and the change of substrate shape will be discussed in detail.

## 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.

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**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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**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 graphite 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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**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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**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, respectively, 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.

# Wednesday Afternoon, December 10, 2014

## Thin Films

Room: Makai - Session TF-WeE

### Thin Film Synthesis and Characterization III

**Moderator:** Hugo R. Navarro Contreras, Coordinación para la Innovación y la Aplicación de la Ciencia y la Tecnología (CIACyT-UASLP)

5:40pm **TF-WeE1 Static and Dynamic Magnetic Properties in FeCoN Thin Films Deposited Under Various Deposition Powers**, *Yuping Wu*, National university of singapore, *Z.H. Yang*, National university of Singapore, *F.S. Ma, B.Y. Zong*, National University of Singapore

In this work, we deposited FeCoN thin films by reactive magnetron sputtering. The applied deposition power was changed from 150 W to 1000 W. The dynamic magnetic properties were measured with the shorted microstrip transmission-line perturbation method, which was developed in our lab. The damping coefficient was estimated by analyzing the measured permeability spectra based on Landau-Lifshitz-Gilbert (LLG) equation. Both the static magnetic properties and the damping coefficient in the magnetization dynamics can be conveniently and effectively tuned by varying the sputtering deposition power, which results in controllable and modified dynamic magnetic properties. The physical origin of the influences is related to the changed deposition rate, which is a critical factor determining the microstructure of films.

6:00pm **TF-WeE2 Substrate Heating during Reactive Magnetron Sputtering**, *Julio Cruz, J. Restrepo, S. Muhl*, IIM-UNAM, Mexico

Substrate heating by the plasma during magnetron sputtering is known to occur, however, there have been very few detailed studies of this process which involves a combination of bombardment by ions, excited and neutral species and UV radiation incident on the substrate. We have studied the heating of the substrate during DC magnetron sputtering of a 4" titanium target as a function of the experimental conditions; plasma power, Ar gas pressure, floating, grounded and biased substrates. We have also studied the substrate heating during reactive sputtering mode by using a gas mixture of argon with nitrogen. On the other hand, it is known that the crystalline orientation of titanium nitride depends on the sputtering conditions. Here we report the effect of the plasma substrate heating, as a consequence of the plasma conditions, on the morphology and the crystalline structure of titanium nitride. The properties of the films were analyzed using SEM and X-ray Diffraction and the film thickness was measured using a stylus profilometer. The measurements of the non-reactive sputtering showed that the substrate temperature could reach temperatures higher than 200°C with a plasma power of 200W and showed a non uniform temperature distribution over the substrate, with the highest temperature in front at the racetrack and the lowest temperatures in front of the edge of the target. Finally by using a Fluke Ti300 camera we show the temperature change in the substrate with time for both reactive and non-reactive processes.

6:20pm **TF-WeE3 The Hollow Cathode Discharges; How They Have Been used to Produce Thin Films and the Novel Toroidal Planar Hollow Cathode System**, *Stephen Muhl*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, *A. Perez*, Universidad Nacional Autónoma de México, Mexico, *A. Tenorio*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico, *E. Camps*, Instituto Nacional de Investigaciones Nucleares, Mexico

In 1916 F. Paschen first report the hollow cathode discharge he demonstrated that the system was capable of producing a high electron flux with relatively low ion and neutral temperatures. Approximately 40 years later Lidsky showed that hollow cathode arc discharges were one of the best plasmas sources available at that time. The term "hollow cathode discharges" has been used in reference to almost any discharge in a cathode with a cavity-like geometry, such that the plasma was enclosed by the walls which are at the cathode potential. Just as trapping of electrons in a magnetron cathode by the magnetic field results in an increase in the plasma density, in the hollow cathode the geometry of the cathode also produces a high plasma density. In general, three types of discharge can be established in a hollow cathode; at low power and / or at relatively low gas pressures the plasma is a "conventional" discharge characterized by low currents and medium to high voltages (a Discharge in a Hollow Cathode or D-HC). However, even this simple plasma has a higher density than a normal planar parallel electrode system because the hollow geometry reduces the loss of electrons. If the combination of gas pressure, applied power and hollow cathode diameter is correct, the negative glow of the plasma almost

completely occupies the interior volume of the cathode. Under this condition the plasma current can, for the same voltage, be 100 to 1000 times the values for the "simple" D-HC discharge and the plasma density is very large (this is the Hollow Cathode Discharge or HCD). If the temperature of cathode can increase so that Thermal-Field electron emission becomes an important additional source of electrons the discharge can change into a dispersed arc (this is the Hollow Cathode Arc or HCA). The accepted explanation for the HCD phenomenon involves the existence of high energy "pendulum" electrons reflected from sheath to sheath on either side of the inside of the cathode; the long trajectory of these electron is thought to produce an increased number of secondary electrons, which produces the high plasma density and plasma current. We will discuss some of the problems associated with the well-accepted model and we will propose a new explanation which has some important implications.

Finally, we will describe how hollow cathodes can be used to deposit thin films and nanostructured coatings, including the use of our novel toroidal planar hollow cathode to produce bismuth thin films, nanoparticles and bismuth/a-C:H nanocomposites.

6:40pm **TF-WeE4 Depth Profiling Organic Thin Films with Argon Cluster Beam**, *Jean-Jacques Pireaux, Nütler, Noël, Houssiau*, University of Namur, Belgium

Many modern devices are based on multilayers of different materials, combined to reach a specific application. Monoatomic ion beam depth profiling did – and still do- immensely contribute to the learning of such multilayered structures containing metallic and oxide films; but one couldn't study (in ToF-SIMS, AES or XPS) an organic/other material interface, or an organic multilayered structure because of the damages induced by the ion beam. For the profiling of organic layers, the development and commercial availability of sputtering sources based on poly-atomic ions (SF<sub>6</sub>, C<sub>60</sub>, coronene) came as a significant and promising evolution; the still more recent Argon cluster-ion source appears now as a revolution for a true quantitative depth analysis of organic films. Numerous applications of gas cluster ion beams have been presented at international conferences; publications study the influence of cluster size, of cluster energy on sputter rates on series of different polymers, and on depth resolution in sputter depth profiles [1]. The present work aims to study by XPS the sputter yield, and the depth resolution in samples consisting of multilayered amino-acid films while profiling with different Ar cluster ions (Thermo Fisher Scientific Escalab 250Xi spectrometer, MAGSIS source). The materials were chosen for their ease to be reproducibly deposited by sequential thermal evaporation in high vacuum under quartz-crystal balance monitoring ; the method revealed successful for the study of delta layers in dual beam Cs+/Bi3+ profiling in ToF-SIMS [2]. Phenylalanine (Phe) and tyrosine (Tyr) were used for this study. Although both amino acids differ only by an OH- group, their characteristic chemical fingerprints could be differentiated throughout the whole depth profile. Both materials surprisingly present a very different sputter yield: the erosion yield of Phe is larger (almost twice the value, depending on the Ar cluster size and energy) than for Tyr – a trend that is completely reversed in ToF-SIMS using Cs+[2,3] ; this strongly suggests different sputtering mechanisms, that will be reviewed during the presentation. Depth resolution at the interface between two layers is found to be better when sputtering from the high sputter yield material to the low one. It is worth to note in addition that, as suggested by Laser scanning confocal microscopy, the gas cluster ion beam profiling does not increase significantly the sample surface roughness.

[1] P.J. Cumpson et al, J.V.S.T. A31 (2013)020605 ; SIA 45 (2013)601

[2] C. Noël, University of Namur, Master Thesis, 2013

[3]C. Noël, L. Houssiau. SIMS Europe 2014 Conf., Münster.

7:00pm **TF-WeE5 Adaptive Functional Surfaces: Ni-Ti(-Cu) Shape Memory Thin Films**, *M. Callisti*, University of Southampton, *Tomas Polcar*, University of Southampton, UK

Shape memory alloys could be effectively used as thin films acting either as active/passive actuators or superelastic interlayers. In this study a series of NiTiCu coatings with increasing was fabricated by magnetron sputtering with a thickness of 2 µm. In order to obtain superelastic properties, the films were isothermally annealed for 1 hour at 500°C in a high vacuum environment. Subsequently the superelastic layers were coated by magnetron sputtering with a functional tribological coating (DLC-W and self-lubricant WSC film).

The chemical composition of every single layer was measured by Energy-dispersive X-ray spectroscopy (EDS), while the structure was evaluated by grazing-incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). The mechanical properties of the single layers as well as those of the bilayers were measured by nanoindentation. Finally, the

tribological behaviour of the bilayers and of the single layers were characterised by pin-on-disc.

We will demonstrate that superelastic interlayer could significantly increase coating adhesion. Pure NiTi interlayers underwent progressive irreversible martensitic transformation during the sliding and lost superelasticity; on the other hand, transformation of NiTiCu film was fully reversible. We will show that we can control compressive and shear stress in functional coating during sliding by selection of an optimum superelastic interlayer.

**7:40pm TF-WeE7 Metal Oxide thin Films for Medical Applications, Sandra Rodil, A. Almaguer-Flores, Universidad Nacional Autonoma de Mexico, P. Silva-Bermudez, Instituto Nacional de Rehabilitación INVITED**

Nowadays, it is generally accepted that surfaces are critically important to nearly all aspects of biomedical technology since most of the biological reactions occur at the interfaces. In vitro studies have demonstrated that the surface properties are directly related to important biological events, such as protein adsorption, bacterial attachment and cell growth. In the case of medical implants, during the last years the research has evolved from the improvement of bulk properties and design of the implants to the development of a variety of bio-functional surface modifications, such as surface topography at the nanoscale, adhesion of growth factors or coating deposition. There is an extensive research to find methods of designing tailored surfaces, which might act as stimuli to guide specific cell responses according to the specific medical application.

This presentation explores one of the many surfaces modifications that have been proposed; plasma deposited coatings. The talk is then divided into two parts. Firstly, a short review about the specific needs to improve odontological implants. Secondly, the results of the physical, chemical and biological characterization of metal oxide thin films ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$ ) deposited by magnetron sputtering are presented. The factors considered of biological relevance in order to understand the surface interaction and that will be presented include: a) protein adsorption on the metal oxides studied by Ellipsometric Spectroscopy, Atomic Force Microscopy and X-ray photoelectron Spectroscopy, b) Corrosion behaviour of the oxides immersed in simulated biological solutions, c) Bacterial attachment and d) Cell adhesion, proliferation and differentiation.

**8:20pm TF-WeE9 Synthesis and Characterization of  $\text{TiO}_2$  and  $\text{Bi}_2\text{O}_3$  Thin Films for Photocatalytic Applications, JuanCarlos Medina, M. Bizarro, IIM-UNAM, Mexico, M. Giorcelli, A. Tagliaferro, Politecnico di Torino, Italy, P. Silva-Bermudez, Instituto Nacional de Rehabilitación, Mexico, S.E. Rodil, IIM-UNAM, Mexico**

The magnetron sputtering technique was used to obtain bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and titania ( $\text{TiO}_2$ ) thin films. The films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. The results indicated that the  $\text{Bi}_2\text{O}_3$  thin films presented the cubic delta phase and the  $\text{TiO}_2$  thin films showed a combination of rutile-anatase. The photocatalytic activity for both films was evaluated testing the degradation of methyl orange dye ( $\text{C}_{14}\text{H}_4\text{N}_3\text{SO}_3\text{Na}$ ) under ultraviolet light and a solution of pH 3.5. The dye degradation and the kinetic of the reaction were estimated using the variation of the corresponding absorption band as a function of the irradiation time. The results pointed out that the photocatalytic activity was always larger for  $\text{Bi}_2\text{O}_3$  films than for  $\text{TiO}_2$  films. Moreover the activity was also larger for  $\text{Bi}_2\text{O}_3$  in comparison to equivalent mass-amounts of  $\text{TiO}_2$  powders (P25) under the same experimental conditions. However XPS tests showed that after a degradation cycle bismuth oxide transforms to Bismuth Oxychloride ( $\text{BiOCl}$ ) due to the interaction with Cl ions from the HCl solution used to decrease the pH, and as a consequence the photocatalytic effect was reduced. After calculating and comparing the reaction kinetic constants for both oxide films, it is concluded that under UV light, the  $\text{Bi}_2\text{O}_3$  reaction rate is three-fold larger than  $\text{TiO}_2$  reaction rate constant. These results suggest that the  $\text{Bi}_2\text{O}_3$  films are a new promising photocatalytic material for water treatment application. Moreover, studies of photoinduced changes in the wettability demonstrated a similar behavior between  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  thin films.

**8:40pm TF-WeE10 Preparation of Ce-doped Hafnium Oxide Thin Films by Sol-Gel Method, Luis Garcia-Cerda, A. Puente, Research Center on Applied Chemistry, Mexico, S. Galvez-Barboza, L.A. Gonzalez, Center for Research and Advanced Studies of the National Polytechnic Institute**

Mono and multilayer Ce-doped hafnium oxide thin films were deposited on silicon wafers and quartz by spin-coating technique using a solution prepared by solgel with hafnium chloride, cerium nitrate, citric acid and ethylene glycol as starting materials. Ce-doped  $\text{HfO}_2$  thin films with 1, 3 and 5 layers were annealed in air for 2 h at 500, 700 and 900 °C. The thin films were then characterized for structural, surface morphological and optical properties by means of X-ray diffraction (XRD), Atomic force

microscopy (AFM), scanning electron microscopy (SEM) and optical absorption. X-ray diffraction analysis indicated that the cubic  $\text{HfO}_2$  films could be obtained by annealing at 500 °C. AFM and SEM images revealed well defined particles which are highly influenced by annealing temperatures.

## Thin Films

Room: Makai - Session TF-ThM

## Graphene

**Moderator:** Suneel Kodambaka, University of California, Los Angeles

8:00am **TF-ThM1 Construction and Characterization of Two Dimensional Atomic Crystals on Transition Metal Surfaces: Graphene, Silicene, Germanene, and Hafnene, Shixuan Du**, Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Epitaxy on a transition metal (TM) substrate is a promising method to produce a variety of two dimensional (2D) atomic crystals which potentially can be used in next generation electronic devices. This method is particularly valuable in the case of producing 2D materials that do not exist in 3D forms, for instance, silicene. In this talk, I will present construction and characterization of graphene, silicene, germanene, and hafnium honeycomb lattice on transition metal surfaces (TMS) (for example, Ru(0001), Pt(111), and Ir(111)). Molecular beam epitaxial growth technique is used to form the large scale 2D atomic crystals on TMS. Low electron energy diffraction (LEED) and scanning tunneling microscopy/spectroscopy (STM/S) together with density functional theory (DFT) calculations are employed to confirm the formed structure on the TMS. We expect that on the TMS more new 2D crystals could be found and these materials will show very interesting physical property and its promising potential applications in nanoscale devices.

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3. L. Meng *et al.*, *Nano Lett.* **13**, 685 (2013).
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8:40am **TF-ThM3 Graphitic Structures on Ru(0001), Valeria del Campo**, Universidad Tecnica Federico Santa María, Chile, *R.H. Henríquez*, Universidad Técnica Federico Santa María, Chile, *P.H. Häberle*, Universidad Tecnica Federico Santa María, Chile

Chemical Vapor Deposition (CVD) is one of the most used techniques for growth of graphitic structures. In the case of graphene, this technique allows the growth of large graphene sheets. However, to obtain monocrystalline graphene (millimeter scale) the CVD process is performed in Ultra High Vacuum (UHV). In this work we grew monocrystalline graphene and carbon nanodiscs on Ru(0001) through LP-CVD (Low Pressure CVD).

To grow our samples, first we heat the substrate (ruthenium crystal) in UHV. Once the desired temperature has been reached, the substrate is exposed to ethylene for some minutes. After exposure, the sample is annealed to allow the formation of carbon structures on the substrate. We performed this process with two different sets of parameters, obtaining different carbon structures on the Ru(0001) surface.

With one set of parameters we obtained graphene sheets on the ruthenium surface. With the second set of parameters we also grew a graphene layer, but on top of this layer we grew carbon nanodiscs. The diameters of these discs vary from few to hundreds nanometers, while their height is always below 1 nm.

The growth of carbon nanodiscs could be explained not only by the different set of parameters but also by the presence of impurities on the ruthenium surface. These impurities enable a preferential nucleation around them. This carbon excess allows the formation of carbon nanodiscs under the CVD conditions used in this experiment.

9:20am **TF-ThM5 On the Wettability of Graphene, Akira Akaishi**, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, Japan, *T. Yonemaru*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST, *J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

While graphite is well known as hydrophobic material, recent studies have revealed that pristine graphitic surfaces are more likely to be hydrophilic. Hydrophobic/hydrophilic nature is closely related to wettability of surfaces. One of the characteristic measures of wettability is a contact angle that is the angle of the edges of a water droplet placed on target surfaces. It has been reported that the contact angle of water on graphite surfaces decreases as removing hydrocarbons on the surface [1,2]. The contact angle estimated

by molecular dynamics (MD) simulations, however, varies depending on a choice of the parameters of interaction potentials between a water molecule and graphitic surfaces [3]. The wettability of pristine graphene surfaces remains unsettled.

We have investigated the behavior of water molecules on graphene surfaces with MD simulations by changing empirical parameters. The simulations are prepared with a graphene sheet and a water droplet which is dropped initially on the graphene surface. With increasing the number of water molecules, the droplet covers the surface and the layered-structure of molecules on the surface is formed. This indicates that, at a level of empirical model, a graphene surface is capable of wetting.

The formation of water layers on the surface can be seen by the density profile of water molecules. The density distribution of oxygen and hydrogen atoms of water along the axis perpendicular to the graphene surface indicates the existence of the layers. Moreover, the distinct peaks of the hydrogen atom distributions indicate that the direction of oxygen-hydrogen (O-H) bonds is not randomly distributed but is certainly oriented. The angle distribution of O-H bonds shows that hydrogen bonds are formed between the water layers on the graphene surface. In other words, the water molecules in the layers tend to form the hydrogen bonding only within the layers. The water molecules above the layer have no unpaired hydrogen bonds that are pointing perpendicular to the layer plane.

### References

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9:40am **TF-ThM6 Unbalanced Standing Wave Patterns at a Graphene Junction, W.-J. Jang, H. Kim**, Korea University, Seoul, Republic of Korea, *M. Wang, S.K. Jang*, Sungkyunkwan University (SKKU), Republic of Korea, *M. Kim*, SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (SKKU), Suwon 440-746, Republic of Korea, *S. Lee, S.-W. Kim, Y.-J. Song*, Sungkyunkwan University (SKKU), Republic of Korea, *Se-Jong Kahng*, Korea University, Republic of Korea

Exotic behaviors such as lensing and perfect transmission are expected in graphene p-n junctions, due to lattice-induced chirality of charge carriers, and experimentally studied using charge transport devices with a scale of several tens of nanometers. However, there has not been a study to confirm such behaviors at the atomic scale. Here, we report the experimental evidence for chiral electron reflections at a graphene junction on hexagonal BN/Cu. We performed scanning tunneling microscopy and spectroscopy to observe unbalanced electron standing wave patterns, which only appeared in one region at an energy lower than 100 meV, or at higher than 250 meV in the other region. Such an energy-dependent crossover of regions of standing wave patterns is explained by solving the Dirac equation with a simple potential step model. Our study shows that chirality of the charge carrier is a key component for understanding their reflections in graphene junctions at the atomic scale.

11:00am **TF-ThM10 Synthesis of Graphene via Surface Segregation and Reaction, Daisuke Fujita**, NIMS, Japan, *K. Sagisaka, H. Guo*, National Institute for Materials Science, Japan

Single-layer, bi-layer and few-layer thick nanosheets of graphene have been attracting significant amount of attention due to their excellent physical, chemical and mechanical properties. The first isolation of few-layer graphene (FLG) was demonstrated in 2004. However, single-layer graphene (SLG) was first synthesized 40 year ago by *surface segregation*, and was identified by Blakely *et al.* in 1974 using surface sensitive techniques. In 1980s, we initiated the growth and characterization of FLG and h-BN nanosheets using *surface segregation* and *surface reaction*. For the graphene growth, there are three important steps; surface segregation of doped atoms, surface reaction to form a monolayer phase, and subsequent 3-D growth (*surface precipitation*). Such surface phase transition was demonstrated on C-doped Ni(111) by *in situ* X-ray photoelectron spectroscopy (XPS) at elevated temperatures, and the growth mode was clarified by inelastic background analysis. Among the three, the surface segregation plays the most important role for the SLG synthesis. The surface segregation approach has been applied to Pt(111) and Pd(111) substrates, where weak coupling is expected, and controllable growth has been demonstrated successfully. As one of the derivatives, we recently proposed a promising method for producing SLG covering an entire substrate at low temperature using a Ni film deposited on an HOPG substrate. By heating the Ni/HOPG in high vacuum, carbon atoms forming graphene are diffused from the HOPG substrate through the Ni template. In this paper, we will put more focus on the effect of competitive surface-site occupation between carbon

and other surface-active impurities on the SLG growth. It is known that sulfur is a typical impurity of metals and the most surface-active element. Even with a high purity single crystal, the surface sites are finally occupied by sulfur at the elevated temperatures by surface segregation. In the case of Ni(110) surface, it is confirmed by scanning Auger microscopy (SAM) and scanning tunneling microscopy (STM) that the available surface sites is nearly occupied by sulfur with a centered 2x2 arrangement. When the Ni(110) is doped with carbon, surface segregation of carbon and following graphene growth shall be strongly affected or restricted by the surface active elements such as sulfur. In this situation, we discovered a strongly directional growth of SLG, exhibiting rectangular-like shapes and nearly straight step edges. The detailed characterization at the nanoscale and interesting growth mechanism shall be discussed based on high resolution microscopes like UHV-STM and scanning helium ion microscopy (SHIM).

11:20am **TF-ThM11 Anomalous Enhancement of Seebeck Coefficients for the Graphene/h-BN Superlattices**, *Jun Nakamura*, The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan, *Y. Yokomizo*, The University of Electro-Communications (UEC-Tokyo) and JST-CREST

The thermoelectric conversion has been of interest for many researchers since Hicks and Dresselhaus showed that the introduction of low-dimensional structures such as quantum well structures would significantly enhance the dimensionless figure of merit [1]. Graphene is a two-dimensional, mono-layer material having honeycomb lattice of carbon atoms [2,3]. It has been suggested that the graphene-based device can be a novel thermoelectric material because of its potential giant Seebeck coefficient larger than 30 mV/K [4]. On the other hand, graphene nanoribbon (GNR) is a one-dimensional (1D) material, a strip of graphene, which has also been investigated theoretically as thermoelectric materials. A molecular dynamics study has shown that a high figure of merit can be obtained for the zigzag GNR (ZGNR) [5]. This result implies that the introduction of 1D structural modulation makes graphene into novel thermoelectric materials. We hereby propose, in this study, superlattice models consisting of ZGNR and zigzag BN nanoribbon (ZBNNR) [6,7]. We have investigated the Seebeck coefficients of ZGNR/BNNRs within the Boltzmann transport theory. It has been shown that a ZGNR/ZBNNR marks up to 20 times larger in the Seebeck coefficient than graphene. The Seebeck coefficients of the superlattices increase with decreasing width of the constituent ZGNR. It has been revealed that the giant Seebeck coefficients of the superlattices stem from the so-called pudding mold band with a finite energy gap.

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11:40am **TF-ThM12 All-graphene Gas Sensor Integrated with Sensing Channel and Graphene Heater**, *Choon-Gi Choi*, Creative Research Center for Graphene Electronics, Electronics and Telecommunications Research Institute (ETRI), Republic of Korea

Graphene leading to high surface-to-volume ratio and outstanding conductivity has been applied for gas molecule sensing with fully utilizing its unique transparent and flexible functionalities which cannot be expected from solid-state gas sensors. However, in order to realize the fast responsive and significantly sensitive graphene gas sensor without hampering of both flexibility and transparency, the high quality of sp<sup>2</sup> carbon bonding for sharp sensing response are demanded. In this work, we demonstrate large-scale flexible and transparent gas molecule sensor devices, integrated with a graphene sensing channel and a graphene transparent heater for fast recovering operation. This combined all-graphene device structure enable an overall device optical transmittance that exceeds 90% and reliable sensing performance with a bending strain of less than 1.4 %. In particular, we could classify the fast (~14 s) and slow (~95 s) response due to sp<sup>2</sup>-carbon bonding and disorders on graphene and the self-integrated graphene heater leads to the rapid recovery (~11 s) of a 2 × 2 cm<sup>2</sup> sized sensor with reproducible sensing cycles, including full recovery steps without significant signal degradation under exposure to NO<sub>2</sub> gas.

This work was supported by the Creative Research Program of the ETRI (14ZE1110) of Korea and by a grant (Code No. 2011-0031660) from the Center for Advanced Soft Electronics under the Global Frontier Research Program of the Ministry of Education, Science and Technology of Korea.

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