

## Thin Films and Surface Modification

### Room Naupaka Salon 1-3 - Session TF-WeP

#### Thin Films and Surface Modification Poster Session II

**TF-WeP-1 Annealing Temperature Effects on Liquid Crystal Behavior and Electro-Optical Properties in Inorganic Alignment Films**, *H. Lee, J. Sim*, Ulsan National Institute of Science Technology, Republic of Korea; **Hong-Gyu Park**, Changwon National University, Republic of Korea

Aligning liquid crystal molecules in a single direction is essential for achieving a uniform and clear display. Additionally, research on the application of new alignment films and methods to enhance the optical, thermal, mechanical, and chemical stability of liquid crystal alignment is ongoing. In this study, we observed the changes in liquid crystal behavior and the resulting electro-optical properties in high-k inorganic alignment films depending on the annealing temperature. While conventional polyimide alignment films are typically annealed at 230°C, we examined how the characteristics of the inorganic films used in this study changed with annealing temperatures of 100°C, 150°C, and 200°C. This allowed us to explore the feasibility of low-temperature processing with inorganic alignment films and to assess their potential as a replacement for traditional polyimide alignment films.

**TF-WeP-3 Synaptic Characteristics of Memristive Au/LiNbO<sub>3</sub>/Pt Device Based on Schottky Barrier Modulation**, *Sejoon Lee, Y. Lee, D. Kim*, Dongguk University, Republic of Korea

The (113) LiNbO<sub>3</sub> layers were grown onto the (111) Pt/SiO<sub>2</sub>/Si substrates at 180 – 320 °C by radio-frequency magnetron sputtering. The samples grown at 250 °C displayed the improved crystallinity as well as the smooth surface morphology without any hillocks and pits. The memristive devices, fabricated in the form of the top-to-bottom Au/LiNbO<sub>3</sub>/Pt two-terminal device scheme, clearly exhibited the external electric field polarity-dependent asymmetric memristive hysteresis loops in their current-voltage characteristic curves. When repeating the current-voltage sweep at an appropriate program voltage range, the on-state current was gradually increased with increasing sweep number. Through analyzing the transport mechanism in Au/LiNbO<sub>3</sub>/Pt, such a behavior was confirmed to be attributable to the Schottky barrier modulation, arising from the ionic migration of oxygen vacancies inside the LiNbO<sub>3</sub> layer. In other words, the electro-migrated oxygen vacancies in LiNbO<sub>3</sub> lead to the Schottky barrier modulation particularly at the LiNbO<sub>3</sub>/Pt side; and it eventually gives rise to the switchable diode effect in the Au/LiNbO<sub>3</sub>/Pt device. Since the degree of the switchable diode effect relies on the pulse parameters of the applied voltage stresses, the memristive characteristics (e.g., data storage speed, multiple resistance states, data retention, etc.) could be effectively controlled by changing the pulse magnitude and the pulse duration of the program/erase voltages. Using these unique features, various synaptic functions such as a short-term memory, long-term potentiation/depression, and spike-timing dependent plasticity were effectively demonstrated. The results suggest that the LiNbO<sub>3</sub> based memristors hold great promise for the future neuromorphic applications.

[1] J. Wang *et al.*, Adv. Electron. Mater. 9, 2201064 (2023)

[2] J. Wang *et al.*, Adv. Intell. Syst. 5, 2300155 (2023)

**TF-WeP-4 X-Ray Photoelectron Spectroscopy and X-Ray Emission Spectroscopy Data Fitting Using a Genetic Algorithm**, *Alaina Humiston, J. Terry*, Illinois Institute of Technology

The ever-growing problem in modern science is that data is being collected at a rate faster than analysis can be performed by characterization experts. The analysis that is done for many recently published x-ray photoelectron spectroscopy (XPS) and x-ray emission spectroscopy (XES) data, is often incorrect/irreproducible and leads to a cycle of incorrect fits in this spectroscopy data. In this work, a genetic algorithm (GA) is being constructed to potentially minimize this human error. This GA code known as XPS Neo/XES Neo, is based on the Neo package which exists for EXAFS (EXAFS Neo) and Nanoindentation (Nano Neo) data. GAs are based on biological methods and depend on parameters such as populations size, number of generations, genes, crossover, and mutation. The GA takes in a certain population size and constructs individual vectors each with their own unique genes i.e the fitting parameters we are trying to optimize. It then performs crossover and mutation to these individual vectors to progress toward a lower global minimum. This GA allows for a variety of

mutation options including, Random Perturbations, Rechenberg, Metropolis mutation, and Self Adapting Differential Evolution. The methods of how a GA works in relation to XPS and XES datasets are discussed. The difficulties in making this work for XPS data arise from complicated backgrounds due to many effects such as plasmon loss, Auger peaks, and satellite peaks. XPS and XES data can also have many peaks that are difficult to distinguish from one another. Currently, the algorithm is only able to fit simplistic XPS spectra such C, O, N, and Si and is being worked on with the hopes of it becoming applicable for more difficult data. The goal is to make the algorithm applicable to all XPS data, with a greater focus given to the actinides, specifically for the use of fitting plutonium data as analysis of this spectra is highly sought after and difficult to fit. Through proper use of an informed GA, and collaboration with the XPS/XES database website XPSOasis.org, theoretically correct fitting of this data is hoped to be achieved.

**TF-WeP-5 Synaptic Characteristics of Au/Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Pt Memristors Based on Double-Barrier Schottky Junctions**, *Youngmin Lee, S. Lee, D. Kim*, Dongguk University, Republic of Korea

The Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> layers were grown onto the (111) Pt substrates at 450 °C by radio-frequency magnetron sputtering, and were annealed at 600 – 800°C. The 700°C-annealed samples showed a smooth surface and an improved orthorhombic lattice phase. The Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> layers exhibited the nonlinear lossy-type ferroelectric characteristics, by which the degree of ferroelectric polarization and its appropriate data retention can be gradually adjustable. The memristive devices, comprising the top-to-bottom Au/Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Pt two-terminal device scheme, clearly displayed the ferroelectric polarization-dependent asymmetric hysteresis behaviors in their resistive switching characteristics. When repeating the current-voltage sweep at a certain and moderate voltage range, the on-state current was gradually increased with increasing sweep number. This could be attributed to the Schottky barrier modulation at the Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Pt side. Since the repeated voltage stresses at the Au/Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> biased region would tenaciously increase the ferroelectric polarization field inside the Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> layer, the increased potential gradient along the Au-Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>-Pt direction could also increase. Then, the effective Schottky barrier height at the grounded Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Pt side will eventually decrease upon increasing the ferroelectric polarization field inside the Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> layer. Since the ferroelectric polarization strongly depends on both the magnitude and the duration of the applied voltage pulses, gradual Schottky barrier modulation could be easily accomplished by controlling the pulse parameters. Furthermore, due to the ferroelectric nature in Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Pt, the Schottky emission rate could be retained at every modulated Schottky barrier heights. This eventually enabled the fine and precise control of the multiple memristive resistance states. Using these unique characteristics, we successfully demonstrated various synaptic functions such as excitatory post-synaptic current, paired pulse facilitation, long-term potentiation/depression, and spike-timing dependent plasticity. The results depict that the present memristive device scheme of the ferroelectric Hf<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>-based double-barrier Schottky junction holds substantial promise for the future neuromorphic applications.

[1] S. Song *et al.*, Adv. Mater. Technol. 7, 2101323 (2022).

[2] B. Chen *et al.*, Nanotechnol. 34, 505205 (2023).

**TF-WeP-6 Isotope Labeling Study of CO<sub>2</sub> Formation Pathways in CO-H<sub>2</sub>O Ice Films under Ultraviolet Irradiation**, *Koichiro Yamakawa, A. Hirayama, I. Arakawa*, Japan Atomic Energy Agency, Japan

Molecular clouds are composed of gases and interstellar dust grains. The dust grains are covered with ice mantles predominantly composed of H<sub>2</sub>O [1]. When the densities of the clouds increase up to 10<sup>4</sup> cm<sup>-3</sup> or more and their temperatures drop below 20 K, CO is condensed on H<sub>2</sub>O-rich ice. The ice mantles are exposed to ultraviolet (UV) radiation, which causes a variety of photochemical reactions. CO<sub>2</sub> is one of the abundant molecules in the ice mantles, and the following two formation channels have been discussed [2]: (1) reaction of two CO molecules, one of which is electronically excited by UV light; (2) reaction of CO with the OH radical which is a dissociation product of H<sub>2</sub>O. We focused on the fact that these two channels can be distinguished from each other by isotope labeling, i.e., by employing H<sub>2</sub><sup>18</sup>O instead of H<sub>2</sub><sup>16</sup>O. In the present study, we investigated the UV photolysis of CO-H<sub>2</sub>O ice and determined the effective rates of the CO<sub>2</sub> formation channels with use of isotope labeling and infrared spectroscopy [3].

A CO gas and an H<sub>2</sub><sup>18</sup>O vapor were mixed in a gas handling system. The mixing ratio was changed in the range of CO/H<sub>2</sub><sup>18</sup>O = 1000-0.1. The gaseous mixture was introduced into an ultrahigh vacuum chamber and was condensed on a gold substrate cooled down to 10 K. After the

condensation, the CO-H<sub>2</sub><sup>18</sup>O ice was irradiated with UV light from a deuterium lamp for 120 min. Reflection-absorption infrared spectra were recorded during the condensation and UV-irradiation.

After the UV irradiation of any sample, we detected infrared absorption bands of C<sup>16</sup>O<sub>2</sub> (2346 cm<sup>-1</sup>) and C<sup>18</sup>O<sup>16</sup>O (2328 cm<sup>-1</sup>), which were generated through the CO-CO and CO-H<sub>2</sub>O reactions, respectively. The absorption band of C<sup>18</sup>O<sub>2</sub> was also detected at 2308 cm<sup>-1</sup> when the mixing ratio was in the range of CO/H<sub>2</sub><sup>18</sup>O = 100-0.1. This indicates that the photodissociation and regeneration of CO<sub>2</sub> took place in ice. We analyzed the irradiation-time dependence of the C<sup>16</sup>O<sub>2</sub> and C<sup>18</sup>O<sup>16</sup>O column densities to determine the effective cross sections of the CO<sub>2</sub> formation through the CO-CO and CO-H<sub>2</sub>O reactions simultaneously.

## References

- [1] E. L. Gibb et al., *Astrophys. J. Suppl. Ser.* **151**, 35 (2004).
- [2] N. Watanabe and A. Kouchi, *Astrophys. J.* **567**, 651 (2002).
- [3] A. Hirayama, I. Arakawa, and K. Yamakawa, *Astrophys. J.* **951**, 132 (2023).

**TF-WeP-10 Synthesis and Characterization of Mo and W Compounds for Disulfide Materials**, *Sunyoung Shin, C. Kim, T. Chung, B. Park*, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Two-dimensional transition metal dichalcogenides (TMDs), particularly MoS<sub>2</sub> and WS<sub>2</sub>, are regarded as potential substitutes for graphene in electronic devices due to their semiconducting properties, exhibiting both indirect and direct band gaps depending on the layer. Various methods have been employed in the synthesis of MoS<sub>2</sub> and WS<sub>2</sub> thin films. In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, metal precursors are typically used in conjunction with a sulfur source, such as hydrogen sulfide (H<sub>2</sub>S), sulfur powder, and so forth. In the majority of cases, the synthesis of crystalline MoS<sub>2</sub> has been achieved at elevated deposition temperatures, with the subsequent treatment at high temperatures being necessary for the attainment of crystallinity. In this study, precursors suitable for the deposition of MoS<sub>2</sub> and WS<sub>2</sub> were synthesized, characterized, and even MoS<sub>2</sub> deposition studies with molybdenum precursors were conducted at relatively low temperatures without any post-treatment process. Precursors (Mo(NtBu)<sub>2</sub>(StBu)<sub>2</sub> (**1**), W(NtBu)<sub>2</sub>(StBu)<sub>2</sub> (**2**)) suitable for the deposition of MoS<sub>2</sub> and WS<sub>2</sub> were synthesized and characterized. The molecular structures of **1** and **2** exhibit a tetrahedral geometry according to single-crystal x-ray crystallography. Thermogravimetric analyses of **1** and **2** showed two-step weight loss. The residues from each step of **1** were MoS<sub>3</sub> and MoS<sub>2</sub>, and these results were consistent with the subsequent deposition results of **1**. We successfully established a PEALD-MoS<sub>2</sub> process using **1** and H<sub>2</sub>S plasma as the precursor and reactant, respectively, at relatively low temperatures of 150–300 °C without any post-sulfurization process. A temperature-dependent selective deposition of Mo<sub>x</sub> phases was observed with the growth of amorphous MoS<sub>3</sub> films (150–200 °C), and crystalline MoS<sub>2</sub> films (250–350 °C).

**TF-WeP-11 Creating Multiple Catalytic Sites for Enhanced CO<sub>2</sub> Photoreduction Activity Through Synergistic Catalysis of MIL-TiO<sub>2</sub>-PI Hybrids**, *Lipei Ren, H. Wang*, Deakin University, Australia, China; *M. Laghaei*, Deakin University, Australia, Iran (Islamic Republic of); *S. Zhao, L. Kong*, Deakin University, Australia

Excessive burning of fossil fuels and changes in land use have led to rising atmospheric concentrations of carbon dioxide (CO<sub>2</sub>), resulting in dramatic and potentially irreversible changes in the world's climate. Nanoscale metal-organic framework (MOF) MIL-101(Cr) with high porosity and large specific surface area is an excellent porous nanomaterial for catalytic reduction of CO<sub>2</sub>. However, its applications have been typically restricted by nanoscale size. Herein, we assembled MIL-101(Cr) nanocrystals on TiO<sub>2</sub>-coated polyimide (PI) substrates via atomic layer deposition (ALD) for high-efficient photocatalytic CO<sub>2</sub> conversion. The high CO<sub>2</sub> capturing capability of MIL-101(Cr) is combined with the unique property of inorganic semiconductor nanoparticles (TiO<sub>2</sub>) to generate photoexcited electrons. Carbon monoxide (CO), methanol (CH<sub>3</sub>OH), and hydrogen (H<sub>2</sub>) were the main products of CO<sub>2</sub> photoreduction. The prepared MIL-TiO<sub>2</sub>-PI felts with 1000 cycles of TiO<sub>2</sub> deposition exhibited the best photocatalytic performance, with high CO, CH<sub>3</sub>OH, and H<sub>2</sub> yields of 158.6, 83.1, and 22.9 μmol g<sup>-1</sup>, respectively. This work opens new routes for CO<sub>2</sub> reduction using MOF-based membrane hybrids prepared by ALD technology.

**TF-WeP-12 Synthesis of Novel Yttrium and Lanthanide Precursors and Fabrication of La<sub>2</sub>O<sub>3</sub> Thin Films Through High-Temperature ALD**, *Yongmin GO, B. Park*, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *T. Park*, Hanyang University, Korea

Yttrium and lanthanide metal oxides are known for their high permittivity and wide band gaps, making them ideal materials for metal-oxide semiconductor field-effect transistors (MOSFETs) and dynamic random-access memory (DRAM). Although various thin film deposition techniques are used to make these metal oxide films, atomic layer deposition (ALD) is a useful method because it produces high quality films, allows self-limited growth, and allows precise control of film thickness.

Achieving the desired crystal structure and crystallinity during ALD requires forming crystallization seeds during the deposition process. To improve the crystal structure and crystallinity of the thin films, deposition must occur at high temperatures. Therefore, developing new precursors with excellent thermal stability, which can withstand high temperatures without decomposing, is critical for the ALD process.

In this study, we developed new yttrium and lanthanide precursors and evaluated their suitability as high-temperature ALD precursors. Various analytical techniques, including NMR, EA, TGA, and vapor pressure measurements, were used to confirm the characteristics of the newly synthesized precursors. Additionally, we proposed an ALD process for La<sub>2</sub>O<sub>3</sub> using the new lanthanum precursor and compared it to the commonly used La(iPrCp)<sub>3</sub> precursor. By processing at high temperatures with the new lanthanum precursor, we successfully obtained La<sub>2</sub>O<sub>3</sub> thin films with excellent crystallinity, higher density, and improved leakage current characteristics. These findings suggest that the new precursors are promising candidates for high-temperature growth of yttrium and lanthanide-based thin films via ALD.

**TF-WeP-13 X-Ray Photoelectron Spectroscopy Analysis of Gallium Nitride Thin Film Prepared by Atomic Layer Deposition**, *Y. Choi, H. Yoo, H. Kim, W. Lee, Sun Jae Kim*, Sejong University, Republic of Korea

Gallium nitride (GaN) is a wide direct bandgap semiconductor with high electron mobility and thermal conductivity. It is widely used in power electronics, RF amplifiers, and optoelectronics such as light-emitting diodes (LEDs). Low-temperature deposition is essential for depositing high-quality GaN thin films on temperature-sensitive substrates or devices. Atomic layer deposition (ALD) is the most suitable technique for this purpose. However, nitride films deposited at low temperatures tend to be nitrogen-deficient, and quantitative compositional analyses of ALD GaN thin films are scarce. X-ray photoelectron spectroscopy (XPS) using an Al Kα source makes the quantitative analysis difficult due to overlapping Ga KLL and N 1s peaks. Although the overlap can be avoided by using a non-monochromatic Mg Kα source, low resolution and many satellite peaks are problems. Auger electron spectroscopy lacks chemical shifts, which limits chemical bond analysis, and its relatively low peak intensity limits quantitative analysis. In this study, we performed XPS analyses of the ALD films prepared at 225 °C or lower. To overcome the problem of overlapping N 1s and Ga LMM peaks, we calculated the ratio of Ga to N using the Ga 2p and N KLL peaks. The GaN wafer was used as a reference, and the sensitivity factors were obtained. We also performed deconvolution of the Ga 3d peak to analyze the chemical states of Ga. This method was then used to investigate the effect of process temperature on the composition of GaN thin films.

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