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℃, we examined how the characteristics of the inorganic films used in this study changed with annealing temperatures of 100℃, 150℃, and 200℃. 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-2 Localized Physical and Chemical Manipulation of Surfaces via Thermal Scanning Probe Lithography (t-SPL)*, **Nicholas Hendricks**, E. Çağin,* Heidelberg Instruments Nano AG, Switzerland

Modification of thin film surfaces is of the utmost importance for various applications ranging from biosensors and spintronics to flat optics and magnonics. To push the performance of such applications to the next level, the optical, electrical, chemical, or magnetic properties need to be locally controlled at the sub-50nm length scale. To convert thin film surfaces, the use of direct-write lithography techniques is often employed where the film is manipulated by electrons, photons, or ions. These energetic particles can induce physical and chemical changes, however, the direct use of thermal energy as the stimulus could provide a more universal stimulus as well as an alternative route for such modifications. With thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor from Heidelberg Instruments, the use of heat to perform direct-write patterning conversions is possible [1-5].

t-SPL generates patterns by scanning an ultrasharp tip over a sample surface to induce local changes with a thermal stimulus. By using thermal energy as the stimulus, it is possible to perform various conversion processes such as functional surface group deprotection, precursor conversion, and crystallization. Along with an ultrasharp tip, with a radius less than 10nm, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor, a capacitive platform for electrostatic activation, and an integrated heating element. By having a cantilever with such properties, it's possible to generate 2D and grayscale chemical gradients where surface chemistry is critical.

In this presentation, the background and workings of t-SPL will be introduced along with the lithography and processing steps necessary to create chemical gradients through the deprotection of functional groups for enzyme and protein patterning. The patterning of a phase change material (PCM) of GeSbTe (GST) will also be discussed where sub-300nm phase changes have been optically observed.

1. S. Howell et al., Microsystems & Nanoengineering, 6, 21 (2020)
2. Y. Meng et al., Adv. Mater. 32, 2005979 (2020)
3. V. Levati et al., Adv. Mater. Technol. 8, 2300166 (2023)
4. O. J. Barker et al., Appl. Phys. Lett., 124, 112411 (2024)
5. Riedo et al., https://doi.org/10.21203/rs.3.rs-3810461/v1

TF-WeP-3 Synaptic Characteristics of Memristive Au/$LiNbO_3$/Pt Device Based on Schottky Barrier Modulation*, **Sejoon Lee**, Y. Lee, D. Kim,* Dongguk University, Republic of Korea

The (113) $LiNbO_3$ layers were grown onto the (111) Pt/SiO_2/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/$LiNbO_3$/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/$LiNbO_3$/Pt, such a behavior was confirmed to be attributable to the Schottky barrier modulation, arising from the ionic migration of oxygen vacancies inside the $LiNbO_3$ layer. In other words, the electro-migrated oxygen vacancies in $LiNbO_3$ lead to the Schottky barrier modulation particularly at the $LiNbO_3$/Pt side; and it eventually gives rise to the switchable diode effect in the Au/$LiNbO_3$/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 $LiNbO_3$ 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/$Hf_xZr_{1-x}O_2$/Pt Memristors Based on Double-Barrier Schottky Junctions*, **Youngmin Lee**, S. Lee, D. Kim,* Dongguk University, Republic of Korea

The $Hf_xZr_{1-x}O_2$ layers were grown onto the (111) Pt substrates at 450 °C by radio-frequency magnetron sputtering, and were annealed at 600 – 800℃. The 700℃-annealed samples showed a smooth surface and an improved orthorhombic lattice phase. The $Hf_xZr_{1-x}O_2$ 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/$Hf_xZr_{1-x}O_2$/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 $Hf_xZr_{1-x}O_2$/Pt side. Since the repeated voltage stresses at the Au/$Hf_xZr_{1-x}O_2$ biased region would tenaciously increase the ferroelectric polarization field inside the $Hf_xZr_{1-x}O_2$ layer, the increased potential gradient along the Au-$Hf_xZr_{1-x}O_2$-Pt direction could also increase. Then, the effective Schottky barrier height at the grounded $Hf_xZr_{1-x}O_2$/Pt side will eventually decrease upon increasing the ferroelectric polarization field inside the $Hf_xZr_{1-x}O_2$ 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 $Hf_xZr_{1-x}O_2$/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 $Hf_xZr_{1-x}O_2$-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 CO2 Formation Pathways in CO-H2O 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_2O [1]. When the densities of the clouds increase up to 10^4 cm^{-3} or more and their temperatures drop below 20 K, CO is condensed on H_2O-rich ice. The ice mantles are exposed to ultraviolet (UV) radiation, which causes a variety of photochemical reactions. CO_2 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_2O. We focused on the fact that these two channels can be distinguished from each other by isotope labeling, i.e., by employing $H_2{}^{18}O$ instead of $H_2{}^{16}O$. In the present study, we investigated the UV photolysis of CO-H_2O ice and determined the effective rates of the CO_2 formation channels with use of isotope labeling and infrared spectroscopy [3].

A CO gas and an $H_2{}^{18}O$ vapor were mixed in a gas handling system. The mixing ratio was changed in the range of CO/$H_2{}^{18}O$ = 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-$H_2{}^{18}O$ 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 $C^{16}O_2$ (2346 cm^{-1}) and $C^{18}O^{16}O$ (2328 cm^{-1}), which were generated through the CO–CO and CO–H_2O reactions, respectively. The absorption band of $C^{18}O_2$ was also detected at 2308 cm^{-1} when the mixing ratio was in the range of CO/$H_2{}^{18}O$ = 100-0.1. This indicates that the photodissociation and regeneration of CO_2 took place in ice. We analyzed the irradiation-time dependence of the $C^{16}O_2$ and $C^{18}O^{16}O$ column densities to determine the effective cross sections of the CO_2 formation through the CO–CO and CO–H_2O 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).

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