

Thin Films Division

Room Ballroom A - Session TF-ThP

Thin Film Poster Session

TF-ThP-1 Effect of Metallic Bonding on the Optical Properties of Transition Metal Based Thin Films, Nimarta Kaur Chowdhary, T. Gougousi, UMBC

Combining electronics and photonic devices on a single chip provides a powerful approach to resolving technological issues, from solar technology to low-power computing systems. Next-generation high-speed photonic devices require materials with large and fast optical nonlinearities. Integrating electronic and photonic devices on a single chip has proved challenging due to the limited availability of nonlinear materials compatible with the semiconductor industry process flow. Transition metal oxide thin films may serve as a potential solution to this problem.

It has been shown that atomic layer deposition (ALD)-grown as-deposited TiO₂ thin films demonstrated large n_2 values, which were 4-6 orders larger than previously reported [1]. X-ray photoelectron spectroscopy (XPS) revealed that these TiO₂ films incorporated Ti-O-N/TiN metallic bonds during growth [1]. The very large enhancement that occurred for ALD films grown at 250 °C was a result of about 1 at. % of Ti-O-N bonds evenly distributed within the films [1]. Although silicon and most dielectric materials used in the electronic industry show little to no nonlinear optical response, it is predicted that the addition of metallic impurities in the bulk during the fabrication process will be an optimal way to induce nonlinearities while maintaining compatibility with the process cycle.

We investigated two complementary ways to incorporate metallic bonding starting with either metal oxide (hafnium dioxide, titanium dioxide) or metal (titanium, titanium nitride) thin films. The former is grown using ALD, and to enhance the metallic bonding, we attempted to promote precursor decomposition by using growth parameters such as temperature and purge times outside the optimal ALD window. Metal films were grown by physical vapor deposition (PVD) and post-deposition thermal treatment was used to control the amount of metal bonding. The ALD films showed some metallic bonding that was accompanied by an increased concentration of bonded carbon impurities. This metallic bonding was found to affect the films' bandgap with absorption extending further into the visible than for pure TiO₂ films.

This approach to accomplishing large nonlinearities may be transferable to other transition metals/transition metal oxides and their nitrides. This will diversify the toolkit of nonlinear optical materials available in the thin-film form, which in its current state is severely lacking.

[1] R. Kuis, T. Gougousi, et al, *ACS Photonics*, vol. 6, no. 11, pp. 2966–2973, Nov. 2019, doi: 10.1021/acsp Photonics.9b01176.

TF-ThP-2 Water Transfer of Electronic Circuits on Flexible and Stretchable 3D Objects, Issraa Shahine, Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN). Iété d'Accélération du Transfert de Technologie, SATT Ouest ValorisatSocion SAS, France; M. Harnois, Université Rennes 1, CNRS, Institut d'Électronique et des Télécommunications de Rennes (IETR), France; P. Tessier, Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France

There is a growing need for products that integrate active electronic devices on the surface of everyday complex objects to make them smarter and more connected. Often the presence of electronic circuits on the surface must remain relatively discreet. It is then necessary to have transparency of the circuit connections. It is a main concern of the field of 3D electronics for "smart objects" and "smart sensors" as an important part of display devices (touch screen and display), energy storage devices (solar cells and super capacitors), and wearable medical devices (electronic skin).

Herein, we use a new and original process for transferring 3D electronic circuits, to produce the interconnection of the transferred circuits over 3D objects conserving their optical, electronic and mechanical properties, to finally serve as flexible transparent conductive electrodes (FTCE). The aim is to connect SMD (surface mounted device) to the defined design circuits to validate the overall operation of the object at the level of detection, display and communication functions.

For this aim, we fabricate, by physical vapor deposition (PVD) method, flexible, stretchable and transparent nanoporous gold designs resulted by applying dealloying process to ultra-thin Au-Cu alloy thin films using acidic vapors.[1] [#_ftn1] These designs are transferred into defined flat and/or

3D surfaces according to the process of film-based patterns transferred to 3D object surfaces.[2] [#_ftn2] This new, powerful and robust technology allows a good transfer of manufactured lines with correct performances concerning the transmittance and sheet resistance of the transferred thin films to deformation.

The transfer into flexible PET surfaces allows the conservation of the electrical properties of the design upon deformation. They have good sheet resistance values ranging from few to about tens of ohms per square (Ω/\square), with a transparency of the order of 50%, while maintaining exceptional stability under severe mechanical deformations (bending).

[1] [#_ftnref1] Chauvin et al. (2019), *NPJ Flexible Electronics*, 3(1), 1-6.

[2] [#_ftnref2] Le Borgne et al. (2017), *ACS applied materials & interfaces*, 9(35), 29424-29429.

TF-ThP-3 Magnetic Field Assisted Epitaxial Growth of Magnetite Films, Adam Dziwoki, Jerzy Haber Institute of Catalysis and Surface Chemistry PAS, Poland; B. Blizniuk, Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Ukraine; K. Freindl, J. Korecki, N. Spiridis, Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Poland

Modern spintronics requires materials, usually thin films and heterostructures, with controllable and programmable magnetic properties. One of the key properties is magnetic anisotropy that determines the orientation of magnetization and its response to an external magnetic field (MF). In well-defined epitaxial films the main contributions to the effective magnetic anisotropy are shape, magnetocrystalline, surface/interface and magnetoelastic/strain anisotropy terms. Molecular beam epitaxy (MBE), which is the most widely used method of growing magnetic heterostructures allows certain level of indirect control of the magnetic properties by controlling elementary growth processes through substrate temperature, deposition rate and partial pressure of reactive gases. Additionally, external agents can be used, such as plasma generation or ion beams. Other factors, including external stimuli, have been only occasionally applied in physical vapor deposition of thin films. In particular, due to the limitations of the MBE technology, examples of application of external fields (in particular MF) *in situ* during growth, as well during *in situ* post-deposition treatment are scarce. Here we present MF-assisted epitaxial growth of magnetite Fe₃O₄(001) films on MgO(001) and Fe₃O₄(111) on Mg(111).

The magnetite films were deposited in a multi-chamber ultra-high vacuum (UHV) system (base pressure 5·10⁻¹⁰ mbar) including MBE facility, typical surface characterization tools (LEED, AES, STM) and Conversion Electron Mossbauer Spectroscopy (CEMS). We used the typical reactive deposition of metallic ⁵⁷Fe in O₂ (partial pressure 5·10⁻⁶ mbar) [1]. The use of the ⁵⁷Fe isotope facilitated CEMS measurements. external MF can be applied during deposition by combination of modular sample holders transferable between two stations of a 4-axis manipulator that are specialized for a given step in the MBE process. The MgO substrates were mounted on "flag-style" (FS) sample plates and the corresponding manipulator station enables those preparation steps that do not require MF. MF can be applied using PTS-style sample holders (PREVAC) incorporating permanent magnets and receiving the FS plates. The magnetic field configurations during deposition can be 100 mT in-plane and 250 mT out-of-plane for the two holder types at maximum deposition temperature of 400°C.

The role of external MF for the in-plane and out-of-plane magnetic anisotropy in the Fe₃O₄(001) and Fe₃O₄(111) film is revealed by the CEMS analysis that is able to distinguish between different magnetization orientation in the virgin magnetization state.

[1] J. Korecki et al. *Thin Solid Films*. 412(2002)14.

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TF-ThP-4 Spectra Analyses of Antireflection Coatings and Hydrogenated Amorphous Silicon Deposited at Room Temperature for Silicon Photovoltaic Cells Applications, *H. da Silva Alvarez, A. Roberto Silva, F. Hummel Cioldin, L. Carvalho Jayme Espindola, José Alexandre Diniz*, University of Campinas, Brazil

For the application in c-Si PV cells, this work has as its main objective, the analysis of antireflection coatings of thin oxides (TiO_2 , Al_2O_3 , Ta_2O_5) and nitride (SiN_x) films, deposited at room temperature, respectively by reactive sputtering or ECR-CVD, for increasing of solar cells efficiency. And of a-Si:H thin films deposited in an ECR-CVD system with RF frequencies of 1W, 3W, and 5W (a-Si:H_{1W/3W/5W}), for variations in their hydrogen concentration, after and before the diffusion of aluminum (Al) at the low temperature of 450 °C for future use as emitter layer. Using a UV/VIS/NIR spectrophotometer with an integrating sphere, the total reflectance of these films was calculated by comparing them with the spectra of a polished c-Si control sample (ΔR_{Total}). For the ARC films, ΔR_{Total} higher than 50% were achieved, with the largest ones coming from SiN_x , with 58.6%, and Ta_2O_5 , 56.5%. Their respective minimum (R_{min}) were 1.4% and 2.5% at 610 nm and 600 nm – close to the maximum energy in the solar spectrum at 630 nm. The TiO_2 and Al_2O_3 films had corresponding ΔR_{Total} of 54.6% and 51.7%, with R_{min} of 5.3% and 5.9%, at 580 nm and 530 nm – shifted towards the UV region compared to the ideal value of 630 nm. For the a-Si:H films, it was observed a reduction of the polished c-Si reflection after their deposition, with the best result coming from the a-Si:H_{3W} film with 47.4 %, with $R_{\text{min}} = 1.4$ % at 630 nm. Followed by the sample with the a-Si:H_{5W} film with $\Delta R_{\text{Total}} = 35.1$ % and $R_{\text{min}} = 11.6$ % at 670 nm. While, for the a-Si:H_{1W} film, a $\Delta R_{\text{Total}} = 8.2$ % was obtained, with $R_{\text{min}} = 3.0\%$ at 570 nm. This low ΔR_{Total} value of the a-Si:H_{1W} sample is due to the presence of greater reflectance values on its spectra in the regions between 440 nm and 500 nm and 660 nm and 1100 nm when compared with the polished c-Si control sample. After a quickly sputtering deposition (20 s) of an ultrathin Al film and its diffusion for 30 min at 450 °C, Al-Si_{5W/3W/1W} films were produced. After this process, the Al-Si_{5W} has now the best results with $\Delta R_{\text{Total}} = 24.8$ %, $R_{\text{min}} = 20.0$ % at 750 nm, and the smallest change in its ΔR_{Total} . While the Al-Si_{3W} has an intermediate value of $\Delta R_{\text{Total}} = 8.2\%$. And the Al-Si_{1W} has a higher reflectance than the polished c-Si substrate with $\Delta R_{\text{Total}} = -12.6\%$, negative for this reason. In addition, as the spectra of the films have a similarity with the polished c-Si in the UV region, a change in their crystalline structure could be inferred, probably induced by the Al diffusion.

TF-ThP-5 Characteristics of Low Temperature Deposited SiO₂ Film based on Very High Frequency Plasma Enhanced Atomic Layer Deposition with Substrate Bias, *Yongki Lee, H. Kim, G. Ahn, G. Yeom*, Sungkyunkwan University (SKKU), Republic of Korea

This study investigated the effect of very high frequency (VHF) plasma and substrate biasing on the surface chemical reaction and the surface damage on SiO₂ film deposited at low substrate temperatures by Plasma-enhanced atomic layer deposition (PE-ALD) system. PE-ALD uses plasma to deliver the energy required for chemical reactions and it can be useful in lowering substrate temperature and increasing the density of material during PE-ALD, however, it can also contaminate or damage the substrate by high energy ions in the plasma. In addition, the substrate biasing may also cause unnecessary effects, especially in non-metallic materials such as preferential sputtering of high sputter yield component, charging, etc. In this study, the effect of substrate biasing was optimized while increasing the density of the plasma using VHF plasma. By applying an appropriate bias voltage to the substrate with VHF plasma, it was possible to deposit stoichiometric SiO₂ films with more rigid properties and even at a lower temperature. These results were investigated for both bare and pattern wafers. Therefore, by using optimal combinations of VHF plasma and substrate biasing, improved properties of SiO₂ films deposited at low temperatures in PE-ALD based systems could be realized. SiO₂ has good insulation performance when it is deposited at least 350°C, therefore, if this can be realized at the level of 50°C by using substrate biasing and VHF plasma, it will be helpful to the fabrication of semiconductor devices using new materials. In this presentation, the detailed properties of materials and plasmas deposited by substrate biasing and VHF plasma will be presented.

TF-ThP-6 SiO₂ Bottom-Up Trench Fill of a High Aspect Ratio Hole by Plasma Enhanced Atomic Layer Deposition Using a Very High Frequency Plasmas and Inhibitor Surface Treatment, *Gyuhwan An, H. Kim, Y. Lee, G. Yeom*, Sungkyunkwan University (SKKU), Republic of Korea

As the semiconductor device size is decreased to nanoscale, even though various trench fill methods such as HARP (High Aspect Ratio Process), HDP

(High Density Plasma), and SOG (Spin On Glass), etc. are utilized, the SiO₂ fill process is facing limitations and has become one of the important processes as semiconductor devices become smaller and as the aspect ratio of the trench is increased significantly. In this study, the effects of capacitively coupled plasma-type very high frequency plasmas (VHF) and inhibitor surface treatment during the plasma enhanced atomic layer deposition with DIPAS (Di-isopropylamino Silane). Formula, $\text{H}_3\text{Si}[\text{N}(\text{CH}_2\text{CH}_3)_2]$ precursor on the SiO₂ trench fill characteristics were investigated to improve performance of trench fill, and especially, to obtain the bottom-up type SiO₂ fill with low defects such as seam and voids. The deposition film quality was verified through wet etch rate (WER. diluted HF), X-ray photoelectron spectroscopy (XPS), and fourier transform infrared (FT-IR) analysis, and the analysis was conducted according to the frequency of the plasma source and with different inhibitor conditions. The improvement of fill performance in patterns using inhibitor was analyzed with scanning electron microscopy while changing the trench aspect ratio from 15:1 to 40:1.

TF-ThP-8 Using Metal Precursors to Passivate Surfaces for Area Selective Deposition, *Kinsey Canova, L. Souqui, G. Girolami, J. Abelson*, University of Illinois at Urbana-Champaign

We previously showed that co-flowing a non-reacting, gas phase inhibitor during chemical vapor deposition (CVD) greatly enhances the area-selective deposition (ASD) of a metal film on metal instead of on oxide substrates. Here, we employ CVD precursors, which ordinarily react to grow metallic films at temperatures ≤ 300 °C, to inhibit nucleation. This occurs in a temperature window above the onset temperature (T_g) where the intended growth precursor will react to grow film, but below the onset temperature where the second precursor – here acting as an inhibitor – reacts. The latter strongly adsorbs on, and decreases the reactivity of, nucleation sites on the intended non-growth surface. The advantages of using precursors as inhibitors are that: (i) potential “inhibitor” precursors can be identified as those with dense adsorption on the non-growth surface and low reactivity towards the ligands of the intended growth precursor; (ii) they are easily integrated into the CVD process flow; and (iii) they can later be removed from the surface by thermal desorption, pyrolysis, or an atomic layer deposition half-reaction. The precursors we use as inhibitors are $\text{Hf}(\text{BH}_4)_4$ ($T_g = 170$ °C) or $\text{Al}(\text{CH}_3)_3$ ($T_g = 300$ °C), and these precursors respectively block growth from $\text{AlH}_3\text{N}(\text{CH}_3)_3$ ($T_g = 130$ °C) or $\text{Hf}(\text{BH}_4)_4$. Experiments with parallel dosing on metal (growth) and oxide (non-growth) surfaces are used to show the enhanced selectivity from this route. We summarize results by proposing selection criteria for other precursor-inhibitor systems: sort precursors by the T_g , select a precursor for the desired film, then choose an inhibitor that has a higher T_g than, and is unreactive towards, the desired film precursor. For ASD, the inhibitor must densely adsorb and passivate the sites that normally lead to nucleation, e.g., hydroxyl or defect sites on oxide surfaces, and there must be surfaces intended for growth where it adsorbs sparsely or not at all.

TF-ThP-9 Amorphous GeSe Thin Films Prepared by Magnetron Co-Sputtering with Rapid Thermal Annealing for UV Optoelectronic Applications, *S. Pech, Chosun University, Cambodia; Sara Kim, Y. Jun, N. Kim*, Chosun University, Republic of Korea

GeSe is one of the IV-VI semiconductors with a p-type conductivity and a modest band gap, which gives rise to potential in optoelectronic applications such as photodetectors for communication, imaging, remote sensing, and spectroscopy due to its relative earth-abundance, simple binary composition, and non-toxicity [1,2]. The GeSe was noted as a good photoresponse over a broad range of wavelengths from ultraviolet (UV) to near-infrared with on/off switching properties [3]. In this study, GeSe was deposited by using the radio frequency magnetron co-sputtering systems with Ge and Se targets. The GeSe thin films were annealed as an increase in the annealing temperature from 300 to 500 °C by using a rapid thermal annealing system. Compositions and surface characteristics of the GeSe thin films were examined by using an energy dispersive X-ray spectroscopy and a field-emission scanning electron microscope. The surface morphological profile and Crystal structure of the GeSe thin films were analyzed by using an atomic force microscope and X-ray diffraction. Optical properties and Hall characteristics of the GeSe thin films were analyzed by using a UV-Visible spectrometer and Hall effect measurement system. As a result of the analyses, the amorphous nature of the selected thin films was verified in all annealing temperature conditions, and a slight compositional difference occurred; however, a sudden difference in UV transmittance of the GeSe thin films occurred in specific annealing temperature conditions. Acknowledgment: This work was supported by the Gwangju-Jeonnam Local Energy Cluster Manpower Training of the Korea Institute of Energy

Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 2021400000560).

[1] Amir Muhammad Afzal et al., ACS Appl. Mater. Interfaces 13, 47882 (2021). [2] Ding-Jiang Xue et al., J. Am. Chem. Soc. 139, 958 (2017). [3] Zhenhua Wang et al., ACS Appl. Electron. Mater. 1, 2236 (2019).

TF-ThP-10 Considering XPS Characterisation of Ultra-Thin Films, J. Counsell, S. Coultas, Kratos Analytical Inc., UK; **Christopher Moffitt**, Kratos Analytical Inc.

Shrinking device dimensions has increased the use of atomic layer deposition (ALD) due to the need for increased control of layer thickness and uniformity. The ability to deposit high dielectric constant (high-k) films via ALD has allowed for their widespread use in a swath of optical, optoelectronic, and electronic devices.

For device design control and optimisation, it is vital to have accurate, quantitative methods to determine thicknesses and structure. We apply and discuss different thickness calculations using both conventional 1486eV and high-energy AgXPS (Ag L α radiation - 2984eV) to elucidate the structure of ALD thin films of hafnia, alumina and a loayer combination of both.

TF-ThP-11 Characterization of Polycrystalline Hf-doped Ga₂O₃, Sara Chamberlin, V. Singh, Washington and Jefferson College; **S. King**, University of Wisconsin - La Crosse

Previous work has shown low concentrations of hafnium (Hf) incorporated into Ga₂O₃ single crystals act as a shallow donor, increasing carrier concentrations and lowering the resistivity of the crystal [1,2]. However, only a single concentration of Hf was considered within these studies. To investigate the impact that Hf concentration has on the optical, structural, and morphological properties of the material, polycrystalline films of Hf-doped Ga₂O₃ were deposited at room temperature by reactive RF-sputtering onto silicon and fused silica substrates with varying concentrations of Hf, and were subsequently characterized by spectroscopic ellipsometry, UV-VIS spectrophotometry, x-ray diffraction, x-ray photoelectron spectroscopy, and atomic force microscopy.

Initial results show that all films, regardless of Hf concentration, are initially amorphous, but crystallize as β -Ga₂O₃ upon subsequent annealing, with the possibility of phase segregation when Hf concentrations reach approximately 3 at. %, giving an indication as to the solubility limit of Hf in Ga₂O₃. Spectroscopic ellipsometry measurements show that the index of refraction of the film is altered by Hf incorporation, while UV-Vis measurements show that the optical bandgap is not significantly altered. These results suggest that Hf-doped Ga₂O₃ may find use in optoelectronic devices and applications.

[1] <https://iopscience.iop.org/article/10.1088/1361-6641/ab75a6>

[2] <https://aip.scitation.org/doi/10.1063/5.0062739>

TF-ThP-12 A Novel Direct Current Chemical Vapor Deposition (DC-CVD) Reactor for Large Area Diamond Deposition, G. Major, A. Lizarbe, Brigham Young University; **B. Lawrence**, Exolv; **Matthew Linford**, Brigham Young University

Diamond has diverse applications because of its high hardness, thermal conductivity, chemical inertness, high melting point, and high refractive index. Synthetic diamond is grown in a variety of ways, each having its advantages and disadvantages. For example, high quality, single crystal material can be grown by the high-pressure high-temperature (HPHT) method. However, the size of HPHT diamonds is limited by the size of the anvils used to produce them, and diamond thin films are not possible. Microwave chemical vapor deposition (MWCVD) is widely practiced, where MWCVD reactors are relatively inexpensive. However, MWCVD suffers from both significant plasma inhomogeneities across its growth area, as well as a limited growth area. Here, we describe a novel system based on direct current (DC) CVD, which, when compared to MWCVD, allows for larger growth areas, single-crystal growth, and more uniform growth due to a more consistent temperature and plasma across the growth surface. Our system has a growth diameter of 130 mm, which, in part, leads to a somewhat slower growth rate. However, the larger growth area allows for increased production overall. Diamonds produced in this reactor have been analyzed by Raman spectroscopy, X-ray topography, electron spin resonance, and optically detected magnetic resonance. These analyses showed minimal non-diamond growth, few defects, and uniformly oriented growth among the samples. Future developments include adding dopants, increasing diamond quality, exploring nitrogen vacancies for use in

quantum computing, and other novel applications that are made accessible because of the reactor design.

TF-ThP-13 Surface Modification of Additively Manufactured Materials via Stress Gradients on Thin Film Growth, Andrew Miceli, S. Stagon, University of North Florida

Thin surface coatings, ranging from nanometers to microns thick, are commonly used to modify the performance of parts made from injection molding, machining, and 3D printing. These surface coatings, often composed of metal or metal oxide/nitride, are commonly added through physical vapor deposition (PVD). As these coatings are grown in kinetically limited conditions, large residual stresses may form during growth. In this work, we hypothesize that these intrinsic residual stresses may be used advantageously to preferentially modify the stress state experienced by the coated part via preloading effect. First, Finite Element Modeling (FEM) is used in this study to analyze the hypothesis. Using FEM, dog-bone specimens are tested in uniaxial tension using simulated coating surface pre-load stress in both tension and compression. Local stress magnitudes are determined on average by the von-Mises stress throughout the model after simulation is completed. This model is then analyzed to determine average stress of the material and which preload stress state reduces average stress through the material. It was found that in the typical tensile test load case, tensile preloading decreases overall stress of the specimen in the gauge section by up to 12%, thus lessening chance of failure due to this lower average stress. This FEM study will be complemented by validation experiments where 3D printing will be used to rapidly fabricate polymeric (ABS) and additively manufactured metal (316SS) parts which will be subsequently coated using PVD and tested in tension. Surface characterization of the thin films will be analyzed visually using Scanning Electron Microscopy and Microhardness tests to validate and characterize the alloy composition based on stoichiometric effects. Following surface characterization, Energy Dispersive Spectroscopy will be used to analyze chemical composition of the thin film alloy created. Following uni-axial testing, fully reserved loading will be investigated to study the effects of compressive stress in PVD coatings on fatigue and results will be translated to high-value metal 3D printed parts.

TF-ThP-14 Decoding Thickness Profiles: Conformality as a Tool to Study Process Kinetics, Andreas Werbrouck, Stanford University, Belgium; **V. Cremers, J. Dendooven, C. Detavernier**, Ghent University, Belgium

While the majority of atomic layer deposition (ALD) research is directed towards developing new precursors, reaction chemistries, and applications, fundamental research on ALD conformality is interesting in its own right. Traditionally the focus in ALD conformality research has been on understanding and optimizing the precursor exposure necessary to completely cover complex 3D structures. On the contrary, this work is concerned with incompletely covered structures – more specifically holes. As the deposition proceeds, various parts of the hole receive different exposures: the top of the structure will be exposed to more precursor than the bottom. As a result, the film thickness depth profile in a hole encodes at least the same kinetic information as a traditional saturation curve but spatially resolved instead of temporally.

In order to decode the information hidden in such a thickness depth profile, two existing feature-scale simulation models were reimplemented. The reactive diffusion in the hole can be described with either a system of coupled differential equations [10.1002/cvde.201106938] or a Markov chain simulation [10.1007/s00214-014-1465-x]. Our implementation of these models was validated and subsequently used to fit experimentally obtained profiles.

The power of fitting simulated depth profiles to experimental data was demonstrated by studying plasma-enhanced ALD. With our approach, we were able to determine the partial pressure of reactive oxygen species generated in various reactor conditions (fig. 1).

A second application is in the study of reaction kinetics. As far as we know, current literature only uses first-order Langmuir adsorption to model kinetic interactions between the precursor and the substrate. Still, real-world reaction kinetics may be more complex. By allowing the model to use a general parametrized adsorption function instead of a first-order model and fitting this along with the profile, useful kinetic information can be obtained. This is demonstrated with the trimethylaluminum (TMA)-water process, where the TMA step exhibits ideal first-order kinetics, but the reaction of water with the substrate is more complex. It has been suggested previously that this reaction might have a coverage-dependent activation energy [10.1021/acs.jpcc.9b11291 [10.1021/acs.jpcc.9b11291]], and our current results confirm this finding.

TF-ThP-15 Low-Temperature Synthesis of Crystalline VO_x Films via Hollow-Cathode Plasma-Assisted ALD: Impact of Vanadium Precursor, Adnan Mohammad, K. Joshi, S. Ilham, B. Wells, University of Connecticut; A. Kemal Okyay, Stanford University; B. Willis, N. BIYIKLI, University of Connecticut

Vanadium oxide exhibits phase-change properties at different stoichiometries including the famous metal-insulator transition (MIT) for VO₂ around 70 °C shifting between monoclinic to tetragonal rutile structure phase with temperature change. Such layers have the potential to be used for low-power electrical switches. The existing VO_x ALD reports demonstrate mainly as-grown amorphous VO_x films via thermal atomic layer deposition (ALD) using TEMAV and VTIP metal precursors and water vapor or ozone as co-reactant. These amorphous films are shown to transform in various crystalline phases using post-deposition annealing process at high temperatures (typically higher than 500 °C). However, no significant report is yet found on low-temperature as-grown VO₂ films grown by thermal or plasma-ALD.

Our main goal in this study is to demonstrate as-grown crystalline VO_x films using our customized hollow-cathode plasma-ALD reactor at substrate temperatures lower than 200 °C and to further improve the crystalline quality and transform the phase structure of the deposited VO_x film into the desired VO₂ stoichiometry. We have grown crystalline VO_x thin films at substrate temperatures as low as 200 °C using TEMAV as the vanadium precursor and O₂ plasma as the oxygen co-reactant. The resulting as-grown film was crystalline V₂O₅. The recipe for the plasma-ALD experiments was as the following: 0.250 s of TEMAV pulse with 10 sccm of N₂-carrier flow, 50 sccm Ar-purge for 10 sec, 50 sccm O₂ plasma for 10 s, plasma power 50-300 W, followed by another 10 s of Ar purge. To provide enough TEMAV dose into the reactor chamber, the TEMAV precursor cylinder is heated at 110 °C. The resulting films are crystalline V₂O₅ with a growth per cycle (GPC) value reaching ~2 Å and a refractive index of 2.45. The corresponding growth process has been real-time monitored with *in-situ* ellipsometry depicting the individual chemisorption and ligand exchange surface reactions.

Having accomplished our first goal, our next step is to explore VTIP as the metal precursor: will we obtain similar as-grown crystalline VO_x films and if yes, which crystal structure and stoichiometry will dominate? The gain knowledge will be used to further improve and transform the crystal structure of V₂O₅ films. The resulting VO₂ films are characterized for their temperature-dependent electrical properties to validate the MIT behavior, paving the way for prototype electronic switch devices.

TF-ThP-16 Dielectric Property on the Post-Heating Treatment of PVDF Thin Film Prepared by Atmospheric Pressure Plasma Deposition, Eun Young Jung, Kyungpook National University, Republic of Korea; C. Park, Milligan University; H. Tae, Kyungpook National University, Republic of Korea

Recent developments of piezoelectric nanogenerators (PENGs) for industrial application, will be flexible and stretchable electronic devices with light weight. The piezoelectric polymers seem to be promising alternatives for flexible PENGs. In present, polyvinylidene fluoride (PVDF) has been widely used due to its unique properties such as mechanical flexibility, high chemical resistance, biocompatibility, and high temperature resistance [1,2]. However, this PVDF polymer has still lower piezoelectric characteristics when compared with piezoelectric ceramics. Thus, it is necessary to improve the piezoelectric and dielectric property of the conventional PVDF material for flexible PENGs. Many researches have been mostly investigated on the piezoelectric polymer-nanocomposites with nano-particles in order to develop dielectric materials with high dielectric coefficient for flexible PENGs [1,3]. Accordingly, we examine the effects of the post-heating on the structural and dielectric properties of PVDF thin film deposited by atmospheric pressure plasma (APP) system. The structural and dielectric properties of PVDF thin film were systematically investigated by using field emission-scanning electron spectroscopy (FE-SEM), X-ray diffraction (XRD), Fourier transforms-infrared spectroscopy (FT-IR), LCR meter according to post-heating in order to remove the N,N-dimethylformamide (DMF) element and enhancing the chemical structure of PVDF thin film. After post-heating treatment, the amount of bubble was reduced. This result implies that the DMF solution is almost removed from PVDF thin film, and the PVDF nanoparticles are clearly observed on the surface of PVDF thin film. In FT-IR, the peak intensity at 1669 cm⁻¹ for -C=O by DMF solution largely decreases after post-heating, and the post-heated PVDF thin film shows mainly two crystalline phases (α and β phases), which represents the peaks at 975 and 1402 cm⁻¹ for α-phase and the peak at 1072 cm⁻¹ for β-phase, respectively. The formation of two phases (α and β

phases) attributed to the increment in the dielectric constant of the post-heated PVDF thin film. The capacitance and dielectric coefficient values were measured to be 96 nF and 15 at 1 kHz frequency in post-heated PVDF thin film, respectively. The detailed characteristics of the post-heated PVDF thin film using FE-SEM, FT-IR, XRD, and LCR meter are under study and will be discussed in detail.

TF-ThP-17 The Microstructure, Roughness, and Electrical Properties of V-Doped SiC Films, Chao-Te Lee Lee, W. Chen, H. Chen, Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

Silicon carbide (SiC) thin film with various V contents were deposited on Si(100) substrate at room temperature by RF magnetron sputtering system using sintered SiC (99.95% purity) and V (99.99% purity) targets. The as-deposited films were annealed in the temperature of 1000 °C under vacuum in 1 hour. Effects of V-doped and annealing on the composition, microstructure, roughness, and electrical properties of films were examined by field emission scanning electron microscopy with an energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), and resistance meter. The XRD and AFM results show that all of the as-deposited films were amorphous with smooth surface. The roughness of the as-deposited films were all below 0.3 nm. After 1000 °C annealing, only the β-SiC(220) phase was observed of SiC and (SiC)_{98.2}V_{2.8} films. The β-SiC(100) and β-SiC(220) two phases were observed of the others annealed films. The roughness of the annealed films were hugely increased with increasing V content when the V content is over 2.8 at.%. The roughness of the annealed (SiC)_{63.6}V_{36.4} film was 9.6 nm. The electrical properties of the annealed films was similar with XRD and AFM analysis. It was demonstrated that the annealed (SiC)_{1-x}V_x film was semi-insulating when the V content was over 28.2 at.%.

TF-ThP-19 Fluorine-Doped SiO₂ Films Applied to Optical Coating Deposited by Reactive Magnetron Sputtering, B. Liao, Taiwan Instrument Research Institute, Taiwan; Chien-Nan Hsiao, National Applied Research Laboratories, Taiwan

Porous SiO₂:F films were deposited by reactive magnetron sputtering with a Si metal target at room temperature. Various ratios of O₂ to CF₄ gas were introduced to deposit SiO₂:F films. The optical properties, microstructure, surface roughness, and crystalline structure, of SiO₂:F films have been studied. The refractive index at 550 nm decreased from 1.46 to 1.39 with increasing CF₄ ratio. Then high reflection coating at 1064 nm were deposited with Nb₂O₅ and SiO₂:F as high and low refractive materials.

TF-ThP-20 Low-Density SiOC Thin Films Grown by Low Temperature Plasma-Enhanced Chemical Vapor Deposition for High Performance Acoustic Bragg Mirrors, Julian Pilz, N. Andrianov, Microsystems Division, Silicon Austria Labs, Austria; T. Sinani, Sensor Systems Division, Silicon Austria Labs, Austria; S. Azeem, T. Dao, M. Moridj, Microsystems Division, Silicon Austria Labs, Austria; G. Bruckner, Sensor Systems Division, Silicon Austria Labs, Austria

Solidly mounted resonators are an important type of bulk acoustic wave resonators, which are applied in devices such as radio-frequency filters. To decrease acoustic losses into the substrate, dielectric Bragg mirrors are applied between the bottom electrode and the substrate within the layer stack. These mirrors typically consist of alternating high (W) and low acoustic impedance (SiO₂) films. To increase the acoustic impedance contrast and thus the performance of the mirror and resonator, one approach is to lower the acoustic impedance of the low acoustic material which depends on the density and elastic modulus. In literature, doping of SiO₂ with C has been shown to be an effective approach to reduce the dielectric function with respect to pure SiO₂.¹

In this study, plasma-enhanced chemical vapor deposition (PECVD) is investigated for growing low acoustic impedance SiOC (carbon doped silicon oxide) thin films on 100 mm diameter Si wafers with native oxide. SiH₄, CH₄, and N₂O are used as the precursors for Si, C, and O, respectively, and Ar is added as neutral species to the processing plasma. The substrate temperature is varied from 50 °C to 350 °C, the total flow rate at a constant pressure (1.2 Torr) from 174 sccm to 698 sccm, and the CH₄/N₂O flow rate ratio from 0 to 0.2.

Generally, increasing the total flow rate and decreasing the substrate temperature leads to a decrease of the refractive index, which is used as a measure of the density of the film. At 50 °C and a total flow rate of 698 sccm, the refractive index (at 633 nm; spectroscopic ellipsometry) and the mass density (gravimetry) can be tuned from 1.37 to 1.42 and 1.6 to 1.9 g/cm³, respectively, by tuning the CH₄/N₂O ratio, with the lowest values found at CH₄/N₂O=0.08. The RMS roughness (atomic force microscopy)

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increases (10-20 nm for around 500 nm thickness) and the films become softer with increasing CH₄/N₂O ratio (0-0.2), where the elastic modulus drops by 50 % (nanoindentation). Fourier transform infrared spectroscopy furthermore shows changes in the chemical structure with changing ratio of Si, C, and O bonds.

In conclusion, the study shows the potential of using a low temperature PECVD process for tuning the acoustic impedance of SiOC thin films. As the main knob the CH₄/N₂O flow ratio is investigated which allows to change the chemical and structural properties of the material, supposedly creating a more open structure and weakening the bond strength. In further studies, the films will be tested in a resonator test device and benchmarked against industrial state-of-the-art layer stacks.

¹Grill, J. Appl. Phys., **93** (3), 1785, 2003

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