Fundamentals and Technology of Multifunctional Materials and Devices
Room On Demand - Session C2
Functional Coatings and Thin Films for Electronic Devices

C2-1 Interference Signal Induced by Ultra-Thin Amorphous Carbon Films Over Flexible Copper Foils Demonstrated by Electromagnetic Boundaries Calculations, ***Ângela Elisa Crespi (angela.crespi@universite-paris-saclay.fr)***, *C. Ballage, M. Hugon, J. Robert,* Université Paris Saclay, France*; D. Lundin,* Linköping University, Sweden*; T. Minea,* Université Paris Saclay, France

Interferences of amorphous carbon thin films (a-C) deposited over flexible copper foils by direct current magnetron sputtering were theoretically and experimentally demonstrated. Destructive interference is observed at specific a-C thicknesses when reflection occurs from the copper foil and the a-C film. As waves are out of phase, they interfere. Experimental diffusive reflectance (DR) was measured using a PerkinElmer lambda35 spectrometer (λ=400-1000 nm) at normal incidence. The theoretical results were calculated using electromagnetic boundary conditions varying from 0 nm to 350 nm a-C thickness. The simple double-layer system presents destructive interferences in thicknesses lower than 100 nm from near-ultraviolet (UV) to near-infrared (IR). At UV visible spectrum around 20-60 nm, a-C films indicate the proximity of an antinode. At IR, the a-C thickness increases to around 70–80 nm due to the skin depth effect. The compromise thickness/minimum DR reflectance depends on the wavelength, although it is lower than 100 nm for the analyzed spectrum. Thicker a-C films are less efficient for reflectance reduction. Keywords: interferences; electromagnetic boundary conditions; amorphous carbon; copper foils.

C2-2 INVITED TALK: High k Dielectrics for MIM Architecture: From Capacitors to Non-volatile Memories Applications, ***Christophe Vallee (CVallee@sunypoly.edu)***, SUNY POLY, Albany, USA*; P. Gonon, M. Bonvalot, A. Bsiesy,* UGA-LTM, France **INVITED**

SC materials were THE materials of SC industry due to their unique properties for switching from conductive to insulator or from transparent to reflective properties thanks to an external stress (most of the time an external voltage applied to the SC device). But nowadays, due to the shrinking of the devices, role of dielectrics materials (such as high k dielectrics) become crucial. First high k dielectrics were developed to improve the SC device performances by increasing the dielectric constant of the capacitor-based device (switching from SiO_2 to HfO_2 in CMOS transistors, from SiO_2 and Si_3N_4 to $ZrO_2/Al_2O_3/ZrO_2$ in DRAM capacitors). The reduction of high k thicknesses below 10 nm also give rises to new potential application of these materials due to unexpected new properties: as for SC materials one can now switch their electrical properties from insulator to conductor. They can be used as memristor (or "memory resistor") which is a Metal-Insulator-Metal (MIM) resistor whose resistance value depends on its past electrical history, i.e. its current-voltage characteristic (I-V) displays a hysteresis loop. In recent years, a large amount of research has been devoted to memristors, focusing on their application to microelectronic non-volatile memories (RRAM - Resistive Random Access Memory). They can also be used as selectors, or MIM diodes, for memories.

With this presentation we will give examples of the use of high k dielectrics and their fabrications for linear MIM capacitors[1], DRAM[2], Resistive Rams[3], MemImpedance[4] and MIM diodes[5]. We will show that whatever the device, due to the very small thickness of the high k dielectrics, the choice of the metal electrodes and the control of the interface is vital.

[1]P. Gonon and C. Vallée, *Appl. Phys. Lett.* 90 (2007) 142906

[2]A. Chaker et al, *Appl. Phys. Lett.* 110 (2017) 243501

[3]P. Gonon *et al*, *J. Appl. Phys*.107 (2010) 074507

[4]T. Wakrim *et al,Appl. Phys. Lett.* 108 (2016) 053502

[5]W. Jeon *et al*, IEEE Trans. on Elect. Dev. 66 (2018) 402-406

C2-4 Study of Polycrystalline BiMnO3 Thin Films Grown by Radio-Frequency Magnetron Sputtering, ***Glory Umoh (glory.umoh@cimav.edu.mx)***, *J. Holguín-Momaca , R. Talamantes,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Mexico*; G. Herrera-Pérez,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), USA*; S. Olive-Méndez, A. Hurtado-Macias,* Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Mexico

Multiferroic magnetoelectric $BiMnO_3$ thin films simultaneously exhibit more than one type of ordering, including

ferromagnetism (FM), ferroelectricity (FM) in a single-phase. Consequently, they have a spontaneous magnetization that can be switched by an applied

magnetic field, a spontaneous polarization that can be switched by an applied electric field, also coupling between them. $BiMnO_3$ thin films were grown

on (111) $Pt/TiO_2/SiO_2/Si$ substrates with 100 nm thickness via radio frequency magnetron sputtering.

The growth of these thin films was extremely sensitive to substrate deposition temperatures, single-phase $BiMnO_3$ could only

be attained in a narrow temperature window of around 700 °C. Working pressure 3×10^{-3} Torr was kept constant throughout the

sputtering deposition process. Loss of Bi during thin film growth of bismuth-based compounds is a major challenge to obtaining

stoichiometric films, because of the desorption nature of Bismuth, to compensate this loss, Bi was added to a crucible were

the sample was annealed at 700 °C in a rich oxygen atmosphere in a tubular furnace for 7hrs with heating and cooling rates

of 3°/min. The $BiMnO_3$ films were found to be strongly (0,2,0) oriented. X-ray diffraction, was in Bragg Brentano configuration,

electronic transmission microscopic (TEM) in scanning image mode (STEM), SAED confirmed a monoclinic structure with space

group C_{12}/C_1. The lattice constants are a = 9.5415 Å, b = 5.61263 Å, c = 9.8632 Å, b = 110.6584°,

with a high-quality textured film. While the surface morphology observed by scanning electron microscopy (SEM) indicates

homogeneity in the grain growth, crack-free and an increased surface uniformity. The root mean square roughness was evaluated

using AFM in tapping mode, with rms = 35±0.7 nm. Moreover, ferroelectric properties were analyzed by means of hysteresis loop.

The structural, chemical composition and ferroelectric properties of these thin films demonstrate that they have the capability

to be used in cantilever-type energy harvesters.

C2-5 Nanostructured Multifunctional Architectural Glass Glazing for Future Green Cities, *S. Woodward-Gagne, R. Beaini, B. Baloukas, O. Zabeida,* ***Ludvik Martinu (ludvik.martinu@polymtl.ca)***, Polytechnique Montreal, Canada

In North America, buildings represent the largest single sector of energy consumption at 39%. This situation can be substantially improved by applying energy-efficient glass and windows provided with smart and multifunctional glazing. In this work, we focus on two types of design-driven nanostructured optical coating systems, namely a) thin films with tailored angular-selectivity (AS) that can be used to tune solar transmission as a function of the sun's position in the sky, or to attenuate parasitic light sources, and b) high performance thermochromic smart radiators (SR).

In the first part, we describe fabrication of slanted columnar thin films (SCTFs) using glancing angle deposition (GLAD) of optically transparent SiO_2 SCTFs overcoated with conformal atomic layer deposited (ALD) TiN films forming a columnar core shell structure. We show that the combination of GLAD and ALD provides an additional degree of freedom to independently adjust the microstructural and optical characteristics, leading to adjustable AS. ALD functionalization of SCTFs can thus be applied for passivation of functional columns, and hence decoupling of device microstructure and surface chemistry, while tailoring the AS independently from the SCTF thickness and density.

In the second part, we use the inherent metal to insulator transition (MIT) of thermochromic VO_2 that allows a coating to act as a lightweight thermal regulator. Using a modeling approach to optimize the optical properties of the individual constituent films, we design an SR with the following architecture: mirror | dielectric resonant cavity | VO_2 | top protective and antireflective film. Using an infrared transparent ultra-low refractive index dielectric materials for the resonant cavity, e.g.: CaF_2 (*n* @ 10 micron = 1.17), we experimentally demonstrate the largest-reported dynamic variation of the emissivity between the hot and the cold states of 66% in the 3 to 25 wavelength range. We discuss the advantages of the described approaches for architectural glass glazing considered for energy solutions in future green cities.

C2-6 Effect of Substrate Bias on Properties and Microstructure of Nanotwinned Copper Thin Films Deposited by Magnetron Sputtering System*, **Tsung Lin (a0917320902@gmail.com)**,* NTHU, Taiwan*; S. Chang,* +886-3-5715131 ext 34321, Taiwan*; F. Ouyang,* NTHU, Taiwan

With the development of advanced nano-electronic devices, the interconnects are necessary to exhibit excellent mechanical properties and electrical properties in the integrated circuit technology. Recently, nanotwinned Cu has drawn much attention in various researches due to its high mechanical strength, good conductivity and thermal stability. In this study, the effect of substrate bias on the properties and microstructure of nanotwinned Cu thin films was investigated. The Cu thin films were deposited on the Si (100) with an adhesion layer of Ti by unbalanced magnetron sputtering (UBMS) system at different substrate bias voltages, ranging from 0 V to -160 V.The results show that the columnar nanotwin structure grows straighter as bias increases. The Cu films deposited under higher bias have columnar nanotwinned structures. On the other hand, Cu films deposited at lower bias voltages have no columnar microstructure and few twins. XRD results indicate that all the deposited Cu films exhibit structure with (111) preferred orientation and the (111)-oriented grains become more dominant in the films with increasing bias. The percentage of (111) orientation can reach 98.4% when bias is -100 V. The optimum substrate bias to form high density nanotwinned structure is -120 V and the films has hardness of 3.12 GPa, which is about 3 times higher than that of its bulk counterpart. The resistivity of the samples is relatively low in bias voltage lower than -80 V, and once the bias voltage increases over -80 V, the resistivity becomes comparably higher. The maximum of resistivity is 2.17 μΩ – cm at the bias voltage of -140 V, but it is still very low and acceptable for being a good conductor. All samples have quite small surface roughness without any CMP process. Small surface roughness is beneficial to Cu-Cu direct bonding process. The residual stress of all samples is tensile. The maximum of residual stress appears at the bias voltage of -140 V, and decreases from 224 GPa to 124 GPa with the bias decreasing to -100 V. Then the residual stresses of samples deposited at relatively low bias voltage region are comparably small. With the further decrease of bias voltage, the residual stress increases a to 127 and 162 GPa at the bias of -20 V and 0 V. The mechanism of the effect of the bias on properties and microstructure will be discussed in details in this study.

C2-7 Nanostructured CuO/WO_3 Thin Films for Hydrogen Gas Sensing Prepared by Advanced Magnetron Sputtering Techniques*, **Nirmal Kumar (kumarn@kfy.zcu.cz)**, S. Haviar, J. Čapek, Š. Batková, P. Zeman, P. Baroch,* University of West Bohemia, Czech Republic

Various architectures of hydrogen sensing multilayers were designed using various combinations of thin films and nanoclusters of both CuO and WO_3. Thin films were prepared using reactive sputter deposition in dc magnetron regime (WO_3) or rf mode (CuO). The nanoclusters were prepared by magnetron-based gas aggregation cluster source which enabled controlling of size and composition of clusters.

There are several architectures described in this work. The combination of two thin films. Decoration of one support film with clusters or thin films overlaying the clusters. By switching the materials in these configurations, various nanostructures were achieved. The sensorial behavior of prepared materials was studied towards hydrogen gas in synthetic air in a form of thin-film conductometric sensor.

The enhancement of the response of WO_3 thin film alone by adding the CuO film on top is described as well as the influence of the amount of nanoclusters deposited on WO_3 thin films. Based on SEM imaging, sensorial behavior analysis, XRD and resistivity measurements, we propose that the sensing mechanism is always based on the formation of heterojunction in between *n*-type WO_3, *p*-type CuO or other phases present in the structures (such as *n*-type $CuWO_4$).

C2-8 Study of Thermal Stability of Highly (111)-Oriented Nanotwinned Ag Films by Using Unbalanced Magnetron Sputtering*, **Po-hsien Wu (sky268455@gmail.com)**, Y. Hao, L. Chang, F. Ouyang,* National Tsing Hua University, Taiwan

The metal strengthening methods generally company a significant reduction in electrical conductivity due to the scattering of electrons. Recently, metals with nanotwins have attractive properties, which can solve the issue on the contradiction of mechanical strength and electrical conductivity. Nanotwinned (NT) metal film, especially copper, possesses high mechanical strength, good ductility, acceptable conductivity and low cost, is still a popular material in academic research and industrial applications until now. Silver seems to be a potential candidate, which possesses prominent electrical and thermal conductivity, most importantly, excellent oxidation resistance. In addition, Ag also contains a lower stacking fault energy value (16 mJ m^{-2}) than copper (45 mJ m^{-2}), causing the glide of a {111}<112> partial easily begets a fault in the FCC stacking sequence. Therefore, the formation of dense twins will prominently increase the obstacle density of dislocation. The transmission in the form of twin boundaries, thereby enhancing the strength and thermal stability of the film, while maintaining a low resistivity.

In this study, the thermal stability of nt-Ag films on (100) Si substrate with Ti interlayer was investigated by annealing at 150˚C, 300˚C, 400˚C and 600˚C under the vacuum for an hour, respectively. Firstly, the cross-sectional FIB images showed that the as-deposited nt-Ag films were mainly columnar structures with high density nanotwins. Furthermore, the random-oriented grains were formed near the Ti interface. The XRD analysis results showed that Ag(111) and Ag(222) were the main diffraction peaks and the ratio of integrated intensities of these two oriented grains was up to 99.9%. Secondly, nanotwins showed stable columnar structures after annealing at 150˚C for 1h. In addition, it was found that the grain growth occurred in random-oriented grains to reduce the total grain boundary energy. When the annealing temperature increased to the 400˚C, the results showed that columnar structures still remain high thermal stability and some of the (111)-orientated nt-Ag grains grew apparently downward to consume the random-oriented grains. Lastly, abnormal grain growth occurred in almost all grains after annealing at 600˚C for 1h. The microstructure evolution and mechanism of the highly (111)-oriented nt-Ag films at various annealing temperature will be discussed in details.

C2-9 Enhanced Reliability and Uniformity for Ge pMOSFET with Low Temperature Supercritical Fluid Treatment*, **Bo-Lien Kuo (eji1i6xu06@gmail.com)**, K. Chang-Liao,* National Tsing Hua University, Taiwan*; D. Ruan,* National Tsing Hua University, China*; J. Li,* National Tsing Hua University, Taiwan

Significant improvement on uniformity and reliability characteristics in Ge pMOSFET are achieved with a novel low temperature supercritical phase CO_2 fluid treatment with H_2O cosolvent. Devices with the proposed treatment also exhibit a lower subthreshold swing, a higher on/off current ratio, and a lower interface trap density. The improvement can be attributed to the reduction of oxygen vacancy and low oxidation states in the interfacial layer (IL), and the quality enhancement on both IL and high-k gate stack.

C2-11 Printed Polymer Heat Sinks for High-Power, Flexible Electronics*, **Katherine Burzynski (burzynskik1@udayton.edu)**[1],* University of Dayton and Air Force Research Laboratory, USA*; N. Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E. Heckman,* Air Force Research Laboratory, Sensors Directorate, USA*; C. Muratore,* University of Dayton, USA

Consumers and military personnel alike are demanding ubiquitous electronic devices which require enhanced flexibility and conformality of electronic materials and packaging, while maintaining device performance. Whether it be high-power devices for faster data speeds, such as fifth generation (5G) wireless communication technology or wearable sensors to facilitate the Internet of Things (IoT), the age of flexible, high performance electronic devices has begun. Managing the heat from flexible electronics is a fundamental challenge. Even on rigid substrates with significantly higher thermal conductivity than polymeric and other flexible substrates, the full potential of semiconducting materials is often thermally limited. The flexible gallium nitride (GaN) high electron mobility transistors (HEMTs) employed in this work are conventionally processed devices that can be released from their growth substrate and transferred to a variety of rigid and flexible substrates. To improve the heat conduction of the flexible substrate material, graphite nanoplatelets were used to improve the thermal conductivity of the polydimethysiloxane (PDMS) by more than 900 percent, from 0.2 to 1.7 W/mK, while maintaining mechanical properties and printability. The GaN HEMTs were directly transferred to this graphite loaded PDMS substrate material and the performance was compared to that of the devices transferred to the unloaded PDMS and the as-grown

[1] **2020 Student Award Finalist**

devices on their sapphire substrates. Using infrared thermography, the GaN HEMTs on graphite-loaded PDMS substrates reach the maximum operating temperature at 60 percent more power than the same device transferred to the PDMS substrate. From the device current-voltage characteristics at 0 gate voltage, the current at saturation is 40 milliamps for devices on the rigid, high thermal conductivity sapphire wafer, compared to 30 and 20 milliamps for devices on flexible, loaded PDMS and unloaded PDMS, respectively. Additionally, the high electrical performance of these devices (i.e., high saturation current) was observed after cyclic bending of these devices on loaded PDMS substrates. These results highlight the fact that high-power device performance is markedly improved when transferred to the higher thermal conductivity flexible substrate. Computational simulations were used to predict flexible substrate architectures to promote point-to-volume heat transfer to further improve device performance. Additive manufacturing for engineered architectures of the flexible, thermally conductive substrate materials was demonstrated to substantially reduce the thermal limitation of high-power flexible electronics.

C2-12 High-performance Thermochromic VO_2-based Coatings Prepared on Glass by a Low-temperature Scalable Deposition*, **Tomáš Bárta (tomasnep@seznam.cz)**, J. Vlček, D. Kolenatý, J. Rezek, J. Houška, S. Haviar,* University of West Bohemia, Czech Republic

Three-layer thermochromic VO_2-based coatings were prepared on soda-lime glass by a low-temperature scalable deposition technique. This deposition technique is based on reactive high-power impulse magnetron sputtering with a pulsed O_2 flow control [1] allowing us to prepare crystalline VO_2 layers of the correct stoichiometry under highly industry-friendly deposition conditions: without any substrate bias at a low substrate temperature of 330 °C. Simultaneous doping of VO_2 by W (resulting in a $V_{1-x}W_xO_2$ composition with x = 0.018 in this work) was performed to reduce the semiconductor-to-metal transition temperature to 20 °C. ZrO_2 antireflection layers both below and above the thermochromic $V_{0.982}W_{0.018}O_2$ layers were deposited at a low substrate temperature (< 100 °C). A coating design utilizing a second-order interference in the ZrO_2 layers [2] was applied to increase both the luminous transmittance, T_{lum}, and the modulation of the solar transmittance, ΔT_{sol}. The crystalline structure of the bottom ZrO_2 layer further improved the VO_2 crystallinity and the process reproducibility. The top ZrO_2 layer provided the mechanical protection and environmental stability of the $V_{0.982}W_{0.018}O_2$ layers. The $ZrO_2/V_{0.982}W_{0.018}O_2/ZrO_2$ coatings exhibited T_{lum} up to 60% at ΔT_{sol} close to 6% for a $V_{0.982}W_{0.018}O_2$ thickness of 45 nm, and T_{lum} up to 50% at ΔT_{sol} above 10% for a $V_{0.982}W_{0.018}O_2$ thickness of 69 nm. This study provides a new solution for a low-temperature fabrication of high-performance durable thermochromic VO_2-based coatings for energy-saving smart windows.

References

[1] J. Vlček, D. Kolenatý, T. Kozák, J. Houška, J. Čapek, Š. Kos, Ion-flux characteristics during low-temperature (300 °C) deposition of thermochromic VO_2 films using controlled reactive HiPIMS, J. Phys. D: Appl. Phys. 52 (2019) 025205.

[2] J. Houska, D. Kolenaty, J. Vlcek, T. Barta, J. Rezek, R. Cerstvy, Significant improvement of the performance of $ZrO_2/V_{1-x}W_xO_2/ZrO_2$ thermochromic coatings by utilizing a second-order interference, Sol. Energy Mater. Sol. Cells 191 (2019) 365-371.

C2-13 Investigation of Resistive Switching in TAOs-Based Memristor With Ultraviolet Irradiation*, **You-Xuan Li (youxuan.eo08g@nctu.edu.tw)**, P. Liu, C. Hsu, K. Gan, D. Ruan, Y. Chiu,* National Chiao Tung University, Taiwan

The effect of ultraviolet (UV) irradiation on TAOs (W doped InZnO, IZO-W) based ECM type memristor has been studied. The typical bipolar I-V curve of TAOs memristors with and without UV irradiation method were revealed in the voltage sweep mode. For the characteristics of IZO-W memristor, high DC endurance cycles (> 8 ´ 10^3), low compliance current (10 mA), large on/off ratio (> 10^4) and long retention time at 85 °C were performed in this study. X-ray photoelectron spectroscopy (XPS) of all devices were analyzed the interaction of metal ion in IZO-W film after UV irradiation. UV irradiation is the low thermal budget method for IZO-W memristors, which is the compatible method for BEOL in future IC industry.

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