

## Fundamentals and Technology of Multifunctional Materials and Devices

### Room On Demand - Session C1

#### Optical Materials: Design, Synthesis, Characterization, and Applications

**C1-1 INVITED TALK: Measurement of Feature Dimension and Shape for Nanowire Test Structures Using Mueller Matrix Spectroscopic Ellipsometry based Scatterometry and Small Angle X-Ray Scattering, Alain C. Diebold (adiebold@sunypoly.edu), SUNY Polytechnic Institute Albany, USA**

INVITED

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. An interesting and challenging example structure is the Nanowire Test Structure which is used to develop etch processes which produce vertically stacked nanowires from a multi-layer film stack of Si/SixGe1-x/Si/SixGe1-x/Si. (1, 2, 3) This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. We also present the use of critical dimension –small angle X-ray scattering characterization. This method uses high energy synchrotron X-Ray scattering to obtain diffraction results from the same periodic array used for scatterometry.

#### References

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[2] Sonal Dey, Alain Diebold, Nick Keller, and Madhulika Korde, Mueller matrix spectroscopic ellipsometry based scatterometry simulations of Si and Si/SixGe1-x/Si/SixGe1-x/Si fins for sub-7nm node gate-all-around transistor metrology, *Proc. SPIE* 10585, Metrology, Inspection, and Process Control for Microlithography XXXII, 1058506 (6 June 2018); doi: 10.1117/12.2296988

[3] Madhulika Korde, Subhadeep Kal, Cheryl Pereira, Nick Keller, Aelan Mosden, Alain C. Diebold, Optical Characterization of multi-NST Nanowire Test Structures using Muller Matrix Spectroscopic Ellipsometry (MMSE) based scatterometry for sub 5nm nodes, *Proc. SPIE Metrology, Inspection, and Process Control for Microlithography XXXIII*, (2019).

**C1-3 Optical Probing of Vanadium Oxide Thin Film Composition and Phase, M. Junda, Nikolas Podraza (nikolas.podraza@utoledo.edu), University of Toledo, USA**

Vanadium oxides have a range of compositions and phases made possible by multiple valence states of vanadium and the high defect tolerance of some phases. Several types of vanadium oxides have found application or are of interest as imaging layers in infrared sensors (VO<sub>x</sub>), phase change materials (VO<sub>2</sub>), and electrodes for energy storage (V<sub>2</sub>O<sub>5</sub>). For each application, different optical and electronic characteristics are required which depends strongly upon the chemical composition, crystal structure (if applicable), and amorphous vs. crystalline ordering of the material. Optical property variations with these characteristics are complicated but enable the use of spectroscopic ellipsometry as a diagnostic of film deposition, post-deposition processing, and operational use. Here, infrared to ultraviolet range spectroscopic ellipsometry is performed on vanadium oxide materials to extract the optical response in the form of the complex dielectric function spectra and relate its characteristics to amorphous film composition, crystal phase after annealing, and changes during temperature driven phase transformations. Amorphous VO<sub>x</sub> films are deposited via reactive sputtering of a pure vanadium target in an Ar+O<sub>2</sub> ambient onto glass substrates at room temperature. Composition is deduced from variations in the amorphous phase complex dielectric functions. Initially amorphous films are then annealed into polycrystalline materials with the phase dictated by starting composition; in two examples room temperature orthorhombic V<sub>2</sub>O<sub>5</sub> and monoclinic VO<sub>2</sub> are produced from initially amorphous x = 2.5 and 2.0 VO<sub>x</sub>, respectively. VO<sub>2</sub> exhibits temperature-dependent opto-electronic properties resulting from a metal-insulator transition (MIT) at the easily accessible temperature of ~67°C from the rutile phase at high temperatures to the monoclinic phase at room temperature. Taking advantage of this switching capability, VO<sub>2</sub> is used for infrared imaging, thermochromic infrared-selective filtering in

windows, and has shown potential to be useful in memory and transistor computing electronics. *In situ* SE measurements of VO<sub>2</sub> films are collected as a function of temperature over the infrared to the ultraviolet (0.08 – 5.9 eV) spectral range. In addition to determining the optical response of the metallic and semiconducting VO<sub>2</sub> phases, incremental changes in the complex optical response are tracked as VO<sub>2</sub> is cycled through the MIT.

**C1-4 INVITED TALK: Metrology for Emerging Semiconductor Devices and Processes, Ndubuisi George Orji (ndubuisi.orji@nist.gov), National Institute of Standards and Technology (NIST), USA**

INVITED

As semiconductor device design undergoes a transformation from laterally-aligned to vertically-aligned gates, and from CMOS-based to beyond CMOS-based architectures, the increased number of materials and device-structure complexity pose new challenges for the metrology needed for characterization and process control. Patterning techniques such as extreme ultraviolet (EUV) lithography, which is expected to be the leading-edge high-volume lithography method for the next decade, also pose a host of measurement problems. In addition, new architectures, such as those based on 2D heterostructures, crossbar memristors, and carbon nanotubes have been proposed. Although the metrology and process control tools needed for some of these new architectures are not yet developed, the challenges are well known. These include smaller sizes, hard-to-obtain optical properties, materials and films with low imaging contrast, and atomic scale defects, among others.

This confluence of small dimensions, new materials and processes, and complex structures requires new approaches. This talk will give an overview of key metrology and characterization requirements for emerging semiconductor devices and processes. The goal is to highlight possible solutions and approaches.

One approach is hybrid metrology, which refers to the use of different techniques to determine the value of a parameter. The large number of process-control parameters for new and proposed device structures means that no single instrument has the required level of resolution, range, and sensitivity needed to adequately characterize the material properties and three-dimensional structure of the devices. I will describe some of the benefits of hybrid metrology and show application examples. I will also describe metrology needed for EUV lithography. Feature sizes and tolerances from EUV lithography are now approaching a level where the molecular size of the resist material affects the printability and size variability of the final features. These variabilities, which are stochastic in nature and show up as surface, linewidth and line edge roughness and defects, are in some cases beyond the detection limits of optical inspection tools.

The importance of metrology in semiconductor manufacturing cannot be overstated. This is underscored by the number of processes where the unavailability of adequate metrology could be a potential showstopper. Although some emerging semiconductor devices fall under this category, there are a variety of new and old techniques and approaches that could be helpful in addressing their metrology needs.

**C1-6 Chemical Bath Deposition of ZnO Nanorods on Ion-plated ZnO:Ga Seed Layers and Their Structural, Photoluminescence and UV Light Detecting Properties, Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp), S. Obara, N. Hashikuni, S. Namba, Ehime University, Japan; M. Yagi, National Institute of Technology (KOSEN), Kagawa College, Japan; Y. Furubayashi, T. Yamamoto, Research Institute, Kochi University of Technology, Japan**

Zinc oxide (ZnO) has many excellent properties, such as a wide band gap ( $E_g$ ) of ~3.37 eV, a large exciton binding energy of ~60 meV, high transparency, piezoelectricity and thermoelectricity. Among various techniques for preparing the ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this technique is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In our previous paper, successful CBD growth of vertically aligned ZnO nanorods (NRs) on ion-plated Ga doped ZnO (IP-GZO) seed layers has been reported. Moreover, we reported that the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited rectifying characteristics in dark and photocurrent under the light illumination [1]. In this paper, structural and PL properties of the NRs and the device performance of the PEDOT:PSS/ZnO NRs/GZO heterostructures will be discussed in terms of the average width of the NRs ( $W_{av}$ ).

The ZnO NRs layers were grown on the IP-GZO seed layers by CBD using the aqueous solution of 0.05 M Zn(NH<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.05 M C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>. Bath temperature was kept at ~86 °C. The growth time was varied in the range of 5-360 min. The PEDOT:PSS layers were deposited on the NRs layers by

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spin-coating (3000 rpm, 30 sec), followed by thermal annealing in the air at 80 °C for 20 min.

It was confirmed that the photocurrent was effectively generated by the illumination of the UV light corresponding to the  $E_g$  of ZnO, indicating that both the electrons and holes contributed to the photocurrent generation. It was also found that the increase in  $W_{av}$  led to the decrease in the barrier height ( $\Phi_b$ ) and the increase in ideality factor ( $n$ ). The larger the  $W_{av}$ , the lower the density of the surface states capturing electrons by forming adsorbed oxygen molecular ions ( $O_2^-$ s). Therefore, the band bending at the surface region becomes smaller with the increase in  $W_{av}$  [2]. Time response curves for the PEDOT:PSS/CBD-ZnO NRs heterostructures exhibited very long response and recovery times, which cannot be explained without the help of the surface reaction. These results indicate that the adsorption and desorption of the  $O_2^-$ s to the surfaces of the NRs dominate the device performance [3].

This work was supported by JSPS KAKENHI Grant Number JP17K04989.

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**C1-7 IR Mirror Coating for Evacuated Thermal Collectors: Design and Optical Characterization, Daniela De Luca (daniela.deluca@na.isasi.cnr.it)**, UniNa and CNR-ISASI, Italy; *E. Di Gennaro*, UniNa Università degli studi di Napoli "Federico II", Italy; *C. D'Alessandro, A. Caldarelli, D. De Maio, E. Gaudino*, UniNa and CNR-ISASI, Italy; *M. Musto*, UniNa Università degli studi di Napoli "Federico II", Italy; *R. Russo*, CNR-ISASI, Italy

Capturing solar radiation as high-temperature heat in solar thermal devices is challenging, especially if flat panels are used instead of concentrating systems. While a high-vacuum encapsulation helps suppressing the conductive and convective losses, the radiative term rise with temperature, according to the Planck's law of blackbody radiation.

To reduce that loss and increase the panel efficiency, we propose an optimized infrared mirror coating. The underlying mechanism is based on the cold-side external photon recycling: the mirror has to be highly reflective in the mid-IR region, to reflect and thus recapture infrared emission back at the absorber. On the contrary, in the visible and near-IR region it has to be highly transparent, to transmit the incident solar power. To obtain its best configuration, optical simulations have been performed and results showed that the best configuration is reached if a rugate filter design is used. Rugate filters are made of alternating layers of dielectric materials, with a continuous and periodic variation of the refractive index as a function of optical thickness.

Previous theoretical [1] and experimental works [2] show that the continuous profile of a rugate filter can be approximated by a reduced number of layers with steps in the refractive indices. Here, we extend prior works and include a realistic set of materials for ease of fabrication.

The Physical Vapor Deposition (PVD) technique has been used for thin films deposition of Si-based materials, i.e. Silicon Oxides, Oxynitrides, and Nitrides. Their strong dependence on the environmental conditions during deposition (pressure, gases flux,...) allow us to obtain different refractive indices from the same cathode of Si, meeting the limitation of most deposition tools on the number of target available.

We present here the optical characterization of the produced samples, including measurements performed with the ellipsometer, integrating sphere connected to an optical spectrum analyser, profilometer, and FTIR spectroscope. This analysis is useful to deeply study all the additional parameters (thickness, roughness, refractive index coupling and matching) that can interfere with the optical and physical properties of the materials. Preliminary results on multilayer structures are also shown and compared, with the aim of choosing the most promising ones for the realization of the final structure.

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## 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 diffuse reflectance (DR) was measured using a PerkinElmer lambda35 spectrometer ( $\lambda=400-1000$  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<sup>1</sup>, DRAM<sup>2</sup>, Resistive Rams<sup>3</sup>, MemImpedance<sup>4</sup> and MIM diodes<sup>5</sup>. 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.

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<sup>3</sup>P. Gonon et al, *J. Appl. Phys.* 107 (2010) 074507

<sup>4</sup>T. Wakrim et al, *Appl. Phys. Lett.* 108 (2016) 053502

<sup>5</sup>W. Jeon et al, *IEEE Trans. on Elect. Dev.* 66 (2018) 402-406

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**C2-4 Study of Polycrystalline BiMnO<sub>3</sub> Thin Films Grown by Radio-Frequency Magnetron Sputtering.** *Glory Umoh* ([glory.umoh@cimav.edu.mx](mailto: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<sub>3</sub> thin films simultaneously exhibit more than one type of ordering, including

ferromagnetism (FM), ferroelectricity (FE) 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<sub>3</sub> thin films were grown

on (111) Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/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<sub>3</sub> could only

be attained in a narrow temperature window of around 700 °C. Working pressure 3×10<sup>-3</sup> 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<sub>3</sub> 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<sub>12</sub>/C<sub>1</sub>. 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](mailto: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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> | top protective and antireflective film. Using an infrared transparent ultra-low refractive index

dielectric materials for the resonant cavity, e.g.: CaF<sub>2</sub> (*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](mailto: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<sub>3</sub> Thin Films for Hydrogen Gas Sensing Prepared by Advanced Magnetron Sputtering Techniques.** *Nirmal Kumar* ([kumarn@kfj.zcu.cz](mailto:kumarn@kfj.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<sub>3</sub>. Thin films were prepared using reactive sputter deposition in dc magnetron regime (WO<sub>3</sub>) 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>, *p*-type CuO or other phases present in the structures (such as *n*-type CuWO<sub>4</sub>).

**C2-8 Study of Thermal Stability of Highly (111)-Oriented Nanotwinned Ag Films by Using Unbalanced Magnetron Sputtering.** *Po-hsien Wu* ([sky268455@gmail.com](mailto: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 ( $16 \text{ mJ m}^{-2}$ ) than copper ( $45 \text{ mJ m}^{-2}$ ), causing the glide of a  $\{111\}\langle 112 \rangle$  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  $150^\circ\text{C}$ ,  $300^\circ\text{C}$ ,  $400^\circ\text{C}$  and  $600^\circ\text{C}$  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  $150^\circ\text{C}$  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  $400^\circ\text{C}$ , 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  $600^\circ\text{C}$  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 (ej116xu06@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  $\text{CO}_2$  fluid treatment with  $\text{H}_2\text{O}$  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)<sup>1</sup>, 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 polydimethylsiloxane (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

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  $\text{VO}_2$ -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  $\text{VO}_2$ -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  $\text{O}_2$  flow control [1] allowing us to prepare crystalline  $\text{VO}_2$  layers of the correct stoichiometry under highly industry-friendly deposition conditions: without any substrate bias at a low substrate temperature of  $330^\circ\text{C}$ . Simultaneous doping of  $\text{VO}_2$  by W (resulting in a  $\text{V}_{1-x}\text{W}_x\text{O}_2$  composition with  $x = 0.018$  in this work) was performed to reduce the semiconductor-to-metal transition temperature to  $20^\circ\text{C}$ .  $\text{ZrO}_2$  antireflection layers both below and above the thermochromic  $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$  layers were deposited at a low substrate temperature ( $< 100^\circ\text{C}$ ). A coating design utilizing a second-order interference in the  $\text{ZrO}_2$  layers [2] was applied to increase both the luminous transmittance,  $T_{\text{lum}}$ , and the modulation of the solar transmittance,  $\Delta T_{\text{sol}}$ . The crystalline structure of the bottom  $\text{ZrO}_2$  layer further improved the  $\text{VO}_2$  crystallinity and the process reproducibility. The top  $\text{ZrO}_2$  layer provided the mechanical protection and environmental stability of the  $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$  layers. The  $\text{ZrO}_2/\text{V}_{0.982}\text{W}_{0.018}\text{O}_2/\text{ZrO}_2$  coatings exhibited  $T_{\text{lum}}$  up to 60% at  $\Delta T_{\text{sol}}$  close to 6% for a  $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$  thickness of 45 nm, and  $T_{\text{lum}}$  up to 50% at  $\Delta T_{\text{sol}}$  above 10% for a  $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$  thickness of 69 nm. This study provides a new solution for a low-temperature fabrication of high-performance durable thermochromic  $\text{VO}_2$ -based coatings for energy-saving smart windows.

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**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  $\text{InZnO}$ , 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 ( $> 8 \times 10^3$ ), low compliance current (10 mA), large on/off ratio ( $> 10^4$ ) and long retention time at  $85^\circ\text{C}$  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.

<sup>1</sup> 2020 Student Award Finalist

## Fundamentals and Technology of Multifunctional Materials and Devices

### Room On Demand - Session C3

#### Thin Films for Energy Applications: Solar, Thermal, and Photochemical

**C3-1 Au and Ag Nanoparticle Effects on the Electrical Properties of Pulsed Laser Deposited CdTe/Cds Photovoltaic Thin Films, Mehmet Alper Sahiner (mehmet.sahiner@shu.edu), J. Emerson, F. Akinlade, M. Herington, V. Castillon, Seton Hall University, USA**

We have used pulsed laser deposition to deposit nanoparticles (Ag, Au) to investigate

the effects of these impurities on the photovoltaic properties of the CdS/CdTe based thin films. The main

objective was to investigate how the inclusion of nanoparticles will affect light scattering in the at the interfaces

and whether the different size and shape of nanoparticles will have a positive effect on the overall electrical

performance of these thin film solar cells. In our previous studies, we have investigated the effects of the

embedded Ag nanoparticles on the photoelectric conversion efficiency on CdS/CdTe based thin film solar cells

as synthesized by Pulsed Laser Deposition (PLD). Silver was shown to enhance the photovoltaic performance

by almost doubling the photovoltaic conversion efficiency of the conventional CdS/CdTe films [1]. A careful

comparison of photovoltaic performance of Au/Si versus Ag embedded thin films of CdS/CdTe on indium tin

oxide coated glass substrates have been performed. Our results on the Ag case revealed electrical

performance of these cells have correlates with the particles density and the particle size on the CdS/CdTe

interface. This study concentrates on the Au and Ag nanoparticle deposition on the CdS/CdTe interface with

varying particle size and distributions. Structural and compositional characterization were performed using

XRD, AFM, and SEM/EDX. Photovoltaic properties were measured using a LabView assisted Keithley

Sourcemeeter set-up. The comparison of Ag vs Au nanoparticles on the structure and photovoltaic

conversion efficiency will be presented. Ag and Au nanoparticles have contrasting effects on the

photovoltaic conversion efficiency in terms of their relative coverage at the interface, This will be discussed in

the light of plasmonic resonances and effective light scattering for Ag and Au particles.

[1] Olivia Rodgers, Anthony Viscovich, Yunis Yilmaz, Mehmet Sahiner, "The Effect of Embedded Ag

Nanoparticle on the Photovoltaic Conversion Efficiency in CdTe/CdS Thin Films", American Physical Society

Bulletin, X17.13 (2018).

This work is supported by NSF Award #:DMI-0420952

**C3-2 Transparent Thermoelectric TiO<sub>2</sub>:Nb Thin Films, J. Ribeiro, F. Correia, Carlos Jose Tavares (ctavares@fisica.uminho.pt), University of Minho, Portugal**

The design of a transparent conducting oxide (TCO) material with thermoelectric properties is a promising technology for touch-screen displays and solar cell applications. In this work, TiO<sub>2</sub> doped with Nb thin films were deposited by d.c. magnetron sputtering. Several process parameters were adjusted, such as reactive gas (oxygen) partial pressure and deposition time and temperature, which affect the morphology and crystalline structure of the thin films. Hence, by modifying the optical, electric, thermal and thermoelectric properties of the produced TiO<sub>2</sub>:Nb thin films, enables their suitability for thermal energy harvesters in devices in order to render them more sustainable. For optimized deposition conditions, TiO<sub>2</sub>:Nb thin films with an optical transmittance up to 85 %, a relatively low electrical resistivity (>10 Ω·cm), low thermal conductivity (<2 W·m<sup>-1</sup>·K<sup>-1</sup>), and a high absolute Seebeck coefficient (>200 μV·K<sup>-1</sup>) corresponding to a power factor of 125 μW·K<sup>-1</sup>·m and ZT figure of merit close to 0.1 were attained, as seen in Figure 1. Both anatase and rutile crystalline phases were discerned in the X-ray diffractograms. Scanning electron microscopy observations provided evidence of a dense microstructure and a smooth film surface with an average thickness of 120 nm. From Figure 2, X-ray photoelectron spectroscopy experiments confirms that Nb<sup>5+</sup> ions substitute Ti<sup>4+</sup> in the TiO<sub>2</sub> lattice, providing a charge unbalance to the matrix. Furthermore, due to larger ionic radii, Nb<sup>5+</sup> scatter phonons more efficiently and reduce the thermal conductivity, which is essential for enhancing the thermoelectric property.

**C3-3 Multilayers for Efficient Thermal Energy Conversion in High Vacuum Flat Solar Thermal Panels, D. De Maio, UniNa and CNR-ISASI, Italy; C. D'Alessandro, A. Caldarelli, E. Gaudino, UniNa and CNR-ISASI, Italy; M. Musto, UniNa - Università degli studi di Napoli "Federico II", Italy; D. De Luca, UniNa and CNR-ISASI, Italy; E. Di Gennaro, UniNa - Università degli studi di Napoli "Federico II", Italy; Roberto Russo (Roberto\_russo@cnr.it), CNR - ISASI, Italy**

The solar thermal flat panel insulated with high vacuum can have excellent efficiency performances in the mid temperature range (150-300°C) if equipped with an optimized selective solar absorber. We present 3 multilayer coatings optimized to work at 100, 200 and 300°C. Optimization has been obtained by maximizing the efficiency at the designed operating temperature by a genetic algorithm. The coatings (based on Cr and Cr<sub>2</sub>O<sub>3</sub>) have been deposited by DC reactive magnetron sputtering starting from a Cr target on glass and on 3 industrial copper substrates (OFE, OF, ETP). The single layers have been measured by standard characterization techniques (ellissometry, integrating sphere, AFM, X-Rays Diffraction...), whereas the produced multilayers have been also investigated by using a proprietary system [1] able to measure the absorber efficiency as function of temperature up to the stagnation temperature and above[2]. Influence of several deposition parameters on the multilayer performance will be presented. To enhance the absorptivity the multilayers have been covered with antireflective coatings based on SiO<sub>2</sub> and/or SiNx.

[1] R. Russo et al. Optic Express 26 (2018) A480

[2] C. D'alessandro et al. submitted to this conference

**C3-4 Development of Efficient Perovskite Solar Cells Under Ambient Conditions via Fine Tuning of Compact TiO<sub>2</sub> Layer, Navjyoti Bhagat (navjyotibhagat@gmail.com), Guru Nanak Dev University, India; V. Saxena, Bhabha Atomic Research Centre, India; A. Mahajan, Guru Nanak Dev University, India**

Organic inorganic perovskites have attracted a great attention as next generation solar cells due to their excellent properties such as high molar extinction coefficient, low temperature processability, ambipolar nature, large diffusion length and small exciton energies. The compact or blocking layers have been studied extensively in dye sensitized solar cells, however, there are only a few reports on the effect of these layers on perovskite solar cells (PSCs). Herein, we employed a thin compact layer of spin coated TiO<sub>2</sub> (c-TiO<sub>2</sub>) (<50 nm) in order to reduce series resistance and improve transmittance. The thickness of c-TiO<sub>2</sub> (7-35 nm) was optimized by changing the precursor concentration as well as spinning speed. The prepared c-TiO<sub>2</sub> as well as mesoporous layer of TiO<sub>2</sub> (m-TiO<sub>2</sub>) were thoroughly characterized using UV-Vis spectroscopy, Raman, Atomic Force Microscopy, Cyclic voltammetry and electrochemical techniques. Further, PSCs were fabricated

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under ambient conditions with high humidity (~RH 80%) using CuSCN as hole transporting layer (HTL). The power conversion efficiency of the optimized device found to be improved by 50 % on increasing the thickness of ETL from 7 nm to 15 nm.

## Fundamentals and Technology of Multifunctional Materials and Devices

### Room On Demand - Session CP

## Fundamentals and Technology of Multifunctional Materials and Devices (Symposium C) Poster Session

**CP-1 Freestanding ZnO Nanowire For Multifunctional Application in RRAM Memory and Gas Sensing, Pragya Singh ([pragyasinh@mail.ntust.edu.tw](mailto:pragyasinh@mail.ntust.edu.tw)),** National Taiwan University of Science and Technology, Taiwan; *T. Tseng*, National Chiao Tung university, Taiwan; *J. Chu*, National Taiwan University of Science and Technology, Taiwan

In current research, the focus of nanoscale community is to produce various nanostructures in such a way that can be easily modified as desired applications ranging from nanoptorotics to biomedical engineering. Nanoscale structure from various metal oxide materials has got great attention due to its various fabrication strategies, characterizations, surface morphology, structure-property correlations, and various remarkable milestones indeed have been entrenched. Zinc oxide (ZnO) is a well-known n-type semiconductor with a wide bandgap (3.37eV) and large excitation binding energy (60eV) material, that has been extensively investigated in multifunctional devices due to the low production cost, chemical stability, doping, and the non-toxic property. In this study, we fabricated the ZnO nanowires by hydrothermal method, applicable in resistive random access memory (RRAM) as well as in gas sensing devices. The hydrothermal growth technique is a solution-based process used to synthesize ZnO nanowires on ITO coated glass substrate. Electrical characteristics were carried out by a semiconductor device analyzer (Agilent Tech. Inc. B1500) and gas sensing electrical measurement system (model 2400, Keithley Source Meter) at room temperature. After introducing ZnO nanowire thin film between conductive electrodes, both devices show significant enhancement in their resistive switching and sensing properties. To check the surface morphology and orientation of nanowire thin film, ZnO nanowires were examined by using scanning electron microscopy (SEM). The crystal structures of the ZnO nanowire thin film were investigated through X-ray diffractometry (XRD). The defect concentrations in the nanowire thin film were evaluated using an X-ray photoelectron spectroscopy (XPS). To understand the filament formation during resistive switching analysis and gas sensing behavior, a schematic representation is used. Our study proposes that ZnO-based devices have been shown effective results and this technique can be easily adopted by other oxide and may encourage the fabrication of various hybrid devices in near future for multifunctional applications.

**CP-2 Introducing Thin HfO<sub>2</sub> Layer to Inhibit the Power Consumption of InWZnO CBRAM, You-Xuan Li ([youxuan.eo08g@nctu.edu.tw](mailto:youxuan.eo08g@nctu.edu.tw)),** *P. Liu, C. Hsu, K. Gan, D. Ruan, Y. Chiu*, National Chiao Tung University, Taiwan

In this study, the memory performance of IWZO-based CBRAM device can be greatly improved by inserting a thin HfO<sub>2</sub> layer with different process methods. The bilayer structure (IWZO/ALD-HfO<sub>2</sub>) device also exhibit excellent memory characteristics, such as high endurance cycle (more than  $2 \times 10^3$ ), long retention time (more than  $2 \times 10^4$  s), lower set and reset voltage. The IWZO-based memory device with bilayer structure can be operated at 10 mA for low-power device application. This improvement in resistive switching characteristics are attributed to Gibbs free energy of HfO<sub>2</sub> lower than IWZO layer, which is easily occur oxidation reaction in HfO<sub>2</sub> layer. These results proposed a method that inserting a thin ALD-HfO<sub>2</sub> layer in IWZO-based CBRAM device can not only reduce the off-state leakage current, but also enhance the reliability of the memory, which has great potential for future memory-in-pixel applications in low-power Internet of Things (IoT) generations.

**CP-3 Improved Electrical Performance for Indium Tungsten Oxide Thin-Film Transistor with Asymmetric Source and Drain Electrode Material, Chia-Yu Lin ([mandylin21107@gmail.com](mailto:mandylin21107@gmail.com)),** *P. Liu*, National Chiao Tung University, Taiwan; *D. Ruan*, National Chiao Tung University, China; *K. Gan, Y. Chiu, C. Hsu*, National Chiao Tung University, Taiwan; *S. Sze*, National Chiao Tung University, USA

In this work, high mobility indium tungsten oxide thin-film transistor (TFT) with asymmetric schottky contact has been fabricated, while the improvement on electrical characteristics was also discussed. In general, metal material with low work function is often selected as the source and drain (S/D) electrode. It can be attributed to a low schottky barrier which was formed with channel material naturally. However, a high conductivity channel material with low schottky barrier may induce an undesirable negative threshold voltage and poor on/off current ratio. Utilizing asymmetric S/D schottky barrier, a lower off-state current and subthreshold swing can be achieved, while the on-state current and field effect mobility have been kept. The research may provide a new approach to enhance the electrical performance and adjust threshold voltage for TFT with high conductivity channel material.

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