Thin Films Division
Room A122-123 - Session TF+EM-WeA

Emerging Thin Film Materials: Ultra-wide Bandgap and Phase Change Materials

Moderators: Cary Pint, Vanderbilt University, Brent Sperling, National Institute of Standards and Technology (NIST), Jin-Seong Park, Hanyang University, Korea

2:20pm **TF+EM-WeA1 MOCVD Growth and Characterization of $ZnGeN_2$-GaN Alloy Films***, Benthara Hewage Dinushi Jayatunga, K. Kash,* Case Western Reserve University*; M.D. Reza, H. Zhao,* The Ohio State University*; O. Ohanaka, R. Lalk,* Case Western Reserve University*; M. Zhu, J. Hwang,* The Ohio State University

$ZnGeN_2$ and GaN are almost lattice matched and both have band gaps of approximately 3.4 eV. A large conduction band offset of ~ 1.4 eV results in a type II band alignment that has great potential for novel device structures. [1,2] For the 50-50 alloy, a slightly positive mixing energy, indicating a tendency toward phase separation, has been predicted. [3] For this mixture the lowest energy configuration is predicted to be an octet-rule-preserving orthorhombic $Pmn2_1$ phase. Other compositions may in principle be made in octet-rule-preserving (and thus lower energy) phases, compared to those that break the octet rule, by random stacking of $ZnGeN_2$ and GaN layers along the orthorhombic *b* axis. [3] Whether random stacking, phase separation, or octet rule violations occur will determine whether, and by how much, the band gap may be tuned with composition, and whether the transport properties are isotropic or anisotropic. The only other work on this alloy reported to date employed a gas reduction nitridation method for synthesis of powders of different compositions, from pure $ZnGeN_2$ to a 50-50 mixture, for photocatalytic applications [4].

Here we report the results of MOCVD growth of this alloy on c-, r-, and a-plane sapphire and c-GaN/sapphire substrates, at temperatures varying from 550 ^{0}C to 700 ^{0}C. Films at the 50-50 composition exhibit better surface morphologies when grown on r-sapphire substrates. Zn incorporation increases with the increase of Ga. The highest growth rate, 3.46 μm/hr, was obtained for a film grown on r-sapphire at 670 ^{0}C and 550 torr, for which a 2θ-ω XRD measurement yielded a wurtzite (110) diffraction peak at 2Θ = 57.70^0 with FWHM of 0.76^0 and an RMS surface roughness of ~ 10 nm by AFM. The Hall mobility is 8.19 cm^2/v-s with an n-type carrier concentration of 8.5 x 10^{18} cm^{-3}. Atomic-resolution HAADF-STEM revealed the atomic arrangement of the film near the substrate interface. Introduction of a low-temperature-grown $ZnGeN_2$ buffer layer (480 ^{0}C at 600 torr with low injection of precursors compared to the film growth conditions) led to improved surface morphology and crystal quality, and yielded a room temperature photoluminescence spectrum indicating a band edge at approximately 3.5 eV, close to that predicted for the $Pmn2_1$ phase. [3]

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2:40pm **TF+EM-WeA2 Device Quality β-Ga2O3 and Related Alloys by MOCVD***, A. Osinsky,* ***Fikadu Alema,*** Agnitron Technology, Inc.*; Y. Zhang, A. Mauze, J.S. Speck,* University of California, Santa Barbara*; P. Mukhopadhyay, W. Schoenfeld,* University of Central Florida

We report on the growth of device quality β-Ga_2O_3 and related alloys using MOCVD method. β-Ga_2O_3 thin films are grown using $Ga(DPM)_3$, TEGa and TMGa as Ga sources, and molecular O_2, H_2O vapor, and N_2O as an oxidizer. Films grown from each Ga source had high growth rates with up to 10 m/hr achieved using TMGa [1]. The effect of the oxidizer identity on the growth rate, electron mobility (μ_e), background carrier concentration, surface and crystalline quality of the films will be discussed. Using pure O_2 as an oxygen source, optimal growth conditions have led to the growth of smooth epitaxial UID Ga_2O_3 thin films with a RT μ_e of 176 cm^2/Vs at n~7x10^{15} 1/cm^3 [2]. The highest μ_e of ~3500 cm^2/Vs has been measured at 54 K. C and H impurities have been shown to be below the SIMS detection limit for a wide range of process conditions, whereby films with n~ 2x10^{14} cm^{-3} were demonstrated. We will also present the growth of device quality β-Ga_2O_3 layers doped with Si, Fe, and N impurities. Critical growth conditions influencing the incorporation of these dopants will be discussed. Using optimum growth conditions, controllable doping with a concentration between 10^{15} and 10^{20} 1/cm^3 were obtained for each dopant. In this work, we will also present on the MOCVD growth of $(Al_x, Ga_{1-x})_2O_3$ alloys. The MOCVD process enables the growth of AlGaO at a temperature >800 ^{o}C, improving the solubility of Al_2O_3 in β-Ga_2O_3 by preventing the formation of volatile suboxides. The MOCVD reactor used in this work has a unique feature that enables it to minimize premature reaction between the species, thereby improving the Al incorporation. AlGaO alloys with Al content of up to 43 % was obtained. The epitaxial growth of high quality strained β-(Al, $Ga)_2O_3/Ga_2O_3$ heterostructures and superlattices will be discussed. The composition homogeneity, structural quality, surface morphology and electrical properties of the heterostructures will be discussed as a function of growth conditions. Finally, the growth of alloys including β-(In, $Ga)_2O_3$ and ZnGaO using MOCVD and their application for photodetection purposes will be discussed.

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3:00pm **TF+EM-WeA3 Development of the β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 (010) Heterostructures by Plasma-assisted Molecular Beam Epitaxy***,* ***James Speck,*** University of California at Santa Barbara **INVITED**

β-Ga_2O_3 is a promising wide bandgap semiconductor for power electronics due to its ~4.8 eV bandgap, reasonable electron mobility, the availability of large area melt grown substrates, and the ability to form heterostructures by alloying on the group III site. In this presentation, we present progress in the plasma-assisted molecular beam epitaxy (PAMBE) growth of β-Ga_2O_3. The presentation will highlight the promise of β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 heterostructures for lateral devices. We will discuss the growth of β-$(Al_xGa_{1-x})_2O_3$ in the context of the predicted high Al solubility in the β-phase (predicted to be up to ~60-70% for growth temperatures > 800 C). Current experiments limit the Al content to ~25% for coherent growth. We will present detailed analysis of the β-$(Al_xGa_{1-x})_2O_3$ alloys that show the compositions agree between atom probe tomography and high resolution x-ray diffraction. We will highlight a new growth technique, metal oxide catalyzed epitaxy (MOCATAXY), that enables higher growth temperatures due to the addition of an indium catalyst layer that serves both to react with molecular oxygen in the flux and to suppress Ga_2O_3 decomposition via the reaction Ga_2O_3 -> Ga_2O+$^1/_2O_2$. We will demonstrate an increase of growth temperature of ~250 C in comparison to conventional PAMBE growth conditions. We discuss the relative merits and challenges for donor doping in MBE (Si vs. Ge vs. Sn) and options for realizing controllable semi-insulating GaN.

4:20pm **TF+EM-WeA7 Phase-Change Memory: A Quest from Material Engineering Towards the Device Performances***,* ***Guillaume Bourgeois,*** *G. Navarro, M.C. Cyrille, J. Garrione, C. Sabbione, M. Bernard, E. Nolot, E. Nowak,* CEA-LETI, France **INVITED**

In this paper, we provide some examples of how phase–change material engineering can allow targeting specific memory applications. We present the trade-off in Phase–Change Memory between high-speed performance, required in Storage Class Memory applications, and high thermal stability of the amorphous phase at high temperature, mandatory to address automotive embedded applications.

Phase-Change Memory (PCM) is today the most mature among innovative back-end non-volatile memory technologies, thanks to a wide set of interesting features making PCM technology enough versatile to meet different applications' requirements [1]. A PCM device experiences a physical change of a chalcogenide material sandwiched between two electrodes made possible by the current induced Joule heating flowing through the cell. To achieve the amorphous phase, the PCM in the crystalline phase has to be melted, then rapidly quenched (RESET operation). Thanks to the switching phenomenon, the material in the amorphous phase changes abruptly its conductivity starting to be highly conductive, and can recover the crystalline phase thanks to a specific thermal profile during the pulse application, that provides the energy necessary to the atomic reorganization (SET operation). Thereby, PCM thermal stability relies on the magnitude of the activation energy of the crystallization that results from the combination of crystals nucleation and growth phenomena, on which also the device programming speed relies. Thus, a general trade–off exists between the time required for the SET operation and the device data retention performance [2] (Figure 1). Sb-rich GeSbTe compounds are suitable for high-speed performances with a

programming time down to tens of ns still ensuring high endurance and scalability, promising for Storage Class Memory applications (SCM) [3]. Reliability at high temperature is the main requirement to target automotive embedded applications. Ge-rich compositions revealed an endurance of 10^7 cycles up to 175 °C and high temperature data retention compatible with embedded standards. We present here the device performance tuning thanks to the phase–change material stoichiometry engineering (Figure 2). Moreover, we highlight the possibility to boost the PCM performances, such as SET speed and Multi Level Cell capability, thanks to dedicated programming strategies [4].

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[2] G. Navarro et al, “Non-Volatile Resistive Memory”, ECS 2016.

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[4] J. Kluge et al, “High Operating Temperature Reliability”, IMW 2016.

5:00pm **TF+EM-WeA9 Neuromorphic Materials and Architectures for Dynamic Learning and Edge Processing Applications***, **Angel Yanguas-Gil**,* Argonne National Laboratory

The ability to dynamically learn and adapt to changes in the environment is one of the hallmarks of biological systems. In the last years there has been a lot of research focused on exploring novel materials, such as those exhibiting memristive behavior, that could enable this type of systems. However, there are comparatively fewer studies focusing on understanding which are the ideal properties that memristive materials should have in order to optimize the performance of architectures capable of dynamic learning. This type of information is crucial to provide design targets for new materials and accelerate the integration of novel devices into architectures optimized for specific applications.

In this work, we identify the subset of the design space of memristive materials that is optimal for dynamic learning applications: in this type of application, a system, in this case a neural network, evolves dynamically and learns as it processes information in real time. This type of behavior is highly desirable for smart sensors or edge processing applications. We have implemented a benchmark architecture consisting of a discrete implementation of spiking neurons where dynamic learning takes place on a set of plastic synapses formed by memristor pairs in a crossbar array. This architecture, which is inspired on the learning center of the insect brain, is capable of dynamically learning standard machine learning datasets such as MNIST and Fashion-MNIST. We have used this model to identify the key properties that memristive materials should have to be optimal dynamic learners, exploring the impact of the kinetics of the memristor's internal state on the system's learning ability, as well as the impact that materials and device variability and errors in tuning the memristor's internal state have on the system's performance.

The results obtained show that a fine degree of control of the memristor internal state is key to achieve high classification accuracy during dynamic learning, but that, within this optimal region, learning is extremely robust to both device variability and to errors in the writing of the internal state, in all cases allowing for 2σ variations greater than 40% without significant loss of accuracy. Moreover, the dynamics of the internal state can show distinct kinetics depending on the polarity, something that is critical for bipolar memristors. These criteria are significantly different from those required for ReRAM applications or even for neuromorphic applications based on offchip training, where the robustness of reading and writing operations are critical.

5:20pm **TF+EM-WeA10 Atomic Layer Deposited VO_2 Thin Films Towards Modulated Infrared Optoelectronic Devices***, **Virginia Wheeler**, C.T. Ellis, M. Currie, J.R. Avila, M.A. Meeker, A.J. Giles,* U.S. Naval Research Laboratory*; J.D. Caldwell,* Vanderbilt University*; J.G. Tischler,* U.S. Naval Research Laboratory

VO_2 is a phase change material that undergoes a first order crystalline phase transition at a critical temperature ($T_c = 68^oC$), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical changes with this phase transition are of particular interest as passive and active components of optoelectronic devices, specifically for thermal regulation and modulated signaling. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is the ideal deposition method in these cases.

Traditional metal-based plasmonic materials suffer from high optical losses, which has promoted research towards alternative low-loss materials that can support plasmonic-like effects. One such approach employs phonon-mediated collective-charge oscillations (surface phonon polaritons, SPhPs) that are supported by nanostructured polar dielectric materials (SiC, AlN, etc), which inherently are low-loss. Geometric design of the nanostructures enables spectral tuning of resonant features between the longitudinal and tranverse optical phonons of the polar material, typically in the infrared regions. However, the spectral position and amplitude of these resonances remain fixed after fabrication. Integrating phase change materials with these structures provides a way to achieve active modulation of resonances.

In this work, nanopillar arrays were etched into SiC and AlN to create narrowband resonances in the long-wave infrared region. These structures were subsequently coated with ALD VO_2 films with different thicknesses (8-75nm). As-deposited VO_2 films are highly conformal and amorphous, and cause the resonances to shift and broaden due to the different dielectric environment. However, after annealing the films at 525°C in $6x10^{-5}$ Torr, the VO_2 films crystallize resulting in sharper resonances and spectral locations close to the initial uncoated structures. Temperature-dependence reflectance and emission measurements show that by heating through the VO_2 transition temperature, the amplitude of the resonances can be modulated. Full signal modulation (ie. on/off) requires at least a 16nm VO_2 film. This work shows the ability to actively tune surface phonon polariton resonances using ALD phase change materials.

5:40pm **TF+EM-WeA11 Deposition Process for Vanadium Dioxide Thin Films for RF Applications***, **Mark Lust**, S. Chen, N. Ghalichechian,* The Ohio State University

Phase change materials (PCM) are attractive due their tunability, wide range of applications, and quasi-passive actuation as compared to traditional active integrated circuits. Vanadium dioxide (VO_2) is particularly appealing because of its high contrast between dielectric and conductive states and the relatively low temperature (68 °C) at which its metal-insulator transition (MIT) occurs. This work details a process for depositing high quality VO_2 thin films on C-plane sapphire wafers as well as alumina (Al_2O_3) buffer layers using atomic layer deposition (ALD) on silicon substrates. We compare resistivity vs. temperature measurements of VO_2 on sapphire with VO_2 on the Al_2O_3 buffer layers both as-deposited and after rapid thermal annealing (RTA) at temperatures ranging from 950 to 1150°C. The VO_2 thin films yielded ratios of resistivity between conductor (heated) and dielectric (room temperature) states of 9.8×10^4 Ω-cm, 5.2×10^3 Ω-cm, and 1.5×10^4 Ω-cm when deposited on crystalline sapphire, amorphous Al_2O_3 buffer layers, and annealed Al_2O_3 buffer layers, respectively. This corresponds to an improvement by a factor of 2.9 in the annealed buffer layers over the amorphous buffer layers. Moreover, we studied various VO_2 thin films using X-ray diffraction, which showed clear indications that the films are highly pure and have a preferred crystal orientation. The deposition process we have developed will allow us to use high quality VO_2 thin films on silicon substrates, especially millimeter-wave devices such as reconfigurable antennas, sensors, and meta-surfaces.

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