

Tuesday Afternoon Poster Sessions, July 31, 2018

Emerging Materials

Room Premier Ballroom - Session EM-TuP

Emerging Materials Poster Session

EM-TuP-1 Structural and Optical Properties of Luminescent Copper (I) Chloride Thin Films Deposited by ALD, Tomáš Homola, R Krumpolec, D Cameron, O Caha, J Humlíček, Masaryk University, Czech Republic; R Zazpe, J Píkrýl, J Macák, University of Pardubice, Czech Republic

Zinc blende-structure g-copper (I) chloride is a wide, direct bandgap semiconductor with the potential for applications in UV optoelectronics. We report on the structural, optical and photoluminescent properties of CuCl thin films deposited by atomic layer deposition. The CuCl films were deposited at a reaction temperature of 125 °C from [bis(trimethylsilyl)acetylene] (hexafluoroacetylacetonato)copper(I) and pyridine hydrochloride precursors with pulsing times 2 and 6 s with corresponding purging times 4 and 6 s respectively. The CuCl growth was deposited on various substrates: amorphous soda-lime glass, amorphous quartz glass, crystalline silicon and crystalline sapphire of different orientations. The deposited coatings at 100, 200, 500 and 1000 ALD cycles were studied by XPS, XRD, AFM, optical reflectance and photoluminescence. We also investigated the effectiveness of a thin capping layer of aluminium oxide against degradation of the CuCl by atmospheric. The presence of CuCl was confirmed by the x-ray diffraction and photoluminescence measurement which showed a strong signal at approx. 3.25 eV characteristic of the excitonic emission. The presence of crystalline CuCl was strongly influenced by the substrate and the best crystallinity was found on quartz glass, whereas silicon wafers showed no evidence of CuCl crystals in the deposited films. Moreover we also showed that quick optical reflectance measurement can be used for fast and reliable detection of the presence of CuCl crystals.

EM-TuP-2 Wafer-scale Fabrication and Optoelectrical Application of Organic-inorganic Perovskite Single Crystal Arrays, Lynn Lee, M Sung, Hanyang University, Republic of Korea

Organic-inorganic hybrid perovskites, especially $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) have received great attention due to their outstanding light-harvesting properties as well as their low-cost device fabrication process. Their superior optoelectrical properties lead to the exceptional device performances of these materials in various applications such as solar cells, LEDs, and photodetectors. Typically, the quality of the crystal is a well-known factor to decide the efficiency of those optoelectronic applications with long carrier diffusion length and high mobility. However, since a thin film of a single crystal cannot be obtained by a typical film fabrication method, films made by most of the manufacturing methods suffer from low crystallinity issue. For these reasons, fabrication of single crystalline perovskite thin film is required for high-efficiency device applications.

Here, we fabricate the wafer-scale perovskite single crystal arrays in thin film form and characterize the crystallinity of the perovskite thin film by X-ray diffraction (XRD) and selected area electron diffraction (SAED). Also, the morphology of perovskite crystals was observed using optical microscopy (OM) and scanning electron microscopy (SEM). Furthermore, the perovskite patterned thin films are applied in lateral solar cell applications. The average efficiency of the perovskite lateral solar cell in low light intensity is over 4%, which are the world-top efficiency in lateral perovskite solar cell field as far. From this work, the probability of the perovskite single crystal array is successfully demonstrated.

EM-TuP-3 Organic-inorganic Hybrid Optoelectronic Device by Atomic Layer Infiltration, Yeongeun Bak, M Sung, Hanyang University, Republic of Korea

Hybrid organic-inorganic solar cell have emerged as a remarkable new alternative energy source over the past few years to solve the global energy problems. The sun is sustainable, reliable and long-term supply of energy, in contrast to conventional resources such as fossil fuels. Silicon is the most widely used as material of solar cell because of its high efficiency, but it has limits; expensive manufacturing cost and limitation of application to flexible or transparent devices. So, alternative types of solar cells are also being researched, Sb_2S_3 solar cell is up-rising candidate for next generation solar cells overcoming the above disadvantage of Si solar cell. The problem of commercialization of Sb_2S_3 solar cell is lower efficiency than Si solar cells, so there were previous studies about interfacial engineering have been proceeding for solving the problems.

We studied new organic-inorganic material nickel-4-mercaptophenol (Ni-4MP), as an interfacial engineering material into Sb_2S_3 -hole transport material interface. Ni-4MP thin film is deposited using atomic layer deposition method. For infiltrate precursors into FTO/mp-TiO₂/ Sb_2S_3 structure, exposing procedure is added. The reference cell structure is FTO/mp-TiO₂/ Sb_2S_3 /P3HT/Au. We measured the photo conversion efficiency using solar simulator with source-meter for comparing two samples. And then we observed impedance measurement with variation of voltage for confirming the effect of Ni-4MP on Sb_2S_3 solar cell. As a result, electron lifetime calculated from this measurement proof the longer lifetime of electron after insert Ni-4MP as interfacial engineering material.

EM-TuP-4 A Common Source/Drain Metallization Scheme for (In)GaAs and Ge Channel Materials Featuring Low Contact Resistances, Szu-Hung Chen, National Nano Device Laboratories (NDL), NARL, Republic of China; K Chen, Y Chen, College of Photonics, National Chiao-Tung University, Republic of China; C Chu, G Luo, National Nano Device Laboratories (NDL), NARL, Republic of China; C Lin, College of Photonics, National Chiao-Tung University, Republic of China

Pursing of the miniaturization of Si-based logic transistors is approaching it's fundamental limits in aspects of geometric scaling, enhancement of intrinsic carrier transport efficiency as well as reduction of parasitic components. Serial extrinsic S/D resistance can seriously degrade the output current of the transistor and constrain it from low-voltage operation. As the transistor channel length (L_g) shrinks, the device's intrinsic channel resistance decreases. Consequently, the parasitic source/drain resistance (R_{sd}) dominates and plays key role in determining the overall device output characteristics, particularly when the technology node is beyond 7 nm and smaller. Despite the stringent challenges in reducing R_{sd} , CMOS technology also requires both n- and p-type transistors in a single chip for various logic functions in integrated circuits. Si is the channel material of current n-/p-type transistors used for industrial mass production. However, due to the potential of incorporating alternative channel materials for future-generation CMOS, n-type and p-type channels may be different materials to maximize the performance. For example, InGaAs, possessing high electron mobility, is used in n-type channel devices and Ge, possessing high hole mobility, is used in p-type channel device, respectively, in an attempt to achieve the best combined performance in CMOS. In such a scheme, the complexity of processing heterogeneous CMOS dramatically increases. From this point of view, it is of great interest and is mandatory to reduce the process complexity, especially in the step of source/drain contact metallization. In this work, targeting the future nano-device application, a single metallization scheme for n-/p-type channel transistors has been developed to reduce the cost of the CMOS manufacturing. W/TiN/Ti multilayer structure is adopted to form metal/ $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and metal/Ge contacts. Both contact structures show specific contact resistance of $<3\text{E-}7 \Omega\text{cm}^2$ by CTLM (circular transmission line model) analysis. However, the interracial relations are distinct as evidenced by material analysis. The promising results show that the developed technology is of great potential for application in future of nano CMOS technology which requires heterogeneous n-/p-channels.

EM-TuP-5 Ruthenium Precursors - Properties and ALD Application, Andreas Wilk, O Briel, D Zeng, A Frey, A Rivas Nass, W Schorn, Umicore AG & Co. KG, Germany

Umicore has its roots in precious metal chemistry and has significant expertise in making new MOCVD and ALD precursors available at high manufacturing volumes. The necessary scale up skills include substantial supply chain involvement, solid chemical background, purification competence, trace metal analytical capabilities and significant packaging knowhow.

Besides the established cobalt and tungsten precursor portfolio we have established new chemistries for ruthenium based compounds as ruthenium tungsten and cobalt are considered by several chipmakers at 5nm and below for upcoming applications.

Ruthenium is a precious metal with interesting chemical, crystallographic and electronic properties. This makes ruthenium chemistry including the related precursors very interesting for chipmakers for logic as well as memory applications. In our poster we will introduce established and new precursors with a variety of ligands currently considered and review their relevant physical and analytical properties for interesting metal and oxide ALD industry applications including the 5 nm node and below.

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EM-TuP-6 Magnetic and Electrical Performance of Atomic Layer Deposited Nanostructures, *Aile Tamm, K Kalam, M Mikkor, H Seemen, A Šutka, U Joast, M Rähn, K Kukli,* University of Tartu, Estonia; *J Link, R Stern,* National Institute of Chemical Physics and Biophysics; *H Castán, S Dueñas,* University of Valladolid

The synthesis of multiferroic materials is of relevance while developing the next generation electronic and spintronic devices [1]. Theoretically, several materials could demonstrate saturating and remnant polarization in both electric and magnetic fields, but it is challenging to actually synthesize thin films which demonstrate multiferroic behaviour, because the physical performance of the materials may considerably depend on their synthesis routes. In this study we compare the nanostructures containing nanoparticles CoFe_2O_4 or MnFe_2O_4 covered by high-k films by ALD with nanolaminate films consisting of high-permittivity oxides (ZrO_2 , Er_2O_3) and magnetic materials (Bi_2O_3 , Fe_2O_3 , Co_3O_4) grown by ALD. Nanolaminate films could be uniformly deposited into three dimensional stacked substrates using the same cycle times otherwise suited to the uniform coverage of planar substrates. The morphology, crystalline phases and composition of nanostructures were described. Those nanostructures promoted both charge polarization and saturative magnetization. Promising results in terms of the simultaneous appearance of the internal magnetization and certain electrical charge polarization were demonstrated in some planar nanostructures. Further electrical and magnetic modelling and analysis will be needed in order to elaborate the phenomenon and optimize the material structure for the magnetoelectric performance.

Acknowledgements

This work was funded by the European Regional Development Fund the project TK134 "Emerging orders in quantum and nanomaterials", Estonian Research Agency (IUT2-24, PRG4), Estonian Academy of Sciences (SLTFYUPROF), and Spanish Ministry of Economy and Competitiveness through the project TEC2014-52152-C3-3-R with support of Feder funds.

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EM-TuP-7 HfZrO₂ Deposited by ALD using TEMA and ZrCMMM Precursors, *Ronald Grundbacher,* IBM Research – Zurich, Switzerland; *Y Ju,* ETH Zurich, Switzerland; *F Eltes,* IBM Research – Zurich, Switzerland; *X Chen,* ETH Zurich, Switzerland

Hafnium zirconium oxide (HfZrO_2) with thickness on the order of a few nanometers to tens of nanometers is of interest as a high-k dielectric material that is integrated into compound semiconductor and CMOS devices, nanowire-based devices, and nanostructured devices based upon novel materials. The ferroelectric properties of HfZrO_2 are of interest for low-power steep-slope transistor applications and nonvolatile memory. The requirements of the HfZrO_2 that is integrated into the above mentioned devices include low concentration of impurities, low interface and bulk trap densities, low leakage current, and often, low temperature deposition due to a limited thermal budget. The characteristics of HfZrO_2 deposited by atomic layer deposition (ALD) has been investigated with the above requirements in mind, and deposition parameters have been determined to optimize the Hf/Zr ratio.

Hafnium zirconium oxide thin films were deposited on silicon wafers by atomic layer deposition using tetrakis(ethylmethylamino)hafnium (TEMAH) and bis(methyl- η^5 -cyclopentadienyl)methoxymethylzirconium (ZrCMMM) precursors and either oxygen plasma or ozone. Oxygen plasma and ozone conditions, Hf to Zr pulse ratio and sequencing, as well as deposition temperature (250°C to 350°C), were varied, and their effects on the HfZrO_2 thin films were investigated. The properties of the ALD deposited films were comparatively characterized. The HfZrO_2 thin films were characterized by ellipsometry to determine the thickness (growth rate) and dielectric constant, and they were characterized by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) to determine the hafnium and zirconium content. Atomic force microscopy (AFM) was used to characterize surface roughness and piezoresponse force microscopy (PFM) was used to determine the ferroelectric nature of the HfZrO_2 films.

EM-TuP-8 Non-destructive And Precise Control Of Electronic Properties via N-Doping Method with Atomic Layer Deposition., *Jong Chan Kim,* Hanyang University, Republic of Korea; *M Sung,* Hanyang University, Republic of Korea

For variety of usage, graphene must be under processed its Fermi level and carrier concentration. In this approach introduced n-doping technique with

atomic layer deposition (ALD) of Zinc oxide. Precise even quite simple and, the produced ZnO thin film on graphene are uniform, conformal, of good quality with a low pinhole density, besides thickness control of 1 Å resolution available. Evaluation of material properties performed which characterization of graphene transistor at the point of carrier density, doping state and Dirac point as a function of the thin film thickness. Our achievement is not only electronic properties' progress, but also stable device performance has gotten. It is caused from ZnO film did a role of effective barrier against air-borne water and oxygen on the graphene. Additionally, ZnO ALD enhanced too to the other promising 2D materials like MoS_2 and WSe_2 those are candidates to promote electron mobility.

EM-TuP-9 Curvature-Dependent Surface Potentials of Zincone Films Grown by Molecular Layer Deposition, *J Lee, Yun Yeong Lee,* Sookmyung Women's University, Republic of Korea

Molecular layer deposition (MLD) is a method for obtaining conformal ultrathin organic films using vapor-phase organic precursors, while their composition and thickness can be controlled at the molecular level. This process is based on self-saturating reactions between the precursors and the substrate surface. Also, in comparison with solution-based technique, it allows epitaxial growth of molecular layer on substrate and is especially good for surface reaction or coating of nanostructures such as nanopore, nanobead, nanowire array and so on.

In this study, we fabricated organic-inorganic zincone polymeric films on surfaces with various curvatures through coupling reactions between diethyl zinc (DEZ) and 2-Butyne-1,4-diol (BYDO) as inorganic and organic precursors, respectively, by molecular layer deposition. Using ellipsometry and transmission electron microscope (TEM), we confirmed the different growth behavior of zincone films grown on curvature substrates with different ratio. And, we investigated their curvature-dependent surface potentials by performing *ex situ* analysis using scanning kelvin probe microscopy (SKPM). Furthermore, their molecular geometries and energies on substrates with various curvatures were predicted by performing density functional theory (DFT) calculations.

EM-TuP-10 Photo-switchable Behavior of Azobenzene-containing Polyamide Films Grown by Molecular Layer Deposition, *J Lee, Hyemi Lee,* Sookmyung Women's University, Republic of Korea

Photo-sensitive polymer film has been attracted in the field of material science including biological system and optical devices which are sensitive on the change of surface topology. Recently, azo compound (R-N=N-R'), as one of the photo-induced reversible transformation unit, has been highlighted in the research related photo-sensitive polymer film including surface science, artificial muscle, biological and optical application, because light used as external triggers for inducing surface transformation is manageable to control without modification of nano-structures and environment concerns.

In this study, we fabricated photo-reversible polyamide film based on coupling reactions between azobenzene-4, 4'-dicarbonyl dichloride (Azo) and one of two diamine compounds, which are phenylenediamine (PDA) and hexamethylenediamine (HDA) by molecular layer deposition through self-limiting surface reaction. And, we investigated the photo-induced reversible transformation of azobenzene-containing polyamide thin film. In situ Fourier Transform Infrared (FTIR) measurement was used to monitor the growth of polyamide film, and the light-induced transformation was characterized by UV-vis spectroscopy.

EM-TuP-11 Phase Selective, Low Temperature Growth of TiO₂ by Atomic Layer Epitaxy, *Virginia Wheeler, D Boris, S Qadri, J Freitas, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored in recent years due to its promise in non-volatile resistive switches, high-k gate dielectrics, solar cell, and photocatalytic applications. This method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. Traditionally, the low ALD growth temperature (Tg) yields amorphous films. To facilitate epitaxial films, many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2 , it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or growth temperature. In this work, we demonstrate high quality epitaxial TiO_2 films at low temperatures and phase selectively by adjusting plasma gas composition, pressure and Tg.

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A Veeco Fiji G2 reactor was used to deposit TiO₂ films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O₂ or pure O₂ plasma at 100-350°C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO₂ film crystallinity and phase [1]. The high pumping speed and large gas flow range available in the system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux ($0.5-1.5 \times 10^{19} \text{ m}^{-2}\text{s}^{-1}$) of very energetic ions (30-50eV); both the flux and energy decrease as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to the plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO₂ phase, and strain. At T_g < 300°C, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O₂ to pure O₂. Additionally, an O₂ plasma produced only rutile TiO₂ films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O₂ plasma show a phase dependence on temperature and substrate. Films on c-plane Al₂O₃ go from anatase at T_g below 200°C to rutile above 300°C. The films on m-plane Al₂O₃ are rutile independent of temperature.

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EM-TuP-12 ALD Deposited Thin Films as Model Electrodes: A Case Study of the Synergistic Effect in Fe₂O₃-SnO₂, J Kint, F Mattelaer, Christophe Detavernier, Ghent University, Belgium

Li-ion batteries are the current state of the art energy storage devices. They have been around since 1991, yet there still is room for improvement. On the anode side, specific capacities are relatively low. High capacity storage mechanisms (conversion, alloying) are gaining attention. However, these reactions impose strain on the material, leading to pulverization, contact loss, SEI formation and poor kinetics. However, synergistic effects were reported when two of these materials are combined.

Since electrodes are complex systems, we used atomic layer deposition to deposit model electrodes. This approach avoids the need for binders or additives and ensures simple, 1-dimensional Li⁺-diffusion pathways. The self-limiting and digital nature of ALD ensures optimal control over the thickness and stoichiometry of the mixed oxides. Furthermore, it enables control of the degree of intermixing of the Fe₂O₃ and SnO₂ at the atomic scale. Here, films of pure Fe₂O₃, pure SnO₂, atomically intermixed Fe₂O₃-SnO₂ and a Fe₂O₃/SnO₂ nanolaminate were deposited with ALD and evaluated as anodes.

Although Li-alloying of SnO₂ delivers a huge capacity, undesirable island formation occurs. During lithiation of the intermixed Fe₂O₃-SnO₂, the conversion of Fe₂O₃ still occurs, yet the conversion and subsequent Li-alloying of SnO₂ is no longer present. Instead, another reaction occurs around 0.9V vs Li⁺/Li which has no analogon in either pure SnO₂ or Fe₂O₃. Therefore it is hypothesized that it is a reaction of Li⁺ with the Fe_xSn_yO_z ternary oxide. Although the mix of these oxides shows no alloying of Sn, it ensures a better cycle life of the material, as the island formation caused by the alloying is avoided. This can be seen from the cyclability test, as the capacity of the mixed material is more stable than the SnO₂. From a kinetics point of view, the fully intermixed material compares well to the Fe₂O₃, especially at high currents.

For the nanolaminate we can also discern abovementioned reactions, as the interfaces between the oxides give rise to the peaks associated with those for the mixed material. Those corresponding with the conversion and subsequent alloying of SnO₂ are also clearly present. This entails that, although the nanolaminate provides a large capacity, the alloying of Sn still occurs and causes great stress and loss of contact, as can be seen from the SEM image after cycling the nanolaminate for a mere 50 cycles. This results in discrete capacity losses during cycling.

We used ALD to prove that in order to maximize the synergistic effect for Fe₂O₃/SnO₂, an atomically intermixed material is preferred over a nanolaminated system with interfaces between the oxides.

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