Thin Films
Room: Makai - Session TF-WeM

Thin Film Synthesis and Characterization II
Moderator: Naho Itagaki, Kyushu University, Japan

8:00am **TF-WeM1 Novel Methods for Fitting the Fe 2p and Sn 3d XPS Data from Metallic and Oxidized Surfaces**, *M. Bravo-Sanchez,* CINVESTAV-Unidad Queretaro, Mexico, ***Jorge A. Huerta-Ruelas***, CICATA-Queretaro, Mexico

Fe and Sn oxides are present in many products and industrial processes. Surface analysis with techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in understanding their properties. Most of the core level spectra from metallic and oxidized Fe and Sn surfaces show very large background signals, highly asymmetrical line-shapes, and a series of shake-up satellites that overlaps with the higher binding-energy branch of the peak doublets. For these reason, a proper fit of these spectra has been elusive. This has prevented the quantification, through the analysis of XPS data, of the composition of oxidized surfaces and of the thickness of thin oxide layers. In this work we jointly employed the SVSC background [1] and the double Lorentzian line-shape [2] to closely model the Fe 2p and Sn 3d spectra. With this approach it was possible to resolve previously unreported shake-up satellites and to quantify the thickness and composition of thin oxide films. The validity of the method is strongly suggested from the reproduction of the thickness assessed with transmission electron microscopy. The expected compositions are also reproduced. Examples of oxide films ranging from 2 to 5 nm will be discussed in full. [1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. Journal of Electron Spectroscopy and Related Phenomena (in press) DOI 10.1002/sia.5453. [2] A. Herrera-Gomez. “A double Lorentzian shape for asymmetric photoelectron peaks.” Internal Report. Cinvestav-Querétaro.(2011).
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8:20am **TF-WeM2 Microstructure Control in Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-sputtering using Selective Metal-Ion Irradiation**, *Greczynski, Lu, Jensen,* Linköping University, Sweden, ***Ivan Petrov***, *J. Greene,* Linköping University, Sweden, University of Illinois at Urbana-Champaign, *Kölker, Bolz, Schiffers, Lemmer,* CemeCon AG, Germany, *L. Hultman*, Linköping University, Sweden **INVITED**

It was realized early on in the HIPIMS literature[1] that there exist a time separation between the Ar and metal-ion dominated fluxes at the substrate which opens the possibility for selection one of the components for ion-assisted by using a pulsed bias voltage with suitable synchronization. Here, we explore systematically this avenue by using pseudobinary TiN-based model systems TiMeN (i.e. TiAlN, TiSiN, and TiTaN) to carry out experiments in a hybrid configuration with one target powered by HIPIMS, the other operated in DCMS[2,3] mode and probe the effects of (i) metal versus rare-gas ion irradiation as well as (ii) the type of metal ion used (Ti vs Me). We employ a metastable NaCl-structure $Ti_{0.39}Al_{0.61}N$ as a model system to demonstrate that switching from Ar^+- to Al^+-dominated bombardment eliminates phase separation, minimizes renucleation during growth, reduces the high concentration of residual point defects, and thus results in dense, single-phase, stress-free films.[4] For metastable alloys, TiAlN and TiSiN, mechanical properties are shown to be determined by the average metal-ion momentum transfer per deposited atom $\langle p_d \rangle$.[5] Irradiation with lighter metal-ion ($M_e = Al^+$ or Si^+ during Me-HIPIMS/Ti-DCMS) procures fully-dense single-phase cubic $Ti_{1-x}(Me)_xN$ films. In contrast, with higher-mass film constituents such as Ti, $\langle p_d \rangle$. Easily exceeds the threshold necessary for phase segregation which results in precipitation of second w-AlN or Si_3N_4 phases. With the TiTaN system we show that synchronized pulsed ion bombardment in the hybrid system with the heavy-metal ions (Ta) permits to grow dense, hard, smooth, and stress-free thin films at lowered substrate temperature, with no external heating.[6] Overall, we demonstrate that using synchronous bias to select the metal-rich portion of the ion flux opens new dimension for ion-assisted growth in which momentum can be tuned by selection of the metal ion in the hybrid/cosputtering configuration and stresses can be eliminated/reduced since the metal ion is a component of the film.

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9:00am **TF-WeM4 Mechanical and Electrical Properties of ZrB_2 Thin Films**, ***Lina Tengdelius***, Department of Physics, Chemistry, and Biology (IFM), Linköping University, Sweden, *E. Broitman, F. Eriksson,* Department of Physics, Chemistry, and Biology (IFM), Linköping University, *M. Samuelsson,* Impact Coatings AB, Linköping, *J. Lu, J. Birch,* Department of Physics, Chemistry, and Biology (IFM), Linköping University, *T. Nyberg,* Department of Solid State Electronics, Uppsala University, *H. Högberg*, Department of Physics, Chemistry, and Biology (IFM), Linköping University

Zirconium diboride (ZrB_2) exhibits a number of favorable properties including high melting point, high hardness, and low resistivity [1,2]. In addition, the compound is chemically inert and shows good wear and corrosion resistance, even at elevated temperatures. These properties make ZrB_2 thin films interesting for applications in demanding environments.

In order to enable reliable evaluation of the mechanical and electrical properties of this material, the films should exhibit well defined properties, including being stoichiometric, show high crystalline ordering, and being free of contaminants. Moreover, the substrate material must be appropriately chosen for the measurements of the functional properties.

The aim of the current study is to investigate and determine the electrical and mechanical properties of ZrB_2 thin films. In order to do so, well defined ZrB_2 thin films, were deposited using direct current magnetron sputtering (DCMS) from a compound source, on Al_2O_3(0001) substrates enabling evaluation of said properties.

It was found that epitaxial growth of ZrB_2 films, up to a thickness of 1.2 μm, is possible by DCMS of a ZrB_2 compound target on Al_2O_3(0001) substrates, and at a temperature of 900 $^\circ$C. The obtained ZrB_2 thin films were characterized with regards to mechanical and electrical properties, and the results showed that the films exhibited resistivity values of ~125-200 μΩ cm, and notably high hardness values of up to 50 Gpa, as well as high elastic recovery.

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9:20am **TF-WeM5 Effect of Vacuum Annealing on the Thin Films Of Copper Oxide prepared by Reactive DC Magnetron Sputtering**, ***Dhanya S. Murali***, *M.K. Jain, A. Subrahmanyam*, Indian Institute of Technology Madras, India

Cu_2O is an interesting p-type semiconductor; it has high optical absorption coefficient in the visible region and reasonably good electrical properties. It finds application in p-n junction based devices such as solar cells and high mobility p-type thin film transistors [1,4]. Among p-type oxides, cuprous oxide (Cu_2O) in single crystal form[1] is known to have the highest hole mobility ~100 cm^2 V^{-1}s^{-1} at room temperature (300 K). Lee *et.al.*[3] reported a Hall mobility of 62 cm^2 V^{-1}s^{-1} for Cu_2O thin films at room temperature. Sohn *et. al*. performed vacuum annealing of copper oxide (CuO) thin films on Si substrate in order to obtain Cu_2O thin film which possesses Hall mobility of 47.5 cm^2 V^{-1}s^{-1} and good optical properties[4].

In the present communication, we report the effect of vacuum annealing (at 623K and 700 K) on polycrystalline copper oxide thin films deposited (at room temperature 300 K) on a borosilicate glass substrate employing reactive DC magnetron sputtering. Argon and oxygen are the sputter and reactive gases respectively. Pure (99.9%) copper is the target. Deposition pressure is 3.5x10^{-3} mbar and the target power density is 1.4 Wcm^{-2}. The films were characterized by X-ray diffraction, Hall effect (with temperature variation in the range 20 K to 300 K) and Raman spectroscopy (excitation wavelength 532 nm and in the temperature range 77 K to 700 K). Optical band gap is evaluated using UV-Vis spectrometer (400 – 1100 nm). The “as prepared" films show CuO phase. At an annealing temperature of 623K (in vacuum at $5x10^{-6}$ mbar), transition to a mixed phase of CuO and Cu_2O is observed. Further annealing at 700 K, CuO transforms completely to a cubic Cu_2O phase. Sohn *et.al.*[4] reported similar transition at 773 K (CuO prepared on Si substrate by RF sputtering**)**. The optical direct band gap is observed at 2.06-2.51 eV. The reduction of phase CuO to Cu_2O is observed to enhance the optical transmittance in the visible region[4]. The Hall mobility measurements showed that the vacuum annealed Cu_2O thin films have high Hall mobility ($51cm^2 V^{-1}s^{-1}$) at 300 K room temperature**.** High temperature (300 K to 700 K) Raman studies were carried out to confirm the phase by keeping the CuO sample on a hot stage in argon atmosphere, the phase change is observed at 723 K.

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9:40am **TF-WeM6 A Study to Reduce Deviations of Sensitivities to Constant CO Gas of Pt Doped SnO_2 Thin Film Based Micro Gas Sensor***, **Jun-gu Kang**,* Sungkyunkwan University, Korea, Republic of Korea*, J.-S. Park,* Korea Electronics Technology Institute (KETI), Republic of Korea*, H. Lee*, Sungkyunkwan University, Korea, Republic of Korea

Gas sensors based on metal oxide semiconductors have been used for detecting low level toxic and explosive gas for a long time, since metal oxide semiconductors enable to make gas sensors operate at low power consumption as well as supply with low price. Recently, researchers have studied nanostructured metal oxide semiconductors to improve sensitivity by enlarging the surface area that react gas directly. However, such gas sensors based on nanomaterials suffer from a large deviation of sensitivities among gas sensors. In the present work, we employed a SnO_2 thin film, with a well-defined surface area and thus a small deviation in sensitivity, and, in addition, doped it with a noble metal to improve stability. For the fabrication of the micro platform, which consists of a micro heater and sensing electrode on SiN_x membrane, we started with a Si substrate(100) by deposition of a low stress 2㎛-thick SiN_x film using a low pressure chemical vapor deposition process. After deposition of a tantalum layer, serving as an adhesion layer, a Pt film was deposited as a heating element. The heater layer of Pt on Ta was patterned and etched using a dry etching process with an advanced oxide-etching equipment. An 1㎛-thick insulating layer was produced on the patterned heater layer. A sensing electrode layer of Pt was sputtered and then patterned using a dry etching process. A SnO_2 thin film, as sensing material, was deposited with RF sputtering on the sensing electrode of a micro platform. And then, Pt doping was done by Pt thin film sputtering, and heat treatment to form Pt islands on SnO_2 thin film. After finishing the front side process of the wafer, we patterned the back-side of the wafer and etched it in a KOH solution to release the SiNx film as a membrane. In this presentation, sensing properties of fabricated gas sensors to indoor pollutant gases such as CO, HCHO and toluene will be presented. We will also show the possibility to reduce deviations of sensitivities to the constant CO gas concentration among thin film based micro gas sensors.

[Acknowledgement] This work was supported by the "Project (10043800) of the Technology Development Program of S/W Convergence Component" by MOTIE and KEIT in Korea. The authors appreciate government for research funding.

10:20am **TF-WeM8 Barium Oxide Glass Targets for Thin Film Dielectric Material***, C. Stutz,* Air Force Research Laboratory*, G. Kozlowski,* University of Dayton Research Insitute*, S. Smith,* University of Dayton Research Institute*, J. Goldstein,* Air Force Research Laboratory*, G. Landis,* University of Dayton Research Insitute*, C. Hollbrook, **John Jones***, Air Force Research Laboratory

Barium-rich, alkali free glasses are expected to be useful for high voltage capacitors due to the high energy storage capacity of Barium, the high resistivity of alkali-free glasses, and the possibility of forming a smooth, glassy surface to minimize the surface electric field intensity. To better understand the structure-property relationships in these glasses, we have synthesized 17 samples of eight different compositions ranging from 22% to 48% mol percent BaO, with a constant ratio of SiO_2 to B_2O_3. These samples were studied with Raman and showed a narrow intermediate range (29-32% BaO) that was independent of BaO content between the stressed-rigid elastic phase (24-29% BaO) and the flexible elastic phase (32-48% BaO). The samples were fabricated into 2.5 cm diameter targets for a pulsed laser deposition (PLD) thin film process. They were nominally clear and made from a melt that was poured into a mold. However the targets would break up when exposed to the 248 nm one joule laser and the deposition onto the substrate was negligible. The targets were also annealed at 50 degrees below the glass transition temperature, but this did not help. A new target process was developed that was more involved and instead of pouring the melt into a form it was poured into de-ionized water to be quenched then ground using a mortar and pestle. After grinding the glass was pressed into a pellet and sintered for densification. The new targets were not transparent. Due to the new process the glass targets were able to withstand the 248 nm one joule laser. Also good coverage of the substrate was obtained during PLD growth. We will discuss the characterization of the thin films based on results from atomic force microscopy, x-ray, and Raman spectra. Also impedance spectroscopy will be presented.

10:40am **TF-WeM9 Near Infrared Photodiodes Comprising Iron Disilicides Prepared by Sputtering***, T. Yoshitake,* Kyushu University, Japan*, M. Shaban,* Aswan University, Egypt*, N. Promros,* King Mongkut's Institute of Technology Ladkrabang, Thailand*, **Motoki Takahara**, T.M. Miostafa,* Kyushu University, Japan*, R. Baba*, Kysushu University, Japan

Semiconducting iron disilicide (β-$FeSi_2$) is a new candidate applicable to near-infrared photoelectronic devices [1-3], because it possesses features such as a direct optical band gap of 0.85 eV above an indirect gap (0.76 eV) and a large absorption coefficient, which is 10^5 cm^{-1} at 1.0 eV[4]. Since β-$FeSi_2$ can be epitaxially grown on Si, a heterojunction diode comprising a β-$FeSi_2$ film and singlecrystalline Si substrate is a device that can be briefly formed by employing vapor deposition. For near-infrared light detection in the Si/b-$FeSi_2$ heterojunction diodes, near-infrared light transmitted through the front-side Si substrate can be absorbed in the depletion region of the back-side β-$FeSi_2$ film.

In our previous works, we have progresses researches on p-type Si/n-type β-$FeSi_2$ heterojunction diodes, totally from the epitaxially growth of β-$FeSi_2$ film on Si(111) by sputtering [5] to the evaluation of p-type Si/n-type β-$FeSi_2$ heterojunctions as photodetectors [6,7]. It was confirmed that β-$FeSi_2$ in the heterojunction evidently contributes to the photodetection of near-infrared light from the photoresponse spectrum. In addition, the heterojunction clearly exhibited current due to photogenerated carriers for 1.33 μm light in the *I-V* curves in comparison with that in the dark. The detectivity at temperatures lower than 100 K reach approximately 2×10^{11} $cmHz^{1/2}/W$, which is comparable with that of existing near infrared photodiodes comprising PbS and InAs at the same temperature. However, the external quantum efficiency is less than 10 % [6,7].

In this presentation, the progress thus far of our research and recent problems that we are facing and should be solved for the next step will be introduced. A serious problem for the heterojunctions is that a barrier due to a band offset appears in the valence band and it prevents from the flow of photogenerated carriers from the n-type β-$FeSi_2$ layer to the p-type Si layer. The opposite combination, namely n-type Si/p-type b-$FeSi_2$, is structurally ideal because of it has no barriers due to the band offset. In order to form p-type β-$FeSi_2$, the residual carrier density should be reduced for controlling the conduction type. Carbon doping, which might be effective for a reduction in the carrier density, will be introduced.

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11:00am **TF-WeM10 Epitaxial Growth of Ag/MgO(001) and Ag/Si(111) by Pulsed Laser Deposition for Use as an Alternative to Single Crystal Metallic Substrates***, **Jeff Terry**, D. Velazquez*, Illinois Institute of Technology

Single crystal metal substrates are often used as platforms for growth. Epitaxial films are potentially cheaper starting points for chemical synthesis single crystal substrates. We report on the epitaxial growth of thin silver films in the crystallographic orientations (001) and (111) using pulsed laser deposition (PLD). The films were deposited on MgO(001) and Si(111) substrates to a thickness of 40 nm at 150 °C and 170 °C, respectively. For the first 2-4 nm, growth was three-dimensional at which point a gradual transition to two-dimensional growth occurred, as monitored by reflection high-energy electron diffraction (RHEED). Scanning tunneling microscopy (STM) was used to show that the surface roughness was less than 5 Å in 100×100 nm^2 for either orientation. Photoelectron spectroscopy (PES) was used to probe the chemical state of the films. The positions of the Ag $3d_{5/2}$ and Auger MNN peaks were used to calculate the Auger parameter to be 726.3 Ev, which corresponds to metallic Ag. These films may be inexpensive replacements for single crystal Ag substrates in certain applications.

11:20am **TF-WeM11 Enhancement of Uniformity and Whiteness of Electrogalvanized Steel Sheet by Deposition of a Transition Metal Thin-Film between Deposited Zinc and Iron Substrate.**, ***Wonhwi Lee***, POSCO, Republic of Korea

Electrogalvanized steel sheets are widely used in automobiles, building interior decorations and home appliances because of its excellent surface uniformity and formability. Among the wide areas of its applications, barely post-treated electrogalvanized steel sheets used in home appliances are processed no further treatments but to form essential resin coating layers for the functions of anti-fingerprinting or Chromate-free. In this case, it is a key quality to have uniformity and good whiteness of its surface.

However, the electrogalvanized zinc layer with partially oriented and enlarged grains is normally produced due to the epitaxial growth along the iron substrate. The oriented zinc grains on the surface lead to the dispersion of reflecting light that results in lowering whiteness.

In addition, iron oxide scales or oil stains remained on the substrate even after the all pre-treatments of rinsing, degreasing and pickling processes may induce poor uniformity of the galvanized surface.

To solve these problems which are derived from the iron substrate, some manufacturers have created a nickel nano-layer on a substrate. The deposition of the nickel layer on a substrate has brought a galvanized surface not only the uniformity but also the better whiteness. This is because the nickel layer significantly enhances the quality of deposited zinc since the condition of substrate is no longer transferable. Recently, however, its high cost as a raw material and harmful fumes during welding processes have arisen as critical problems to solve.

In this article, we suggest to deposite a thin film of a single or as an alloy of transition metals between the deposited zinc and the iron substrate. The thin layers were made by electrodeposition method and several transition metals were selected for the coating materials. These coating materials were electrodeposited with the coating weights in the range of 10 to 50mg/m^2. The results show that the better whiteness and uniformity of the galvanized zinc can be achieved by the thin layer which minimizes the influences from the substrate and interrupts coarsening of zinc grains as well. Furthermore, it is a remarkable finding that the zinc grains are randomly oriented on the surface with much smaller sizes.

11:40am **TF-WeM12 Effect of Organic Substrate Materials on Electrical and Mechanical Properties of Cr Thin Film Prepared by DC Magnetron Sputtering**, *H. Park, D. Kim, I. Park, K. Bae,* Pusan National University, ***Young-Rae Cho***, Pusan National University, Republic of Korea

Sputtering is one of the most popular physical vapor deposition methods due to their versatility and reproducibility. Effect of organic substrate materials on electrical and mechanical properties of chrome (Cr) thin films was investigated. For the application of wearable or flexible electronic devices, the materials for substrate were selected from flexible organic materials such as leather, cloth (melton), paper and plant. The Cr films were deposited on the several different substrates by DC magnetron sputtering. The thickness of Cr films was varied from several tens to 500 nm. For the explanation of the electrical and mechanical properties, a sheet resistance and fatigue properties in cyclic stress of the samples were characterized. When we deposited Cr film over 400 nm in thickness, the sheet resistance of Cr film on smooth substrates (leather, A4 paper, melton) showed small values. However, the sheet resistance of Cr film on rough substrates (toilet paper, wool) showed very large values. Furthermore, we will try to prepare more wide range of organic substrates such as rubber and plant. Finally, the relationships between their physical properties of samples and the change of substrate shape will be discussed in detail.

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