Functional Thin Films and Surfaces
Room Palm 5-6 - Session MB2-1-MoM

Thin Films for Electronic Devices I

Moderators: Jiri Houska, University of West Bohemia, Czechia, **Spyros Kassavetis**, Aristotle University of Thessaloniki, Greece

10:00am **MB2-1-MoM-1 Microstructure – Properties Relationship in New Zn-Iv-N2 Thin Films for Photovoltaics Applications***, **Jean-Francois Pierson [jean-francois.pierson@univ-lorraine.fr]**,* IJL / CNRS / Univ. Lorraine, France **INVITED**

Zn-IV-N_2 (IV = Sn or Ge) semiconductors are promising optoelectronic materials and good candidates for thin film photovoltaic absorbers. Due to their tunable band gap (1.4-3.2 eV) and the choice of earth-abundant and non-toxic elements, they may replace $In_xGa_{1-x}N$ alloys materials commonly used for optoelectronics devices. Recently, few works investigate the disorder caused by unintentional oxygen incorporation, and the grains boundaries oxygen contamination in $ZnSnN_2$ thin films. To reduce oxygen contamination and improve physico-chemical properties, a new approach is investigated by the use of bias during film growth.

This work shows the results of $ZnSnN_2$ thin films grown by reactive co-sputtering using zinc and tin metallic targets in a nitrogen reactive atmosphere. The stoichiometry control of the film composition was managed by optimizing the target currents and the nitrogen partial pressure. The composition was measured by electron probe microanalysis (EPMA) to study the evolution of oxygen content under bias conditions. The application of different bias powers (from 0 to 50 W) modified the morphology and the composition of the films by densifying and decreasing significantly the oxygen contamination from 6.7 to 2.0 at. %. The optical band gap has been deduced from UV-visible spectroscopy and electrical properties was investigated by I-V experiments and Hall effect measurements. Ab initio calculations estimate an optical band gap in the order of 1.37 eV (calculated with a hybrid functional mBJ), the practical use of this system has been limited because of the difficulty to reach expected value. Here, we demonstrate that the optical band gap energy can be decreased (from 1.7 to 1.34 eV) to the range of the predicted one by using bias magnetron sputtering at room temperature. UV-visible spectroscopy highlights the reduction of the absorption by free electrons in the IR range responsible for the Burstein-Moss effect. Using first principle calculations, we explore the electronic structure and optical properties to compare with experimental results and we observe a good agreement. The study of bias effect power from 0 to 50 W underlines that an optimal parameter of 20 W bias is a compromise to gain the best structural, electrical and optical properties. Our results provide an interesting method to obtain a potential candidate for photovoltaic application, in an environmental friendly way, for a low-cost industrialization.

Keywords: photovoltaic, $ZnSnN_2$, bias effect, thin films, magnetron co-sputtering.

10:40am **MB2-1-MoM-3 Enhanced Etching Resistance of Y2O3 Films Through Microstructure Control via Thermal Annealing***, Shiao Wang, Qiuming Fu, Hongyang Zhao,* Wuhan Institute of Technology, China*; **Tomasz Liskiewicz [t.liskiewicz@mmu.ac.uk]**,* Manchester Metropolitan University, UK*; Ben Beake,* Micro Materials Ltd, UK*; Yanwen Zhou,* Wuhan Pudi Vacuum Technology Co., China

Yttrium oxide (Y2O3) is a promising material for etch-resistant coatings in semiconductor manufacturing due to its high hardness, high melting point, and excellent chemical stability. This study investigates the effect of thermal annealing on the microstructure and etching resistance of Y2O3 thin films, aiming to improve their performance without introducing additional phases. Current methods for improving Y2O3 etching resistance involve costly phase introductions, and the effect of annealing temperature on the etching resistance of Y2O3 thin films has been understudied.

Y2O3 films were deposited on P-type Si substrates using RF magnetron sputtering. The films were then annealed in a vacuum at 300°C, 600°C, and 900°C. The crystal structure was characterised using XRD, and surface morphology was observed with FESEM. Etching tests were conducted using inductively coupled plasma with two different environments, chemical etching (CF4 and O2) and mixed etching (CF4, Ar, and O2). The etching rates and surface roughness were determined using a step profiler and AFM respectively. Chemical bond analysis was performed using XPS.

XRD analysis revealed that the Y2O3 films exhibited a polycrystalline cubic structure. The sharpness of the diffraction peaks increased and then decreased with increasing annealing temperature, indicating grain size changes. FESEM images showed that the film annealed at 900°C had a dense, laminated structure with no pores or defects, while films annealed at 600°C and 300°C displayed rod-shaped grain structures with noticeable gaps. The etching rates of Y2O3 films were significantly lower than those of Al2O3, Si, and other materials. The 900°C annealed film exhibited the lowest etch rates. AFM analysis showed the roughness of Y2O3 thin films decreased after both chemical and mix etching. XPS analysis confirmed the formation of Y-F compounds during etching, with deeper F penetration in mix etching due to Ar+ sputtering.

The enhanced etching resistance of the 900°C annealed Y2O3 film is attributed to its high density and low surface roughness. In chemical etching, F radicals react with Y2O3, forming a Y-F protective layer, which reduces further etching. In mix etching, the additional Ar plasma facilitates the detachment of the formed Y-F compounds, increasing the etching rate compared to chemical etching.

This study demonstrates that thermal annealing is a cost-effective method to improve the etching resistance of Y2O3 films. The 900°C annealing resulted in a dense film with superior etching resistance, making it a promising material for protective coatings in semiconductor manufacturing.

11:00am **MB2-1-MoM-4 Effects of Room Temperature Sputtered Nano-Interfaced WxMoyO$_3$ Nanograins on Highly Responsive NO Sensing***, Somdatta Singh,* Indian Institute of Technology Roorkee, India*; Ravikant Adalati,* University of Mons, Belgium, India*; Prachi Gurawal, Raman Devi,* Indian Institute of Technology Roorkee, India*; Gaurav Malik,* Jeonbuk National University, Republic of Korea, India*; Davinder Kaur, **Ramesh Chandra [ramesh.chandra@ic.iitr.ac.in]**,* Indian Institute of Technology Roorkee, India

This work demonstrates a heterostructure of monoclinic molybdenum trioxide (n-MoO_3) and tungsten trioxide (n-WO_3) with nano-interfaced (n-i@WxMoyO3) based NO gas sensing material. The nanocrystalline n-i@$W_xMo_yO_3$ thin film was coated using a single-step magnetron sputtering technique on an n-type (100) silicon substrate. Within the temperature range of approximately ambient temperature (50°C) to 350°C, this sensing material, $W_xMo_yO_3$ (where x = 0.71 and y = 0.29), detects NO gas and investigates the impact of crystal structure and nanointerfaces on sensing performance. A heterostructure composed of several materials can enhance the interaction between the gas molecules and the sensor surface by producing interfaces that promote charge transfer. With a response/recovery time of around 300 seconds/125 seconds at 300°C, the n-i@$W_xMo_yO_3$ has a low limit of detection (DL) of about 39 ppb and an excellent sensor response (SR = R_g/R_a) of about 44.15 for 50 ppm NO gas. Even at 50°C, the enhanced sensitivity of the sensing material with the nanointerface shows a strong affinity for NO molecules. It provides around 1.03 SR with response/recovery times of 53 and 71 seconds, respectively. The robustness of the n-i@$W_xMo_yO_3$ thin film sensor was established by its excellent selectivity (SR = ~44.15) and long-term stability (60 days) towards 50 ppm NO at 300°C. The remarkable sensing properties of MoO_3 functionalized WO_3 nanograins indicate an exciting potential for NO gas sensors that operate close to ambient temperature (50°C).

11:20am **MB2-1-MoM-5 Study on the Effect of Different Oxygen Flow Rates on Vanadium-Doped Zinc Oxide Thin Film Piezoelectric Pressure Sensors***, **Cheng Han Hsu [e204242271@gmail.com]**,* National Cheng Kung University (NCKU), Taiwan

The piezoelectric effect is a phenomenon where certain materials generate an electric charge when subjected to mechanical stress.This property is widely utilized in sensors,and energy-harvesting devices because it converts mechanical energy into electrical energy.ZnO is a promising material for energy-harvesting devices due to its piezoelectric and semiconductor properties,along with good biocompatibility and low environmental impact.However,its relatively low piezoelectric coefficient (12.4 pC/N) limits its potential in these applications.To enhance the piezoelectric coefficient,vanadium was doped into ZnO thin films.Vanadium ions have a higher valence than zinc ions,which improves electric polarization and increases the piezoelectric coefficient.Additionally,V^{5+}ions,having a higher positive charge than V^{3+}ions,create stronger polarity,further boosting the piezoelectric properties.By adjusting the oxygen flow rate during the sputtering process,the V^{5+}content in the films is increased,enhancing the piezoelectric coefficient.In this study,we utilized an RF sputtering system with varying oxygen flow rates to prepare vanadium-doped zinc oxide thin films, which were then used to fabricate piezoelectric pressure sensor devices.The results show that as the oxygen flow rate increases,the grain shape of the thin films changes,and the grain size decreases. SEM reveal significant changes in the grain structure.XRD shows that the intensity of the 002 peak weakens as the oxygen flow rate increases,indicating structural changes in the thin films.XPS reveals that the content of pentavalent vanadium increases with higher oxygen flow rates, but decreases after reaching a critical value,which correlates with the trend observed in piezoelectric coefficient measurements.Further analysis of the O1s XPS shows that the lattice oxygen content in the films is higher than the surface adsorbed oxygen,with the lowest number of oxygen vacancies at a certain oxygen flow rate,which then increases as the oxygen flow rate rises.UV-visible spectra indicate that,due to the Burstein-Moss effect,the energy band structure of the thin films initially decreases and then increases with increasing oxygen flow rates.Finally,piezoelectric pressure sensors were fabricated from these thin films,and the stress sensitivity at different oxygen flow rates was measured.This study provides a comprehensive investigation of the structural,optical,piezoelectric properties of V-doped zinc oxide thin films at varying oxygen flow rates and explores their application as piezoelectric pressure sensors.The findings offer insights for optimizing thin film performancein piezoelectric sensing devices.

Author Index

Bold page numbers indicate presenter