New Horizons in Coatings and Thin Films
Room On Demand - Session FP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-1 Optical, Structural and Morphological Properties of NiO_X Thin Films Obtained by E-Beam*, **Jhonathan Castillo (jhonathan.castillo@uabc.edu.mx)***,* Universidad Autónoma de Baja California, Colombia*; N. Nedev,* Universidad Autónoma de Baja California, Bulgaria*; B. Valdez,* Universidad Autónoma de Baja California, Mexico*; M. Bernechea,* University of Zaragoza, Spain*; M. Mendivil,* Centro de Investigación en Materiales Avanzados (CIMAV, Mexico*; M. Curiel,* Universidad Autónoma de Baja California, Mexico

Non stoichiometric nickel oxide (NiO_x) is a transparent conductive oxide (TCO) that has attracted a lot of attention because of its electrical and optical properties.Most of the available TCOs are n-type semiconductors, while NiO_x is a promising p-type candidate because of its excellent chemical stability and optical transparency. Some potential optoelectronic applications of NiO_x are as a p-type channel in transparent thin film transistors (TFTs) and as a hole transport layer in organic or quantum dot solar cells solar. In this work thin NiO_x films were obtained by thermal oxidation of ~20 nm thick Ni films deposited by electron beam evaporation. The films were deposited on glass substrates with size of 2.5×2.5 cm and n-type <100> silicon wafers. The oxidation process was carried out at 400, 500 and 600°C.

All samples were characterized by transmission electron microscopy, scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy, UV-Vis spectroscopy, X-ray diffraction and diffuse reflectance spectroscopy. Results for the obtained NiO_x films will be presented and a discussion of their possible application in TFTs and in solar cells as hole transport layers will be given.

Keywords: NiO_x, e-beam, thin films

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FP-2 Characterization and Photoluminescence of Al- and Ga-doped V_2O_5 Nanostructures Synthesized by Thermally Activated Process*, **Chih-Chiang Wang (twinbads@yahoo.com.tw)***,* National Chung Hsing University, Taiwan*; C. Lu,* Chinese Culture University, Taiwan*; F. Shieu,* National Chung Hsing University, Taiwan*; H. Shih,* Chinese Culture University, Taiwan

V_2O_5 has an orthorhombic crystal structure, and narrow direct and indirect bandgaps of 2.4 and 2.0 eV. Its optoelectronic properties can be modified by adding various dopants, such as Ga, Al, and Nd, due to the formation of the defect-levels. The applications of V_2O_5 are widely used in gas sensors, catalysts, and electrochromic devices. In this study, Al- and Ga-doped V_2O_5 nanostructures were fabricated by the thermally activated process at 850℃ via the V-S mechanism. The Raman and XRD patterns have showed the typical V_2O_5 orthorhombic crystal structures of Al- and Ga-doped V_2O_5. The variations of c/a and c/b ratios estimated from the XRD patterns confirmed the substitutions of the Al^{3+} and Ga^{3+} into the V^{5+} lattice sites. HRTEM images showed that the growth direction of Al- and Ga-doped V_2O_5 nanostructures were along the [110] direction. The XPS results for the Al-doped V_2O_5, metallic Al was formed inside the nanostructure and the amorphous Al-O and Al-OH phases were generated on the nanostructure surface; for the Ga-doped V_2O_5, Ga-O phase was formed in the V_2O_5 nanostructures. PL spectra showed the increasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 nanostructures while the Ga dopant was in 0.5 wt.%, which can be contributed to the formation of and -defects; the Al dopant showed a decreasing intensities in blue (1.94 eV) and green (1.77 eV) emissions of the V_2O_5 while the adding of Al, which can be attributed to the formation of the metallic Al inside the V_2O_5 nanostructures. This study showed that the photoluminescence properties of V_2O_5 nanostructures can be modified by the dopants of Al and Ga. The Al dopants revealed a significantly suppressing effect while starting the addition of Al, and the Ga showed an enhancing effect while the Ga contents were in 0.5 wt.%.

FP-3 On the Grain Size Dependence on Film Thickness*, **Dulmaa Altangerel (dulmaa.altangerel@ugent.be)***, R. Dedoncker, F. Cougnon, D. Depla,* Ghent University, Belgium

A meta-analysis of published data in combination with measurements on Al, Cu, CuO, CrCoFeMnNi, $Ni_{90}Cr_{10}$, TiN, and V sputter deposited thin films, permits to demonstrate that the grain size-thickness correlation can be described by a power law. The exponent depends on the homologous temperature which is defined as the ratio between the deposition and the melting temperature of the studied material. The exponent is close to 0.4 at a homologous temperature between approximately 0.15 and 0.3. Theoretical film growth models that depict an evolutionary overgrowth mechanism obtain the same exponent. Above a homologous temperature of approximately 0.3, a slightly higher exponent is observed which agrees with the general idea that at higher homologous temperatures the grain size is also influenced by restructuring mechanisms occurring during film growth. The exponent becomes substantially lower at low homologous temperatures (<0.15). From a theoretical point of view its value should be close to zero. The aforementioned boundaries of the homologous temperatures corresponds with those observed in published structure zone models which describe the microstructure of physical vapor deposited thin films. The good agreement suggests that the underlying reason for the observed boundaries is the atom mobility. This hypothesis was further investigated by a study on the influence of intentionally added impurities on the power law behavior for Al and Cu thin films. A decrease of the grain size is observed for both materials when the impurity-to-metal flux ratio is increased. No change of the exponent is observed for Al, while for Cu the exponent becomes equal to zero at sufficiently high impurity-to-metal flux ratios.

FP-4 Structural and Photoluminescence Properties of ZnO Nanorods Grown on Various TCO Seed Layers by Chemical Bath Deposition*, **Tomoaki Terasako (terasako.tomoaki.mz@ehime-u.ac.jp)***, K. Hamamoto,* 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) with a wide band gap (E_g) of ~3.37 eV and a large exciton binding energy of ~60 meV has received much attention because of its wide range of applications. The use of quasi-one-dimensional (1D) nanostructures, such as nanowires, nanorods (NRs) and nanobelts, in ZnO based gas-sensing devices and photodetectors is expected to be effective for achieving higher performance. Among various methods for preparing the 1D-ZnO nanostructures, we have paid our attention to chemical bath deposition (CBD) because this is usually performed at low temperatures (<100 °C), which allows us to use polymers as substrate materials. In this paper, the influences of the difference in seed layer on the structutral and photoluminescence properties will be discussed.

The ZnO NRs layers were grown on ion-plated ZnO:Ga (IP-GZO), SnO_2:F (FTO) and In_2O_3:Sn (ITO) seed layers, by CBD using the mixed aqueous solutions of $Zn(NH_3)_2 \cdot 6H_2O$ (ZnNit) and $C_6H_{12}N_4$ (HMT). Both the concentrations of ZnNit and of HMT were varied in the range of 0.025-0.075 M. Bath temperature was kept at ~86 °C. Growth time was varied in the range from 30 to 180 min.

SEM observations revealed that the vertically aligned NRs were successfully grown on the IP-GZO seed layers. After the growth time of 60 min, their average diameter and length tended to be saturated at 80 and 600 nm, respectively. On the other hand, on the FTO and ITO seed layers, many NRs were inclined with respect to the the seed layer surface. Both the average widths and lengths of the NRs grown on the FTO and ITO seed layers were lager than those on the IP-GZO seed layers and became lager with the growth time.

All the photoluminescence (PL) spectra were composed of a near-band-edge (NBE) emmission at ~380 nm and an orange band (OB) emission at ~600 nm. Regardless of the difference in seed layer, PL intensity ratio of the NBE emission to the OB emissin (I_{NBE}/I_{OB}) became larger with the increase in the average width of the NRs. There is a possibility that the reduction of the band bending formed at the NR surafce contributes to the increse in I_{NBE}/I_{OB} with increasing the average width of the NRs [1,2].

This work was supported by JSPS KAKENHI Grant Number JP17K04989.

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FP-5 Superior Hydrophilicity in a Magnetron Sputtered Fe-Cr-Ni Thin Film With Nano-Pyramid Surface Structure*, **Pak Man Yiu (pmyiu@mail.ntust.edu.tw)***, J. You, S. Wang, J. Chu,* National Taiwan University of Science and Technology, Taiwan

In this study we sputter deposited a Fe-Cr-Ni alloy film using SUS316 stainless steel as the target material. We deposited the film across a range of argon working pressure from 3 mTorr to 12 mTorr, and thickness ranged from ~200 nm to 1200 nm. Water contact angle of each specimen was measured. We found that the film surface showed a gradual transition from hydrophobic to hydrophilic behavior as the working pressure increased. At 12 mTorr / 1200 nm thickness the water contact angle measured was as low as ~20 degrees. We investigated the surface morphology with AFM and SEM, the images revealed that the specimens with high hydrophilicity possess a nano-pyramid structure, consisted of fibrous grains with a pyramid-like tip.

FP-6 Synergistic Effect of Ultra-thin Ag Film Coupled ITO Sandwich Structures*, Ying-Jie Gao (www25635179@gmail.com), H. Song, W. Wu,*
Da-Yeh University, Taiwan

With the fast developments in modern optoelectronic devices including organic light emitting diodes (OLEDs), light-emitting diodes (LEDs), solar cells, and touch screens, the demand of flexible transparent conductive oxide (TCO) is increased. Tin-doped indium oxide (ITO) is most widely adopted because of its high optical transparency and electrical conductivity. For TCO on flexible electronic device, manufacturing challenges such as processing temperature, annealing temperature, total film thickness, and film stress become crucial.

High-power impulse magnetron sputtering, (HiPIMS) technology exhibits a high plasma density and target ionization rate through a duty cycle of less than 5 % and high peak power. Compared with traditional magnetron sputtering technology, the HiPIMS-deposited film has a higher density, adhesion, flatness, and processing temperature below 100 °C. HiPIMS has several advantages for the deposition of TCO structures on polyethylene terephthalate, (PET) and polyethylene naphthalate, (PEN) substrates because of the low heat resistance of the flexible substrate. Due to ITO alone can not fully meet the demand for flexible electronic devices, various materials or structure design have been developed. Among them, the sheet resistance was effectively reduced by stacking the oxide and ultrathin metal film to form a sandwich structure of oxide/metal/oxide (OMO). The ultrathin metal film provides a continuous electronic conduction and the upper and lower oxide layer provide anti-reflection effect and increases transmittance.

In this study, sandwich ITO/Ag/ITO structure have been prepared onto 1.2 mm thick soda lime glass, (SLG) substrates, flexible polymer substrates including PET and PEN using HiPIMS technology after investigating the single layer of Ag and ITO. Through the optical simulation and the thickness optimization, the synergistic effect of ultra-thin Ag film Coupled ITO sandwich structures was studied. The flexible sandwich ITO/Ag/ITO structure in our study gives a sheet resistance of less than 10 Ω/sq, a resistivity of less than 10^{-5} Ω·cm, and an average visible light transmittance of more than 80 %.

Keyword：ITO、HiPIMS、TCO、OMO

FP-7 Development of Hydrogen Barrier Coatings based on Tungsten-doped Alloys*, Issam Lakdhar (issam.lakdhar@utt.fr), A. Alhussein,*
Université de Technologie de Troyes (UTT), France*; J. Creus,* LASIE, CNRS-Université de La Rochelle, France

Hydrogen energy, classified as one of the cleanest energy sources, developed in the industrial countries around the world presents a substitution for oil and other fuels [1]. However, the transport and the storage of the smallest chemical element at ambient conditions still a crucial issue because hydrogen can dissolve then permeate in any metallic material and cause its embrittlement and failure (pipelines, tanks).

The coating barriers are an effective and practical option to reduce hydrogen permeation. In general, two crucial parameters govern the process of hydrogen permeability: the diffusion coefficient and solubility. Some bulk materials have a low hydrogen permeability in particular W, Mo, Ti, Ni and ceramics [2].

This work focuses on the development of hydrogen barriers based on tungsten-alloy thin films (ternary alloys Al-Ti-W/Ti-W-N) and alternative multilayers (Al-Ti-W/Ti-N-W) elaborated with physical vapor deposition technology in presence of plasma environment. According to some specifications, protective coatings must be dense and without defects. The optimization of elaboration parameters was necessary to obtain good films. Many characterizations were carried out (SEM, XRD, Scratch and Nano-indentation…). The coating efficiency was evaluated under hydrogen by chemical and electrochemical charging and the hydrogen quantity absorbed was determined with analytical and experimental methods (Thermal-Desorption Spectroscopy (TDS).

The mechanical characterizations (tensile and fatigue tests) are performed to evaluated the real behavior of a coated structure under hydrogen[3]. The coating performance as a barrier will be compared with other films reported in the literature and should allow us to continue our development for advanced coatings to increase the life duration of structures under hydrogen.

Keywords: Thin films, Barrier coatings, Hydrogen industry, PVD plasma technology, Electrochemical and mechanical properties.

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FP-8 Structure and Mechanical Properties of ZrB_{2+x} and $ZrAlB_{2+x}$ Hard Coatings*, Tomáš Fiantok (tomasfiantok1@gmail.com), T. Roch, M. Truchlý,*
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Transition metal diborides (TMB_2) of the IVB to VIB group are in the form of films, attractive for use in the mechanical engineering industry due to their high temperature stability, excellent mechanical properties, in particular high hardness, and wear resistance. Here, we present two approaches to influencing stoichiometry, structure and mechanical properties of the perspective ZrB_{2+x}. In the first approach, we focus our efforts on investigating the effect of the amount of Ar particles and their energy on the sputtering of a stoichiometric ZrB_2 target resulting in a change in the character of the growing films. Using High Target Utilization Sputtering (HiTUS), where it is possible to influence the energy of target bombarding Ar particles (target voltage) at their constant amount (constant target current), we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 2.4 ÷ 3.2). The highest hardness of 44.6 ± 2.0 GPa and the lowest hardness of 35.9 ± 1.0 GPa were achieved for $ZrB_{2.39}$ and $ZrB_{3.2}$, respectively. The films have a brittle character, expressed by the high Young's modulus, with the highest value of 446.0 ± 11.6 GPa for $ZrB_{2.39}$.

In the second approach we focused on investigating thermally-induced changes in the structure and mechanical properties of ZrB_{2+x} films alloyed with aluminium. The ternary system Zr-Al-B_{2+x} was prepared by magnetron sputtering of sintered $ZrAlB_2$ target with aluminium content 10 at.%. The idea is based on the theoretical prediction of B. Alling et al. [1] who, based on the different bulk moduli and volume misfits of the binary constituents ZrB_2 and AlB_2, predict that Zr-Al-B_2 is a metastable system with a tendency to spinodal decomposition during annealing. This phase separation can be accompanied by age hardening, similar to the known Ti-Al-N system. Here, we have grown Zr-Al-B_{2+x} films containing approximately 5 at.% Al, where the B/Zr ratio is approx. 2.6. The films have a hexagonal highly orientated (0001) structure. The addition of aluminium to the films reduces the hardness to 28.8 ± 1.0 and the Young's modulus to 335.6 ± 6.4 GPa. Subsequently, the annealed Zr-Al-B_{2+x} films are investigated by wave-dispersive x-ray spectroscopy (WDS), x-ray diffraction (XRD), transmission electron microscopy (TEM) and nanoindentation measurements. The experiments are supported by density functional theory (DFT) calculations.

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FP-10 Fabrication of Nanocomposite Thin Films of Metallic Nano Particles in Amorphous Carbon*, Stephen Muhl (muhl@unam.mx), F. Maya,*
Universidad Nacional Autónoma de México, México*; S. Rodil,* Universidad Nacional Autónoma de México, México*; R. Calderon,* Universidad Nacional Autónoma de México, México*; A. Perez,* Unidad de Investigación y Desarrollo Tecnológico (UIDT-CCADET), Hospital General de México, México

A new planar hollow cathode design based on a combination of a toroidal electrode and the gas flow sputtering source has been developed; the Toroidal Planar Hollow Cathode (TPHC). Here a resonant discharge occurs between the upper and lower electrode surfaces and the only way that electrons can leave the discharge is via the upper or lower aperture in these electrodes. We have used the system to deposit bismuth and aluminium based thin films and nanoparticles as a function of the experimental parameters. The cathode can be operated from 1 few militorr up to >5 torr. The deposition rate is mainly dependent on the plasma power and gas pressure, and to some extent on the gas flow. The size of the nanoparticles mainly depends on the gas pressure and plasma power. Nanocomposite coatings have been made by using the plasma plume at the exit of the TPHC to remotely decompose acetylene or methane and deposit a combination of the nanoparticles and an a-C:H film. We report that the distribution of the nanoparticles is uniform throughout the thickness of the deposit, and the density of nanoparticles in the nanocomposite can be easily controlled.

FP-11 Growth and Characterization of Ga_2O_3/Ag-Cu /Ga_2O_3 Multilayers by High Power Impulse Magnetron Sputtering, ***Shih-Hsin Lin (jimmylin344@gmail.com)***, *W. Wu, D. Wuu, J. Chiang, H. Sung,* Da-Yeh University, Taiwan

High-energy ultraviolet radiation (λ <300 nm) is widely used for surface sterilization of surface, static water, and flowing water. In the past, mercury lamps have always been the only choice for ultraviolet radiation sources, but due to the "Minamata Convention on Mercury", it will be restricted internationally in the future. Therefore, ultraviolet radiation emitting device have become the most potential substitute. The UV device must use transparent conductive electrode materials to prevent electrodes from covered light-emitting elements. However, the most commonly used indium tin oxide (ITO) has a very serious absorption problem at UV. Therefore, reducing the Ultraviolet radiation-absorbing transparent conductive oxide (Transparent Conductive Oxide, TCO) is one of the key technologies to effectively improve component efficiency. Gallium oxide (Ga_2O_3) has a very wide band gap (4.87 eV) and has excellent transmittance in the shorter wavelength UVC (100~280 nm). However, the wide band gap also led to electrical performance almost insulating in Ga_2O_3. According to many literature studies, sheet resistance could be effectively reduced by using a multilayer OMO (Oxide/Metal/Oxide) stacking method. Moreover, an ultrathin metal film has a certain degree of transmittance in UV and visible spectrum. Therefore, developing Ga_2O_3/Metal/ Ga_2O_3 nano-multilayer film structure as the TCO electrode for the UVC element is necessary.

In this work, the use of HiPIMS co-sputter deposition of Ag-Cu alloy structure reduce the island growth of pure metal thin films and further improve the performance of OMO multilayer film. The dense and continuous ultra-thin metal film improves the optical and electrical properties of the overall structure of the OMO. By fixing the power of Ag and adjusting the current of Cu, various composition of Ag-Cu film was deposit for investigating the influence of the concentration of Cu on the sheet resistance and optical transmittance continuity of the ulta-thin metal film.

Author Index

Bold page numbers indicate presenter