Functional Thin Films and Surfaces
Room Pacific F-G - Session C1-1-WeM

Optical Materials and Thin Films I

Moderators: Dr. Silvia Schwyn-Theony, Evatec AG, Switzerland, **Dr. Juan Antonio Zapien**, City University of Hong Kong

8:40am **C1-1-WeM-3 High-Rate Deposition of Calcium Fluoride Coatings Using Radio-Frequency Magnetron Sputtering**, ***Sharon Waichman**, I. Zukerman, M. Buzaglo, S. Barzilai,* NRCN, Israel

Calcium fluoride (CaF_2) is a ceramic material that exhibits versatile properties such as broadband transparency, lubrication behavior at high temperatures (up to 900 °C), high mechanical stability, and hydrophobicity. CaF_2 can be utilized as an antireflective (AR) coating for different optical needs and applications. Due to its enhanced transmission, mainly in the UV and IR regime, a broader transmission range can be achieved, greater than the common oxide-based coatings (SiO_2, TiO_2, or their combination). Moreover, CaF_2 as a constituent in composite-based coatings can effectively reduce wear and friction in mechanical devices and working tools that are subjected to heavy loads and high temperatures. One of the challenges in CaF_2 sputtering concerns with the low stability of the target under high sputtering power (above ~ 2 W/cm^2). Therefore, CaF_2 deposition is usually characterized by low deposition rates. In the current research, CaF_2 coatings were deposited on silicon (Si) substrates by means of a radio frequency (RF, 13.56 MHz) magnetron sputtering technique in an argon atmosphere, and fixed power of 4.4 W/cm^2, whereas the substrate bias voltage (V_b) was varied from 0 to - 150 V. The role of V_b is to enhance the adatoms' mobility and to increase their probability of residing in permanent binding sites. This lowers the roughness and increases the layer density. The coatings were characterized using SEM/EDS, XRD, and XPS. A spectrophotometer was utilized to study the optical properties of the deposited films. The residual stress was studied using the Stoney formula, while the adhesion was studied by a scotch-tape method. In this research, we report a high deposition rate of 8-25 nm/min, depending on the V_b value, with a maximum deposition rate at the low voltages applied, 0 and -30 V, as expected. To the best of our knowledge, this high deposition rate of CaF_2 coatings, using RF magnetron sputtering technique, is reported for the first time. The morphology of the surface was changed with increasing V_b, from a rough surface obtained at the low V_b regime to smoother at - 50 to - 75 V, which finally became rougher again at high V_b of - 150 V, because of pits and holes that were generated by the excessive ion bombardment. Moreover, at - 150 V, coatings were delaminated from the Si substrate immediately after deposition. Due to preferential sputtering of the light fluorine, the composition of the CaF_2 coatings turned fluorine deficient with increasing V_b.

9:00am **C1-1-WeM-4 Reactive Sputter Deposition of Nanoporous Black Zinc and White Zinc Oxide Coatings**, ***Jakub Zawadzki,*** Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Faculty of Materials Science and Engineering - Warsaw University of Technology, Poland*; M. Borysiewicz,* Łukasiewicz Research Network - Institute of Microelectronics and Photonics, Poland

A group of metallic materials characterized by low reflectivity is known as black metals. The transition of the metal from being highly reflective to nearly black can be achieved by its preparation in a way providing a highly porous structure . This phenomenon has been widely applied to the synthesis of macroscopic black metal materials based on Ag [1], Au [2], Al [3], Cr [4], Ni [5], Mo [6], P [7], Zn [8] etc. The dominant applications of black metals are in solar cell collectors [9], optical sensing10, electrochemical sensing11 and decorative coatings12. On the other hand, white coatings can find applications where a high degree of specular light reflection is required – e.g. in cooling coatings [13] or decorative coatings [14]. Depending on the function, several properties must be considered, such as absorbance of electromagnetic radiation in specific wavelengths, thermal emittance, thermal stability and wear resistance.

Our study presents a way to make thin porous zinc and zinc oxide nanosystems obtained by reactive sputter deposition with additional postdeposition annealing as functional black coatings. We show that a wide array of morphologies from highly porous nanocoral and branched structures to densely-porous ones can be obtained by addition of oxygen to inert working gas [15,16]. The purely Zn films are characterized by a wide degree of black or off-black colours. They can be oxidized at an elevated temperature to form matt white ZnO nanoporous films. We show the strategy to increase the mechanical stability and the optical quality of the films, by applying additional protective overcoats. We show that the doping with Al increases the thermal stability of the Zn films for harsh applications. We investigate creating patterns in the black and white films. The influence of morphology, crystal structure and chemical composition on the optical and mechanical properties of the films is discussed.

The comprehensive approach allowed us to achieve highly functional black and white coatings based on zinc with the use of a solvent-free deposition technique widely spread in large-scale thin film industries.

References:

[1] 10.1143/JJAP.39.551

[2] 10.3762/bjnano.8.46

[3] 10.1039/D0RA00866D

[4] 10.1016/j.proeng.2013.09.123

[5] 10.3103/S1068375515040055

[6] 10.1016/0927-0248(95)00021-6

[7] 10.1016/S1003-6326(06)60099-X

[8] 10.1016/0040-6090(84)90387-0

[9] 10.1016/j.solener.2022.01.042

[10] 10.3847/1538-4365/ab7af8

[11] 10.1016/j.bios.2013.12.002

[12] 10.1016/j.solmat.2010.05.019

[13] 10.1038/s41467-022-32409-7

[14] 10.1016/S0257-8972(99)00076-6

[15] 10.1002/pssa.201228041

[16] 10.1016/j.apsusc.2016.07.098

9:20am **C1-1-WeM-5 High Hall Mobility W-Doped In_2O_3 Conductive Films with Thicknesses of Less Than 10 Nm Deposited on Glass Substrates**, ***Tetsuya Yamamoto**, R. Palani, H. Makino,* Kochi University of Technology, Japan

We have achieved polycrystalline W-doped In_2O_3 (*p*-IWO) films with thicknesses ≤ 10 nm showing high Hall mobility ≥ 50 cm^2/(Vs). Amorphous IWO (*a*-IWO) films with thicknesses in the range from 5 to 50 nm were deposited on glass substrates without intentionally heating of the substrates by reactive plasma deposition with dc arc discharge (RPD). Then, the *a*-IWO were subjected to under-vacuum solid phase crystallization in the RPD chamber at a pressure of 5×10^{-4} Pa without any additional gas for 30 min at 250 °C, to realize *p*-IWO films. Structural, electrical, and optical properties are characterized by X-ray diffraction and reflectivity (Rigaku SmartLab), Hall-effect combined with the van der Pauw geometry (Nanometrics HL5500PC), and spectrometer measurements (Hitachi U-4100), respectively. For obtaining high Hall mobility *p*-IWO films, flat surfaces of the IWO films and reduced roughness of film/substrate interface are essential. Resolutions to the above issue are follows: (1) control of the energy of flying particles such as positively charged indium (In^+) ions of less than 25 eV; (2) to prevent the generation of low-melting-point In metals at the early growth stage of the films, optimization of the flow rates of oxygen (O_2) gasses introduced into the deposition chamber during the film growth. In this talk, we discuss thickness-dependent electrical and optical properties and elucidate the cause of the high carrier transport, on the basis of the analysis of the data obtained by high resolution Rutherford back scattering and hydrogen (H) forward-scattering spectroscopy measurements and combined with classical size effect theoretical models.

9:40am **C1-1-WeM-6 The Effects of Growth and Post-Annealing Temperatures on MoS_2 Thin Films Deposited by Magnetron Sputtering**, *C. Chao,* National Dong Hwa University, Taiwan*; P. Tsai,* National Chung-Shan Institute of Science & Technology, Taiwan*; P. Wu,* Stone & Resource Industry R&D Center, Taiwan*; **Ing-Song Yu,*** National Dong Hwa University, Taiwan

Molybdenum disulfide (MoS_2), one of two-dimensional semiconductors, can be applied in various fields such as electronics, optoelectronics, energy storage, catalysis, etc. In our work, large-area and highly-continuous MoS_2 thin film was prepared by magnetron sputtering process at different growth parameters. Then, a post-deposition annealing process was conducted in ultra-high vacuum and in the nitrogen-plasma environments in order to improve the crystallinity and optical properties of the MoS_2 layers. After the deposition and annealing process, MoS_2 thin films were characterized by reflection high-energy electron diffraction, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy. The phase transformation of MoS_2 layers was studied by differential scanning calorimetry. The optical properties of MoS_2 thin films were further investigated by photoreflectance spectroscopy. From the observations, the crystallinity of MoS_2 films can be significantly improved after annealing at 300 °C for 45 minutes in ultra-high vacuum. The increase of the annealing temperature did not further improve the crystallinity, but the surface chemical composition ratio of sulfur and molybdenum decreased at higher temperatures. Moreover, the enhancement for crystallinity of MoS_2 can be also achieved by the deposition temperature of 150 °C.

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