Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B7-TuA

Plasma Diagnostics and Growth Processes

Moderators: Arutiun P. Ehiasarian, Sheffield Hallam University, **Yolanda Aranda Gonzalvo**, Consultant, USA

1:40pm **B7-TuA-1 On the Growth of TiO_x Coatings by Reactive Magnetron Sputtering from Metallic and Ceramic ($TiO_{1.8}$) Targets: A Joint Modelling and Experimental Story**, ***Romain Tonneau***, *P Moskovkin,* University of Namur, Belgium*; W De Bosscher,* Soleras Advanced Energy, Belgium*; A Pflug,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; S Lucas,* University of Namur, Belgium

This work reports the study of the growth mechanisms involved in TiO_x thin film deposition by magnetron sputtering. An Ar-O_2 plasma chemistry obtained by dual magnetron setup operating in DC mode is used. Growth from both metallic and $TiO_{1.8}$ targets are compared. Isotopic $^{18}O_2$ is used as reactive gas for all different configurations. The aim is to differentiate oxygen coming from ceramic targets and oxygen coming from the gas phase. Indeed, using ion beam analysis techniques such as Rutherford Backscattering Spectroscopy it is possible to precisely analyze Ti, ^{16}O and ^{18}O content of the samples. Other investigation techniques such as AFM, SEM … are also used to fully characterize deposited coatings. In order to study the effect of energetic ions bombardment of samples during deposition, 70° and normal incidence samples are compared. In addition to sample's characterization, Langmuir probe and energy flux probe are used to obtain plasma phase properties.

In a second part, simulations tools are used to predict both discharge and coating's properties. In order to simulate the complete plasma process, three different software are used. Each one is handling a defined step of the process (i) neutral particle motion, (ii) charged particle motion and (iii) film growth. We will discuss the comparison between simulation predictions and experimental investigations. Those two approaches allow us to achieve a better understanding on the growth of oxide layers by reactive magnetron sputtering and how plasma parameters influence coating properties.

2:00pm **B7-TuA-2 Titanium Atom and Ion Number Density Evolution in Reactive HiPIMS with Oxygen, Nitrogen and Acetylene Gas***, M Fekete,* Masaryk University, Brno, Czech Republic*; D Lundin,* Université Paris-Sud/CNRS, France*; K Bernatova, P Klein, J Hnilica,* ***Petr Vasina,*** Masaryk University, Brno, Czech Republic

Reactive high power impulse magnetron sputtering (R-HiPIMS) offers a great opportunity for high quality coating production thus understanding the processes accompanying deposition is of great importance. The hysteresis curve in R-HiPIMS generally exhibits a narrower shape compared to dcMS, or it can even be entirely suppressed, which is beneficial for high-rate deposition of stoichiometric compound films. The main reason of the hysteresis suppression is not yet completely understood. A recently developed effective branching fraction method is utilized to determine absolute ground state number densities of sputtered titanium species from the optical-emission signal. We report on evolutions of titanium atom and ion ground state densities in R-HiPIMS discharges in oxygen, nitrogen and acetylene gases for constant mean power and pulse duration, when varying the repetition frequency. A fast feedback system is employed to allow working in the transition region of the hysteresis curve in a well-controlled manner. The ionization fraction of sputtered species increases with the partial pressure of the reactive gas. The increased ionization of titanium is attributed to the combination of the following effects: a longer residual time of sputtered species in the target vicinity; a higher maximal discharge current attained at the end of the pulse; lower amount of sputtered species due to the target poisoning which may positively affect electron distribution function. It is furthermore found that the hysteresis curve shape changes when varying the repetition frequency at the same mean power. The difference is more pronounced for R-HiPIMS with higher sputtered species ionization fraction. The experimental results are compared to the results obtained by a reactive ionization region model (R-IRM). The absolute ground state number densities of Ti atoms and Ti ions measured at the target vicinity are also substituted into the Berg model modified to include ion back attraction, and a rather good match between the measurements and simulation results for different experimental conditions is found.

2:20pm **B7-TuA-3 Phase Formation during Sputtering of Copper in Argon/Oxygen Mixtures***, D Altangerel,* ***Diederik Depla,*** Ghent University, Belgium

Structure zone models give an overview of the microstructure as a function of the deposition conditions. It has been shown by our research team that these overviews can be interpreted in a quantitative way by studying the ratio between the diffusivity (D) and the deposition flux (F)[1-3]. The deposition flux can easily be derived from the deposition rate. To calculate the diffusivity the available energy per deposited atom (EPA) needs to be quantified which becomes possible by measuring the total energy flux with a passive calorimetric probe. In this paper, this approach is applied to understand the phase formation during reactive sputtering of copper in an argon/mixture. The influence of the total pressure, and the discharge current was investigated. Within the experimental range hardly any changes in the EPA could be noticed, illustrating that the phase formation in the case of copper oxide thin films is solely defined by the oxygen partial pressure in the system. In the case of pure tenorite (CuO) thin films deposited at relative high oxygen partial pressures, the EPA could by increased, and it is shown that this leads to less crystalline films. The origin of this behavior is further investigated by energy-resolved mass spectrometry.

[1] Review paper : S. Mahieu, D. Depla, Journal of Physics D: Applied Physics 42 (2009) 053002

[2] Critical review paper : D. Depla, B. Braeckman, Thin Solid Films, (2016) 90-93

[3] J. Xia, W. Liang, Q. Miao, D. Depla, Applied Surface Science 439 (2018) 545–551

2:40pm **B7-TuA-4 Plasma Diagnostics During Growth of Transparent Conductive Oxide Thin Films by Magnetron Sputtering***,* ***Eugen Stamate,*** Technical University of Denmark, Denmark **INVITED**

Transparent and conductive materials are important for a large number of applications including: touch screens, solar cells, smart windows and light emitting diodes. Oxides doped with metals, generically known as transparent conductive oxides (TCO) are successfully used nowadays, with indium tin oxide (ITO) as the best material. However, the high demand for large area applications, conflicts with the reduced abundance of indium. This motivation sustains an intensive research on alternative materials with aluminum doped zinc oxide (AZO) as one of the most promising choices. There are several methods used to deposit AZO. Among them, magnetron plasma sputtering is successfully used for ITO on large area substrates and it is also investigated as a viable cost effective method for AZO. However, the resistivity of AZO thin films is about 5 to 10 time higher than ITO, with promising values only for limited areas on the substrate. One of the main reasons is the electronegativity of oxygen that forms negative ions, resulting in a growth mechanism assisted by energetic ions with a spatial distribution correlated with the erosions tracks. In this context, a proper deposition process requires spatially-resolved plasma diagnostics in direct correlation with spatially-resolved thin film properties. This work reviews the status in plasma diagnostics during TCO growth with special emphasis on AZO. New results by mass spectrometry, optical emission and probes are also presented, both for disk and rotatable cathodes operated in DC, RF and MF using oxide (ZnO/Al_2O_3, 2, 2.5 and 3% Al) and metallic targets (Zn, 2 and 3% Al). Pressure, target to substrate distance and discharge power have been investigated as discharge parameters with the aim of obtaining a resistivity below 10^{-3} W cm over the whole length of the sample (50 mm for disk cathode and 200 mm for rotatable cathode). The resistivity, transmittance and film thickness were measured with a spatial resolution of 2 mm. XPS, XRD, TOF-SIMS and SEM were used for surface characterization. It is shown that the AZO resistivity can change with two orders of magnitude over 10 mm span on the substrate, a behavior that can be correlated with plasma parameters and the growth mechanism.

4:20pm **B7-TuA-9 On Three Different Ways to Quantify the Degree of Ionization in Sputtering Magnetrons***, A Butler,* Université Paris-Sud, Université Paris-Saclay, France*; N Brenning,* Université Paris-Sud, Université Paris-Saclay, Sweden*; M Raadu,* KTH Royal Institute of Technology, Sweden*; J Gudmundsson,* University of Iceland, Iceland*;* ***Tiberiu Minea****, D Lundin,* Université Paris-Sud, Université Paris-Saclay, France

Quantification and control of the fraction of ionization of the sputtered species are crucial in magnetron sputtering, and in particular in high-power impulse magnetron sputtering (HiPIMS), yet proper definitions of the various concepts of ionization are still lacking. In this contribution, we distinguish between three approaches to describe the degree (or fraction) of ionization: the ionized flux fraction F_{flux}, the ionized density fraction $F_{density}$, and the fraction α of the sputtered metal atoms that become ionized in the plasma (sometimes referred to as probability of ionization). By studying a reference HiPIMS discharge with a Ti target, we show how to extract absolute values of these three parameters and how they vary with peak discharge current. Using a simple model, we also identify the physical mechanisms that determine F_{flux}, $F_{density}$, and α, as well as how these three concepts of ionization are related. This analysis finally explains why a high ionization probability does not necessarily lead to an equally high ionized flux fraction or ionized density fraction.

5:00pm **B7-TuA-11 Characterization of Microwave Surfatron Plasma-enhanced-ALD System for Low-temperature Deposition of Thin Oxide Films**, ***Martin Cada,*** *D Tvarog,* Institute of Physics CAS, v. v. i., Czech Republic*; J Kim,* ISAC Research Inc., Republic of Korea*; A Poruba,* SVCS Process Innovation s.r.o., Czech Republic*; Z Hubicka,* Institute of Physics CAS, v. v. i., Czech Republic

The preparation of ultra-thin film is crucial for the development of cutting-edge technologies in the field of microelectronics, optoelectronics, nanotechnology or catalysts. Furthermore, covering 3-D objects in a nanometer scale requires a high degree of uniformity of deposited thin films preserving high aspect ratio of complex shape objects. Atomic layer deposition (ALD) has proven to be almost an indispensable deposition technique for conformal deposition of mostly metal or oxide thin films. Plasma-enhanced ALD (PE-ALD) process brings energy for surface reactions between precursors and reactants through electrons, ions, radicals or excited particles. Many studies have shown that the PE-ALD process is able to operate at significantly lower substrate temperatures. In this work, a microwave surfatron plasma source as alternative to CCP, ICP or other remote plasma sources was used for activation of reactants during the PE-ALD process. We carried out measurements with the Langmuir probe to obtain spatial map of electron temperature, plasma density and potentials in the ALD chamber designed for deposition on wafers with diameter 100 mm during typical deposition conditions of TiO_2, Al_2O_3 and TiN thin films. The plasma parameters were investigated for different working gas pressures and mixtures. Obtained results proved that radial homogeneity of the plasma density could be improved if mass flow rate of working gas is reduced. On the other hand, for higher pressure of the working gas the plasma density rapidly decreased in axial distance from the surfatron nozzle outlet. Results clearly demonstrated that spatial inhomogeneity of the plasma parameters correlates with thin film properties. The possibilities of deployment of the multi-nozzle surfatron system for achieving a sufficient level of homogenization of the plasma parameters was suggested. Effect of substrate temperature and microwave power delivered into the surfatron on deposited thin film properties was studied too. The Raman spectroscopy proved that substrate temperature above 200°C led to anatase phase formation of TiO_2 thin films whilst lower temperatures produced amorphous thin films. Further, gradually increased microwave power resulted in the rise of thin film thickness measured by the spectroscopic ellipsometry for constant number of ALD cycles. Impact of the microwave power on the Growth per Cycle (GPC) parameter was studied by the optical emission spectroscopy detecting evolution of oxygen or nitrogen atoms and radicals.

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