

Wednesday Morning, October 21, 2015

Plasma Science and Technology

Room: 210B - Session PS+2D+SE-WeM

Plasma Diagnostics, Sensors and Control II

Moderator: Colin Wolden, Colorado School of Mines

8:20am **PS+2D+SE-WeM2 Diagnostics for Ionized Physical Vapor Deposition Chambers**, *YuiLun Wu, P. Piotrowicz*, University of Illinois at Urbana-Champaign, *I.A. Shehelkanov*, National Nuclear Research University (MEPhI), *D.N. Ruzic*, University of Illinois at Urbana-Champaign

As the critical dimension of the semiconductor device continues to shrink and aspect ratio continues to rise, more diagnostics are needed to accurately predict the deposition profile of features on the wafer. Traditionally, the incident ion fluxes are considered to be perfectly normal to the wafer plane due to the electric field of the plasma sheath. However from simulation results [1] the ion flux from a magnetron discharge has a narrow angular distribution and this distribution is becoming more significant as the aspect ratio increases. In order to confirm and adjust this predicted distribution a sensor to measure angular distribution of ions in an industrial scale chamber is designed and developed. The sensor is a combined gridded energy analyzer (GEA) and a quartz crystal microbalance (QCM) [2], with a high aspect ratio collimator in place of the normal electron repeller grid for angular measurement distribution measurements. The collimator is made of 3D-printed plastic elements with 600 μ m nominal openings which provides 1 degree angular resolution. This combined QCM and GEA setup is capable to determine fluxes of metal ions, metal atoms and argon ions at 30kW DC magnetron nominal target power. The setup is able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the discharge. A time resolved triple Langmuir probe was also employed to measure the plasma parameters such as electron temperature and density and scanning in a three dimensional map.

References:

1. Stout, P. J., et al. "Comparing ionized physical vapor deposition and high power magnetron copper seed deposition." *Journal of Vacuum Science & Technology B* 20.6 (2002): 2421-2432.
2. Meng, Liang, et al. "Downstream plasma transport and metal ionization in a high-powered pulsed-plasma magnetron." *Journal of Applied Physics* 115.22 (2014): 223301.

8:40am **PS+2D+SE-WeM3 Probing the Plasma Chemistry that Underpins Diamond Chemical Vapour Deposition**, *Michael Ashfold*, University of Bristol, United Kingdom of Great Britain and Northern Ireland, *M.W. Kelly, B.S. Truscott*, University of Bristol, UK, United Kingdom of Great Britain and Northern Ireland, *Y.A. Mankelevich*, Moscow State University, Russia, Russian Federation

INVITED

Most diamond chemical vapour deposition (CVD) employs microwave (MW) activated C/H (typically CH₄/H₂) gas mixtures. Many previous studies have sought to explore (and optimise) radical formation in such activated gas mixture, and the ways in which these radicals add to, and are accommodated on and in, the growing diamond surface.

Our activities in this area employ an interrelated three-pronged approach, *i.e.*

i) electronic spectroscopy methods (cavity ring down absorption and optical emission spectroscopies) to determine the spatial distributions of selected species (*e.g.* H atoms, CH and C₂ radicals) as functions of process variables like the process gas mixing ratio, flow rate and total pressure, and MW power,

ii) complementary 2-dimensional (2-D) modelling of the plasma chemistry and composition with the aim not just of rationalising the spatial resolved column density data obtained in (i), but also enabling prediction of the concentrations of other key gas phase species (*e.g.* CH₃ radicals, which are generally regarded as the dominant growth species) that are not amenable to spectroscopic detection, as functions of process condition, and

iii) quantum mechanical (QM) and QM-molecular mechanics (MM) calculations of the energetics of the elementary steps involved in radical addition to, migration on, and eventual accommodation on, a growing diamond surface.

This invited presentation will summarise the current understanding of diamond CVD from traditional C/H gas mixtures and results of recent studies designed to explore and explain the significant growth rate

enhancements that can be achieved by adding trace amounts of nitrogen to such gas mixtures.

9:20am **PS+2D+SE-WeM5 Ionization Zones and the Deposition of Thin Films in the Transition Region from Non-Reactive to Reactive Magnetron Sputtering including dc, HiPIMS, and Burst-HiPIMS Modes**, *Yuchen Yang, X. Zhou, A. Anders*, Lawrence Berkeley Lab, University of California, Berkeley

Research has been done for copper and chromium targets in conventional non-reactive HiPIMS, revealing the disappearance of localized ionization zones when operating at high power due to high metal neutral supply from the target. However, relatively little research has been done for reactive HiPIMS. In this work we investigate the existence of ionization zones in various forms of reactive magnetron sputtering: direct current (dc) and HiPIMS for conventional pulse patterns and in burst mode. Copper and chromium targets are selected with nitrogen as reactive gas because (i) in the non-reactive regime Cu and Cr can be operated with or without ionization zones, and (ii) these target materials form application-relevant compound films, *e.g.* of interest in wear and corrosion-resistant applications, medical implants, metallization layers, etc.

Work at LBNL is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:00am **PS+2D+SE-WeM10 Modelling of the Reactive High Power Impulse Magnetron Sputtering (HiPIMS) process**, *JonTomas Gudmundsson*, University of Iceland, *D. Lundin*, Université Paris-Sud, France, *N. Brenning*, KTH Royal Institute of Technology, Sweden, *T. Minea*, Université Paris-Sud, France

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of the sputtered material and a high dissociation fraction of the molecular gas. We demonstrate this through an ionization

region model (IRM) [2] of the reactive Ar/O₂ HiPIMS discharge with a titanium target that was developed to study the temporal behavior of the discharge plasma parameters. We explore the influence of oxygen dilution on the discharge properties such as electron density, the ionization fraction of the sputtered vapour, the oxygen dissociation fraction and the onset and role of self sputtering. We discuss the important processes and challenges for more detailed modeling of the reactive HiPIMS discharge. Furthermore, we discuss experimental observations during reactive high power impulse magnetron sputtering (HiPIMS) of Ti target in Ar/N₂ and Ar/O₂ atmosphere. The discharge current waveform is highly dependent on the reactive gas flow rate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the effective secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [3] or oxide [4] forms on the target.

[1] J. T. Gudmundsson, N. Brenning, D. Lundin and U. Helmersson, *J. Vac. Sci. Technol. A*, 30 030801 (2012)

[2] M. A. Raadu, I. Axnäs, J. T. Gudmundsson, C. Huo and N. Brenning, *Plasma Sources Science and Technology*, 20 065007 (2011) 065007

[3] F. Magnus, O. B. Sveinsson, S. Olafsson and J. T. Gudmundsson, *J. Appl. Phys.*, 110 083306 (2011)

[4] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, *J. Vac. Sci. Technol.*, 30 (2012) 050601

11:20am **PS+2D+SE-WeM11 Pulsed Magnetron Sputtering Plasma Optimization for Large Area Growth of Two-dimensional MoS₂**, *Andrey Voevodin*, Air Force Research Laboratory, *C. Muratore*, University of Dayton, *A.R. Waite, J. Bultman, A. Safriet, J. Hu*, Air Force Research Laboratory

Pulsed magnetron sputtering process provides an alternative scalable and reduced temperature growth pathway for the direct synthesis of two-dimensional (2D) materials for electronic device applications [1]. To avoid defect generation by excessive ion bombardment, while maintaining sufficient adatom mobility on the condensation surface at low substrate temperatures, the ion flux and kinetic energy must be modulated. In this study a variable intensity magnetic field was used to control chemistry, energy, and spatial density distribution characteristics of plasma produced by pulsed magnetron sputtering of MoS₂ in 15 mTorr argon. An electromagnetic coil positioned above the substrate generated a 5-15 G magnetic field near substrate surface, causing redirection of magnetron particle flux for tuning of electron and ion densities at the substrate surface. Both plasma emission and mass-spectroscopy analysis showed an abundance of excited and ionized Ar as well as Mo and S species with no

evidence for MoS radicals. Wavelength specific plasma imaging and mass/energy spectroscopy studies demonstrated that the applied magnetic field mostly affects excited and ionized Ar generated in background gas collisions with electrons trapped by the magnetic field lines, while the trajectories of Mo and S species generated from the target surfaces are influenced to a much lesser degree. The imposed magnetic field intensity was adjusted to selectively filter Ar species from reaching the substrate and to find a balance between reducing unnecessary Ar bombardment and preventing shifting energy distributions of all arriving ions above 8 eV, where point defect generation is expected for hexagonal MoS₂. Plasma studies were used to select optimum growth conditions for 2D MoS₂ synthesis on SiO₂ surfaces at 700 °C. Film thickness uniformity was verified by producing 2-3 monolayer layer thick hexagonal polycrystalline MoS₂ films over 25-50 mm scale area sizes as confirmed by in-situ Raman spectroscopy and TEM microscopy.

[1]. C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jespersen, P.J. Shamberger, M. E. McConney, R.D. Naguy, A.A. Voevodin, "Continuous ultra-thin MoS₂ films grown by low-temperature physical vapor deposition", *Applied Physics Letters* 104 (2014) 261604 1-5

11:40am **PS+2D+SE-WeM12 Molybdenum Nitride Formation by N₂ Plasma Exposure on Molybdenum Disulfide: In-situ Surface Study.** *Angelica Azcatl, X. Qin, Q. Wang, N. Lu, M.J. Kim, C.L. Hinkle, R.M. Wallace*, The University of Texas at Dallas

Two-dimensional molybdenum disulfide (MoS₂) is currently considered as a potential channel material for CMOS applications. Electron mobilities on the order of 470 cm²/Vs [1] have been reported for few-layer MoS₂ based FETs. Such promising results have fueled the efforts on synthesis of large area and high quality mono and few-layer MoS₂. Yet, the development of MoS₂ processing techniques of interest for device fabrication (i.e. doping, etching, functionalization) is still in an early stage.

Recently, it has been reported that when MoS₂ is exposed to SF₆, CF₄ or CHF₃ plasma treatments, fluorine can be introduced in the MoS₂ structure as an acceptor dopant, resulting in p-type doping. In parallel, due to the weak van der Waals interlayer forces, layer etching occurred as a side effect after these fluorine-based plasma exposures. [2]

Following the exploration of the effect of plasma exposures on MoS₂, in this study nitrogen plasma exposures on MoS₂ were performed, while the surface chemistry was monitored by in-situ by X-ray Photoelectron Spectroscopy. Theoretical studies have shown that substitution of sulfur with nitrogen in MoS₂ leads to p-type doping. [3,4] Here, the chemical analysis obtained by XPS indicates that nitrogen will covalently interact with molybdenum to generate molybdenum nitride. It was found that the nitrogen content in MoS₂ can be controlled with exposure time. The thermal stability of MoN_x formed due to sulfur replacement with nitrogen will be discussed. Finally, Raman Spectroscopy studies and Scanning Transmission Electrons Microscopy imaging on the MoN_x/MoS₂ structure will be presented to discuss the impact of the Mo-N bonding environment on the MoS₂ structure. This study will give an important insight for the understanding of the interaction of MoS₂ with a non-metal dopant atom, nitrogen, which has implications on the electrical properties of MoS₂.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

References

- [1] W. Bao, et al. *Applied Physics Letters* 102, 042104 (2013).
- [2] M. Chen, et al., *Appl. Phys. Lett.* 103, 142110 (2013).
- [3] H.-P. Komsa, et al., *Phys. Rev. B* 88, 035301 (2013).
- [4] Q. Yue, et al., *Phys. Lett. A* 377, 1362 (2013).

12:00pm **PS+2D+SE-WeM13 Low Temperature Synthesis of AlYB₁₄ by High Power Pulsed Magnetron Sputtering.** *Oliver Hunold, Y.T. Chen, D. Music*, RWTH Aachen University, Germany, *P.O.A. Persson*, Linköping University, Sweden, *J.M. Schneider*, RWTH Aachen University, Germany

The influence of ion bombardment on the structure evolution of AlYB₁₄ was studied by using high power pulsed magnetron sputtering (HPPMS). The structure was analyzed by X-ray and electron diffraction. The diffraction data are consistent with the formation of crystalline AlYB₁₄ domains in an amorphous matrix. As the growth temperature was 675 °C synthesis was conducted at 725 °C below the bulk synthesis temperature. It is reasonable to assume that this decrease in the growth temperature is facilitated by bombardment of ions formed in the HPPMS discharge resulting in enhanced surface diffusion and hence higher adatom mobility. This work may be relevant for synthesizing other boron rich solids with low symmetry

crystal structures at temperatures well below their bulk synthesis temperature.

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