

Plasma Science and Technology  
Room: 102 B - Session PS+TF-MoA

## Plasma Deposition

Moderator: S. Agarwal, Colorado School of Mines

2:00pm **PS+TF-MoA1 Practical Aspects of using Tailored Voltage Waveforms for Thin Film Processing of Photovoltaic Devices**, E.V. Johnson, B. Bruneau, LPICM-CNRS, Ecole Polytechnique, France, P.A. Delattre, T. Lafleur, J.-P. Booth, LPP-CNRS, Ecole Polytechnique, France  
The use of Tailored Voltage Waveforms (TVWs) to manipulate the Electrical Asymmetry Effect in a capacitively coupled plasma-enhanced chemical vapour deposition (CCPECVD) chamber has been shown to be an effective technique for device quality thin-film deposition [1,2], and a useful tool to study the interaction of the bulk and sheath properties of processing plasmas [3] and their impact on growth surfaces [4].

We have used this technique to directly study the influence of mean ion-bombardment energy (IBE) on the growth of hydrogenated microcrystalline silicon ( $\mu\text{-Si:H}$ ) in a CCP chamber, with otherwise unchanged plasma conditions. In this work, we discuss recent results on a specific aspect of  $\mu\text{-Si:H}$  growth for photovoltaic applications, the amorphous to  $\mu\text{c}$  phase transition. The dependence of this transition on many other parameters (power, pressure, dilution) makes the direct observation of the effect of IBE very difficult, as recently demonstrated by the efforts of other authors [5]. We instead use TVWs to vary the IBE, and in-situ ellipsometry to observe the transition in real time for a number of deposition chemistries, such as  $\text{H}_2/\text{SiH}_4$  and  $\text{Ar}/\text{H}_2/\text{SiF}_4$ . Furthermore, in addition to maximizing or minimizing the IBE by changing the waveform shape, the sheath expansion/contraction rates at the powered electrode can equally be controlled. The unexpected impact of these conditions for the  $\mu\text{-Si:H}$  nucleation rate are presented, underlining the importance of "Tailoring" the waveform to the specific plasma processing goal.

Finally, we address an outstanding issue that has challenged the use of TVW's in an industrial setting – the difficulty of matching a TVW source to a CCP chamber. This has previously limited their use to only two harmonics for exciting a large area reactor at high power. We present experimental results for a prototype, high-power multifrequency matchbox that allows the effective coupling of the full output power of the amplifier to the PECVD chamber, enabling high deposition rate  $\mu\text{-Si:H}$ . These increased deposition rates, along with in-situ observation of the film evolution during growth, will be shown.

[1] E.V. Johnson, P.A. Delattre, and J.P. Booth, *Appl. Phys. Lett.* **100** (2012) 133504.

[2] D. Hrunski, *et al*, *Vacuum* **87** (2013) 114.

[3] T. Lafleur, P.A. Delattre, E.V. Johnson, and J.P. Booth. *Appl. Phys. Lett.* **101**, (2012)124104.

[4] E.V. Johnson, S. Poulouen, P.A. Delattre, and J.P. Booth, *J. Non-Cryst. Solids* **358**. (2012), 1974.

[5] A. C. Bronneberg, N. Cankoy, M. C. M. van de Sanden, and M. Creatore, *J. Vac. Sci. Technol.* **A30**, 061512 (2012).

2:20pm **PS+TF-MoA2 Characteristics of Plasma Generated by ICP-CVD with Various  $\text{H}_2/\text{SiH}_4$  Ratios and the Resultant Properties of nc-Si:H Thin Films**, J.H. Hsieh, Y.L. Lie, S.C. Lin, Ming Chi University of Technology, Taiwan, Republic of China

nc-SiH thin films were deposited with an ICP-CVD system attached with four internal antennas, under the variation of  $\text{H}_2/\text{SiH}_4$  ratios (R). During deposition, the generated plasma was characterized using a Langmuir probe and an optical emission spectrometer (OES). The films' properties were characterized using Raman spectrometry and FTIR. The results were correlated with those obtained from probe and OES studies. It was found that the crystallinity of nc-Si:H film was significantly affected by plasma density which was increased with the increase of R, but only to a certain extent. Both the plasma density and Xc reached the maximum at R=10, then leveled off. The deposition rate decreased with the increase of IHa\* which is obtained from the OES results. Also, it was also found that the crystallinity could be proportionally related to the increase of  $I^*(\text{SiH}_2+\text{SiH}_3)/I(\text{SiH}+\text{SiH}_2+\text{SiH}_3)$  in FTIR spectra. This is could be due to that di-/poly- hydride bonding could serve to passivate the grain boundaries of Si nano-crystalline clusters.

2:40pm **PS+TF-MoA3 Medium Range Order (MRO) in "Amorphous (a-Si(H))" Alloys in PV and TFT Devices with Intrinsic, B and P Doped a-Si(H) and a-Si,Ge(H) Layers: Reduction of Photo- and Stress-induced Defects by O-bonding**, G. Lucovsky, D. Zeller, C. Cheng, Y. Zhang, North Carolina State University **INVITED**

Intrinsic photo-absorbing regions, and B and P doped contacts comprised of hydrogenated amorphous silicon,  $\text{a-Si}_{1-x}\text{H}_x$ , with  $\sim 10$  at.% or  $x \sim 0.1 \pm 0.02$ , are used in photovoltaic devices (PV), and thin film transistors (TFT's). A-Si thin films, assumed to be free of H, are used as precursors for polycrystalline gate electrodes in microelectronics. Intrinsic, and p-type and n-type layers in multi-layer stacks that include "a-Si,Ge(H)" have been assumed to be "amorphous continuous random networks (CRN)", with limited short range order (SRO) extending to 1st nearest neighbor (NN) bond lengths, and 2nd N-N bond-angles. A-Si(H) films are not CRNs. They have medium range order (MRO) extending to self-organized and symmetry determined dihedral angles. MRO and formation of non-periodic organized nm-scale ordered regions with crystalline-Si symmetries is responsible for enabling properties in a-Si(H) devices. Intrinsic a-Si(H) thin films have been deposited by glow discharge (GD), remote plasma-enhanced chemical vapor deposition (RPECVD), and reactive magnetron sputtering (RMS). The concentrations of bonded-H are determined by deposition precursors and substrate temperatures. Two conditions are necessary for low Si dangling bond densities to  $\sim 0.5$  to  $1 \times 10^{16} \text{ cm}^{-3}$ : (i) a bonded mono-hydride, Si-H, concentration of  $\sim 10$  at.% H, and (ii) a deposition, and/or a post-deposition anneal at  $\sim 240^\circ\text{C}$  to  $300^\circ\text{C}$  [1]. These combine to reduce strain-induced defects by introducing MRO as 1 nm-ordered clusters. Si  $L_{2,3}$  X-ray absorption spectroscopy (XAS) confirms MRO by yielding non-vanishing ligand-field splittings (DLF) of  $e_g$  and  $t_{2g}$  atomic d-states. The MRO basis states are symmetry-adapted linear combinations (SALC) of atomic states and form molecular orbital valence bands. MRO symmetry promotes a H-atom transfer reaction from a the Si-H bond at the apex of the MRO cluster into a Si-H-Si bond at NN sites. This reaction establishes the low level of dangling bond defect sites. The same H-atom transfer is induced by sunlight absorption in PV devices. This increase dangling bond concentrations is the Staebler-Wronski effect (SWE). The local bonding arrangements of P and B dopant atoms are qualitatively different. If the bonding sites were the same as substitutional sites in c-Si, each of these dopants would be 4-fold coordinated. The incorporation of P is the same as in crystalline Si, 4-fold coordinated, and the ionization energy of the P<sup>+</sup> site is small giving rise to a high doping efficiency, i.e., in electrons/P atom [2]. B is 3-fold coordinated, and p-orbitals perpendicular to the 3-fold coordinated bonding plane act as an electron acceptor creating hole transport.

Each of the preferred bonding arrangements for P- and B-atoms includes remote induction stabilized Si-H reducing Si-atom dangling bond densities. This accounts for a reduction of the E' center signal strength in electron spin resonance (ESR) measurements. Finally, the local bonding of 2-fold coordinated O-atoms, and 3-fold coordinated N-atoms have similar effects as 1-fold coordinated H-atoms, introducing new MRO local bonding arrangements. When combined with 1-fold coordinated NN Si-H bonds, the 2- and 3-fold local symmetries introduce coupled mode motions that stabilize unique MRO clusters by increasing their total binding energy. This stabilization provides a reduction in the Staebler-Wronski Effect photo-degradation in PV devices by process-controlled low densities ( $< 10^{18} \text{ cm}^{-3}$ ) of plasma processing incorporation of O- and N-atoms and coupled O-H/H-H bonds.

Similar reductions reduce electron trapping in TFTs.

1. G. Lucovsky and F.L. Galeener, J. of Non-Cryst. Solids 35 & 36 (1980) 1209.
2. G.N. Parsons, C. Wang and M.J. Williams, Appl. Phys. Lett. 56, 1985 (1990).
3. D.E. Steabler and C.R. Wronski, J. Appl. Phys. 51 (6), (1980) 3262.

3:40pm **PS+TF-MoA6 Plasma Prize Talk - Plasma Processing Advances at Illinois**, D.N. Ruzic, University of Illinois at Urbana Champaign **INVITED**

Recent advances in plasma processing at Illinois will be discussed. The first is the investigation of high-powered pulsed magnetron sputtering (HiPIMS) by creating a hole in the target racetrack and placing a gridded energy analyzer and quartz-crystal monitor (QCM) behind it. In this way the metal ion and Ar ion flux can be measured, as well as the neutral metal atom flux. These measurements show the true mechanism behind the high surge in current during a HiPIMS pulse. The next subject is creating PVD-like coatings at atmospheric pressure. This is done by introducing atoms of the coating material directly into the plasma plume of an atmospheric-pressure torch either through laser ablation or by evaporation. These coatings have

many industrial applications and since they can be made in the field instead of inside a vacuum chamber, their utility is increased and their cost reduced. Lastly, the use of a metal-surface-wave plasma source will be described. Low-damage crystalline and amorphous silicon can be produced with it leading to higher-efficiency solar cells and other applications.

**4:20pm PS+TF-MoA8 PECVD, Rf vs Dual Frequency : Investigation of Plasma Influence on Metalorganic Precursors Decomposition and Material Characteristics.** *F. Piallat*, STMicroelectronics, France, *C. Vallee*, Ltm - Minattec - Cea/leti, France, *R. Gassilloud*, *P. Michallon*, CEA-LETI, France, *B. Pelissier*, Ltm - Minattec - Cea/leti, France, *P. Caubet*, STMicroelectronics, France

In the last decade, Dual Frequency (DF) reactors have been considerably developed as fine etching tool for microelectronic manufacturing. In this case, the CCP source is driven by a high frequency (HF) and a LF sources attached on either one electrode or two electrodes separately. Usually one frequency is chosen to be much higher than the other in order to achieve an independent control of ion bombardment and electron density (i.e. ion flux). In the case of deposition process, it has been observed for Silicon Nitride deposition that the HF to LF ratio in the plasma modify the ion flux and energy and so the mechanical properties of the material [3]. Moreover, addition of LF to HF can modify the sheath thickness of the plasma and so increase the electron temperature of the gas [4]. In this way, the precursor fragmentation can be tuned by tuning the LF power what will impact the deposition rate and thin film properties.

In this study we compare RF and Dual frequency deposition of materials for metal gate applications such as TiCN and TaCN. The reactor used is a 300 mm Metal Organic PECVD industrial tool in which the plasma is sustained capacitively by a RF power supply (13.56 MHz) and a LF (350 kHz) source. Impact of LF addition on the metal composition and its physical properties is analyzed and correlated to plasma modification observed by OES (Optical Emission Spectroscopy). For both metalorganic precursors we observe a strong modification of the metal properties and deposition rate when adding 25 to 100 W LF to a 200 W RF plasma. As an example, in case of TiN, with 50 W LF added to a 200 W RF, the deposition rate increased more than twice, the film appears to be less resistive (50%) and denser. These modifications highlight the change of deposition mechanisms/reactions. The beneficial effect of adding a weak LF power to the RF power can be correlated to a modification of the precursor fragmentation as observed by OES. These results are less pronounced and not obtained when only RF plasma is used, whatever the increasing power (from 200 to 300 W). Finally, with LF addition, we also hope, to reduce the RF plasma impact on the dielectric leading to a regrowth of Equivalent Oxide Thickness (EOT) observed previously in our p-like metal MOS capacitors [5].

- [1] H. N. Alshareef *et al*, Electrochemical and Solid-State Letters **11** (2008) H18
- [2] H. Zhu *et al*, Phys. Review B **80** (2009) 201406
- [3] W.S. Tan *et al*, Journal of Electronic Materials **33** (2004) 400-407
- [4] W-J Huang *et al*, Phys. Plasmas **16** (2009) 043509
- [5] F. Piallat *et al*, AVS 59th Tampa (Florida, USA)

**4:40pm PS+TF-MoA9 Reactive High Power Impulse Magnetron Sputtering (HiPIMS), J.T. Gudmundsson**, University of Iceland, *F. Magnus*, Uppsala University, Sweden, *T.K. Tryggvason*, *S. Shayestehaminzadeh*, *S. Olafsson*, University of Iceland

Reactive high power impulse magnetron sputtering (HiPIMS) [1] provides both a high ionization fraction of a high dissociation fraction of the molecular gas. Here we discuss reactive high power impulse magnetron sputtering (HiPIMS) of Ti target in Ar/N<sub>2</sub> and Ar/O<sub>2</sub> atmosphere. The discharge current waveform is highly dependent on the reactive gas flowrate, pulse repetition frequency and discharge voltage. The discharge current increases with decreasing repetition frequency. This we attribute to an increase in the secondary electron emission yield during the self-sputtering phase of the pulse, as nitride [2] or oxide [3] forms on the target. We also discuss the growth of TiN films on SiO<sub>2</sub> at temperatures of 22-600 °C. The HiPIMS process produces denser films at lower growth temperature and the surface is much smoother and have a significantly lower resistivity than dc magnetron sputtered films on SiO<sub>2</sub> at all growth temperatures due to reduced grain boundary scattering [4,5].

- [1] J. T. Gudmundsson, N. Brenning, D. Lundin and U. Helmersson, J. Vac. Sci. Technol. A, **30** 030801 (2012)
- [2] F. Magnus, O. B. Sveinsson, S. Olafsson and J. T. Gudmundsson, J. Appl. Phys., **110** 083306 (2011)
- [3] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, J. Vac. Sci. Technol., **30** (2012) 050601

[4] F. Magnus, A. S. Ingason, S. Olafsson and J. T. Gudmundsson, IEEE Elec. Dev. Lett., **33** (2012) 1045 - 1047

[5] S. Shayestehaminzadeh, T. K. Tryggvason, L. Karlsson, S. Olafsson and J. T. Gudmundsson, Thin Solid Films, submitted 2012

**5:00pm PS+TF-MoA10 Sputtering Yields and Selectivity of Magnetic Materials by Chemically Reactive Plasmas.** *H. Li*, *Y. Muraki*, *K. Karahashi*, *S. Hamaguchi*, Osaka University, Japan

Based on highly developed reactive ion etching (RIE) technologies, micro-fabrication of Si-based semiconductor devices has been considerably developed for the last few decades. However, as non-conventional micro devices, such as magnetic random access memory (MRAM) devices, have been developed recently, there has been a considerable demand for RIE processes of non-conventional materials such as magnetic materials with nonconventional gases such as CO/NH<sub>3</sub> and methanol. In this study, we examine sputtering yields and surface reaction characteristics for MRAM etching by CO/NH<sub>3</sub> or methanol plasmas. Especially we focus on effects of oxygen and nitrogen in incident ions that are likely to induce selectivity of magnetic materials over Ta, i.e., a widely used mask material in such processes. In this study, we use a multi-beam system (i.e., mass-selected ion beam system), which allows only selected ions with specified energy to be injected into a sample substrate set in an ultra-high-vacuum (UHV) chamber. Using the beam system, rather than an actual plasma etching system, we can examine specific surface reactions caused by a specific combination of a sample material and incident ions (and/or radicals). In the beam system, chemical surface compositions are analyzed by *in-situ* XPS. In this study, the incident ion energy and angle of incidence were varied from 300eV to 1000eV and from 0° to 75°. The sputtering yields were measured as functions of energy and/or angle of incidence for various materials including Ni, Fe, Co, Ta, and TaO<sub>x</sub>. It has been found that, in most cases, etching processes for these materials are nearly of physical sputtering. For simple physical sputtering (by, e.g., Ar<sup>+</sup> ions), the sputtering yield of Ta is much lower than the magnetic materials (Ni, Co, Fe), which justifies the use of Ta as a mask material. Furthermore, from XPS spectrum observation, it has been found that, when N or O are in the incident ionic species, Ta forms a nitride or an oxide and its sputtering yield becomes even lower. These results have confirmed that, in CO/NH<sub>3</sub> or methanol plasma etching processes of magnetic materials with Ta masks, the observed selectivity is essentially caused by the formation of hard-to-etch oxides and/or nitrides of masks, rather than enhanced etching yields of magnetic materials by these plasmas.

**5:20pm PS+TF-MoA11 Two-dimensional Growth of Novel ZnO based Semiconductor ZnInON with Tunable Bandgap by Magnetron Sputtering.** *K. Matsushima*, *R. Shimizu*, *D. Yamashita*, *G. Uchida*, *H. Seo*, *K. Kamataki*, *K. Koga*, *M. Shiratani*, *N. Itagaki*, Kyushu University, Japan

Materials with tunable bandgap are required for optoelectronics applications such as photo detectors, solar cells, light emitting diodes, and so on. Recently we have developed a novel ZnO based semiconductor, ZnInON (ZION), with tunable bandgap from 1.6 eV to 3.3 eV, being fabricated by sputtering method [1]. ZION has wurtzite crystal structure and high absorption coefficient of 10<sup>5</sup> cm<sup>-1</sup>. Here we have studied effects of Ar partial pressure during the sputtering deposition on the crystal growth of ZION films by means of plasma parameter measurements and evaluation of film properties such as crystallinity and electrical properties. Furthermore, we have demonstrated two-dimensional growth of single crystalline ZION films.

First, 10-nm-thick ZnO buffer layers were fabricated on c-Al<sub>2</sub>O<sub>3</sub> substrates via nitrogen mediated crystallization (NMC) in N<sub>2</sub>-Ar atmosphere at 700°C [2]. Then, 1-μm-thick ZnO templates were fabricated on the ZnO buffer layers by RF magnetron sputtering at 700°C in Ar-O<sub>2</sub> atmosphere. Finally, epitaxial ZION films were fabricated on the ZnO templates by RF magnetron sputtering. For fabrication of ZION films, N<sub>2</sub>, O<sub>2</sub> and Ar gasses were used. The total pressure was 0.28 Pa and the partial pressure of Ar was 0.04-0.17 Pa. The supplied RF power was 0.49-3.95 W/cm<sup>2</sup> and the deposition temperature was 360°C. The ZION film thickness was 30-50 nm.

X-ray diffraction measurements show that the full width at half maximum (FWHM) of rocking curves from (002) plane for the ZION films are noticeably small of 0.09°, being independent of the partial pressure of Ar in the sputtering atmosphere. Hall-effect measurements using the Van Der Pauw configuration reveal that the carrier density of ZION films decreases from 1.1×10<sup>20</sup> cm<sup>-3</sup> to 3.7×10<sup>19</sup> cm<sup>-3</sup> and the electron mobility increases from 66 cm<sup>2</sup>/Vsec to 87 cm<sup>2</sup>/Vsec with decreasing the partial pressure of Ar from 0.17 Pa to 0.04 Pa. This is because electron temperature in the plasma increases with decreasing the partial pressure of Ar, and thus the dissociation of oxygen and nitrogen molecules is enhanced, which can suppress the lattice defects related to nitrogen and/or oxygen deficiencies. Moreover, two-dimensional crystal growth of ZION films was observed at a low Ar partial pressure of 0.04 Pa. These results show that Ar partial

pressure in sputtering atmosphere is an important parameter to control the growth mode and to improve electrical properties of ZION films.

This work was partially supported by JSPS and PRESTO.

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[2] N. Itagaki, et al., Appl. Phys. Express 4 (2011) 011101.

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