Thursday Afternoon, November 10, 2016

Plasma Science and Technology
Room 104B - Session PS-ThA

Plasma Chemistry and Plasma Surface Interactions

Moderator: Steven Vitale, MIT Lincoln Laboratory

2:20pm **PS-ThA1 Nonthermal Plasma Driven Power to Gas*, Tomohiro Nozaki,*** Tokyo Institute of Technology, Japan **INVITED**

Renewable energy is recognized as indispensable CO_2-free energy source in our future society and tremendous increase in renewable energy has been demanded worldwide. However, it is also well-known that energy generation and timing strongly fluctuate depending on the climate and geological conditions. Energy storage by secondary batteries and smart grid concept have been investigated extensively by now. More recently, power to gas (PtG) concept is highlighted. The key component of PtG is the electrochemical conversion of H_2O into H_2 and O_2 with renewable electricity, enabling direct conversion of electrical energy to chemical energy. Basic concept of PtG can be extended to the synthetic CH_4 production from CO_2 and renewable hydrogen for increased energy storagibility and transportability. The key strategy is that electrochemical H_2O conversion and conventional C1 chemistry, which utilizes thermal energy at various temperature range, is combined appropriately in order to maximize overall electrical to chemical conversion processes.

In this study, nonthermal plasma enhanced catalytic conversion of CH_4 and CO_2 into syngas (CO and H_2) is presented. Electrical energy is converted into chemical energy of syngas via nonthermal plasma (electrical energy) driven endothermic reaction. Syngas is then converted into not only CH_4, but also carbon containing liquid fuels with the existing C1 chemistry. Liquid hydrocarbon would be more preferable than synthetic CH_4 because transport and storage capability of liquid hydrocarbons is improved with great flexibilities. CH_4 and CO_2 reforming is known as dry methane reforming (DMR): CO_2 can be oxidizer as well as carbon source for C1 chemistry. There are two major problems in DMR: one is coke formation which readily deteriorates catalyst activity. The other is high temperature thermal energy is needed (above 800 °C). Therefore, combustion of initial feed is unavoidable. Nonthermal plasma enables low temperature conversion of CH_4 and CO_2 at relatively low temperature (below 600 °C), yet fast reforming is guaranteed because plasma-generated reactive species promote catalytic surface reaction. We have developed pulsed dry methane reforming as comprehensive diagnostic method of plasma catalytic methane reforming [1]. This diagnostic method is further enhanced by the combination of optical emission spectroscopy, isotope labeling, and admixture of reaction promoters. In the symposium, mechanistic study of plasma catalysis and prospects for practical application (PtG) will be presented.

[1] S. Kameshima, K. Tamura, Y. Ishibashi, T. Nozaki, *Catalysis Today*, **256** (2015) 67-75.

3:00pm **PS-ThA3 Plasma-based CO_2 Conversion: Experiments and Modeling*,*** *A. Bogaerts,* ***Ramses Snoeckx,*** University of Antwerp, Belgium **INVITED**

Plasma-based CO_2 conversion is gaining increasing interest. We try to obtain better insight in the underlying mechanisms by experiments and computer modeling. Our experiments are carried out in a (packed bed) DBD and in a vortex-flow gliding arc (GA) reactor, focusing mainly on the conversion and energy efficiency at different conditions and reactor setups. Our model calculations focus especially on the detailed plasma chemistry in a DBD, GA and microwave (MW) plasma, for pure CO_2 as well as mixtures of CO_2 with N_2, CH_4 and H_2O. For this purpose, we make use of a zero-dimensional chemical kinetics model.

When studying the plasma chemistry in pure CO_2, we focus especially on the the role of vibrationally excited CO_2 levels, which are the key species for enhanced energy efficiency of the CO_2 conversion [1].

We have also studied the plasma chemistry in CO_2/CH_4 [2,3] and in CO_2/H_2O [4] mixtures in a DBD reactor, for producing value-added chemicals. The main products formed are a mixture of H_2 and CO, or syngas, with a tuneable H_2/CO ratio depending on the gas mixing ratio. The production of oxygenated compounds is very limited. A detailed chemical kinetics analysis allows to elucidate the different pathways leading to the observed results, and to propose solutions on how to improve the formation of value-added products.

Finally, we also studied the plasma chemistry in a CO_2/N_2 mixture, both in a DBD [5] and in a MW [6] plasma, to investigate the effect of this important impurity in effluent gases on the CO_2 conversion, energy efficiency and product formation. Our model and experiments reveal that N_2O and NO_x compounds are produced in the range of several 100 ppm. The reaction pathways for the formation of these compounds are again explained based on a kinetic analysis, which allows proposing solutions on how to prevent the formation of these harmful compounds.

References

1. T. Kozák, A. Bogaerts, *Plasma Sources Sci. Technol.* 23 (2014) 045004.

2. R. Snoeckx, R. Aerts, X. Tu, A. Bogaerts, *J. Phys. Chem. C* 117 (2013) 4957-4970.

3. R. Snoeckx, Y.X. Zeng, X. Tu, A. Bogaerts, *RSC Advances* 5 (2015) 29799-29808.

4. R. Snoeckx, A. Ozkan, F. Reniers and A. Bogaerts, paper in preparation.

5. S. Heijkers, R. Snoeckx, T. Kozák, T. Silva, T. Godfroid, N. Britun, R. Snyders and A. Bogaerts, *J. Phys. Chem. C* 119 (2015) 12815-12828.

6. R. Snoeckx, S. Heijkers, K. Van Wesenbeeck, S. Lenaerts and A. Bogaerts, *Energy & Environm. Sci.* 9 (2016) 999-1011

4:00pm **PS-ThA6 Revisiting HgCdTe Etching Mechanism in High Density CH_4-H_2 Plasmas in Terms of Langmuir Adsorption Kinetics and Taking into Account Etching Inhibition*, Christophe Cardinaud,*** *A. Pageau,* CNRS - IMN, France*; L. Le Brizoual,* IETR - Univ. Rennes, France*; F. Boulard, J. Baylet,* CEA, LETI, MINATEC Campus, France

In the past 20 years, intrinsic properties of $Hg_{(1-x)}Cd_xTe$ have placed this semiconductor compound as the standard material for the fabrication of high performance infrared detection devices [1]. CH_4-H_2 based plasmas have proven to be efficient to etch HgCdTe [2]. In terms of mechanism, it is usually admitted that methyl radicals, coming from the dissociation of methane CH_4, form volatile metal organic species, mainly $Cd(CH_3)_2$ and $Te(CH_3)_2$, while atomic hydrogen, coming from CH_4 and H_2 dissociation, forms volatile TeH_2, and that Hg, due to its high vapor pressure, desorbs spontaneously from the surface. Strong Cd accumulation is always observed on the processed surface, underlining that Cd removal is the limiting step of HgCdTe plasma etching. In a previous study we have identified that the surface stoichiometry change appears as soon as the etching starts and that the etch rate is closely related to the incoming flux of methyl species [3]. Consequently, the $Hg_{(1-x)}Cd_xTe$ alloy removal takes place through a Cd-rich surface layer rather than through the bulk material itself. Low-pressure high-density plasma sources and independent control of sample bias enable operation of the process with more chemical than physical etching mechanisms. Such conditions should meet the main fabrication requirements: high anisotropy, smooth sidewalls, reasonable etch rate, and low level of surface damage. However they typically fall in the HgCdTe etching / hydrocarbon deposition borderline.

Plasma-surface interaction mechanisms are investigated when varying source power, sample bias, CH_4 flow rate and total pressure. Mass spectrometry and electrostatic probes are respectively used to evaluate methyl and positive ion flux onto the surface. X-ray photoelectron spectroscopy provides surface composition. Results and etch rate measurements are discussed in the view of an ion-neutral species synergy model based on Langmuir adsorption kinetics [4] and taking into account the competition between hydrocarbon film formation and HgCdTe etching.

1 A. Rogalski, Infrared Phys. and Technol. (2011) **54**, 136

2 R.C. Keller, M. Seelmann-Eggbert, and H.J. Richter, J. Electron. Mater. (1995) **24**, 1155

3 F. Boulard, J. Baylet, and C. Cardinaud, J. Vac. Sci. Technol. A (2009) **27**, 855

4 T.M. Mayer and R.A. Barker, J. Vac. Sci. Technol. (1982) **21**, 757

4:20pm **PS-ThA7 Temporal Evolution of Surface Chemistry in Ion and Radical Dominated Etch of Hydrocarbon Polymers*, Barton Lane,*** *P. Ventzek, N. Eibagi,* Tokyo Electron America, Inc.*; A. Ranjan, V. Rastogi,* TEL Technology Center, America, LLC

Precise and selective etching requires the control of the chemical and physical nature of thin surface layers. We discuss here the specific example of hydrocarbon polymer etching in an argon/oxygen chemistry. An important issue is the temporal evolution of the layer started from an initial condition established by a preceding step. It is important to ascertain whether the surfaces evolve continuously or not. We find for this chemistry and film set, that there are transients which give way at longer times to steady state conditions. Through the use of a novel *in situ* OES based technique which mimics traditional SIMS surface analysis we demonstrate the time dependent effect of argon ions on a hydrocarbon polymer surface which has been previously oxidized and separately the re-oxidation of a previously graphitized surface. Both these processes show sharp transients followed by much less active steady states. We characterize how these transients depend on the starting surface condition. We apply these same analytic techniques to the more complicated situation of the time evolution of photoresist lines which have been defined by 193i lithography. We show that the time dependence of the morphology of the surfaces of these lines which can be related to the lamellar structure of the photoresist.

4:40pm **PS-ThA8 Etching Mechanisms of Transparent Conducting Oxides by Hydrocarbon Plasmas***, **Hu Li,*** Osaka University, Japan*; P. Friederich, K. Fink,* Karlsruhe Institut for Technology (KIT)*; K. Karahashi,* Osaka University*; M. Fukasawa, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan*; W. Wenzel,* Karlsruhe Institut for Technology (KIT)*; S. Hamaguchi,* Osaka University, Japan

Zinc oxide (ZnO) and tin-doped indium oxide (ITO) are some of the most promising transparent conducing oxides (TCOs) for optoelectronic devices such as solar panels and head-mounted liquid crystal displays. With the demand of high-resolution optoelectronic devices increasing in the market, more efficient fabrication technologies for sub-micron- or nano-scale patterning of TCOs are required. Reactive ion etching (RIE) is a key technology for such fine patterning of materials, which has been widely used in the fabrication of semiconductor devices. RIE processes for TCOs have been developed with non-corrosive gases such as $CH_{4.}$ However, etching reactions and mechanisms of such processes are not fully understood yet. The goal of this study is therefore to clarify plasma-surface interactions of CH_4 based plasmas with TCOs.

It has been found in our earlier beam experiments that the etch rate of ZnO by energetic CH_x^+ ions strongly depends on the amount of hydrogen (i.e., value of x) of each incident CH_x^+ ion. The results have also shown that ZnO stores hydrogen after the surface was exposed to energetic hydrogen ions. The modified surface layer of ZnO, which we call a “hydrogen-embedded ZnO” layer, has a higher sputtering yield for incident (inert) ions. In this study, we have examined how hydrogen can be stored in a hydrogen-embedded ZnO layer, using *ab initio* calculations. It has been found that, when a hydrogen atom is introduced to the surface or bulk of ZnO, it forms a hydroxyl group and weakens the Zn-O bond, converting ZnO to ZnOH. The result indicates that, in terms of energy levels, ZnOH has a higher sputtering yield than ZnO. A similar discussion of hydrogen effects on ITO will be also given in this presentation.

5:00pm **PS-ThA9 The Role of the Dense Amorphous Carbon (DAC) Overlayer in Photoresist Etching***, **Adam Pranda,** Z. Tomova, S. Gutierrez Razo, J.T. Fourkas, G.S. Oehrlein,* University of Maryland, College Park

Multicolor photolithography is an alternative to extreme ultraviolet (EUV) lithography in attaining device feature sizes below 10nm. The use of this technique requires modification of existing acrylate-based photoresists in order to enable selective photochemistry with multiple wavelengths of light. In the following work, we establish the viability of multicolor photoresists by comparing their plasma etching behavior to industry-standard 193nm and 248nm photoresists.

The 193nm and 248nm photoresist polymers commonly used in industry are abundant in C-H bonds that scission when exposed to high energy ions that are characteristic of plasma etching. The rapid removal of volatile hydrogen- and oxygen-based carbon products results in the formation of a dense amorphous carbon (DAC) overlayer in the nm range. Steady-state etching of the bulk photoresist entails the constant removal and reformation of this overlayer, and the DAC layer acts as an etch-inhibiting layer on top of the bulk resist. The overall density of the overlayer will determine the etching behavior of the underlying photoresist.

In this work, we define a baseline for comparing multicolor photoresists by investigating the relationships between chamber conditions, formation of the DAC overlayer, and the resultant etch yields for a poly(methyl methacrylate)-based 193nm photoresist polymer (PR193) and a polystyrene-based 248nm photoresist polymer (PR248) using an inductively-coupled plasma (ICP) reactor as well as an electron cyclotron wave resonance (ECWR) reactor. The thickness and refractive index of both the DAC overlayer and bulk photoresist layer were monitored in real-time using *in-situ* ellipsometry.

We observe a correlation between the ambient chamber oxygen concentration, magnitude of the DAC overlayer refractive index (reflective of material density), and photoresist steady state etch rate. In the absence of ambient oxygen, the primary steady-state etching mechanism is physical sputtering. In the presence of ambient oxygen, the etching mechanism has contributions from physical and chemical sputtering, the latter mainly through adsorbed oxygen on the sample surface. Removal of carbon from the overlayer is enhanced by chemical sputtering, resulting in a less dense DAC overlayer which yields a higher steady state etch rate compared to the oxygen-deficient condition. These observations are useful as a baseline for evaluating the behavior of multicolor photoresists and provide a benchmark to guide which photoresists to synthesize to achieve the desired etching behavior.

The authors gratefully acknowledge the financial support of this work by the National Science Foundation (NSF CMMI-1449309).

5:20pm **PS-ThA10 Transport Mechanism on Reactive Species in Downflow Reactors for F-based Etch***, **Kenji Ishikawa**, T. Tsutsumi, Y. Zhang, M. Sekine, T. Hayashi, M. Hori,* Nagoya University, Japan*; Y. Horiike,* Tsukuba University, Japan

In chemical dry etching (CDE) of F-based etch chemistry such as CF_4, SF_6, etc. [1], it has been believed that F atoms transport as long as 1 meters downflow of plasma source and etch Si with etch rates around 500 nm/min [2]. The etch results for SiO_2 and SiN films were shown stable even low rates but relevant values regardless of the distance [3,4]. Otherwise, whilst the cases of NO + F_2 gas mixture generates F atoms, the etch rates significantly decreases with the distance from the location generated F atoms [5]. These apparently paradoxical results remain an open question, which needs to revisit. In particular of O_2 addition, the etch rate-dependence versus distance is evident, thus the the effects of peroxy radicals, OOF, and peroxides, F_2O_2, are hypothesized. Here, we report the transport mechanism on reactive species in downflow for F-based etch.

The chemical dry etching apparatus was constructed by a long-length quartz tube. A mixture of CF_4 and O_2 gases was flown into the tube and a microwave cavity (2.45 GHz, 50W) was used for plasma generation. At the downflow, F atom or FOO signals were measured by electron spin resonance (ESR) instrument [6,7]. Quantum-chemical calculations were done with B3LYP/6-311+G(d) by Gaussian 09.

Ground-state of O_2 ($^3\Sigma g$) is reacted with F atom and stabilized 0.36 eV to generate OOF. Subsequently, OOF reacts with F atom to form F_2O_2. The OOF and Si reaction takes place Si + OOF -> SiF + O_2($^3\Sigma g$), rather than Si-oxidation pathways.

Experimentally, concentrations of F atoms at downflow depended on mixture ratio of O_2 and distances from the plasma source. The O_2 addition enhanced to transport F atom toward further positions. In general, although F atom recombination to F2 is known to be relatively low reaction rate, however the recombination cannot be negligible during transport. Thus, we revisited the radical complex mechanism, i.e., F + O_2 -> OOF and OOF -> F + O_2, *vise verse*. In summary, we suggest that the transport of reactive species needs to revisit effects of the radical complex of F atom with O_2., in particular of the O_2 added F-based chemistry.

[1] Y. Horiike *et al*. Jpn. J. Appl. Phys. suppl. 15 (1976) 13; [2] N. Hayasaka *et al*., 11th Proc. DPS (1989), p.57;[3] B. E. E. Kastenmeier *et al*., J. Vac. Sci. Technol. A 14 (1996) 2802; [4] G. S. Oehrlein *et al*., Plasma Sources Sci. Technol. 5 (1996) 193; [5] S. Tajima *et al*., J. Phys. Chem. C 117 (2013) 5118; [6] H. E. Radford *et al*., Phys. Rev. 123 (1971) 153; [7] A. D. Kirshenbaum *et al*., J. Am. Chem. Soc. 88 (1966) 2434.

5:40pm **PS-ThA11 Surface Reactions of Magnetic Materials by CO Cluster Beams***, **Kazuhiro Karahashi,*** Osaka University, Japan*; T. Seki, J. Matsuo,* Kyoto University, Japan*; K. Mizotani, K. Kinoshita, S. Hamaguchi,* Osaka University, Japan

Dry etching of magnetic thin films is a critical issue in the fabrication of magnetic random access memories (MRAMs). Currently argon (Ar) ion milling seems the only etching technique available in the manufacturing processes. However Ar ion milling is incapable of achieving anisotropic and selective etching of magnetic films and therefore extensive research is underway to establish highly selective anisotropic reactive ion etching (RIE) processes for magnetic thin films [1]. The formation of volatile metal carbonyl compounds produced by reactions of a metal surface with incident CO molecules may be used as a chemical etching process but such reaction probabilities are known to be very small. In this study we propose gas cluster beam processes as a means to etch magnetic metal surfaces. Gas clusters can provide a large number of reactant molecules to the metal surface at low incident energies and are expected to cause multiple collision processes at impact [2]. Especially we have examined surface reactions of Ni thin films by CO neutral clusters as well as energetic CO ion clusters. First we studied Ni etching reaction by incident CO cluster ion irradiation with typical single cluster ion energy being $E_{cluster}$ = 20 keV (and a single CO molecule ion incident energy being E_{CO}= 11 eV). It was found that amorphous carbon deposition occurred on Ni surfaces and the beam did not etch the Ni films. These results suggest that each CO cluster is broken apart to CO molecules at impact by the excessive kinetic energy. Such excess kinetic energy prevents the formation of carbonyl compounds. Second, we examined interactions between low-energy incident CO neutral clusters ($E_{cluster}$ = 300 eV, E_{CO}= 60 meV) with Ni surfaces. NiCO (Mass 86), which are fragments of nickel carbonyl compound [$Ni(CO)_4$], were detected with a quadrupole mass spectrometer equipped in the chamber of the beam system. These results suggest that carbonyl formation reaction occurred by CO neutral cluster irradiation. Currently the probability of such carbonyl-formation reaction seems low and we shall discuss how the carbonyl-formation reaction rate on a metal surface can be increased. This work was supported by the Semiconductor Technology Academic Research Center (STARC)

References

[1]K. Kinoshita et al., Jpn. J. Appl. Phys. 49(2010) 208JB02.

[2]I. Yamada, J. Matsuo, et al., Mater. Sci. Eng. A, 253(2005) 249.

6:00pm **PS-ThA12 A Method to Accelerate Creation of Plasma Etch Recipes Using Physics and Bayesian Statistics***, **Meghali Chopra**, R.T. Bonnecaze,* The University of Texas at Austin

Creating and optimizing plasma etch recipes for microelectronic and other nanostructured devices is costly and time consuming. Fully optimized plasma etch recipes can take several months to two years to create, which slows time to market. Here we introduce a method combining physics-based global plasma models, Bayesian statistics and experimental data to rapidly develop and optimize recipes for plasma etching. The method predicts optimal process windows with two- to three-fold fewer experiments than using factorial design of experiments. We first demonstrate this method for prediction of etch rates in CCP and ICP-RIE plasma reactors. These predictions are then successfully compared to synthetic and experimental data. We next use the method to determine the anisotropic etch rates through a single material including level set modeling. Lastly, we apply the method to the etch recipe development of a high aspect ratio trench through a multi-layer stack. Our results show that we can reduce three-fold the cost and time required to develop an etch recipe.

Author Index

Bold page numbers indicate presenter