Wednesday Morning, October 31, 2012

Energy Frontiers Focus Topic
Room: 15 - Session EN+PS-WeM

Plasmas for Photovoltaics and Energy Applications

Moderator: J.-P. Booth, LPP-CNRS, Ecole Polytechnique, France

8:00am **EN+PS-WeM1 Electron Driven C_1-chemistry: Direct Conversion of Methane to Synthetic Fuels**, ***T. Nozaki***, Tokyo Institute of Technology, Japan **INVITED**

Currently, industrial material and energy conversion technology platform consists of thermochemical processes including various catalytic reactions. Existing industry scale technology and related science has already been well established; nevertheless, further improvement in energy efficiency and material saving are demanded. Drastic reduction of CO_2 emission is also drawing keen attention with growing concern of energy and environmental issues. Green chemistry is a rapidly growing field of science and technology, and often highlights renewable bioenergy, bioprocesses, solar photocatalysis of water splitting, and CO_2 regeneration as synthetic fuels. Plasma catalysis of hydrocarbon feedstock is also highlighted as an important part of the innovative next generation green technologies that meet the need for energy saving, environment protection, and material preservation [1-4]. Non-thermal plasma uniquely generates reactive species independently of reaction temperature, and these species are used to initiate chemical reactions at unexpectedly lower temperatures than normal thermochemical reactions. Non-thermal plasma thus broadens the operation window of existing chemical conversion processes, and ultimately allows modification of the process parameters to minimize energy and material consumption. We specifically focus on dielectric barrier discharge (DBD) as one of the viable non-thermal plasma sources for practical fuel reforming. In the presentation, room-temperature one-step conversion of methane to synthetic fuels such as methanol, hydrogen, and syngas (H_2+CO) using a microplasma reactor is highlighted. Not only practical background of the project, but also unique characteristics of plasma fuel reforming such as non-equilibrium product distribution is presented [5-7].

1. T Nozaki et al: *Journal of the Japan Petroleum Institute*, **54**(3) (2011) 146.

2. The special issues on " Non-thermal Plasma Assisted Fuel Conversion for Green Chemistry ", *J Phys D: Appl Phys.*, **44**(23), 2011

3. A Gutsol: Handbook of Combustion, Vol.5 New Technology, Wiley-VCH, 323 (2010)

4. H L Chen et al: *Appl. Catal. B: Environmental*, **85** (2008) 1.

5. T Nozaki et al: *Chemical Engineering Journal*, **166** (2011) 288– 293.

6. T Nozaki et al: *Energy & Fuels*, **22** (2008) 3600–3604.

7. T Nozaki et al: *Pure and Applied Chemistry*,**78**(6) (2006) 1147–1162.

8:40am **EN+PS-WeM3 Plasma-assisted CO_2 Conversion as Candidate Element in Future Solar Fuel Economy**, *S. Welzel, S. Ponduri, F. Brehmer, M. Ma, M.C.M. van de Sanden,* ***R. Engeln***, Eindhoven University of Technology, the Netherlands

Recently research in 'solar fuels' has been stimulated by the forthcoming depletion of fossil fuels along with a slowly increasing share of intermittently available renewable sources. New efficient methods of harvesting renewable (e.g. solar) energy and its storage in high energy density chemical fuels are therefore highly desirable. CO_2 and its recycling into 'solar fuels' will be an essential element in the future transport and energy infrastructure. Plasma-processing of CO_2 in the gas phase under low-temperature non-equilibrium conditions is thereby a promising alternative to specifically tackle the rate-limiting dissociation into CO. Two aspects of such a plasma-assisted CO_2 treatment have been studied and are detailed in this contribution.

Firstly, the direct hydrogenation of CO_x in a plasma-expansion created from mixtures of Ar and H_2 was investigated. Different (metallic) surface materials were employed to assess the influence of surface reactions on the molecule formation. Mass-spectrometry and infrared absorption spectroscopy were applied to quantify the gas phase composition of such argon-ion and hydrogen-radical enhanced plasmas. Although CO was a main product with up to 50 % conversion yield, the separation of CO_2 dissociation and subsequent hydrogenation was strongly suggested to optimise both processes individually. Furthermore it transpired that plasma-catalysis require new surface materials that are different from conventional catalysts: a copper surface typically reduced the CO and CH_4 yields by 50 %.

Secondly, to particularly account for the individual optimisation of the CO_2 dissociation and scrutinise the (energy) efficiency of the conversion process dielectric barrier discharges in CO_2 were studied. The focus was on establishing a consistent energy-balance of the proposed plasma-assisted route and involved the analysis of energy injected to the power supply, the transfer to the discharge and the correlation with the CO_2 conversion. Through reduction of loss channels in the resonance circuit operated in the kHz-range clearly more than 50 % of the input power were directly injected to the plasma. Plasma parameters such as electron and vibrational temperatures and the population distribution of excited species were determined to further characterise the excitation and dissociation channels in the CO_2 plasma.

9:00am **EN+PS-WeM4 Novel Processing Routes of Silicon Nanocrystals in a Remote Expanding Thermal Plasma for Photovoltaic Applications**, ***I. Dogan****, Eindhoven University of Technology, Netherlands, *S.L. Weeks*, Colorado School of Mines, *K. Dohnalova, T. Gregorkiewicz*, University of Amsterdam, Netherlands, *S. Agarwal*, Colorado School of Mines, *M.C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research, Netherlands

The interest in silicon nanocrystals (Si-NCs) has considerably increased since the observation of carrier multiplication and separation between adjacent Si-NCs. This mechanism might potentially enable a more efficient solar spectrum conversion. For successful integration of Si-NCs into solar cells, the key issues are size control, crystalline quality, surface preparation and cost efficient production of Si-NCs. Previous works have failed to address the latter point because they require multiple production steps yet with an insufficient amount of produced Si-NCs. Here, a novel synthesis method of Si-NCs by using a remote expanding thermal plasma (ETP) is presented, that allows a direct utilization for large scale production. One-step route synthesis of Si-NCs is realized in an argon/silane plasma with remarkable throughputs above 100mg/min of Si-NCs. Formation of Si-NCs is favoured by means of silane polymerization reactions. In contrast to the common belief of particle coagulation, all Si-NCs are found to be formed by nucleation as revealed from TEM analysis of the Si-NCs produced. TEM, Raman spectroscopy (RS) and photoluminescence spectroscopy (PL) consistently demonstrate that the Si-NCs have a size distribution in the range 2-140nm which is related to differences in residence times in the different zones of the reactor. To move towards a better control of the size distribution, a series of size separation experiments is discussed. Two approaches are proposed: spatial confinement of the plasma zones where the smaller Si-NCs are formed or a time modulation of the silane flow injected into the reactor. It will be shown that using these methods an average Si-NC size distribution of 5nm can be reached. Moreover, based on the results of time modulation, the role of different plasma species on the formation of small and large Si-NCs will be discussed. The observation of step-like enhancement of luminescence quantum yield with increased photon energy, which is a sign of carrier multiplication between Si-NCs will be discussed. It is expected that the ETP approach is capable to dramatically increase the production efficiency of Si-NCs to scalable throughputs without any loss of quality.

9:20am **EN+PS-WeM5 Growth of Microcrystalline Silicon using Tailored Voltage Waveform Driven Plasma Processes: From Materials to PV Devices**, ***E.V. Johnson***, LPICM-CNRS, Ecole Polytechnique, France, *S. Pouliquen, P.A. Delattre, J.-P. Booth*, LPP-CNRS, Ecole Polytechnique, France **INVITED**

The use of non-sinusoidal, radio-frequency (RF) « tailored » voltage waveforms (TVW's) to drive plasma processes in a capacitively coupled plasma reactor allows one to decouple the injected power from the mean ion bombardment energy (IBE) at the substrate. Also known as the Electrical Asymmetry Effect (EAE), this decoupling stems from a controllable division of the sheath voltage between the two electrodes when an asymmetric voltage waveform is applied to one of the electrodes. In a symmetric reactor, this effect manifests itself through the presence of a self-bias voltage (V_{DC}), and as dramatic changes in this parameter in an asymmetric one. For example, the application of a "peaks" waveform to the RF electrode - consisting sharp pulses separated by plateaus - results in a large, negative V_{DC}, and thus a reduction in the IBE at a substrate on the grounded electrode. A "valleys" waveform results in the opposite, while both waveforms inject the same power into the plasma.

Such independent control over the sheath voltages is very useful when applied to the deposition by PECVD of thin-films of materials needing a high radical flux but low IBE, such as hydrogenated microcrystalline silicon

***** Coburn & Winters Student Award Finalist

(μc-Si:H). By controlling the growth conditions of the μc-Si:H thin films through the shape of the waveform, one can control many aspects of the film properties (Raman crystallinity, density, hydrogen bonding, surface morphology, and electronic properties) without changing any other process conditions. In particular, the optical response of the films (and film surfaces) can be observed in-situ during growth using spectroscopic ellipsometry, thus linking the redistribution of the sheath voltages to the growth dynamics. Furthermore, we show that when TVW's are used to decrease the IBE during the growth of the absorber layer of thin-film solar cells, good device properties at acceptable deposition rates are obtained.

A promising aspect of this technique is the prospect of achieving process control without modifying the core of an existing reactor chamber. However, the counteracting challenge is that of efficiently coupling multiple harmonics to the reactor simultaneously, and these two facets will also be discussed.

10:40am **EN+PS-WeM9 Measurement and Control of Ion Energies in Dual Frequency Capacitive Hydrogen Discharges**, ***E. Schuengel***, *S. Mohr, J. Schulze, U. Czarnetzki*, Ruhr-University Bochum, Germany

In plasma processing applications, capacitively coupled radio frequency (CCRF) discharges are widely used. A typical example is the manufacturing of silicon thin film solar cells using PECVD in a geometrically almost symmetric capacitive parallel plate discharge. For these applications, one of the major aims is the control of the fluxes and properties of radicals and ions at the substrate surface, thus controlling the surface chemistry and optimizing the (electrical) properties of the deposited film and/or the deposition rate. In particular, the shape of the ion velocity distribution function (IVDF) plays a crucial role [1]. The IVDF can be controlled to some extent in CCRF discharges driven by two substantially different frequencies, where the low frequency component is used to modify the ion energy while the total ion flux should be adjusted via the high frequency component. However, recent investigations have shown that this method is limited to a rather narrow window of discharge operating conditions [2]. As opposed to this concept, the Electrical Asymmetry Effect (EAE) uses the excitation via two consecutive harmonics to generate an asymmetric discharge even in geometrically symmetric discharge configurations [3]. Here, the symmetry of the discharge, the DC self bias, and the ion energy at the electrode surfaces are controlled via the phase angle between the two frequencies. In this study, the EAE is investigated in a discharge setup, which is similar to the ones described in the above example. A combination of 13.56 MHz and 27.12 MHz is applied to one electrode. The discharge is ignited in pure hydrogen at pressures of several hundred Pascals. Under these conditions, H3+ ions are the dominant ion species. A plasma process monitor is implemented into the center of the grounded electrode, allowing to measure the H3+ IVDF. The results show that the mean ion energy changes as a function of the phase angle, while the ion flux is kept almost constant. However, the control range of the ion energy via the EAE is limited and the shape of the IVDF shows a dependence on the phase angle. These experimental findings are understood in the frame of a simple model.

Funding by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (0325210B) is gratefully acknowledged.

[1] S. Nunomura and M. Kondo 2008 Appl. Phys. Lett. **93** 231502

[2] J. Schulze et al. 2009 Plasma Sources Sci. Technol. **18** 034011

[3] U. Czarnetzki et al. 2011 Plasma Sources Sci. Technol. **20** 024010

11:00am **EN+PS-WeM10 Raman Study of the Properties of Free Standing Silicon Nanocrystals Using Laser Induced Thermal Heating**, ***L. Han***, *A.H.M. Smets, M. Zeman*, Delft University of Technology, Netherlands

Nanocrystals (NCs) exhibit unique physical properties which might open routes to new photovoltaic concepts conquering the Shockley-Queisser limit of single junction solar cell devices, such as multiple-exciton-generation (MEG) and down conversion using space-separated-quantum-cutting (SSQC). In addition, the strong dependence of the band gap of NCs on their sizes, allows the design of novel multi-junction solar cells. For these reasons, NCs made of variety of direct and indirect semiconductor materials, have been extensively studied in recent years. In this contribution we focus on silicon, the most dominant material in PV technology. Challenges in the processing of Si NCs are controlling their size distribution and passivation of surfaces to prevent unwanted Shockley-Read-Hall recombination of generated charge carriers.

The Si NCs studied in this paper are synthesized using the expanding thermal plasma chemical vapor deposition (ETP-CVD) technique with the advantage of incredible high yield, deposition rate, room temperature fabrication, low cost, high purity and post-surface passivation treatment based on plasma processing. Using the ETP-CVD technique free standing Si NCs with a wide variety of properties have been processed. The dependence of the processing conditions are studied using high resolution transmission electron microscopy. Furthermore, the surface oxidation kinetics of free standing Si NCs without any post-deposition surface-passivation-treatment is studied using IR absorption spectroscopy.

The main focus in this contribution is an unconventional Raman spectroscopy analysis on the free standing Si NCs. In this approach, Si NCs are additionally heated using a laser probe to study the quantum confinement effects of the Si NCs in more detail. An interesting huge red Raman peak shift for the transverse optic mode (520 cm-1) of around 30 cm-1 and a width enhancement of 19.1 cm-1 are observed with the increasing power of the probe laser. We argue that the shift is due to the laser induced thermal heating of the Si NCs in line with analysis based on the ratio of the Anti-Stokes-to-Stokes peak of the free standing Si NCs [1]. As a reference, the Raman spectra of amorphous silicon and microcrystalline silicon thin films are studied using the same approach. This experiment shows that thermal conduction between the free standing Si NCs is inefficient in contrast to the Si films, which allows the Si NCs to be heated up by laser light more efficiently.

[1] Khriachtchev et al., JAP 100, 053502 (2006)

11:20am **EN+PS-WeM11 Fabrication of 3D Array Si Quantum Dots Superlattice using Biotemplate and Neutral Beam Etching**, ***M.E. Fauzi***, *M. Igarashi, W. Hu, S. Samukawa*, Tohoku University, Japan

Quantum dots have been used in many novel optoelectronic devices due to its quantum effect characteristics. To further improve quantum dots light absorption efficiency, it is vital to increase number of quantum dots while keeping straight alignment in vertical direction. However, in the conventional method using bottom-up approach, fabricated quantum dots structure is not uniform and well-aligned in vertical direction, while the conventional top-down etching has limitations in fabrication of nanometer size and leaves high-density defects. In previous study, we have fabricated well-ordered arrangement of high-density 2 dimensional (2D) array (7×10^{11} cm^{-2}) silicon nanodisk (Si-NDs) with a new process using bio-template and damage-free neutral beam etching (NBE). In this paper, we developed technology for fabricating 3D array of Si NDs with single step NBE technique and biotemplate technology, focusing on well-aligned structure in vertical direction.

Firstly, we deposited 4 layers of 4 nm-thick Si layer with 2 nm-thick silicon carbide (SiC) as its matrix using thin film deposition technique. Then, bio-template was quasi-hexagonally arranged and used as mask during our etching process.These bio-templates provide 6 nm space between etching masks. After NBE process, high aspect ratio of 12 is achieved. The key technology in our approach is to utilize low-selectivity etching process to etch high aspect ratio structure in single step. Single step etching is made possible for three reasons. First, oxide layer on top of our Si/SiC structure was first removed by NF_3 gas/hydrogen radical treatment. Secondly, SiC that was used as matrix material has a comparable etching rate compare to Si. In our research, we make use of Si/SiC's low selectivity (1.3) to conduct a well-aligned vertical etching process. Thirdly, a high selectivity for Si/SiC structure to iron-core etching mask. After chlorine NBE process, iron-core mask pattern was precisely transferred, and anisotropic etching profile was achieved. Our SEM images of the top-view and cross-section view exhibits well-aligned, uniformity, high aspect ratio nano-columns. Lastly, we deposit SiC layer to complete Si/SiC matrix. As a result, we successfully fabricated 4 layers-stacked Si-NDs with sub-10 nm in diameter and 2 nm space between nanodisks.

We hope quantum dots superlattice fabricated by our technology could be used in quantum dot solar cell application for higher conversion efficiency.

11:40am **EN+PS-WeM12 Two-dimensional Simulations of Hydrogen and Hydrogen/Silane Capacitively Coupled Dual Frequency Discharges**, ***S. Mohr***, *E. Schuengel, J. Schulze, U. Czarnetzki*, Ruhr University Bochum, Germany

Capacitively coupled radio-frequency (CCRF) discharges are commonly used in surface processing applications, for example the deposition of thin films. One of the most important challenges in optimizing CCRF discharges for this usage is achieving the ample and independent control of flux and energy of ions and reactive species at the surfaces, as these properties determine the quality and deposition rate of the films. This independent control can be attained by using electrically asymmetric discharges which use two consecutive harmonics to excite the plasma; the ion energy can be controlled by the phase between the two frequencies while the flux stays constant. The feasibility of this method has been demonstrated by both experiments and simulations in various gas mixtures [1-3], although limitations have been observed, for example in highly electronegative discharges.

Hydrogen is part of many gas mixtures used in industrial applications such as hydrogen/silane mixtures in the production of solar cells. Two traits, which distinguish hydrogen discharges from the already investigated gas mixtures, are the high ion mobility and the regular occurrence of field reversals during the sheath collapse. Additionally, deposition processes are usually carried out at quite high pressures of several 100 Pa. We conduct two-dimensional simulations of such discharges covering a wide range of discharge conditions (pressure: 20 Pa – 500 Pa, pure hydrogen discharges and hydrogen/silane mixtures) using the simulation tool Hybrid Plasma Equipment Model (HPEM) by Mark Kushner [4]. The focus of our investigations lies on the influence of high pressures, field reversals, and high ion mobilities on the separate control of ion energy and ion flux. For example, we observe a significant reduction of the ion energy control range, if field reversals are the main ionization source of the discharge. The physical mechanisms behind this effect and others occurring in hydrogen and hydrogen/silane - discharges will be discussed.

Funded by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (0325210B).

[1] U. Czarnetzki et al. 2011 *PSST***20** 024010

[2] E. Schüngel et al. 2011 *J. Phys. D.***44** 285205

[3] J. Schulze et al. 2011 *PSST***20** 045008

[4] M. Kushner 2009 *J. Phys. D***42** 194013

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