Energy Frontiers Focus Topic
Room: 103 - Session EN+PS-MoM

Plasmas for Photovoltaics & Energy Applications

Moderator: S. Agarwal, Colorado School of Mines

8:20am **EN+PS-MoM1 Plasma Energy R&D at National Fusion Research Institute (NFRI): Fusion Energy, Silicon Quantum Dot Solar Cell, and Plasma-Enhanced Coal Gasification**, ***S.J. Yoo***, National Fusion Research Institute, Republic of Korea **INVITED**

National Fusion Research Institute (NFRI) is a unique national laboratory dedicated to conducting research and development of the most powerful plasma energy application, the fusion energy, in Korea: We have constructed and a fully superconducting Tokamak device named KSTAR (Korea Superconducting Tokamak Advanced Research) which is now successfully in operation, and actively involved in the world's largest joint fusion project - International Thermonuclear Experimental Reactor (ITER), in which seven countries are participating to investigate engineering feasibility of fusion power commercialization.

Besides the fusion research, the NFRI has actively developed various plasma applications related to energy harvesting such as silicon quantum dot solar cells and plasma-enhanced coal gasification.

We have challengingly developed a new fabrication method of the silicon quantum dot solar cell by using hyperthermal neutral beams which are neutral beams with an energy range of 1 ~ 100 eV and very effective tools for thin film deposition at much lower substrate temperature without plasma-induced damages. The hyperthermal neutral beams can be effectively applied to each fabrication step of the silicon quantum dot solar cells: Deposition of a silicon thin film consisting of nano-crystal silicon and amorphous silicon matrix, then selective etching of the amorphous silicon matrix by keeping only nano-crystal silicon remained in order to obtain the silicon quantum dots, thereafter dielectric barrier coating on the silicon quantum dot surface, and then repetition of the procedure until a required thickness achieved.

We also have developed a steam plasma torch driven by microwave powers of 2.45 GHz and 915 MHz for effective gasification of various hydrocarbon materials and even low grade coals which can be hardly gasified by conventional thermal gasification methods since the steam plasma torch can produce much more abundant reaction catalysts such as O*, H*, OH*, H_2O_2, and O_3 than the thermal gasification methods. And, furthermore, the microwave plasma torch has a great advantage of the system life time compared to conventional arc plasma torches for which metallic electrodes are inevitable and thus easily eroded by the reaction catalysts produced for the coal gasification.

9:00am **EN+PS-MoM3 Synthetic Fuel Processing through Plasma-Assisted CO_2 Conversion**, ***S. Welzel***, *S. Ponduri, F. Brehmer, M. Creatore, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, Netherlands

Continuously increasing green house gas emissions and forthcoming (fossil) fuel depletion has stimulated research in novel fuel processing, cleaner combustion as well as CO_2 capturing and conversion. Conventional fuel processing usually aims at producing syngas (CO/H_2) mixtures that may be further converted into value-added hydrocarbons and oxygenates ($C_xH_yO_z$). Photocatalytic CO_2 hydrogenation is now considered as alternative approach which would simultaneously lead to a global green carbon cycle. It could reduce atmospheric CO_2 concentrations, while at the same time provide fuels on a renewable basis that can directly be supplied to our present energy infrastructure. Since the efficiency of such an artificial photosynthesis is low, we propose the plasma-assisted hydrogenation of CO_x into hydrocarbons.

This contribution focuses on the efficiency of CO_2 depletion and selectivity of CH_4 production in a low-temperature plasma expansion. The plasma is created from mixtures of argon and hydrogen while CO_x is injected into the expansion part where the dissociation mechanism might be radical- and/or ion-driven. Results on measurements of the (steady state) gas composition obtained by mass spectrometry and mid-infrared tuneable diode laser absorption spectroscopy will be reported.

Especially under argon rich conditions, where the chemistry is mainly driven by combined charge exchange with the Ar ions and dissociative recombination, a CO yield of 50 % was achieved. CH_4 formation was particularly detected at high hydrogen admixtures. C_2H_y hydrocarbons were in most cases absent while H_2O and CO turned out to be the main stable products. The results suggest an inherent syngas step during the plasma-assisted conversion approach, particularly a successive hydrogenation of CO.

9:20am **EN+PS-MoM4 Effective Light Trapping for Crystalline Silicon Solar Cells by Plasma Texturing**, *F.M.M. Souren*, Eindhoven University of Technology, Netherlands, ***J. Rentsch***, Fraunhofer Institute for Solar Energy Systems (ISE), Germany, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Currently, in the photovoltaic (PV) industry, wet chemistry based etching is used for saw damage removal and surface texturing. It is known that plasma based dry etching leads to an improved light trapping on multi-crystalline silicon material and, therefore, it has the potential to increase the solar cell efficiency. However, up to now plasma based texturing has not been implemented in the PV industry, because of the very low etch rate (<1 µm/min) and the high cost of ownership. In this study, different front surface textures obtained by means of the Linear Microwave Plasma (LMP, commercialized by Roth&Rau) technique and the high rate Expanding Thermal Plasma (ETP, commercialized by OTB-Solar) technique, are investigated to reduce the overall reflection losses of mono-crystalline silicon solar cells and compared to KOH/IPA (Potassium hydroxide/Isopropanol) which is the standard process in solar cell manufacturing industry. The created textures employing the different etching techniques are characterized by reflectometry (250-1200 nm) to determine the weighted reflection and by Atomic Force Microscopy (AFM) to measure the surface topography so as to determine statistical roughness parameters. We have found that the average scatter angle, determined from the AFM measurements, shows a clear correlation to the measured weighted reflection. Effective light trapping has been obtained for two typical textures based on the described etching techniques. A texture which leads to a successive hit of the incident light ray towards the solar cell surface, can result in effective light trapping, as for example, the KOH/IPA process which creates a pyramidal texture. Efficient light trapping can also be obtained by the creation of a diffuse front surface (resembles the topography of "black silicon"), as for example by using the LMP technique, under the conditions used, which creates micro roughness. This micro roughness can be described as an effective medium with a refractive index between air and silicon and a typical thickness of up to (60±10) nm [1]. The micro roughness leads to an effective light trapping of a broad range of wavelengths from 250 nm up to 1200 nm. The light trapping of the wafer etched by the ETP technique is smaller than the as cut wafer and can be explained by a smaller average scatter angle compared to the as cut wafer. A short post treatment of the ETP textured wafer by the LMP technique, creates a diffuse front surface and results, therefore, in an improved light trapping. Moreover this combination shows great promise for a cost-effective approach towards plasma based texturing.

[1] R.B. Stephens and G.D. Cody, Thin Solid Films 45 (1977) 19.

9:40am **EN+PS-MoM5 RF-PECVD Processes Excited by Asymmetric Voltage Waveforms**, ***P.-A. Delattre***, *S. Pouliquen*, Laboratoire de Physique des Plasmas, France, *E.V. Johnson*, Laboratory of Physics of Interfaces and Thin Films, France, *J.-P. Booth*, Laboratoire de Physique des Plasmas, France

Voltage Waveform Tailoring (VWT) is a promising new technique for Radio-Frequency (RF) process plasma excitation. It is known that asymmetric waveforms resembling *peaks* (short positive and long negative voltage) or *valleys* (long positive, short negative voltage) can produce a voltage self-bias, even in a symmetrical reactor [1], known as the Electrical Asymmetry Effect (EAE). We have implemented a system to provide such voltage waveforms on the RF electrode of our Capacitively Coupled Plasma (CCP) reactor. For a peak to peak voltage (V_{PP}) of 300 V, we can control the self-bias from -190 V to 15 V, without changing any other process parameter. A new differential RF probe gives us the real-time current and voltage derivatives, and therefore, the instantaneous power. For a voltage waveform composed of a 15 MHz fundamental and three harmonics, instantaneous power changes from +1 kW to –1kW in 10 ns. Using a hairpin resonator probe in hydrogen at 13 Pa, we have measured an electron density of 2E8 cm^{-3} with a standard sine waveform, 2E9 cm^{-3} with a valleys waveform and 2E10 cm^{-3} with a peaks waveform (all with V_{PP}= 300V). With a view towards photovoltaic applications, using a gas mixture of 4 % of SiH_4 in H_2 at 65 Pa, we have achieved a deposition rate of high-quality amorphous silicon of 1 Å/s for sine, 2.7 Å/s for valleys, and 3.8 Å/s for peaks voltage waveforms.

[1]Brian G Heil *et al* 2008 *J. Phys. D: Appl. Phys.* **41** 165202

10:00am **EN+PS-MoM6 Spontaneous and High Rate Synthesis of Nanocrystalline Silicon by Expanding Thermal Plasma**, ***İ. Doğan***, *NJ. Kramer, M.A. Verheijen,* Eindhoven University of Technology, Netherlands, *K. Dohnalova, T. Gregorkiewicz,* University of Amsterdam, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Silicon nanocrystals (Si-NCs) draw attention since they exhibit size dependent luminescence, improved charge storing capacity and increased surface reactivity. For instance, the size dependent optical properties of Si-NCs show great promise for increasing the efficiency of solar cells. Si-NCs could be used as spectrum down converters by converting the excess energy of a hot photon to generate multiple exciton pairs. For successful applications, the main issues on Si-NC synthesis are size control and surface engineering for improved optical properties, and high throughput. Among these points, the amount of throughput is highly critical for large scale applications however, it is not possible to achieve with current production techniques. Our research goal is to show that it is possible to fulfill these demands with a novel route by using the remote expanding thermal plasma (ETP) technique. Synthesis of Si-NCs in a remote Ar/SiH_4 plasma occurs by means of a reaction sequence of ion-SiH_4 charge exchange and subsequent addition of SiH_4 molecules. This realizes spontaneous and nearly complete conversion of SiH_4 into Si-NCs with very high throughputs of about 25mg/min, the fastest deposition rate reported in the literature so far. Moreover, ETP has the freedom of tuning the size of the Si-NCs by controlling the flow rates of SiH_4 and Ar, i.e. the residence time in the plasma. Synthesized Si-NCs have a bimodal distribution of small (4-7nm) and large (50-80nm) sizes as confirmed by TEM, which is a consequence of the plasma expansion and reactor geometry. Bimodality has been analyzed with Raman spectroscopy by studying the asymmetry and shift in the transverse optical vibration mode of bulk-Si at 521cm^{-1}. Photoluminescence spectroscopy confirms the presence of monodisperse size distribution of small Si-NCs (4-7nm) leading to luminescence in the region 600-900nm. Observation of luminescence illustrates the quality of the nanocrystal surface passivated by the rapid native oxidation. Preliminary results show separation of the bimodal distribution can be controlled by means of geometrical isolation of the regions, in which small and large particles are formed.

10:40am **EN+PS-MoM8 SiH_4 and SiF_4 Dissociation in Matrix Distributed ECR Sources, and Potential for High Deposition Rate of Thin Film Silicon Alloys**, ***S. Kasouit,*** Total S.A, France, *P. Bulkin, P. Roca i Cabarrocas*, LPICM, France

Depositing at high rates and on ever larger areas are important objectives for the reduction of thin film silicon modules costs. High deposition rates have been achieved so far using different plasma sources but uniformity over large areas is still problematic. Matrix distributed electron cyclotron resonance (MDECR) systems consist of individual ECR plasma sources, which can be arranged in arrays with virtually no size limitations. Deposition rate of silicon alloys exceeding 10 nm/s, has been demonstrated, but little is known so far about the precursors' dissociation and species fluxes onto the surface.

We study here the dissociation of Silicon film precursors, using optical emission spectroscopy and quadrupole mass spectrometry, both in the plasma phase and in the fore line. We correlate the dissociation on the one hand to the electron density and temperature measured using Langmuir probes and microwave interferometry, and to film growth rate and structure on the other.

It is found that more than 90% of SiH4 is used across a wide range of microwave powers, with a small dependence on gas residence time and pressure. Deposition rate depends primarily on the total flow of SiH4, and values above 3 nm/s are easily obtained. Transition from amorphous to microcrystalline silicon growth, on the other hand, occurs at high powers, and correlates to the electronic temperature and the high H/Si ratio observed in the gas phase. Direct dissociation of SiH4 by electron impact, followed by deposition from atomic Si and subsequent crystallization by hydrogen is therefore a satisfactory explanation.

On the contrary, for deposition from SiF4 , consumption is found to be lower than 60%, and independent of the gas residence time and microwave power. The deposition rate is also much lower, on the order of 0.3 nm/s. SiF4 consumption increases with the total hydrogen flow rate added to the mixture. The total concentration of atomic Si in the gas phase varies linearly with the product of SiF and H species, estimated by actinometry, suggesting fluorine abstraction by hydrogen as a possible mechanism. Deposition rate is also proportional to the Si content in the plasma phase and increases with the hydrogen flow rate added to the plasma. We propose that film growth from MDECR plasmas of SiF4/H2 mixtures occurs through the deposition of atomic silicon, obtained from hydrogen abstraction of fluorine in the gas phase, direct electron impact dissociation of SiF4 playing a smaller role.

This illustrates the importance of gas phase reaction for achieving high deposition rates, even in the case of high density low pressure plasma sources.

11:00am **EN+PS-MoM9 The Effects of Showerhead Hole Structure on the Deposition of uc-Si:H Thin Films by VHF PECVD**, ***S.-S. Wi,*** *Y.-G. Kim, H.-J. Lee,* Pusan National University, Republic of Korea, *D. Kim, D. Hwang, W.S. Chang*, LG Electronics, Republic of Korea

We presents the characteristics of hydrogenated microcrystalline silicon thin films deposited from SiH_4/H_2 in 40 MHz plasma enhanced chemical vapor deposition (PECVD)equipped with multi-hole-array showerhead. The effects of hole array structure are analyzed in terms of their diameter and depth. Cross dependences between the hole structure and process parameters, such as SiH_4 concentration, rf power, pressure, substrate temperature and total gas flow rate, are also investigated. The results show that deposition rate is not a strong function of hole structure compared with other process parameters. However, it is found that uniformity can be controlled by varying the surface density of hole array. With decreasing total flow rate, faster increase in deposition rate is found at the multi-hole array compared with flat electrode. This may be attributed to the high electron density and longer residence time of within the holes. It is demonstrate that the multi hole array electrode can be used as an effective control variable for optimization of Si thin film solar cell PECVD process.

11:20am **EN+PS-MoM10 Plasma-Enhanced CVD and ALD Prepared Nanolayers for High-Efficiency Solar Cell Manufacturing**, ***W.M.M. Kessels***, Eindhoven University of Technology, the Netherlands **INVITED**

Photovoltaics has become a very innovative field of research and manufacturing due to the continuous improvement in the solar cell cost/performance ratio and its tremendous growth opportunities (past average annual growth rate of 40%). Several innovations with respect to the improvement of the cell efficiency lie in the field of thin film technology, not only for thin-film solar cells but also for crystalline silicon solar cells which are currently still dominating the market (87% market share in 2010). One particular trend is the application of ultrathin films or "functional nanolayers" for solar cell interface engineering. In crystalline silicon technology these nanolayers have as a main application the reduction of charge carrier recombination at interfaces through "surface passivation". Plasma-based deposition processes such as plasma-enhanced chemical vapor deposition (CVD) are key for the preparation of such films and recently the interest also shifted to (plasma-enhanced) atomic layer deposition (ALD) processes due to their precise growth control and their excellent uniformity and conformality [1]. Moreover, ultrathin films of < 10 nm have been found feasible in terms of reaching very-well passivated surfaces. In this contribution, the application of ultrathin films of various materials such as a-Si:H, a-SiN_x:H, SiO_2, and in particular Al_2O_3 will be addressed. The preparation methods will be described as well as the relevant surface reaction mechanisms during the film synthesis. Passivation and solar cell results will be presented with a main emphasis on the key mechanisms underlying the good passivation performance of the ultrathin films. Also the market feasibility of new ALD technologies, e.g., in terms of high throughput processing, will be addressed.

[1] Atomic layer deposition: prospects for solar cell manufacturing, W.M.M. Kessels, et al., Proc. 33rd IEEE Photovoltaic Specialist Conference, San Diego, U.S.A. (2008).

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