

Thursday Afternoon, November 13, 2014

Plasma Science and Technology

Room: 305 - Session PS-ThA

Plasma Processing of Nanoparticles and Nanomaterials

Moderator: Mohan Sankaran, Case Western Reserve University

2:20pm **PS-ThA1 Raman Spectroscopy as Diagnostics for Size Distribution and Surface Chemistry of Remote Plasma Synthesized Silicon Nanocrystals**, *I. Dogan*, Eindhoven University of Technology, Netherlands, *R. Gresback*, *T. Nozaki*, Tokyo Institute of Technology, Japan, *Mauritius C.M. van de Sanden*, Dutch Institute for Fundamental Energy Research (DIFFER), Netherlands

The possibility to realize advanced photon management in solar cells and ultrahigh capacity charge storage in Li-ion batteries with silicon nanocrystals (Si-NCs) have boosted the interest on them, thanks to their size dependent optical properties and surface reactivity. To promote the use of these properties of Si-NCs in solar cells and batteries in an optimized manner, particle size control and surface engineering are the critical requirements. Therefore, accurate analysis of the size distribution is essential to optimize the process parameters to reach an ultimate control on nanocrystal size, which raises the requirement of a suitable diagnosis and post-analysis route. The analysis technique to be used is expected to provide quantitative data of size and morphology related features in a fast and non-destructive manner. Common techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence spectroscopy (PL) are time consuming and only provide qualitative data of the size distribution especially when the Si-NC size distribution is not monodisperse, which is hardly achievable in most of the nanocrystal processing tools. Thus, these techniques are far from being considered as ideal tools for effective size analysis. Our aim in this work is to demonstrate that, Si-NCs with multimodal size distributions can be quantitatively analysed in a fast and non-destructive way by using Raman spectroscopy (RS). Free standing densely packed Si-NCs are synthesized in Ar/SiH₄ and Ar/SiCl₄ gas mixtures by using a remote expanding thermal plasma and a ultra-high frequency non-thermal plasma. Synthesized Si-NCs have a multimodal size distribution with peak sizes of 5 nm and 70 nm, respectively. Experimental Raman spectra are deconvoluted for separate analysis of the sub-distributions by using the size dependent phonon confinement model. Comparison of the extracted size distributions with the distributions obtained from TEM and PL show that RS provides highly reliable, quantitative information of size distribution and volume fraction. Analysis of the surface chemistry of Si-NCs is performed by depositing a monolayer of Si-NCs on a 10 nm thick Ag. Using a 514 nm laser enhances the Raman signal by two orders of magnitude, which reveals the presence of Si-H_x, Si-O_x and Si-Cl_x bonds on Si-NC surface. In addition, disappearance of Si-H_x signal with oxidation is observed. With this observation, we show that, Raman spectroscopy can be used for probing the surface chemistry of Si-NCs. These results propose that Raman spectroscopy has the potential to become a standard diagnostic tool for the size and surface chemistry analysis of Si-NCs.

2:40pm **PS-ThA2 High Rate Production of Silicon Nanoparticles Through a Microwave Torch Production Process**, *David Oakes*, *M.A. Costolo*, *J.D. Lennhoff*, Physical Sciences Inc.

Nanometer sized aluminum particles are currently utilized as an energetic additive in propellant, pyrogen, and explosives formulations. Nano-silicon is potentially an attractive replacement for nano-aluminum in these applications since it has a similar energy density while being less sensitive, and thus safer to handle. In addition silicon forms a thin passivation layer which makes it a stable additive compared to aluminum which can oxidize in-depth. Incorporating nano-silicon into energetic formulations is currently limited by the high cost of the material which is generally formed in low production rate, batch processes.

This paper describes the development of a scalable, continuous (non-batch) high production rate method for nano-silicon utilizing a microwave driven plasma torch-based process. Silane (SiH₄) is injected near the throat of the supersonic output nozzle of the torch where it dissociates in the near atmospheric pressure nitrogen plasma formed by the microwave discharge. The local gas temperature in the torch plenum is approximately 2800 K which is sufficient to produce greater than 0.9 moles of silicon atoms for each mole of SiH₄ (>90% efficiency). The resulting silicon atom rich gas is rapidly quenched (~2x10⁸ K/s) in a supersonic expansion into a vacuum chamber (~50 torr) producing the seed particles that then grow to 10 – 20 nm in approximately 0.1 ms. The process meets the criteria specified by

Kodas and Frielander for producing monodisperse particles in a flow reactor by namely: 1) Separating seed particle production in the supersonic expansion from subsequent growth of the seeds downstream of the nozzle, 2) Providing a flat velocity profile in the growth region enabling a uniform residence time for the particles in the growth region, and 3) Utilizing a high velocity jet which results in a short residence time in the growth region to minimize particle agglomeration.

Growth conditions will be described that produce 6 g/min of 10 -20 nm diameter silicon particles with a 140 m²/g surface area from a 2 kW microwave discharge. Material analysis will be described including SEM and TEM to assess the particle morphology and size distribution, single point and BET surface area measurements, and EDX, differential scanning calorimetry, and electrochemical performance to assess purity and energetic characteristics of the material. Future efforts will extend the growth region of the process to enable larger particle sizes and scale up the microwave system to 5 kW to enable 15 – 30 g/min production rates.

3:00pm **PS-ThA3 Plasma-Produced Nanomaterials for Energy Recovery and Storage**, *Lorenzo Mangolini*, University of California, Riverside **INVITED**

Despite being heavily utilized in industry, the unique capabilities of non-thermal plasmas with respect of materials processing have yet to be fully realized. In this talk we will describe our effort in understanding the nucleation and growth of silicon nanoparticles in non-thermal plasmas and we will discuss their application for energy-related applications.

Several research groups have focused on nanoparticle nucleation and growth in silane-containing plasmas. Yet a clear understanding of the correlation between plasma parameters and the properties of silicon particles is missing. There is no theory explaining how a non-thermal process can produce nanocrystals of a material with a relatively high melting point within few milliseconds of reaction time. We have performed *in-situ* FTIR measurements and aerodynamically extracted particles along the length of a flow-through reactor similar to the one described in [1], and have found that silane is rapidly consumed and converted into amorphous particles with size close to their final one. Crystallization takes place after the precursor is fully consumed and within few milliseconds. An independent measurement of the crystallization rate of small silicon particles [2] suggests that their crystallization kinetics exceeds that of bulk amorphous silicon films. Despite this the current models describing the plasma-nanoparticle interaction [3,4] cannot justify the substantial heating necessary to achieve crystallization in such short time. Results from our ongoing efforts in this area will be presented.

By leveraging the processing capabilities of non-thermal plasmas it is possible to provide improvements in the performance of devices that are relevant for energy-related applications. By sintering plasma-produced nanocrystals it is possible to fabricate bulk samples with precise control of grain size and grain size distribution. These samples show some of the lowest thermal conductivities ever reported for the case of bulk nanostructured silicon. This is a promising step towards the development of highly efficient waste-heat recovering devices that do not require alloying with expensive materials such as germanium. Furthermore, plasma-produced silicon particles can also be integrated into anodes for lithium-ion batteries. Their excellent dispersibility into polymer matrices allows achieving stable operation over hundreds of charge-discharge cycles.

[1] L. Mangolini et al., Nano Letters 5 (2005) 655.

[2] T. Lopez and L. Mangolini, Nanoscale 6 (2014) 1286.

[3] L. Mangolini and U. Kortshagen, Physical Review E 79 (2009) 026405.

[4] N. J. Kramer et al., Journal of Physics D: Applied Physics 47 (2014) 075202.

4:00pm **PS-ThA6 Atmospheric-Pressure Microplasma Synthesis of Colloidal Metal Nanoparticles**, *Caroline De Vos*, *J. Baneton*, *J. Dille*, *S. Godet*, Université libre de Bruxelles, Belgium, *M. Sankaran*, Case Western Reserve University, *F.A.B. Reniers*, Université libre de Bruxelles, Belgium

Microscale plasmas are electrical discharges where at least one geometrical dimension is sub-millimetric. In consequence, they present a remarkable stability at high pressure as reducing the size of the plasma allows keeping breakdown voltages sufficiently low to avoid the glow-to-arc transition. [1] The development of non-thermal atmospheric pressure microplasmas facilitates the coupling with the liquid phase and offers new potential applications in water treatment, medicine and material synthesis. [2]

This study focuses on the synthesis of silver and gold nanoparticles in aqueous solution. The plasma, supplied with argon, is initiated at the surface of silver nitrate or chloroauric acid solution. The electrons from the discharge lead to electrochemical reactions and reduction of the metal

cations. Different stabilizers such as polyvinyl alcohol and sodium dodecyl sulfate are mixed with the solution to prevent uncontrolled particle growth.

X-ray photoelectron spectroscopy (XPS) spectra exhibit the metallic nature of the Ag and Au nanoparticles and particles growth is monitored by ultraviolet-visible absorbance spectroscopy. The two plasmon bands, characteristic of spherical Ag and Au nanoparticles, can be observed at 415 and 530 nm respectively. The morphology and the size of as-grown colloidal metal nanoparticles are evaluated by transmission electron microscopy (TEM). For silver nanoparticles, the average size rises from 10 to 20 nm when the discharge current increases from 2 to 5 mA. Moreover, bigger nanoparticles are observed at higher concentration and reaction times. For gold experiments, particles about 10 nm in diameter are synthesized at higher current than for silver experiments. Lower precursor concentration is necessary to avoid aggregates formation. In both cases, particles below 20 nm are spherical whereas at larger diameters, various shapes such as triangle, hexagon, appear.

In the project continuity, a comparison of the reduction mechanisms is performed for the two studied metals. At first, the proportion of reduced metal cations is quantified by potentiometric analyzes. Thereafter, the active species involved in the reduction process (e.g., H_2O_2 , electrons) are discriminated. Finally, a bimetallic synthesis is studied to help the comprehension of the fundamental mechanisms. Indeed, metal ratio and alloy formation provide information about the reduction kinetic of both metals.

This work is supported by PSI-IAP 7 (plasma surface interactions) from the Belgian Federal Government BELSPO agency.

References

- [1] D. Mariotti, Appl. Phys. Lett. **92** (2008) 151505.
[2] D. Mariotti, R. M. Sankaran, J. of Phys. D: Appl. Phys. **44** (2011), 174023.

4:20pm PS-ThA7 Gas Chromatography and Mass Spectrometry Characterization of Nanoparticle-Producing Atmospheric-Pressure Microplasmas, Jonathan Cole, R.M. Sankaran, Case Western Reserve University

Plasma processes are becoming increasingly important for the production of nanoparticles by homogeneous nucleation.^{1,2} The high-purity conditions that have made plasmas essential for thin film etching and deposition in the semiconductor industry similarly allow nanoparticles to be synthesized without organic stabilizers or other types of contaminants. In addition, high temperature and/or pressure materials such as silicon and diamond can be produced in plasmas because of non-equilibrium conditions. A novel class of plasmas for nanoparticle synthesis is microplasmas. Microplasmas operate stably at atmospheric pressure as a result of pd scaling (p being the gas pressure and d the electrode gap), eliminating the need for vacuum infrastructure. In addition, particle nucleation, growth, and agglomeration are controlled by the rapid quenching that results from the small volume and flow-through geometry.

Here, we present gas chromatography and mass spectrometry measurements of atmospheric-pressure microplasmas with reaction chemistries relevant to nanoparticle synthesis by homogeneous nucleation. We focus on two different gas chemistries that are used to produce nanoparticles: 1) metal-organic vapors that allow the synthesis of metal nanoparticles, such as Ni and Fe, and 2) hydrocarbon gases that allow the synthesis of carbon nanoparticles, including nanodiamonds. Measurements are performed on the effluent at the exit of the microplasma. To sample gases at high pressure (>1 atmosphere), we have built a mass spectrometry system consisting of an open ion source, quadrupole trap, 1-300 AMU detection range RGA (Dycor Technologies, Ltd.) and capillary inlet. The gas chromatography system (Shimadzu, Inc.) is equipped with a recently developed barrier ionization discharge detector, which is capable of universal detection of molecular gases with sensitivity at the ppm and ppb levels. The results are thus comprehensive, but restricted to the neutral vapor or gas molecule reaction products because of the high sampling pressure. Important insight is nonetheless obtained about reactant conversion, gas product selectivity, process efficiency, and influence of plasma characteristics. The gas chemistry studies are complemented by optical emission spectroscopy (Ocean Optics, Inc.) and scanning mobility particle sizer spectrometry (TSI, Inc.) of the nanoparticle aerosol. Materials analysis of collected product by high resolution transmission electron microscopy is also carried out in support of the in situ measurements.

References

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U. Kortshagen, J. Phys. D **42**, 113001 (2009).
2D. Mariotti and R. M. Sankaran, J. Phys. D **43**, 3223001 (2010).

4:40pm PS-ThA8 Top-down InGaAs/GaAs Nanopillars Fabrication using a Bio-Nano-Process and a Neutral Beam Etching Process, Cédric Thomas, K. Yoshikawa, C.Y. Lee, Y. Tamura, A. Higo, Tohoku University, Japan, T. Kiba, A. Murayama, Hokkaido University, Japan, I. Yamashita, Nara Institute of Science and Technology, Japan, S. Samukawa, Tohoku University, Japan

Quantum dot (QD) lasers have been extensively studied in the last few decades due to their device characteristics benefits. However, fabrication of a high density and uniform two-dimensional array of QDs is still a high challenge. We have developed a damage-free top-down process for creating InGaAs QDs by combining a high-density bio-template [1] and a neutral beam (NB) etching process [2]. The bio-nano process consists of a high-density (up to $7 \times 10^{11} \text{ cm}^{-2}$), two-dimensional array of cage-shaped proteins called ferritins with encapsulated metal oxide nanoparticles (NPs). Ferritins can be functionalized with polyethylene glycol (PEG) to control distance between them and avoid QDs in-plane coupling. After removal of the protein shell, 7 nm in diameter iron oxide NPs were used as etching masks. The NB etching consists of an inductively coupled plasma chamber separated from the process chamber by a carbon electrode with a high-aspect-ratio aperture array. As a result, the charged particles are efficiently neutralized whereas almost no UV photons can reach the sample.

A self-assembled monolayer of PEG-ferritins was formed by spin coating on a GaAs cap surface with native oxide. Samples grown by metalorganic vapor phase epitaxy (MOVPE) with the following structure were used: 10-nm-thick GaAs cap, three 8-nm-thick $\text{In}_{0.24}\text{Ga}_{0.76}\text{As}$ active layers separated by two 20-nm-thick GaAs barrier layers on top of a semi-insulating substrate. A low-temperature oxygen annealing in vacuum was used to remove protein shell and form etching mask with the iron oxide cores. Subsequently, a hydrogen radical treatment was performed during 30 min at 350°C to remove native oxide, followed by hydrogen passivation at room temperature. Nanopillars were etched by neutral beam etching process with a mixture of argon and chlorine. Substrate temperature, neutrals energy and mixture ratio were investigated to find the optimized conditions in term of etching profile and nanopillars density. It has been found that a mixture ratio of $\text{Ar}:\text{Cl}_2 = 27:73$ with a substrate temperature of 50°C were the best conditions to obtain high-density and anisotropic nanopillars, with diameters about 20 nm and height about 80 nm. After regrowth of the GaAs barrier layer by MOVPE, photoluminescence was observed. PL emission from InGaAs QDs could be detected. The results showed that III-V compound QDs can be realized by this damage free top-down nanoproces.

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[2] S. Samukawa et al., Jpn J. Appl. Phys. **40** (2001) L997

5:00pm PS-ThA9 Nanostructuring of Metal Surfaces by Low Energy He Ions, Irem Tanyeli, FOM Institute DIFFER, Netherlands, L. Marot, University of Basel, Switzerland, M.C.M. van de Sanden, FOM institute DIFFER, Netherlands, G. de Temmerman, ITER Organization, Netherlands

The effect of low energy (<50 eV) helium ion irradiation on surface modifications of metals has been studied [1,2]. The most pronounced works have been done on tungsten and molybdenum surfaces [2]. Nanostructure formation on these surfaces by high fluxes of low energy helium ions is identified as a self-growth process of He bubbles. In this study, we provide a size-controlled nanostructure formation by surface temperature and plasma exposure time on iron surfaces consistently with the experiments on tungsten and molybdenum. Besides, various metal surfaces such as titanium, aluminum and copper are irradiated by low energy He ions. We investigated the behavior of these surfaces under the He ion irradiation as a function of surface temperature, plasma exposure time and He ion flux. Different surface morphologies are observed for these metals. Nanostructure growth kinetics shows dependency on surface temperature and plasma exposure time. It has been shown that the nanostructured surfaces present high surface area and hence high light absorption [3]. The photo-catalytic activity of our metal surfaces will be presented.

- [1] K. Tokunaga, et al., J. Nucl. Mater. **337–339**, 887 (2005).
[2] G. De Temmerman, et al., JVSTA, **30** (2012).
[3] S. Kajita, et al., Appl. Phys. Express., **3** (2011).

5:20pm PS-ThA10 Nucleation of Microcrystalline Silicon Thin Films on Nano-Imprint Textured Substrates, Jurgen Palmans, T. Faraz, W.M.M. Kessels, M. Creatore, Eindhoven University of Technology, Netherlands

Hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) is important in thin-film silicon solar technology where it is combined with amorphous silicon (*a-Si:H*) in tandem cells for enhanced light absorption. However, efficient light absorption requires thick (>1 μm) $\mu\text{c-Si:H}$ films compared to thin *a-Si:H* (~350 nm). Since reduced absorber thickness is desired, the potential of light management, typically induced by texture-etched transparent conductive oxides (TCO), has been explored, demonstrating a strong

dependence of absorber layer quality on TCO chemical nature and morphology. Generally, electrical, optical and structural properties require optimization. Due to parameter interdependence, nano-imprint lithography (NIL) was introduced to decouple electrical/optical and structural properties by inducing texture on glass prior to TCO deposition, allowing independent optimization of light diffraction and electrical/optical requirements. The potential of NIL textures has been demonstrated in this respect. However, such novel morphologies (periodic/random) impact absorber layer quality. Therefore, the nucleation of *uc*-Si:H thin films (~100 nm), deposited under high power-high pressure conditions in a capacitively coupled plasma reactor, has been studied on various NIL textured substrates. To replicate a solar cell structure, NIL textured and flat glass have been coated with ~500 nm magnetron sputtered aluminum doped zinc oxide (AZO). Characterization through Raman spectroscopy and crystal grain analysis has been performed. For flat glass, the crystalline volume fraction (X_c) increased a factor 2 upon AZO addition joined by a narrower phase transition. This was related to a different microstructure evolution. Introducing a NIL texture increased nucleation delay on randomly textured compared to periodically textured substrates. Since nucleation depends on process conditions, i.e. silane flow rate (Φ_{SiH_4}), the role of ions and radicals is considered a determining factor. A reduced Φ_{SiH_4} enhances the ion-to-growth flux ratio and ion energy, promoting surface diffusion^[1]. However, on rough morphologies the ion contribution per unit area is reduced, therefore reducing X_c on NIL substrates. When shifting to the phase transition, preferential etching of *a*-Si:H by atomic hydrogen dominates while the ion contribution is reduced. This is confirmed by the microstructure parameter (R^*) experiencing a transition from void-rich to (di)vacancy-dominated films. Furthermore, a direct correlation of R^* and X_c was obtained. The insights obtained as such directly impact process control when dealing with challenging morphologies.

^[1] J. Palmans *et al.*, *J. Phys. D: Appl. Phys.* **47** (2014)

5:40pm **PS-ThA11 Synthesis of AZO Film on Polymer by Nano-Process Control with Confined Magnetic Field Sputtering**, *J.G. Han*, NU-SKKU Joint Institute for Plasma-Nano Materials, Republic of Korea, *Subong Jin*, *B.B. Sahu*, *J.B. Kim*, NU-SKKU Joint institute for plasma nano materials, Republic of Korea, *K. Takeda*, *M. Hori*, Plasma Nanotechnology Research Center, Japan

Al doped ZnO(AZO) film has been attracting as one of promising candidate film replacing ITO film for transparent conductive oxide film of next generation flexible digital electronics devices. The relatively low resistivity and transparency of AZO film deposited at low temperature are still hurdles to overcome for replacing ITO film even though its unique advantages in low cost and high toughness over those of ITO film. It is well known that resistivity is closely associated with carrier concentration and mobility which are controlled by stoichiometry, binding energy of atoms and lattice defects of film including oxygen vacancy as well as Al replacement in Zn atom sites.

The control of those atomistic structure and lattice defects is affected by surface energy accumulated with atoms and molecules deposited at top surface layer during film nucleation and growth depending on process parameters during deposition process. The surface energy is mostly comprised of kinetic energy of neutrals, electronic energy of activated neutral molecule and atoms and ions as well as flux density. We have investigated effect of those atomic and molecular level energy analysis on structure formation and related electrical property changes by in-situ diagnostics during sputtering process under confirmal confined magnetic field. The kinetic energy and flux of sputtered atoms are controlled by independent variation of power density for direct sputtering and in-direct sputtering targets on polymer substrate at low temperature below 100 C. Optical emission spectroscopy and radical diagnostics as well as Langmuir probe analysis have been performed to measure plasma parameters. Carrier concentration and mobility have been analyzed depending on microstructure changes including binding energy of atoms and Al replacement of Zn site etc.. The resistivity is significantly reduced with atomic level nano process control and can be reached less than 4E-4 at low temperature.

This paper discusses on fundamental mechanism of film nucleation and growth with top surface energy accumulation with atomic and molecular energy diagnostics for AZO film synthesis by magnetron sputtering, and then illustrate control of resistivity associated with control of carrier concentration and mobility.

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