

Plasma Science and Technology

Room: 102 B - Session PS+AS+NS+SS-ThM

Plasma Synthesis of Nanostructures

Moderator: R.M. Sankaran, Case Western Reserve University

8:00am **PS+AS+NS+SS-ThM1 Nanoscale Interface Engineering of Silicon Nanocrystals by Non-equilibrium Microplasma**, V. Svrcek, Advanced Industrial Science and Technology (AIST), Japan **INVITED** Silicon nanocrystals (Si-ncs) created vast interests and Si-ncs interfaces are at the basis of application in water splitting, for bio-imaging and may open up great opportunities for the development of most advanced technologies. For instance, in photovoltaic community enormous interests is mainly due to their enhanced multiple exciton characteristics. The fundamental aspects of exciton dissociation are highly important to improve the efficiency of solar cells and therefore the employment of Si-ncs in a range of applications requires careful investigation on the surface conditions. Indeed, the interplay of quantum confinement with surface effects reveals a complex scenario, which can strongly affect of Si-ncs properties and prediction of their corresponding behaviour. In this context, a variety of carefully surface-engineered Si-ncs are highly desirable both for understanding of Si-ncs photo-physics and for their successful integration in application devices. Surface surfactant free functionalization techniques that can assess the functionalities of the Si-ncs interface need to be developed so that efficient charge transport and excitons dissociation could be achieved. In this talk we firstly highlight a selection of theoretical efforts and experimental surface engineering approaches. Secondly we present our results on surfactant free surface engineering of Si-ncs, which have utilized novel microplasma-liquid interactions. The possibilities of surface engineering and tuning overall Si-ncs properties by two independent techniques will be pointed out. Particularly, we will show that the atmospheric pressure RF and DC microplasmas in liquid media offer a wide range of opportunities for Si-ncs surface engineering due to multiple mechanisms induced by the microplasma process and more efficient electron driven non-equilibrium liquid chemistry. The flexibility and results on superior capabilities of the microplasma-based surface engineering approach will be presented. Then, an influence of Si-ncs surface engineering on photovoltaic based devices and the possibilities of enhancement optical density and role of Si-ncs surface engineering on integration within nanotubes will be shown. Finally the potential for scaled-up to achieve large scale surface engineering as would be required for industrial applications will be discussed as well.

8:40am **PS+AS+NS+SS-ThM3 Single Step Plasma Synthesis of Core-shell Group IV Nanoparticles**, R.P. Chaukulkar*, Colorado School of Mines, K. de Peuter, Eindhoven University of Technology, Netherlands, P. Stradins, National Renewable Energy Laboratory, S. Agarwal, Colorado School of Mines

There has been an increased interest in group IV nanoparticles (NPs) for a variety of applications including photovoltaics, lithium ion batteries, and bio-imaging. The properties of these quantum-confined NPs are governed by their size as well as the surface passivating layer. Si NPs, 3-7 nm in size, were synthesized in a tubular, capacitively-coupled, radio-frequency SiH₄/Ar plasma at pressures ranging from 5-8 Torr. The H-terminated surface of the as-synthesized Si NPs is highly reactive, and requires surface passivation to prevent oxidation. We have developed a single-step synthesis and in-flight surface passivation technique wherein we use a dual-plasma setup, which consists of a second capacitively-coupled C₂H₂ plasma, downstream from the SiH₄/Ar synthesis plasma. The Si NPs can be coated with amorphous carbon (a-C) to obtain core-shell nanostructures, with a thin SiC interface between Si and a-C. These core-shell NPs are transported by flow into a surface analysis chamber, which is equipped with *in situ* attenuated total reflection Fourier transform infrared and photoluminescence spectroscopy setups to determine the surface composition and the optical band gap of the NPs, respectively. The NPs are also extensively characterized using *ex situ* x-ray diffraction, Raman spectroscopy, and transmission electron microscopy (TEM). The thickness of the coating, determined from TEM, is ~2-4 nm. We have also studied the effect of varying the C₂H₂ plasma parameters on the structure and composition of the a-C coating and the SiC interface. This plasma synthesis and passivation technique has been extended to other group IV NPs such as Ge and Sn, which are less likely to have a carbide interface.

9:00am **PS+AS+NS+SS-ThM4 On the Structure of Non-Thermal-Plasma Produced Nanocrystals**, T. Lopez, L. Mangolini, University of California, Riverside

The use of continuous flow non-thermal plasma reactor for the formation of silicon nanoparticles has attracted great interest because of the advantageous properties of the process [1]. Despite the short residence time in the plasma (around 10 milliseconds), a significant fraction of precursor, silane, is converted and collected in the form of nanopowder. The structure of the produced powder can be tuned between amorphous and crystalline by adjusting the power of the radio-frequency power excitation source, with high power leading to the formation of crystalline particles [2]. Numerical modelling suggests that higher excitation power results in a higher plasma density, which in turn increases the nanoparticle heating rate due to interaction between ions, free radicals, and the nanopowder suspended in the plasma [3]. An understanding of the mechanism that leads to the crystallization of the powder while in the plasma is lacking. In this work, we present an experimental investigation on the crystallization kinetic of plasma-produced amorphous powder. Silicon nanoparticles are nucleated and grown using a non-thermal plasma reactor similar to the one described in [1], but operated at low power to give amorphous nanoparticles. The particles are then extracted from the reactor and flown through a tube furnace capable of reaching temperatures up to 1000°C. Raman and TEM have been used to monitor the crystalline fraction of the material as a function of the residence time and temperature. A range of crystalline percentages can be observed from 750 °C to 830 °C. We have also used *in-situ* FTIR to monitor the role of hydrogen on the crystallization kinetic. It has been proposed that that hydrogen induced crystallization is the mechanism for deposition of microcrystalline silicon thin films in PECVD systems. We find that the plasma-produced amorphous silicon powder is rich with surface SiH_x species, but no detectable signature from bulk Si-H bonds has been observed. A discussion of particle growth and plasma-particle interaction will be presented with its relation to the overall effect on crystallization mechanisms.

1. Mangolini, L.; Thimsen, E.; Kortshagen, U., *High-yield plasma synthesis of luminescent*

silicon nanocrystals. Nano Letters **2005**, 5 (4), 655-659.

2. O. Yasar-Inceoglu, T. Lopez, E. Farshihagro, and L. Mangolini, *Silicon nanocrystal*

production through non-thermal plasma synthesis: a comparative study between silicon

tetrachloride and silane precursors. Nanotechnology, **23**(25): p. 255604.(2012)

3. Mangolini, L.; Kortshagen, U., Selective nanoparticle heating: another form of

nonequilibrium in dusty plasmas. Physical review E **2009**, 79, 026405 1-8.

9:20am **PS+AS+NS+SS-ThM5 Detection of Nanometer Scale Ni Clusters Formed in an Atmospheric Pressure DC Microplasma by Ion Mobility Spectrometry**, C.J. Hogan, University of Minnesota, A. Kumar, Case Western Reserve University, S. Kang, C. Larrriba-Andaluz, H. Ouyang, University of Minnesota, R.M. Sankaran, Case Western Reserve University

Using a high resolution differential mobility analyzer (1/2-mini DMA, Nanoengineering) coupled to a Faraday cage electrometer for ion mobility spectrometry, we have investigated the formation of Ni clusters in a DC atmospheric pressure Ar microplasma. To produce Ni clusters, nickelocene (bis(cyclopentadienyl)nickel) vapor was continuously introduced into the microplasma by sublimation of a heated solid powder into an Ar gas flow. Particles were nucleated, grown, and rapidly quenched to limit their diameter to less than ~10 nm. Prior to mobility measurement, a steady-state charge distribution of the aerosol particles was achieved via diffusion charging with background gas ions produced in a Kr-85 source (TSI, Inc.). Both positive and negative mobility distributions were measured. A background high intensity peak around ~0.75 nm equivalent "mobility diameter", corresponding to the ions produced by the Kr-85 source, was always observed. The introduction of nickelocene vapor in the microplasma resulted in a lower intensity distribution of particles, spanning from the peak corresponding to Kr-85 generated ions to 10 nm in mobility size. Under all circumstances, the mobility distribution from the ion peak to the largest produced particles was continuous, indicating the microplasma reactor can form stable Ni clusters below 2.0 nm in size. To obtain structure-mobility relationships, density functional theory and gas molecule scattering calculations were carried out. The nanoparticles were also collected by electrostatic precipitation and further characterized by atomic

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force microscopy to confirm their size and distribution. These results confirm that a continuous distribution of particles is formed in microplasma processes down to less than 1.0 nm which could have both fundamental and technological implications ranging from the study of particle formation in the vapor phase to novel applications of quantum confined materials.

9:40am **PS+AS+NS+SS-ThM6 One-step Synthesis of Gold Bimetallic Nanoparticles with Various Metal Compositions**, *M.A. Bratescu, N. Saito*, Nagoya University, Japan

In our group, Solution Plasma Processing (SPP) is a useful and simple method for metal NPs (nanoparticles) synthesis [1, 2]. In the present work, we demonstrate a special merit of the SPP method for the fabrication of bimetallic NPs using a combination of the reduction reaction of the metal (M) ion to the neutral state, while simultaneously eroding the electrodes during the discharge, which generates the second metal in the structure of the bimetallic NPs [3].

The gold bimetallic NPs were synthesized by alloying gold with various types of metals, which are divided in four categories: (i) divalent *sp* metals, Zn and Cd, (ii) trivalent *sp* metals, Ga and In, (iii) *3d* metals Fe, Co, Ni, and Cu, and (iv) *4d* metals Pd and Ag. We used SPP between two gold electrodes immersed in a nitrate solution of the corresponding metal M. We studied the optical properties of the gold nanoalloys, as well as their crystallinity, composition, size and morphology, and we have evaluated the interaction of various gold bimetallic NPs with free radicals for possible consideration as catalysts. SPP characterization has been done using electrical and optical probes. We found that the properties of the gold bimetallic NPs are connected with the category to which the metal belongs. We analyzed that the amount of the intermetallic compound in the composition of the gold bimetallic NPs depends on the electrochemical potential and the electron density of the Wigner-Seitz cell. The obtained gold bimetallic NPs using one step in Solution Plasma have sizes in the range from 5 to 20 nm. The difference in electronegativity between gold and the other metal was the main reason for the formation of the intermetallic compounds found in the composition of the gold bimetallic NPs. This work was supported in part by Kakenhi, Challenging Exploratory Research, JSPS, Japan.

[1] M.A. Bratescu, et al., *J. Phys. Chem. C* 115 (2011) 24569.

[2] S.P. Cho, et al., *Nanotechnology* 22 (2011) 455701.

[3] M.A. Bratescu, et al., *J. Alloys and Compounds* 562 (2013) 74.

10:40am **PS+AS+NS+SS-ThM9 Synthesis of Platinum Nanoparticles on Carbon Powder by the Means of an RF Plasma Torch for Fuel Cells Applications**, *D. Merche, T. Dufour*, Univ. Libre de Bruxelles, Belgium, *L. Devant*, Facultés Univ. Notre Dame de la Paix, Belgium, *F. Deschamps*, Univ. de Liège, Belgium, *J.-J. Pireaux, L. Houssiau*, Facultés Univ. Notre Dame de la Paix, Belgium, *N. Job*, Univ. de Liège, Belgium, *F.A.B. Reniers*, Univ. Libre de Bruxelles, Belgium

The grafting of noble metal nanoparticles on porous carbon supports has attracted a great interest over the last few years, due to potential applications in Proton Exchange Membrane Fuel Cells (PEMFC). Plasma processes for the synthesis of such electrodes could be a major asset for the production of the fuel cell elements at lower cost.

In this study, Pt nanoparticles are synthesized from the decomposition of Platinum (II) acetylacetonate [Pt(acac)₂] and deposited on porous carbon by the means of an RF atmospheric plasma torch running with argon in an open air environment. This one single step technique is very simple, fast and robust. It also presents substantial economic advantages, such as the non requirement of a high-vacuum and the possibility to easily implement this process in a continuous production line. The Pt nanoparticles were principally grafted on carbon-black powder. Some tests were also conducted on Carbon Xerogel matrices presenting well-controlled porosity.

The organometallic-carbon powder mixture pressed on a copper tape was treated in the post-discharge of the Ar plasma torch. A kinetic study has been carried out by XPS to evaluate the optimal exposure time to the post-discharge required for synthesizing a significant amount of Pt nanoparticles. 6% of Pt was detected after only 30 seconds of plasma treatment, and 14% after 600 seconds. According to the fitting of the Pt XPS peaks, the most intense component of the Pt for the sample treated by plasma was the Pt(0). 68% of the platinum was under metallic form after 30 seconds of plasma treatment, and 78 % after 600 seconds.

The effect of the distance between the powder and the torch, and the addition of a small quantity of hydrogen to the vector gas was studied by XPS regarding the elemental composition and the oxidation state of the platinum nanoparticles. A comparison with Pt synthesized in a controlled atmosphere was also realized. For a study more focused on the PEMFC applications, the powder mixture was overlaid on a Gas Diffusion Layer

(GDL), namely Carbon Toray Paper (CTP), before being exposed to the Ar post-discharge.

The size and the dispersion of the nanoparticles grafted on carbon black powder or on carbon Xerogel were observed by a FEG-SEM and by TEM.

11:00am **PS+AS+NS+SS-ThM10 Growth of Nanocomposites on Heat-Sensitive Polymers using Cold, Dielectric Barrier Discharges at Atmospheric Pressure**, *J. Profili*, Université Paul-Sabatier, France and Université de Montreal, Canada, *N. Gherardi*, CNRS-LAPLACE, France, *L. Stafford*, Université de Montreal, Canada

Cold, atmospheric-pressure plasmas have already demonstrated their potential for homogeneous thin film deposition in polymers functionalization. In order to achieve multifunctional properties, a new challenge is the plasma-assisted deposition of nanocomposite coatings. This contribution is focused on the growth of nanocomposites based on TiO₂ nanoparticles embedded in a silica-like matrix with the objective of synthesizing barrier layers with improved resistance to UV irradiation. Experiments were carried out in a parallel plate dielectric barrier discharge with the substrate placed on the bottom electrode. The gas mixture is composed of either N₂ or He as the carrier gas, a mixture of hexamethyldisiloxane, and either nitrous oxide (for experiments in N₂) or O₂ (for experiments in He) for the growth of the SiO₂ matrix, and TiO₂ nanoparticles which are introduced by nebulizing stable colloidal solutions. Preliminary results show that TiO₂ nanoparticles can successfully be incorporated in the film. In addition, as in low-pressure plasma conditions, electrostatic forces were found to play a very important role on the transport of nanoparticles in the discharge. As a result, an appropriate tuning of the applied voltage waveform (shape, amplitude and frequency) was found to directly impact the spatial distribution of nanoparticles in the film.

11:20am **PS+AS+NS+SS-ThM11 Fabrication of Asymmetric Nanopores by Pulsed PECVD**, *S.S. Kelkar, C.A. Wolden*, Colorado School of Mines

The field of nanopore fabrication has attracted a lot of attention recently due to their potential application in DNA sequencing, ionic field effect transistors, and detection and separation of biomolecules and nanoparticles. The objective of our research is to develop a simple approach for large area fabrication of nanopores (pore size ~ 1–10 nm) with atomic level precision. In this work, we first employ relatively large template structures (~ 100–250 nm) produced by track-etching or e-beam lithography. The pore size is then refined to the desired level by deposition of material using pulsed plasma enhanced chemical vapor deposition (PECVD). Pulsed PECVD has been developed as an alternative to atomic layer deposition (ALD) to deliver self-limiting growth of oxides like alumina and silica. Pulsed PECVD has two growth components that act sequentially: ALD-like growth during the plasma off step ($\gamma \sim 0$); and PVD-like growth during the plasma on step ($\gamma \sim 1$), where γ is the reactive sticking probability. The ALD contribution is constant at ~1 Å /pulse whereas the PECVD contribution can be typically varied from 0.5 - 5 Å/pulse by appropriate control of operating conditions. The degree of conformality in pulsed PECVD can be engineered by controlling the relative contribution of these 2 growth components. As such this technique can produce novel morphologies that are distinct from those produced by conventional deposition processes. We have developed feature scale models to predict the pore closure phenomenon in pulsed PECVD. This model successfully predicts experimentally observed profiles in features such as trenches and cylinders. The model findings will enable us to determine optimal operation conditions for obtaining the desired nanopore opening and geometry. Flux experiments on nanopore-based membranes are further employed to validate the feature scale models. Such well-defined nanopores can serve as an ideal platform for rigorous evaluation of hindered transport at the nanoscale.

11:40am **PS+AS+NS+SS-ThM12 Microplasma Reduction of Metal-Organic and Metal-Polymer Films for Single-Step Fabrication of Flexible, Conductive Patterns**, *S. Ghosh, R. Yang, C.A. Zorman, P. X.-L. Feng, R.M. Sankaran*, Case Western Reserve University

In situ approaches to synthesizing metal nanoparticles from metal-organic or metal-polymer films have recently emerged as a simple and viable method to fabricating flexible, conductive patterns.^{1,2} In general, a metal precursor is mixed or reacted with an organic or monomer, cast as a film, and exposed to ultraviolet, laser, heat, or electron beam (e-beam). Recently, we have demonstrated that an atmospheric-pressure microplasma can be similarly used to initiate reduction of metal ions and formation of metal nanoparticles in polymer films.³ In this study, we present electrical characterization of the reduced lines and show that conductive patterns are achieved similar to other methods including e-beam irradiation.

Polymer films containing ionic metal precursors were prepared by first dissolving metal salts [e.g., silver nitrate (AgNO₃), palladium acetate (Pd(OAc)₂] with polymers [e.g., polyvinyl alcohol (PVA),

polymethacrylate (PMMA)] in solution. The solvent was chosen according to the metal salt-polymer system. For AgNO₃ and PVA, we used a 1:1 ratio of water:ethanol, and for Pd(OAc)₂ and PMMA, acetonitrile was used. The mixed metal-organic solutions were drop cast or spin coated onto Si substrates to form thin films (100nm~1µm thick). The films were dried in vacuum and then exposed to the microplasma process. An Ar microplasma was formed by applying DC power to a stainless steel capillary tube and the substrate holder. Patterns were generated by scanning the microplasma at constant discharge current. After exposure, the films were peeled off from the substrate and transferred to a glass substrate. The conductivity was measured using a two point probe method. The as-prepared films were also characterized by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDX) to confirm metallization (*i.e.*, reduction) over the exposed areas.

Our results show that plasma exposure leads to conductive patterns on a free-standing flexible substrate. SEM and EDX confirm the reduction of metal ions to metal nanoparticles. We have also compared these results with exposure to an e-beam. In the case of the plasma, the polymer is removed, probably due to oxidation, whereas the e-beam causes conformational changes to the polymer. The effects of annealing following exposure to increase the conductivity of the films will also be discussed.

References:

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2. S. W. Lee et al., Adv. Funct. Mater. 21, 2155-2161 (2011).
3. S. W. Lee et al., Macromolecules 45, 8201–8210 (2012).

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