12th Asia Pacific Conference on Plasma Science and Technology

including

27th Symposium on Plasma Science for Materials

31 August – 5 September 2014
**Location:** Adelaide Convention Centre, North Terrace, Adelaide

### Sunday 31st August

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.00</td>
<td>Check in Desk open (Riverbank Room)</td>
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<tr>
<td>6.30 – 8.30</td>
<td>Welcome Reception – cocktail function</td>
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<tr>
<td></td>
<td>Riverbank Room – Foyer 4</td>
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<td>Adelaide Convention Centre, North Terrace, Adelaide</td>
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</tbody>
</table>

### Monday 1st September

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>08:30</td>
<td>Check in Desk Open (Foyer 1)</td>
</tr>
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<td></td>
<td>Presentations can be uploaded from 8.45</td>
</tr>
<tr>
<td>8:55</td>
<td>Hall A</td>
</tr>
<tr>
<td>09:00 – 09:20</td>
<td>Conference Opening – Dr Jason Whittle</td>
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<tr>
<td></td>
<td>Welcome Address</td>
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<tr>
<td></td>
<td>Professor Rob Short</td>
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<td></td>
<td>Pro-Vice Chancellor, Division of Information Technology</td>
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<td>and the Environment</td>
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<td>University of South Australia</td>
</tr>
<tr>
<td>09:20-10:00</td>
<td>Plenary Speaker: Professor Yakov Krasik</td>
</tr>
<tr>
<td></td>
<td>Underwater electrical discharges: main features and applications</td>
</tr>
<tr>
<td>10.00-10.20</td>
<td>Dr Musarat Ishaq</td>
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<tr>
<td></td>
<td>Molecular mechanisms of selective melanoma cancer cell</td>
</tr>
<tr>
<td></td>
<td>apoptosis induced by atmospheric gas plasmas</td>
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<tr>
<td>10.20-10.40</td>
<td>Dr Melanie Ramiasa</td>
</tr>
<tr>
<td></td>
<td>Plasma polymer films as a platform for selective cell capture</td>
</tr>
<tr>
<td>10.40-11.10</td>
<td>Tea Break – served in Foyer 1</td>
</tr>
<tr>
<td>11.10-11.40</td>
<td>Invited Speaker: Prof Masaharu Shiratani</td>
</tr>
<tr>
<td></td>
<td>Plasma CVD nanostructured films for energy applications</td>
</tr>
<tr>
<td>11.40-12.00</td>
<td>A/Prof Krasimir Vasilev</td>
</tr>
<tr>
<td></td>
<td>Nanoengineered Plasma Polymer Films For Biomaterial Applications</td>
</tr>
<tr>
<td>12.00-12.20</td>
<td>Xiao-Ning Zhang</td>
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<tr>
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<td>Calculation of transport coefficients in a non-equilibrium argon plasma</td>
</tr>
<tr>
<td>12.20-12.40</td>
<td>Mrs Elena Kosobrodova</td>
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<tr>
<td></td>
<td>Plasma Immersion Ion Implanted Polycarbonate for Antibody Microarray Applications</td>
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<tr>
<td>12.40 – 2.00</td>
<td>Lunch Break – Served in Foyer 1</td>
</tr>
<tr>
<td>2.00</td>
<td>Session resumes – Hall A</td>
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<tr>
<td>Time</td>
<td>Session Name</td>
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<tr>
<td>2.00</td>
<td>Session resumes – Hall A</td>
</tr>
<tr>
<td>2.00-2.30</td>
<td>Invited Speaker: Prof Masaaki Nagatsu</td>
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<tr>
<td>2.30-2.50</td>
<td>Dr Leslie Lea</td>
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<tr>
<td>2.50-3.10</td>
<td>Mr David Rubin de Celis</td>
</tr>
<tr>
<td>3.10-3.30</td>
<td>Mr Yoshihiro Torigoe</td>
</tr>
<tr>
<td>3.30-3.50</td>
<td>Dr Anne Mai-Prochnow</td>
</tr>
<tr>
<td>3.50-5.00</td>
<td>Poster Session – Day 1</td>
</tr>
<tr>
<td>P-01</td>
<td>Aleksandr Lisafin</td>
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<td>-----------------------------------------------</td>
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<tr>
<td>P-02</td>
<td>Mikhail Lukashevsky</td>
</tr>
<tr>
<td>P-03</td>
<td>Shi Nguyen-Kuok</td>
</tr>
<tr>
<td>P-04</td>
<td>Yuri Malakhov</td>
</tr>
<tr>
<td>P-05</td>
<td>Zahra Marvi</td>
</tr>
<tr>
<td>P-06</td>
<td>Rafael Neves</td>
</tr>
<tr>
<td>P-07</td>
<td>Homero Maciel</td>
</tr>
<tr>
<td>P-08</td>
<td>Fatemeh Rezaei</td>
</tr>
<tr>
<td>P-09</td>
<td>Paul Sibley</td>
</tr>
<tr>
<td>P-10</td>
<td>Kentarou Kita</td>
</tr>
<tr>
<td>P-11</td>
<td>Alex Cavallaro</td>
</tr>
<tr>
<td>P-12</td>
<td>Heping Li</td>
</tr>
<tr>
<td>P-13</td>
<td>Zhang-hu Hu</td>
</tr>
<tr>
<td>P-14</td>
<td>Darryl Jones</td>
</tr>
</tbody>
</table>
Underwater electrical discharges: main features and applications

Yakov Krasik

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A short description of main models ("bubble", "explosive emission", "ionization" and "thermal") of underwater electrical discharge and its parameters (breakdown electric field versus polarity of the high-voltage pulse, its duration and frequency, pressure, inter-electrode gap and area of electrodes; velocity of streamer propagation, density and temperature of the plasma, strong shock waves and radiation) will be shortly reviewed together with different electrical and optical diagnostics which are used in this research. Such main applications of underwater electrical discharge as electro-hydraulic forming, destruction of rocks, low-inductance spark gap switches, treatment of pollutants in water and extracorporeal shock wave lithotripsy will be discussed. Finally, application of underwater electrical explosion of single wires in $10^{-7}$s – $10^{-6}$s timescales for research related to Equation of States of different materials and underwater electrical explosion of spherical wire arrays for generation of converging strong shock waves for research of compressed water at extreme conditions will be presented.
Molecular mechanisms of selective melanoma cancer cell apoptosis induced by atmospheric gas plasmas

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Background: Atmospheric gas plasmas (AGP), which is able to selectively induce apoptosis in cancer cells, offers a promising alternative approach to conventional therapies which have unwanted side effects such as drug resistance and toxicity. However, the mechanism of AGP-induced cancer cell death is unknown.

Aim: The aim of this study was to explore the intracellular mechanism, how AGP induced apoptosis in cancer cells without effecting normal cells

Methods: Melanoma cancer cell lines (Mel007, Mel-RM and Mel-JD) and normal cells (melanocytes and human lung fibroblasts:MRC5) were used to study the effect of AGP by measuring the cell viability, capases 3/7 activity, intracellular ROS/GSH/NO production, intracellular gene expression by qPCR, immunoblotting and ELISA and enzymatic activity of kinases (ASK1, p38 and JNK).

Results: In this study, AGP was shown to up-regulate intracellular reactive oxygen species (ROS) levels and induce apoptosis in melanoma but not in normal melanocyte cells. Through screening of genes involved in apoptosis, tumor necrosis factor (TNF) family members were identified as the most differentially expressed cellular genes upon AGP-treatment of melanoma cells. TNF receptor 1 (TNFR1) antagonist-neutralizing antibody specifically inhibited AGP-induced apoptosis signal regulating kinase 1 (ASK1) activity and the subsequent ASK1-dependent apoptosis. Treatment of cells with intracellular ROS-scavenger N-acetylcysteine (NAC) also inhibited AGP-induced activation of ASK1 as well as apoptosis. Moreover, depletion of intracellular ASK1 reduced the level of AGP-induced oxidative-stress and apoptosis.

Conclusion: The evidence for TNF-signaling dependence of ASK1-mediated apoptosis suggests possible mechanisms for AGP activation and regulation of apoptosis-signaling pathways in tumor cells.
Plasma polymer films as a platform for selective cell capture

Melanie Ramiasa, Krasimir Vasilev

Mawson Institute, UniSA

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Whether it is for research purposes or for direct use by clinicians, biosensors and diagnostic devices that can selectively capture a specific cell type from whole body fluids are potent tools in high demand. Yet, such devices are not readily available and researchers are still looking for simple and effective ways to isolate specific cells from complex cells mixtures (e.g. Circulating Tumour Cells from whole blood). The first and crucial step towards the development of such devices is the successful immobilisation of functional proteins, in particular antibodies, to biomaterial surfaces.

Plasma polymerisation is a simple way to create bioactive films and recent work from our group has shown that, following a multistep protocol, aldehyde based plasma polymer surfaces could be used as a platform for specific T cell binding [1]. Here we present new fabrication strategies based on the plasma polymerisation of nitrogen rich precursors for the design of novel biomaterials coatings. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infra-Red spectroscopy (FTIR) have been used to characterise the chemistry of the polymer films obtained using various experimental conditions. Namely, different precursors, plasma powers, precursor flows and deposition times were used. As a result of the structural fragmentation and recombination of the precursors occurring during plasma polymerisation, a range of reactive chemical groups are formed such as amide, amine, isocyanate, imine, nitrile etc. The presence of these reactive groups on the plasma polymer surface enables chemical reactions with the carboxyl functions present on biomolecules.

The surface developed were tested for bioconjugation with selected proteins and cell marker ligands. Results from real time Quartz Crystal microbalance (QCM) protein adsorption studies and surface analysis show that differences in the plasma polymer chemistry lead to different protein adsorption mechanisms. In particular, optimum conditions were found where the surfaces spontaneously and covalently bind proteins from physiological buffer solution and without using reducing agents, thus minimising contamination by reaction side products and avoiding protein denaturation.

Plasma CVD nanostructured films for energy applications

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Hyunwoong Seo, Nao Itagaki, Giihiro Uchida, Kazunori Koga,

Graduate School of Information Science and Electrical Engineering,
Kyushu University, Japan
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The pressing urgent need for massively scalable carbon-free energy sources has focused attention on both increasing the efficiency and decreasing the cost of energy conversion devices “green energy devices”. To realize such green energy devices using nanoparticles, we are developing a “plasma nano-factory” which is a miniature version of macroscopic conventional fabrication, based on the knowledge of nanoparticle formation in reactive plasma. A plasma nano-factory produces nanoblocks and radicals (adhesives) in reactive plasmas, transports nanoblocks toward a substrate and arranges them on the substrate. There are three advantages of a nano-factory in plasma: controlled agglomeration and transport of nanoblocks as well as parallel processing over large area at relatively low temperature. This concept is useful for realize nano-systems far from the thermodynamically equilibrium with low processing energy and low material consumption. First, we describe the concept of plasma nano-factory and methods to realize the concept. Then, we explain, based on the methods, fabrication of core-shell Si nanoparticle films (plasma CVD nanostructured films) using SiH₄/H₂ and CH₄ or N₂ double multi-hollow discharge plasma CVD. Finally, we show application of nanoparticles to next generation lithium ion batteries and solar cells. Regarding the Li ion battery, the charge capacity is 4000mAh/g, which is 9 times higher than that of conventional graphite anode. The Li ion battery with Si/SiC coreshell nanoparticle anode produced by plasma CVD also shows high capacity of 370 mAh/g after 10 cycles. Thus SiC/Si coreshell nanoparticle anode is promising for the next generation Li ion batteries.

Work supported by JSPS.

Nanoengineered Plasma Polymer Films For Biomaterial Applications

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In my talk, I will present recent developments from our group on various nanoengineered biomaterial coatings prepared by plasma polymerisation. These include antibacterial coatings, drug release platforms and cell guidance surfaces.

We have developed various strategies for generation of antibacterial surfaces which are based on silver nanoparticles, controlled release of antibiotics and immobilised antibacterial compounds. Several of these strategies involve silver nanoparticles which are either in situ synthesized into amine reach plasma polymer films by first loading the films with silver ions and subsequent reduction or electrostatically attached using appropriate surface functionalities of both plasma polymer films and nanoparticles. By careful tuning of the nanoparticle surface concentration and silver ion release rate we were able to achieve complete inhibition of bacterial attachment. Importantly, we demonstrated that our coatings are not cytotoxic to mammalian cells and do not cause adverse inflammatory responses. I will also present several strategies to develop antibacterial coatings by surface immobilization of antibacterial polymers and QAC. We have also developed procedures for the synthesis of hybrid antibacterial nanocapsules and nanoparticles.

I will also outline our research on developing various advanced plasma polymer based coatings which we use to guide and direct cellular behavior. This include surface gradients which have become powerful tools for studying and guiding cellular responses such as adhesion, proliferation, migration, differentiation, etc. We have developed a range of surface gradients such as of chemistry, bound ligands, proteins, nanomechanics and nanoparticles. We have used these gradients to investigate the behaviour of various cell types, including stem cells. In my talk, I will focus on recent work where we used gradients of nanoparticles density to interrogate the influence of surface nanotopography of cell behaviour. Our data demonstrates that fibroblast and osteoblast cell lines preferentially adhere to specific surface nanotopographies defined in terms of lateral spacing and height of nanotopography features. I will also present a strategy for developing gradients of surface elastic modulus. Our studies on the adhesion and proliferation of primary human fibroblasts show that these cells prefer stiffer surfaces. I will also touch on our surfaces that are capable of driving the differentiation of stem cells only based on surface chemistry.

References:

2. Taheri et al Biomaterials 35 (16), 4601-4609 (2014)
Calculation of transport coefficients in a non-equilibrium argon plasma

Xiao-Ning Zhang\textsuperscript{1,2}, He-Ping Li\textsuperscript{3,*}, Anthony B Murphy\textsuperscript{2} and Wei-Dong Xia\textsuperscript{1}

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\textsuperscript{2}CSIRO Materials Science and Engineering, PO Box 218, Lindfield NSW 2070, Australia
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Here, the species compositions of an argon atmospheric-pressure thermal plasma under both local thermodynamic equilibrium (LTE) and non-LTE conditions are first obtained using the two-temperature (2-T) Saha equation [1] under the assumption of local chemical equilibrium. A new transport theory for non-LTE thermal plasmas [2], based on the modified Chapman-Enskog method, is then applied to the calculation of the transport properties of the argon plasma. The transport theory considers the coupling between the electrons and heavy species, allowing the species diffusion fluxes to satisfy the mass conservation law in the plasma system, but includes simplifications based on the physical fact that the mass of electrons is much smaller than that of heavy species. The calculated transport coefficients have been compared with those obtained using previous transport theories: the completely-decoupled method of Devoto [3] and the completely-coupled method of Rat [4]. The consistency between the formulas used for calculating the 2-T plasma properties and those for LTE plasmas, which are used widely in previous studies [5], are also discussed.

Acknowledgement: This work has been supported by the National Natural Science Foundation of China (11035005).

Plasma Immersion Ion Implanted Polycarbonate for Antibody Microarray Applications

*E. Kosobrodova*¹, A. Kondyurin ², C.G. dos Remedios ³, D. R. McKenzie ¹, M. M. M. Bilek ¹

¹ School of Physics, University of Sydney, Sydney, NSW, Australia, 2006.
² Muscle Research Unit, Discipline of Anatomy and Histology, Bosch Institute, University of Sydney, Sydney, NSW, Australia, 2006.

Plasma immersion ion implantation (PIII) modifies the structure and properties of polymers making them attractive for anti-cluster of differentiation (CD) antibody microarray applications. PIII treatment creates a high density of radicals in the polymer surface layer and dramatically increases its surface energy. Being hydrophilic, the PIII treated surface does not have much influence on protein conformation and, consequently, does not significantly affect the biorecognition properties of antibodies. In contrast to other hydrophilic materials, PIII treated polymers have a high protein binding capacity. Radicals embedded in the PIII treated surface layer enable the formation of covalent bonds with proteins resulting in the irreversible immobilization of a dense protein monolayer on the polymer surface [1].

The anti-CD antibody microarrays can be useful in preliminary tests of antibody therapeutics. Monoclonal antibody therapeutics can target specific molecules in patients and provide an efficient and safe treatment of cancer, autoimmune disease, anemia and heart disease. However, due to the foreign nature of biotherapeutics, even successful medicines can be hemotoxic and cause immune responses and other adverse events in patients. Anti-CD antibody microarrays provide an ability to test antibody cross-reactivity by observing the reactions of living human cells on foreign proteins under conditions as close as practical to in-vivo.

We describe the use of PIII treated polycarbonate (PC) slides as a novel platform for producing anti-CD antibody microarrays. We compare their performance to identical antibody microarrays printed on nitrocellulose-coated glass slides that are currently the industry standard. Populations of leukocytes are applied to the anti-CD microarrays and unbound cells are removed revealing patterns of differentially immobilized cells that are detected in a simple label-free approach by scanning the slides with visible light. Intra-slide and inter-slide reproducibility, densities of bound cells, and limits of detection were determined. Compared to the nitrocellulose-coated glass slides, PIII treated PC slides have a lower background noise, better sensitivity, and comparable or better reproducibility. They require three-fold lower antibody concentrations to yield equivalent signal strength, resulting in significant reductions in production cost. The improved transparency of PIII treated PC in the near-UV and visible wavelengths combined with superior immobilization of biomolecules makes them an attractive platform for a wide range of microarray applications.

Plasma Surface Functionalization of Nano-structured Materials for Bio-medical Applications

Masaaki Nagatsu$^{1,2}$, Chou Han$^2$, Anchu Viswan$^1$, Tomy Abuzain$^1$, Mihai A. Ciolan$^1$, Kazunori Koga$^3$, and Masaharu Shiratani$^3$

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In this study, we will present the recent experimental results on plasma surface functionalization of nano-structured materials for bio-medical applications. The main objectives are; first to fabricate nano-structured materials by various plasma processing, secondly to modify their surfaces by plasma chemical modification, and finally to immobilize the desired biomolecules onto the surface of nano-structured materials for medical application. In order to achieve our objectives described above, graphite-encapsulated magnetic nanoparticles, vertically aligned carbon nanotube dot-arrays (for a biochip sensor) and ZnO nanoparticles (as fluorescent materials) were used and investigated.

The Ar plasma pre-treatment followed by NH$_3$ plasma post-treatment plays an important role to introduce the amino groups onto the surface of the graphite-encapsulated magnetic nanoparticles. With conventional chemical procedures, the amino group population of magnetic nanoparticles having a typical diameter of 20 nm was evaluated to be about 8 x 10$^9$ molecules per nanoparticle. Immobilization of the antibody of influenza virus onto the surface of aminated magnetic nanoparticles has been carried out for aiming at developing the feasibility of the collection and condensation of virus. We observed the significant enhancement of collection rate of the influenza virus by a factor of 10$^{~18}$ using the antibody-immobilized magnetic nanoparticles. The present result suggests the feasibility of the magnetic condensation method for rapid detection of influenza virus.

We also demonstrated the selective ultrafine surface modification of functional groups onto the polymeric substrate or vertically aligned CNT dot-array (with a dot size of 5 μm and 50 μm spacing) using the atmospheric pressure plasma jet with a nano/micro-sized capillary. The micro-sized surface modification of amino or carboxyl groups introduced onto the substrate were confirmed by the fluorescence labelling technique. The present result supports the feasibility of future biochip sensor fabrication in atmospheric pressure.

In addition to these results, the other results will be also presented and discussed at the conference.
Etching of Silicon: Matching Process to Application

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Demand is growing to etch medium to high aspect ratio features into silicon for a range of applications such as through wafer electrical contacts, microfluidic systems and moulds for nano imprinting of features for optical gratings. To etch relatively large features almost through wafer, where the aspect ratio is of order 10:1 and sidewall roughness is less critical, a fast Bosch [1] process may be used which will produce relatively large “scallops” on the sidewalls. If smoother sidewalls are required it has been necessary with previous generations of etch tools to significantly reduce the etch rate. Recent developments enable cycle times for the Bosch process to be reduced down to 1-2 seconds, enabling etch rates to be maintained at high levels while achieving reduced scallop size. This can be very important for High Aspect Ratio features where smooth sidewalls are often required, e.g. for 3d x-ray detectors. For very small features it can be advantageous to switch from the Bosch etch process to a non-switched “cryo” process where no scallops are produced and side wall roughness can be as low as 2-3 nm, while achieving an etch rate of 4 - 5 μm/min. The changeover between process types is easy to achieve in the latest etch tools.

The Bosch etch process comprises alternating deposition and etch steps. In the etch step it is the isotropic chemical etching of the silicon that produces the scallops which may be reduced in size by reducing the number of radicals reaching the exposed silicon during the etch step, a result that may be achieved by either reducing primary plasma parameters of plasma source power, gas flow or process pressure so that net etch rate is decreased or by reducing the duration of each etch step and using shorter cycle times.

In the alternative cryogenic etch or “cryo” process SF₆ and O₂ gases are both continuously fed to the plasma producing a silicon oxyfluoride passivation of the surface of exposed silicon [2]. Ions from the plasma continuously remove the passivation from the base of the feature and fluorine radicals then react with the exposed silicon, steadily etching the mask defined feature into it.

A novel plasma process tool can now offer production level reliability combined with extreme flexibility allowing high rate Bosch processes to be performed and within the same process chamber the “cryo” process for nano [3] or microscale features where the requirement is for extremely smooth feature sidewalls while maintaining good etch rates.
Figure 1, shows a Through Silicon Via (TSV) etched almost through wafer using the Bosch process while figure 2, shows in detail the scallops on the sidewalls of the via which are of an acceptable size for this requirement. In figure 3, a 3μm wide very high aspect ratio trench is shown with aspect ratio comparable to that required in 3D sensors, where the scallop size has been reduced to around 60nm. In figure 4, the result of a “cryo” etch in the same process tool of a 1μm wide trench is shown, of aspect ratio 10:1 with etch rate at 4μm/min while sidewall roughness shown in figure 5 is < 2nm. Figure 6 shows that for a series of Bosch process runs on a particular tool, the etch rate and scallop size are close to linearly related. For reference the cryo etch result from the same tool is shown.

Tailoring of metal oxides by combining cold plasma with heat

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The potential of combining cold plasma with heat has been explored. The combination enables controllable doping and nanostructuring of semiconductors that cannot be achieved by either treatment alone. The system (Fig 1) is effective at doping metal oxides with elements such as nitrogen and can produce nano-structure. Both thin films and powders can be used as the starting material.  

It has been found that the amount and the type of nitrogen doping (interstitial or substitutional) can be controlled by altering parameters such as RF power, temperature and plasma treatment time. Measurements of metal oxides show the band-gap has been lowered by the plasma nitrogen doping.  

Theoretical calculations have been performed to understand the changes in the electronic structure of these doped materials, including the behaviour of the band-gap energy. Preliminary results show that there is an optimum doping percentage which corresponds to a minimum band-gap.  

Nanostructure in the oxides can be achieved by the formation of nano-crystals during treatment. Different working gases, including Argon, pure N₂ and N₂ (85%) + H₂ (15%), have been used to help understand the mechanism. The results suggest that nitrogen reactive species play a critical role in the formation of the nano-crystals.  

The doped and nano-structured metal oxides have excellent potential as anode materials for energy generation and energy storage devices.  

Note: The first and second names in the list are both the first authors.
Effects of hydrogen dilution to nanoparticle formation in silane hydrogen mixture multi-hollow discharge plasmas

Yoshihiro Torigoe, Susumu Toko, Weiting Chen, Daisuke Yamashita, Hyunwoong Seo, Nao Itagaki, Kunihiro Kamataki, Kazunori Koga, Masaharu Shiratani

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Light-induced degradation of hydrogenated amorphous silicon (a-Si:H) is a key issue for intensifying the competitiveness of thin film silicon solar cells in the solar cell market. Amorphous silicon nanoparticles below 10 nm in size (clusters) are formed in CVD plasmas for a-Si:H film deposition and some of them are incorporated into a-Si:H films, leading to light induced degradation of the films [1-3]. Here we study the effects of hydrogen dilution to nanoparticle formation in CVD plasmas.

Experiments were carried out using a multi-hollow discharge plasma CVD method [3]. For the method, most clusters are transported towards the downstream region because their diffusion velocity is less than the gas velocity. SiH₄ was fed from the bottom of the chamber at 20 sccm, then flew thorough the hollows. The total pressure was 0.5 Torr. Substrates were set in the upstream region from the electrodes. Their temperature was set at 100 °C. High frequency discharge voltage of 60 MHz was applied to the powered electrode. The discharge power was 20 W.

Figure 1 shows H₂ flow rate dependence of emission intensity ratio of Si* 288 nm to SiH* 414 nm. The ratio decreases from 0.244 for 10 sccm to 0.215 for 40 sccm. This result indicates the effective electron temperature decreases with increasing the H₂ flow rate. The temperature decrease is correlated with nanoparticle formation in gas phase.


Fig. 1. Dependence of Si*/SiH* on H₂ flow rate.
Bacterial biofilm response, and mechanisms of resistance, to argon plasma treatment

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Biofilms are the predominant mode of growth for bacteria. They are cell clusters encapsulated by an extracellular matrix attached to a surface. It is now widely recognized that more than 60\% of all infections are caused by biofilm-forming bacteria. These biofilm infections can become resistant to treatment with traditional antibiotics and often develop into a chronic state.

A number of studies show very promising results for atmospheric-pressure plasma (APP)-mediated killing and removal of biofilms, including pathogenic bacteria such as \textit{Pseudomonas aeruginosa}. However, the mode of action of APP and resulting bacterial response is not fully understood.

Here we show the successful removal of \textit{P. aeruginosa} PAO1 biofilms using the ‘kinpen 09’ argon non-thermal plasma jet (1). Biofilms were allowed to form for 24 h on glass coupons in a CDC biofilm reactor (2) before plasma treatment of 0, 1, 3, 5 or 7 min. Bacterial cells were then either removed from the coupon for cell counting (CFU) or stained with LIVE/DEAD\textsuperscript{®} BacLight\textsuperscript{™} viability kit for visualization using a confocal laser scanning microscope.

A 7 min plasma treatment led to a 3 log reduction in viable cells compared to the untreated control. Interestingly, only a few surviving, attached cells could be observed with confocal microscopy and LIVE/DEAD staining for this treatment time. Bacterial survival rates after plasma treatment depended on the age and thickness of the biofilm.

To investigate a possible bacterial resistance mechanism to plasma treatment, a lawn of \textit{P. aeruginosa} cells was spread onto agar plates and exposed to argon plasma treatment. Surviving bacterial colonies were selected for whole genome sequencing. Seven distinct polymorphisms were detected, with three of the affected genes related to phenazine biosynthesis, which is known to be involved in protection to environmental oxidative stress. Interestingly, plasma-resistance colonies also show an increased tolerance to hydrogen peroxide.


The Treatment of Oxide Powder in the RF Plasma Torch

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This work presents the main results of the treatment of refractory oxide fractions (50÷500) μm of materials (Al₂O₃, ZrO₂, MgO) in the RF plasma torch 1000 kW/0.44 MHz.

RF plasma torch 1000 kW/0.44 MHz used to process refractory oxide materials (Al₂O₃, ZrO₂, MgO). The paper identifies the main technological parameters of the process of obtaining MgO, ZrSiO₄: thermal efficiency is equal to the MgO (68.6÷83.1)%, ZrSiO₄ – (67÷74)%, Al₂O₃ – (75÷86)% of heating, temperature and velocity of particles in the plasma (particle velocity in the reactor νₚ = 30 m/s; melting temperature of the particles T_{MgO} = 3100 K, T_{ZrO₂} = 2800 K, T_{Al₂O₃} = 2300 K), the movement and heating of the plasma torch (speed in the center of the plasma torch νₑ = 113 m/s, maximum temperature 9246K) loaded particle flux with regard to their interaction (the effect cool down) weight limit processing of particles in given parameters of the plasma set (for the MgO – 240 kg/h fraction of 100 μm, for ZrSiO₄ – 520 kg/h, 100 μm fraction, for ZrO₂ – 350 kg /h, 100 μm fraction).

The results of treatment of oxide powder fractions (50÷500) μm are shown in Fig. 1-8.

Fig. 1. MgO powder 50÷150 μm fractions prior to treatment in Air plasma - RF 1000 kW/0.44 MHz.

Fig. 2. MgO powder 50÷150 μm fractions after treatment in Air plasma - RF 1000 kW/0.44 MHz.
Fig. 3. Heat flux of heating particles MgO for different factions.

Fig. 4. Heat flux of heating particles Al$_2$O$_3$ for different factions.

Fig. 5. The maximum loading on the particle size ZrSiO$_4$, MgO, Al$_2$O$_3$.

Fig. 6. Efficiency particle size for ZrSiO$_4$, MgO, Al$_2$O$_3$.

Fig. 7. The temperature of the RF plasma torch 1000 kW/0.44 MHz in the loading 80÷240 kg/h MgO.

Fig. 8. The temperature of the RF plasma torch 1000 kW/0.44 MHz in the loading 200÷360 kg/h Al$_2$O$_3$.

Using the obtained estimates [1-4] can be concluded that the limit load MgO oxide powder is 245 kg/h for a fraction of 50 μm. Thermal efficiency MgO powder processing is at the limit
(67.8±82.6)% for the particle fraction of 350 and 50 μm respectively. Maximum upload ZrSiO₄ oxide powder is 530 kg/h for a fraction of 50-300 μm. Thermal efficiency MgO powder processing is at the limit (67.1±74.4)% for the particle fraction of 500 and 50 μm respectively. Given the fact that in zircon ZrSiO₄ contains a percentage of 66% zirconium oxide ZrO₂, then the maximum output will be 350 kg/h. Using the obtained estimates can be concluded that the limit load Al₂O₃ oxide powder is 340 kg/h for a fraction of 50 μm. Thermal efficiency processing of Al₂O₃ powder is in the limit (74±86)% fraction of particles 350 and 50 μm respectively.

References


The Results of Calculation of Thermoemission Cathodes in Ar at Atmospheric Pressure

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This work gives results of calculating the cathode processes of the Arc plasma torches at atmospheric pressure with the thermal cathodes. Calculations were performed on the basis of the method of integral balances for the cathode made of the pure tungsten W and the thoriated tungsten W(2% ThO\(_2\)) over a wide range of temperatures of cathodes \((T_c = 3000 - 4400\) K for W and \(T_c = 2000 - 3200\) K for W(2% ThO\(_2\))) and argon plasma \((T_e = 20000 - 40000\) K).

In practice, with the work of Arc plasma torches in the inert gases, nitrogen, hydrogen and their mixtures, widely are used thermoemission cathodes on the basis of tungsten. The study of processes near the electrode is necessary for understanding the physical picture of the phenomena near the electrode and helps to solve the problem of increasing the life of Arc installations.

The simplified picture of phenomena in the cathode region of arc can be presented with the two-layered model (Fig. 1) [1-3]. The first layer, if the count to lead off the surface of the cathode is called the space-charge layer has a length of the order of the Debye length \(n_0\) and less than the mean free path of electrons and ions \(l_{\text{el}}\). The second layer separates the space-charge layer and the arc column called ionization. It runs neutrality condition occurs intense generation of charged particles due to the energy acquired by electrons in the first layer.

![Schematic of the two-layered model of the cathode region of Arc plasma torches.](image)

Fig. 1. Schematic of the two-layered model of the cathode region of Arc plasma torches.
We present the results of the calculations of the cathode region for the tungsten W and the thoriated-tungsten W (2% ThO₂) for the arc plasma torches in argon. Pressure in both cases $P = 1$ atm. The electric field on the cathode is represented in Fig. 2. The dependence of a voltage drop in the layer of space charge $U_d$, in the ionizing layer $U_i$ and in the cathode region $U_k$ from the temperature of the cathode surface is given in Fig. 3.
Fig. 4. Balance of current density on the cathode surface: $j_{em}$ - current density of thermoemission from the cathode; $j_{ec}$ - current density of opposite electrons to the cathode; $j_i$ - current density of ions to the cathode.

Fig. 5. Share of electron and ion currents on the cathode.
Fig. 6. Energy balance on the cathode surface: \(q_{em}\) — the heat flux of thermoemission from the cathode; \(q_{ec}\) — the heat flux of opposite electrons to the cathode; \(q_i\) — summary of the ion heat flux to the cathode, including energy of the ion bombardment, energy of the neutralization of ions on the cathode and energy of the atoms, which leave the cathode surfaces; \(q\) — summary of the heat flux to the cathode.

Fig. 7. Total power into cathode and radius of cathode spot depending on arc current: a) line — calculation; b) point - the experiment: 1 — [4, 6]; 2 — \(l_c = 0\); 3 — 0.6 cm; 4 — 1.2 cm; 5 — 6 cm [5, 6], \(l_c\) — length of the water-cooled region of cathode.

The balance of current density on the surface of cathode is represented in Fig. 4. The share of electron (thermoemission and opposite electrons) and ion current depending on the temperature of the cathode surface with the different values of temperatures of electrons is represented in Fig. 5. Energy balance on the cathode surface is represented in Fig. 6. In Fig. 7 are represented data of total power into the cathode and a radius of cathode spot.
depending on arc current. A good agreement of calculated and experimental data makes it possible grow prettier the applicability of this model of the cathode region and method of integral balances for calculating the processes of arc plasma torches near the cathode.

References
Calculation of e-Ar Scattering of the Higher Order

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This paper presents the calculation results of the differential cross sections of electron-atom in the argon with the low energies of electrons to \(e = 10\) eV and comparison with experimental and theoretical data from other sources. In contrast to the works of other authors we used the approximation of higher order (up to four) to calculate the phase shift \(\eta_i\) and a large amount of packet waves (up to a million). Calculation was performed for the scattering angles (\(\theta = 10^\circ - 100^\circ\)). We used also higher orders \(L = 1...6\), \(S = 1...11\) to calculate averaged cross sections of the electron-atom in argon. The results of our calculations have a good agreement with the experimental data.

Electron scattering on the atoms for inert gases, including argon, with the low energies is characterized by wave properties and is described by quantum-mechanical model. The quantum-mechanical description of the theory of particle scattering is based on the solution of Schrödinger wave equation taking into account potential interaction energy of the particles \(\phi(\vec{r})\). The solution of Schrödinger wave equation is produced with the method of separation of variables. For this the wave function is determined in the form two functions, one of which depends on coordinates, and the second – from the scattering angle \(\theta\). Quantum-mechanical description makes it possible to determine the probability of scattering (i.e., differential cross sections) the particles to the specific angle only \(\theta\). This probability is expressed as the phase shift \(\eta_i\) of the radial wave function \(\psi(\vec{r})\). Phase shift \(\eta_i\) depends on the wave number \(k\) and the function \(U(r)\), which are determined as follows:

\[
k = \frac{2\pi}{\lambda} = \frac{p}{\hbar} = \sqrt{2mE}, \quad U(r) = \frac{2m\phi(r)}{\hbar^2}
\]

where \(p, m, E\) – pulse, reduced mass and the total energy of system respectively. The Schrödinger equation can be written down in the spherical coordinates taking into account the symmetry as:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \left( k^2 - U \right) \psi = 0
\]

With the use of the corresponding boundary conditions it is possible to obtain expression for the function of scattering amplitude in the following form:

\[
f(\theta) = \frac{1}{2ik} \sum_{l=0}^{c} (2l+1)(\exp(2i\eta_l) - 1)(P_l(\cos \theta)) = \frac{1}{2ik} \sum_{l=0}^{c} (2l+1)\exp(i\eta_l)\sin \eta_l P_l(\cos \theta)
\]

where \(P_l(\cos \theta)\) – Legendre's polynomials.

A phase shift \(\eta_i\) can be used for determining the differential cross section in the following form:
The results of our calculation with large amount of packet waves (up to a million) have a good agreement with the experimental data. A comparison with experimental and theoretical data from other sources presents on Fig. 1.

\[ \frac{d\sigma}{d\Omega} = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) \exp(i\eta_l) \sin \eta_l P_l(\cos \theta) \right|^2 \]  

(4)

A phase shift \( \eta_l \) determined with the Modified Effective Range Theory (MERT) of the fourth approximation degree [7]. We used also higher orders \( L = 1...6 \), \( S = 1...11 \) to calculate averaged cross sections of the electron-atom in argon (Fig. 2). The averaged effective cross sections are determined as follows:

\[ Q^{(L,S)}(T) = \frac{2(L+1)}{(S+1)!(2L+1-(-1)^S)} \int_0^\infty \exp(-x)x^{S+1}Q^{(L)}(kT)x)dx \]  

(5)

where \( x = \frac{m^2 g^2}{2kT} = \frac{E}{kT} \) – the initial relative speed of the being encountered particles.
Fig. 2. The averaged effective interaction cross sections $e$-Ar.

References
Electron Temperature and Density of Argon in the RF Plasma Torches

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The paper presents experimental results of determining electron temperature and density of an argon RF plasma at atmospheric pressure. The utilization of an optic-fiber three-channel diffractive spectrometer with radiometric calibration and a developed technique to automatically process experimental data allowed to increase precision of temperature determination by means of spectrum line relative intensity method. The obtained measurements and estimates are used to evaluate the usability of relative thermodynamic equilibrium model for diagnostics of argon RF plasma at atmospheric pressure.

Electron temperature is one of the main plasma parameters. It is necessary for calculating plasma composition and its transport coefficients, for determining electric, electromagnetic and thermal characteristics of a plasma discharge. The electron temperature also allows to obtain many interaction cross-sections of particles in plasma.

The RF plasma torches employed in this work operate at the frequency of 27.12 MHz and allows to obtain an RF plasma torch with the diameter of 20 – 25 mm at an atmospheric pressure. The power transferred to plasma is ~ 2 – 2.5 kW and the maximum electron temperature is ~ 7000 – 10000K and electron density is about ~ 10^{16} cm^{-3}. One of the features of RF plasma is that radial intensity changes non-monotonously caused by skin-effect in the torch. The most significant power output in the RF plasma torch occurs in the outer curricular zone of the discharge. Therefore the temperature and density in this zone may be higher than at the axis of the discharge. RF plasma radiation spectrum consists of continuous radiation ("continuum") and atomic ion line radiation. For the given RF discharge electron energy may be insufficient to excite ions. For the studied RF plasma local thermodynamic equilibrium model (LTE) is used and the following methods can be utilized for the spectrum analysis:

1. Electron temperature determination from analyzing relative distribution of excited argon atoms by excitation energy (Fig. 1). The variation of excitation energies should be equal to or more than kT.
2. Electron density determination from ArI atomic line Stark width (Fig. 2).

The plasma radiation at the atmospheric pressure in the considered temperature range \( T \sim 7000 – 10000 \text{ K} \), electron density range \( n_e \sim 10^{14} – 10^{16} \text{ cm}^{-3} \) and wavelength range 200 – 1000 nm leaves the plasma without reabsorption, i.e. plasma is optically thin.
Fig. 1. The determination of the temperature in the center of RF plasma torches by the relative intensity method.

Since we employ the LTE approach, the Maxwell-Saha-Boltzmann equations are applicable. Our main information source is the absolute and relative intensities of spectral lines and continuum. Electron temperature is determined from the functional dependence analysis for \( \ln \frac{n_e(E_x)}{g_x} \) for atomic Ar I lines, for the maximum possible excitation energy variation range [2]. The distribution \( \ln \frac{n_e(E_x)}{g_x} \) is also a method for evaluating the applicability of Boltzmann’s law for the connection between the population of certain argon atom and ion states and plasma temperature.

References


Radicals and ions transport effects on the catalysed growth of carbon nanotubes in a low-pressure low-temperature plasma

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The growth kinetics of carbon nanotubes on the catalyst nanoparticle in a low-temperature, low-pressure reactive plasma is investigated using a multiscale numerical simulation including the plasma sheath and surface diffusion modules. The plasma related effects on the characteristics of the carbon nanotube growth are studied. The effective carbon flux and CNT growth rate are calculated. Also, the dependence of growth parameters on the substrate temperature is investigated. It is found that in the presence of reactive radicals in addition to energetic ions inside the plasma sheath area, the effective carbon flux and total growth rate of CNT increase. The results show that the effects of plasma sheath parameters on the growth parameters are different in low and high substrate temperature regimes. It is also found that the substrate temperature $T_s=800$ K and applied DC bias $V_{dc}=100$ eV are appropriate reactor control parameters for obtaining maximum growth rate of carbon nanotubes.
Electron scattering from phenol

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We report results from a joint theoretical and experimental study on electron impact excitation of electronic states in phenol (C$_6$H$_5$OH). We initially present results from measurements of electron energy loss spectra (EELS), and how we interpret the observed features in those spectra through our detailed calculations of the electronic structure of phenol. In addition differential and integral cross sections are derived from the measured EELS, with those data being compared where possible against corresponding Schwinger Multichannel (SMC) calculation results that were undertaken as a part of this investigation. The qualitative similarity between the electronic-state spectroscopy of phenol and benzene will also be explored.
Experimental investigation and modelling of power characteristics of AC gliding arcs with oxidative and reducing plasmas

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Ambient pressure gliding arcs, as one of the kind of non-equilibrium gas discharges, have been utilized in plasma assisted combustion processes, among various other applications, due to their promising technical properties. Our study is focused on the experimental investigation of AC powered gliding arc (GA) with reverse vortex flow in air and in their mixtures with natural gas (NG) as well as on the physical modeling of this GA based on generalization of power characteristics with new similarity relations.

The experiments with the GA were fulfilled in a reactor comprising a quartz tube of 0.062 m length and 0.0225 m diameter. Its geometry corresponds to an advanced GA reactor with “tornado”, that includes a high voltage wire electrode in a helical profile. The ranges of operating parameters for the series of discharges made in air + NG mixtures were as following: RMS discharge voltage \( U = 1.73-3.41 \text{ kV} \), applied power to the power AC transformer before GA heater \( W = 175-395 \text{ W} \), mass flow rate of NG \( G_{NG} = 0.02-0.14 \text{ g/s} \), maintained constant the air flow rate in the system, at \( G_{AIR} = 0.8 \text{ g/s} \). The experiments were directed towards the studies of generalization of power characteristics of the discharges and, additionally, we explored the GA reactor as a plasma assisted combustion device. By varying the equivalence ratio \( \phi \), of the NG+air mixture, we determined the inflammability limits, for various values of discharge power, as illustrated in the Fig. 1.

Cellular Response to Atmospheric Pressure Dielectric Barrier Discharge Plasma Modified Polymethylmethacrylate Surfaces

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Polymeric materials have a wide variety of applications in medical areas, because of their desired mechanical strength, chemical stability, light-weight, as well as their tailor made design possibilities [1]. The most noticeable properties of polymers in medical applications are their inertness and biocompatibility. However, in contact with biological systems, these materials are not always compatible. So, surface modifications may be needed to perform the requirements of the desired medical applications. Among a wide range of polymeric materials, polymethylmethacrylate (PMMA) has good mechanical strength. It is biocompatible and biostable, so it is an attractive candidate for medical applications especially in the fields of orthopaedia, orthodontia and ophthalmology [2,3].

Plasma surface treatment is a good technique for surface modification without altering the bulk properties [4]. The majority of plasma assisted technologies are based on low pressure processes that need the high vacuum equipment [5,6,7]. However, in recent years, due to the lower operational and maintenance costs and simplicity of the equipment, atmospheric pressure plasmas in dielectric barrier discharge (DBD) configuration have attracted considerable interest for surface modification. These systems are also capable of continuous treatments in single step and simple processes. Nevertheless, examples of polymer surface modifications in such configurations are not as abundant [5,8,9].

In this study, PMMA films are modified by atmospheric pressure oxygen DBD plasma for biomedical applications. The oxygen gas flow rate was kept constant at 500 sccm. The role of plasma process parameters, exposure time (5-90 s) and applied voltage (140-300 V), on the surface characteristics, especially cell attachment, was studied. The biocompatibility of samples is investigated by MTT assay. It is found that oxygen DBD plasma treatment enhances the biocompatibility and also hydrophilicity of PMMA films.

References:
Characterisation of plasma emission broadening for double-pulsed laser induced breakdown spectroscopy

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Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique which provides elemental composition information through observation of spectral lines emitted from a plasma generated by laser ablation of a material. A variation on this technique in the form of double-pulsed LIBS, utilises a second laser pulse incident on the material and has been used to significantly enhance the spectral signal.\textsuperscript{1} This allows for an improved limit of detection, which is highly important for applications requiring the detection of trace elements.

A thorough examination of the potential mechanisms for this signal enhancement requires determination of plasma properties such as electron density and plasma temperature. For the constantly evolving laser induced plasma, this is often achieved through the analysis of spectral line properties, with calculation of the electron density achieved through the analysis of the broadening of the peaks.\textsuperscript{2} The most significant contributions to broadening arise from the Stark and Doppler broadening effects.

This research examines the contributions to the broadening of spectral emissions from a double-pulsed LIBS apparatus through a deconvolution of the peaks into the Stark and Doppler broadening effects, using their Lorentzian and Gaussian line shapes respectively. A time resolved spectroscopy system is used to obtain spectra as the laser induced plasma develops, both before and after the second laser pulse for a copper beryllium alloy target. The analysis of the broadening contributions to the overall spectral allows for the assessment of the validity of using Stark broadening to measure electron density. Additionally, the developing plasma is visualised using high speed imaging and shadowgraphy.

High Production Rate Synthesis of Fe-doped TiO₂ Nanopowder using Pulse-Modulated Induction Thermal Plasmas with Time-Controlled Feedstock Feeding

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A large amount of Fe-doped TiO₂ nanopowder was synthesized using pulse-modulated induction thermal plasmas (PMITP) [1]. The feedstock of Fe/Ti powder mixture, 5wt%Fe+95wt%Ti or 2wt%Fe+98wt%Ti, was intermittently supplied, being synchronized with the coil current modulation for PMITP. The production rate of synthesized nanopowder was estimated to be 500 g/h for 5wt%Fe, and 450 g/h for 2wt%Fe at 20 kW. These production rates are 10-20 times higher than those by the conventional thermal plasma method. Synthesized particles were analyzed by FE-SEM, BET, XPS, XRD and a spectrophotometer.

Figure 1 shows the FE-SEM images of synthesized nanopowder. About 90% of synthesized particles have sizes less than 100 nm. Figure 2 shows XPS results of synthesized nanopowder at Ti 2p peaks. Ti 2p peaks of Fe-doped TiO₂ were shifted to lower binding energy compared to those of pure-TiO₂. This result indicates that chemical bonding for Ti-O was changed by Fe doping. Fe 2p peaks around 712 eV were also detected in XPS results for both samples, while iron crystal structure could not be detected by XRD. From these results, Fe ion may be doped to TiO₂ in the synthesized nanoparticles.


![Figure 1. FE-SEM images of synthesized nanopowder.](image)

![Figure 2. XPS Ti2p spectra of Fe-doped/pure TiO₂ nanopowder.](image)
Substrate independent concentration gradients of immobilized quaternary ammonium compounds for reduction of bio-burden

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Despite advances in infection control, there are over 175 thousand cases of healthcare acquired infections observed annually in Australian hospitals. The associated cost of this exceeds 1 billion dollars per annum in extra bed spaces alone.¹ Bacterial adhesion and the subsequent biofilm formation on medical devices is the leading cause of post-surgical complications and usually results in further surgery.² After initial bacterial adhesion bacteria develop into biofilms and show enhanced resistance to conventional antimicrobial treatments. Although the introduction of aseptic technique into the medical field dramatically reduced infection rates, infections continue to threaten human health and are the second most common cause of death, after heart related diseases.³ This, combined with the increased prevalence of multi-drug resistant bacteria, is of major concern within the medical community. One method utilized to decrease infection rates is the addition of surface immobilized compounds that are capable of killing pathogens upon contact; such as quaternary ammonium compounds (QACs).⁴

Using plasma polymerization of allylamine and controlled dip coating techniques, QACs were immobilized to substrates and the surface density of QACs was controlled in a gradient manner from high to low concentrations. Bacterial interaction with these surfaces was investigated using microbiological imaging techniques and the viability of E. coli was shown to decrease towards the high concentration of the gradient. Additionally no decrease in viability of human dermal fibroblasts grown on these substrates is observed suggesting minimal cytotoxicity of these antimicrobial substrates towards mammalian cells.

Optical emission analysis of an AC-excited discharge using a gas-liquid two-phase plasma reactor

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Electrical and optical analysis of an AC-excited discharge are presented in this study by using an innovative gas-liquid-phase (two-phase) plasma reactor, employing powered needle electrode enclosed in a conical quartz tube and grounded deionized water electrode. The small orifice at the end surface of the conical tube stabilizes the discharges at a low power by reducing the interference between the gas- and liquid-phase discharges. It also maintains the gas-phase discharge by stopping the penetration of the deionized water into the conical tube. The two-phase discharge initiates in the same fashion as the gas-phase discharge, diffusing and occupying the surrounding volume of the needle. And then, the continuous increase of the applied voltage suddenly extends the discharge in the entire gap spacing. The dependence of the estimated rotational temperatures of the two-phase discharges, based on the spatially resolved measurements of the emission intensities of the OH band ($A^2\Sigma^+ \rightarrow X^2\Pi$, $\Delta v=0$), on the currents and flow rates is investigated, and is also compared with that of the gas-phase discharges. On one hand, the rotational temperatures both in the gas-phase and two-phase discharges strongly depend on the flow rate and discharge current. On the other hand, the OH emission intensity enhances at an elevated level by decomposition of the deionized water in the two-phase discharges, which results in relatively higher rotational temperatures (850-1400 K) than those in the gas-phase discharges. The significant increasing trend of the OH emission intensity and the relatively high rotational temperatures in the two-phase discharges are more convenient for the degradation and hydrogen production than those in the gas-phase discharges.

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Current neutralization and plasma polarization for ion beams propagating through plasmas

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The investigations of transport and focusing of charged ion beams show important applications in the ion beam-material interactions. Simulations and experiments have proven that background plasma can be provided as an ideal media for ion beam focusing and transport. A two-dimensional electromagnetic Particle-In-Cell (PIC) simulation model is proposed to study the propagation of intense ion beams with beam radius $r_b$ small compared to the electron skin depth $c/\omega_{pe}$ through background plasmas in the presence of external applied magnetic fields. The effective electron gyroradius $r_{ge}$ is found to be an important parameter for ion beam transport in the presence of magnetic fields. In the beam regions, the background plasmas respond differently to the ion beam of radius $r_b<r_{ge}$ and $rb>r_{ge}$ for the given magnetic field and beam energy.

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A Dynamical (e,2e) Investigation of Phenol

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We present an experimental and theoretical investigation into the dynamics of electron-impact ionization of the unresolved combination of the highest (4a'') and next-highest (3a'') occupied molecular orbitals of phenol. Here a coincident (e,2e) experiment [1] is performed to measure angular distributions of the ejected electron with energy of 20 eV when a 250 eV incident electron ionizes phenol and scatters at an angle of either -5, -10 or -15°. These measurements are compared to calculations performed within a molecular three-body distorted wave framework [2].