Sustainable Energy Applications Performed by the Duo-Plasmaline Microwave Plasma Source and the Plasma Array

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1 Introduction – Characteristics of Low-pressure Microwave Plasmas

Microwave plasma excitation at low-pressure conditions is based on acceleration of free electrons in the electric field of the microwave. Heavy charged particles such as ions are not able to follow the fast changing polarity of the electric field of the microwave in the GHz range due to inertia and virtually remain at their original energy level, which is generally correlated with ambient temperature. By collisions of accelerated free electrons with electrons from the shell of neutral atoms or molecules and charged ions, respectively, kinetic energy of these accelerated free electrons will be transferred to the shell electrons. Consequently, shell electrons will be excited or even overcome the attractive force of the nucleus, and bonding electrons in molecules can be separated. This leads to emission of light characteristic for the element or molecule when the shell electron falls back from the excited state into its original energy state, to the generation of additional free electrons as well as positively charged ions and to the formation of radicals in the latter case, respectively. The exponential generation of additional free electrons – the so-called avalanche effect – is causal for the formation of a plasma, characterized by a significant ratio of ionization of the gas particles and a correspondingly high density of free electrons.

The pressure is another important parameter for the characteristics of the microwave plasma, since the pressure directly correlates with the collision frequency of the free electrons. At low-pressure conditions and the mean free path of the accelerated free electrons being significantly shorter than the dimensions of the vacuum chamber, a non-equilibrium plasma is formed, characterized by neutrals and ions at ambient temperature and by "hot" accelerated free electrons. When the pressure in the vacuum chamber is reduced so that the mean free path of the free electrons is in the range of the dimensions of the vacuum chamber, the probability of collisions of the free electrons with the walls of the vacuum chamber significantly increase, thus inhibiting the avalanche effect which is essential for forming and sustaining a plasma. Increasing the pressure will allow energy transfer to heavy particles like neutrals and ions, too, causing the plasma to gradually thermalize. Thus, the gas temperature of the plasma increases, too. In addition, when keeping the microwave energy constant by increasing particle density, the excitation energy will not be sufficient to maintain the plasma volume, which results in the formation of plasma filaments.

Increasing electron density at constant pressure finally inhibits the propagation of the microwave. At the so-called critical density, the electromagnetic wave can no longer penetrate the plasma and is reflected. The plasma then acts like a conducting wall. The critical density is proportional to the square of the frequency of the electromagnetic wave.

Based on these principles, many technical microwave plasma sources have been realized to exploit the high reactivity of microwave plasmas due to the high density of radicals. However, the formation of specific modes and of standing waves, respectively, according to the vacuum wavelength of the microwave, which is in the same geometrical dimension as the material to be treated, can lead to inhomogeneous plasma treatment of the surface of the this material. Easy upscaling of microwave plasma sources for plasma treatment of large substrates is another challenge. The Duo-Plasmaline microwave plasma source as well as the plasma array, which is based on the Duo-Plasmaline, perfectly meet these challenges.

2 Duo-Plasmaline and Plasma Array Low-pressure Microwave Plasma Sources

2.1 Duo-Plasmaline

The Duo-Plasmaline is a low-pressure microwave plasma source. The plasma is formed by microwave excitation only, i.e. without the effect of an additional magnetic field. In a simplified description, the Duo-Plasmaline is like an inverse fluorescent tube excited by microwaves: a coaxial line is mounted through the vacuum vessel (i.e. the process chamber) made of electrically conducting material and powered by microwaves from both sides. Inside the vacuum vessel, the outer coaxial conductor is replaced by a dielectric tube made of e.g. glass, quartz or ceramics. The inside of the dielectric tube is at atmospheric pressure (for proper cooling of the antenna), whereas the outside (i.e. the process chamber) is at low pressure, preferably in the range between 10 Pa and 1000 Pa (the pressure is defined by the related application, i.e. etch, deposition etc.). Microwaves can pass the dielectric tube and propagate into the low-pressure regime of the vacuum vessel. When the electric field strength of the microwave exceeds the breakdown field strength, a discharge ignites in the low-pressure regime at both ends of the Duo-Plasmaline where the outer coaxial conductor is replaced by the dielectric tube. The short plasma hoses formed at both ends of the Duo-Plasmaline are electrically conducting media and thus replace the missing outer coaxial conductor. With increasing microwave power, the plasma extends from both ends alongside the dielectric tube, until an axially homogeneous plasma is finally formed (see Figure 1).

Figure 1: Axially homogeneous plasma formed around the Duo-Plasmaline low-pressure microwave plasma source [1].

The formation of an axially homogeneous low-pressure plasma around a Duo-Plasmaline with a length of more than 3 m has been demonstrated by application of only some kW of microwave power at the frequency of 2.45 GHz.

2.2 Plasma Array

A two-dimensional plasma array is obtained when arranging two or more Duo-Plasmalines equidistantly and in parallel. While a Duo-Plasmaline provides an axially homogeneous plasma, a large homogeneous plasma can be formed by a plasma array (see Figure 2). Consequently, a Duo-Plasmaline is preferably used for plasma surface treatment in continuous in-line processes, whereas a plasma array is suitable for continuous and batch processes, respectively. Both Duo-Plasmaline and plasma array provide highly efficient surface treatment of even thermally sensitive materials due to high radical densities at simultaneously low ion energy of the non-equilibrium microwave plasma at low-pressure.

Their modular design makes it easy to adapt plasma arrays to the dimensions of the material to be treated in a plasma surface process by configuring the number and the length of the Duo-Plasmalines in the plasma array. In this way, the active plasma area can be scaled both in width and length.

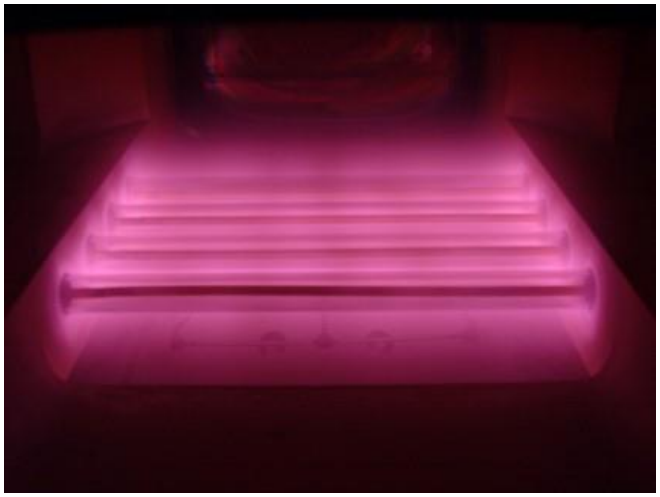

Figure 2: Two-dimensional homogeneous plasma formed by a plasma array microwave plasma source at low-pressure conditions [2].

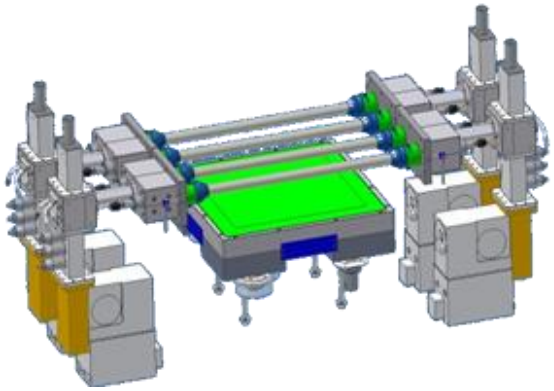

Figure 3: Schematic of a plasma array consisting of four Duo-Plasmalines (including magnetron head, tuner and isolator, power supply is not shown) for plasma treatment of the green surface below at low-pressure conditions.

A schematic of a plasma array consisting of four Duo-Plasmalines in a process chamber for plasma surface treatment at low-pressure conditions is shown in the Figure 3. The four Duo-Plasmalines are supplied with microwave energy from the left and from the right. The microwave energy is generated by two magnetrons on each side. Each magnetron supplies two Duo-Plasmalines via power splitter with microwave energy. Splitting microwave power equally to two or more Duo-Plasmalines provides for increased homogeneity of the plasma area formed by the plasma array. Figure 4 shows a plasma array consisting of six Duo-Plasmalines with a length of 160 cm each, thus forming an active plasma area of approximately 150 cm x 200 cm for e.g. coating of solar cells with silicon nitride films. In general, the size of the active plasma area can vary from a fraction of a square meter to a few hundred square meters.

Figure 4: Plasma array consisting of six Duo-Plasmalines integrated into a process chamber for e.g. low-pressure plasma deposition of thin films used in the production of solar cells (courtesy of Meyer Burger Germany).

Apart from deposition of thin films, Duo-Plasmalines and plasma arrays are also used for plasma assisted surface treatment like surface activation, etching, cleaning and even sterilization.

3 Examples for Sustainable Energy Applications Performed by the Duo-Plasmaline Microwave Plasma Source and the Plasma Array

3.1 Plasma Deposition of Anode Materials for Lithium-ion Battery Applications

In 2007, researchers at Stanford University discovered a solution to the challenges associated with silicon in batteries. They were able to store lithium in tiny silicon nanowires by using new techniques and methods from nanotechnology. The dimensions of these silicon nanowires are about one thousand times thinner than the thickness of a sheet of paper. The silicon nanowires are able to swell when they take-up lithium, while physical effects on nanoscale inhibit the silicon from fracturing and breaking apart.

Therefore, silicon is widely considered to be the future material of choice in anode technology – battery-builders and automakers are working on ways to take advantage of its high theoretical charge capacity. Batteries with silicon anodes achieve significantly higher energies per unit volume and per unit weight than today's commercially available batteries based on carbon-anode designs.

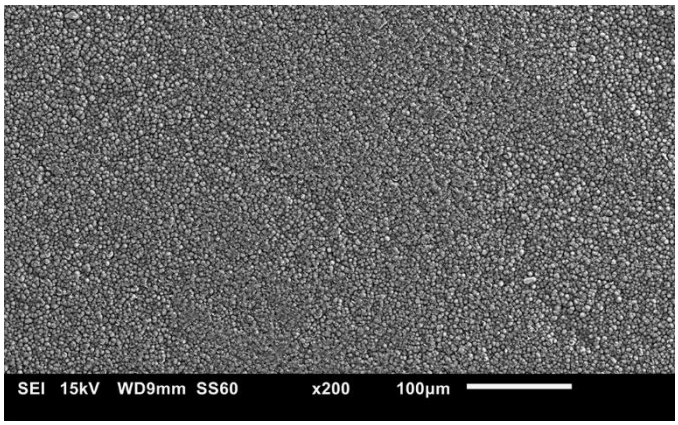

Figure 5: Three-dimensional growth of silicon columns by low-pressure microwave plasma deposition for pure silicon anodes [3].

Manufacturing facilities relying on Duo-Plasmaline technology for plasma enhanced chemical vapor deposition (PECVD) of three-dimensional porous silicon layers have the potential for producing silicon nanowire anodes. Figure 5

shows silicon columns three-dimensionally grown by low-pressure microwave plasma deposition for pure silicon anodes.

3.2 Plasma Deposition of Silicon Nitride for Photovoltaic and Semiconductor Applications

Thin films of silicon nitride (SiN) are widely used in microelectronics, optoelectronics, optics and hard surface coatings. Figure 6 shows a thin plasma-polymerized SiN film on a silicon wafer used in microelectronics. This SiN film was deposited in a low-pressure plasma deposition process by application of a microwave-powered plasma array.

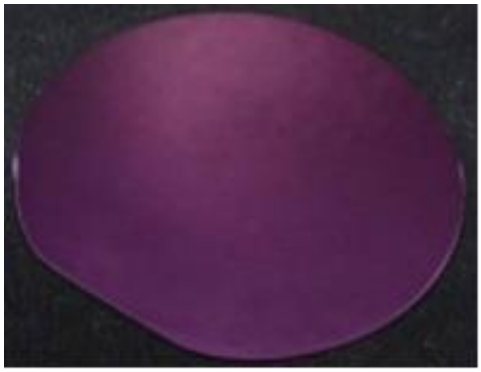

Figure 6: SiN film plasma deposited in a low-pressure plasma deposition process on a silicon wafer by application of a microwave-powered plasma array [4].

Effective silicon solar cells require minimal reflection losses and minimized surface recombination. Thin plasma-polymerized SiN films are used to minimize both properties, the reflection behavior by adjusting the refractive index of the anti-reflection coating and the surface properties to avoid recombination at and near to the surface.

Their hardness and chemical resistivity are further advantages of SiN films. For this reason, they can be applied as insulator material and barrier layer in many industrial applications, too.

3.3 Plasma Deposition of Barrier Layers for Photovoltaic Applications

Today, application of photovoltaic devices is an economical means for producing green electrical energy. However, photovoltaic devices will be more profitable if their price can be significantly reduced, e.g. by large-scale production. Thin film solar cells are of particular interest regarding large-scale production. Glass plates are state-of-the-art substrates for thin film solar modules made of e.g. copper indium gallium di-selenide (CIGS). They can be replaced by thin metal foils to reduce weight as well as material costs. Standard CIGS solar modules consist of monolithically connected solar cells. Therefore, the metal foil has to be insulated. In addition, diffusion of material impurities and of material elements from the metal foil into the CIGS must be prevented by a diffusion barrier, too. However, there are also some advantages when using thin metal foils as substrate material: they provide new flexibility to the modules, making them suitable for mobile applications and other niche domains.

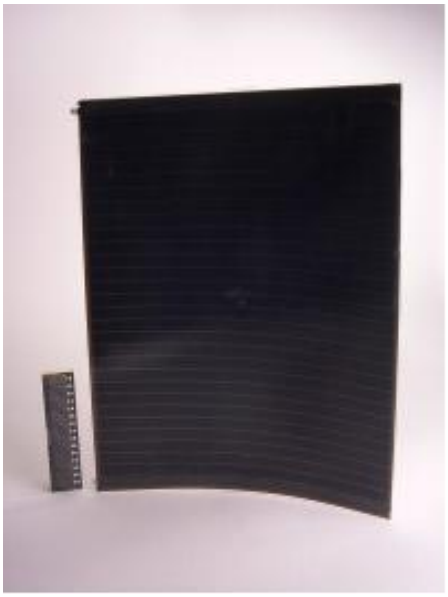

Figure 7: Monolithically connected copper indium gallium di-selenide (CIGS) solar modules on a flexible metal foil with a plasma-deposited diffusion layer in between [5-7].

The glass substrate (as well as the glass covering) can be replaced by a systems of thin polymer films deposited in a low-pressure microwave sustained plasma process on the metal plate (and on the optical layers on top of the CIGS solar modules, respectively). A monolithically connected copper indium gallium di-selenide (CIGS) solar modules on a flexible metal foil with a plasma-deposited diffusion layer in between is shown in Figure 7. These plasma processes for deposition of thin polymer films acting as diffusion barriers establish new technologies for economical production of flexible photovoltaic modules.

Furthermore, plasma processes can be used for deposition of thin film amorphous silicon (a-Si) solar cells and microcrystalline silicon (µc-Si) solar cells, too, thus providing important new markets for plasma technology.

3.4 Plasma Surface Modification and Activation for Applications in Fuel Cell Technology

Fuel cells based on ionomer membranes are very important e.g. for zero emission vehicles. The major disadvantage of commercially available membranes such as Nafion in direct methanol fuel cells (DMFC) is their relatively large permeability of methanol, which leads to a drastic degradation of the efficiency of the fuel cell. Figure 8 shows the schematic of a DMFC. Plasma surface treatment of such membranes can reduce the permeability of methanol. In addition, the bond strength of the membrane to the catalyst can be improved by plasma surface treatment.

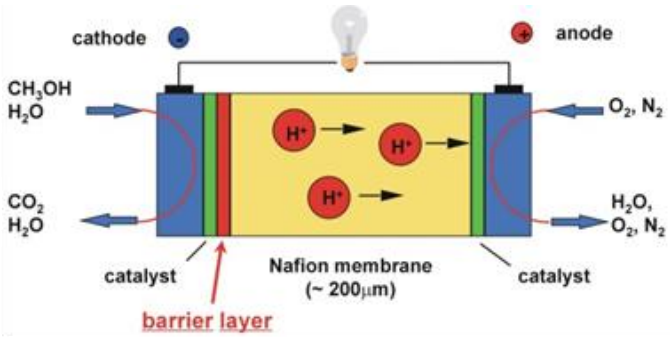

Figure 8: Schematic of a direct methanol fuel cell (DMFC) [8-9].

The porous gas diffusion layer (GDL) is another important component of a fuel cell. It provides a homogeneous gas flow to the catalyst and controls the water content of the cell. In particular, the water management in a wide range of the voltage/current polarization curves of the fuel cell is very important for the efficiency of the fuel cell. However, GDLs mostly consist of a strongly hydrophobic material which is critical for a proper water management. A partially hydrophilic GDL is a better choice, because it can retain a certain amount of water in the fuel cell.

Figure 9: Originally completely hydrophobic surface of a gas diffusion layer (GDL), showing hydrophilic properties on the areas exposed to the plasma (cf. water droplets adhered to these hydrophilic areas after low-pressure microwave plasma treatment) [9-10].

Partially hydrophilic properties of the GDL can be achieved by a surface treatment of the GDL in a nitrogen plasma process for example. When the GDL is covered by a perforated plate, only the uncovered areas of the surface of the GDL will be modified in the plasma process. Consequently, the uncovered areas of the surface of the GDL show hydrophilic properties after plasma treatment (cf. the water droplets adhering to these areas in Figure 9), whereas the covered areas of the surface of the GDL retain their hydrophilic properties. The fuel cell with plasma treated GDL shows significantly higher cell voltages than the reference fuel cell without plasma treated GDL. This is due to the fact that the membrane of a fuel cell without plasma treated GDL runs dry, especially at higher current densities. When using a plasma treated GDL, a certain amount of water can be retained in the cell leading to a better fuel cell performance.

4 Summary

Today and even more in future, there are and there will be many different applications of surface modification by low-pressure microwave plasma processes in the field of sustainable energy production and storage. The examples presented for deposition of silicon nanowires for novel lithium-ion batteries, for deposition of silicon nitride films and of polymer-based diffusion barriers for photovoltaic and semiconductor applications as well as for surface modification in fuel cell technology require non-equilibrium microwave plasma processes at low-pressure conditions. High radical densities,

homogeneity of the plasma on a large area as well as easy upscaling are major characteristics of these non-equilibrium microwave plasmas at low-pressure conditions, which can be easily generated by the Duo-Plasmaline microwave plasma source and by the plasma array based on the Duo-Plasmaline.

For further readings

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*Microwave Assisted Bulk Production of High-quality Reduced Graphene Oxide for Battery Applications**

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***A brief account on the recent paper (an open access article under CC BY 4.0 License) published by Loughborough's Advanced Ceramics Group [9]**

Rapid production of high-quality reduced graphene oxide (rGO) with less oxygen functional groups (OFGs) and large lateral dimensions is pursued worldwide owing to the fascinating intrinsic properties of graphene such as highly flexible but mechanically robust structure, excellent electronic