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Linearized Hollow Cathode Plasma for PECVD

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Abstract

Scientists and engineers at AGC/Interpane have developed a novel plasma generation system and industrialized the devices for Plasma-Enhanced Chemical Vapor Deposition [PECVD] coatings on substrates up to jumbo sized glass (3.2m x 6.0m).

Plasma generation is accomplished between multiple linear hollow cathodes, alternately driven by mid-frequency AC or pulsed power. Extremely high input power densities of 40-80 kW per meter of plasma length are achievable with robust electrode designs and a plasma generation mechanism which does not require magnets in the plasma source.

Stable plasmas can be maintained using a variety of input gases, such as Oxygen, Nitrogen, Argon, Helium, and Hydrogen.

Depending upon the choice of precursor materials and the desired film properties, dynamic deposition rates for inline coatings of 200-500 nm*m/min have be achieved for SiO2.

Plasma operation is possible in an extremely wide range of pressures from 1 mTorr to 1 Torr, while the most useful process pressures for PECVD are generally in the 1 mTorr to 30 mTorr range. Hollow Cathode PECVD pressures are compatible with conventional Physical Vapor Deposition [PVD] pressures to allow for the deposition of multi-layer coating stacks by PVD and PECVD in an inline coating system.

Introduction

While Physical Vapor Deposition [PVD] coating methods remain the standard for many vacuum deposition processes, the prominence of Plasma-Enhanced Chemical Vapor Deposition [PECVD] is steadily increasing. PECVD can provide a means for depositing materials with specialized properties or for coating traditional materials at deposition rates that are much higher than PVD can normally provide.

A variety of plasma formation methods are used for decomposition of precursor materials into surface coatings, many of which must employ complex designs for the plasma generating device or use expensive power supplies with limited scalability.

This work focuses on a novel plasma generation method based on alternating plasma discharges between multiple linear hollow cathodes, and the use of these devices for PECVD. Major benefits are realized through the relative simplicity of the plasma devices and their ability to operate at high power densities using off-the-shelf plasma excitation power supplies.

While AGC has a number patents granted and in-process for linear hollow cathode PECVD technology, there is a growing interest to collaborate with academic and industrial partners to make full use of this novel and widely adaptable technology.

Device design

General device design

The plasma devices being discussed here are generally designed as multiple linear hollow cathodes (HC) which are alternately driven using AC or bipolar pulsed power. Each hollow cathode electrode takes the form of an elongated cavity with multiple gas inputs and an arrangement of plasma outputs facing toward the substrate.

When any one electrode is in the negative voltage phase and is acting as cathode, electrons that are contained within the hollow electrode cavity are repelled from the surrounding surfaces. An electron oscillation is induced within the electrode cavity and the process gas input, which is fed through the electrode cavities, is ionized into an extremely dense plasma.

The driving of these multiple hollow cathodes with alternating current (or pulsed power) allows for plasma to be spread throughout the electrode cavity and uniformly exit into the process chamber through a series of holes or slots. The power is normally supplied by a conventional AC or bipolar pulsed power supply with a frequency in the range of 20-100kHz, as would often be used for plasma excitation for dual magnetron sputtering.

Typically, two electrodes are provided in the process chamber and are connected to the two legs of a standard mid-frequency bipolar power supply. The general design described here is shown in Figure 1. Additional electrodes may, however, be included in a single process chamber to provide a larger reaction area.

Operating voltage can vary greatly depending upon the geometry of the plasma formation cavities, the material of the

plasma generating surfaces, and the process gasses, but many designs operate at discharge voltages of 300-700V. This is, again, fairly similar to dual magnetron sputter cathode operation.

By introducing a precursor material either through the area in between the multiple linear hollow cathode electrodes or from a manifold that is external to the plasma source, a uniform thin film can be deposited on substrates in the process chamber.

The separation of plasma generating surfaces from the process chamber by way of the plasma exit holes or slots makes these devices particularly useful for long term PECVD coating. This separation can help to keep the plasma generating surfaces free of extraneous coating material.

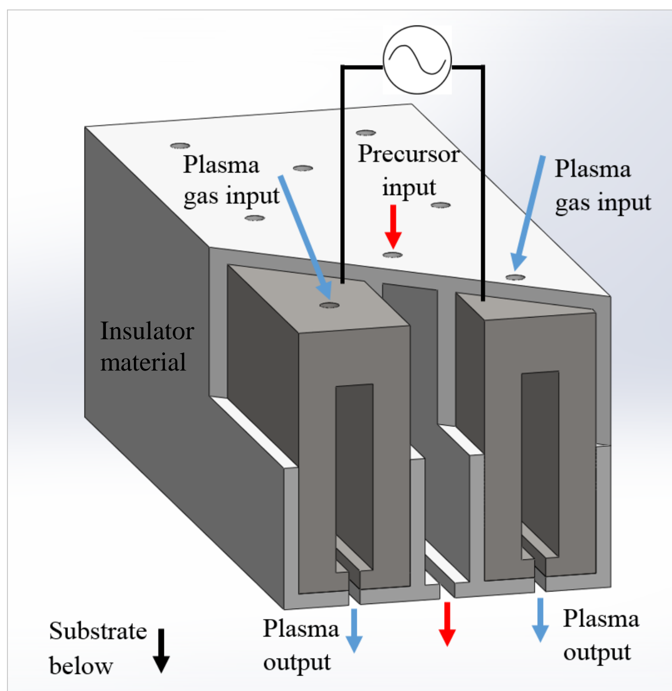

Figure 1: Simplified general design of a linear hollow cathode plasma device driven by alternating current.

Electrodes typically include water cooling circuits and cooling capacities are comparable to magnetron sputter cathodes. External surfaces of the electrodes are electrically insulated to avoid plasma formation in areas other than the plasma cavity.

The design of the hollow cathode cavities can be quite flexible, and various cross sectional shapes and sizes may be employed. Typical shapes may include large cylindrical cavities or thin cavities of rectangular cross-section, as is shown in Figure 1. The characteristic dimension for electron oscillation in the plasma cavity is typically in the range of 1 to 5 cm, although further variation is possible.

A wide range shapes and sizes of electrode cavity cross sections may be considered depending upon the specific process requirements and the physical constraints of the vacuum chamber.

This description represents the basic design of the device, while more specialized applications may include additional HC electrodes, employ magnetic fields to steer the plasma within the process chamber, or provide additional means to extract and accelerate ions toward a substrate.

Additionally, the embodiment that is described here has evolved from a focus toward coatings on flat substrates using large-area inline coating processes. Other processes for coating stationary or three-dimensional substrates are also possible with modified devices.

Scalability

While these devices could be extremely useful for coating of smaller substrates, a primary goal for their development has been the large area coating of flat glass substrates. This is typically done on substrate sizes of up to 3.21m x 6.0m, a size which is often referred to as jumbo glass or PLF [for Plateau Largeur Fabrication].

AGC has demonstrated the scalability of this PECVD process to include these challenging applications. 3.6 meter hollow cathode plasma devices have made it possible to incorporate this PECVD technology into large-area horizontal glass coaters.

Coating uniformity for inline systems is limited only by the precursor uniformity profile and, as such, can be maintained to ±5% or ±1% over the coating area for these larger devices of 1 to 4 meter plasma lengths.

Application of this technology to other industrial uses is also of considerable interest. Smaller substrate sizes, vertical coaters, and shorter coating campaign lengths could all allow for hollow cathode-based PECVD systems to be operated at extremely high power densities to allow for more effective use of difficult to react precursor materials.

High-power operation

Having no need for magnetic fields to support plasma formation, of course allows for a plasma source design that does not require any magnets to be incorporated into the device. This is an important point due to the sensitivity of magnets to heat, and is one of the factors that allows these devices to reliably operate at extremely high power densities.

AGC has operated hollow cathode PECVD plasma devices at power densities in excess of 80kW of input power per linear meter of plasma length. For specialized applications, even greater power densities may be obtainable. This can allow for high-rate coating deposition using more difficult-to-crack precursor materials such as titanium isopropoxide or titanium tetrachloride for the deposition of materials like titanium dioxide. While most PECVD devices have trouble to

outperform PVD for deposition of TiO_2, the high power capabilities of hollow cathode-based PECVD can overcome these challenges.

Adaptability to various vacuum coater types

The mechanical simplicity of hollow cathode PECVD devices, combined with flexibility in electrode geometry, process pressure, operating power, and gas flow, all allow for incorporation of these devices into a wide variety of coater applications.

As has been previously mentioned, the large scale plasma capabilities with tight control of coating uniformity make these devices especially well-suited for large area horizontal coaters.

The possibility of using thin electrode cavity cross-section shapes can allow for extremely compact devices that may be well suited for roll-to-roll web processing.

These PECVD devices tend to be much less sensitive to vacuum quality than many PVD applications, and allow for startup of a coating process rapidly after pump-down.

A 'standard' hollow cathode device that has been designed to operate alongside of sputter processes generally has a much wider plasma operating range than its PVD counterparts. By further varying the electrode geometry with respect to characteristic electron oscillation dimension, plasma outlet size, and plasma outlet spacing, linear hollow cathode devices can be adapted to an extremely wide variety of processes and vacuum coaters.

Electrode surface coatings

While bare electrodes may be used from a variety of materials like copper, stainless steel, and titanium, plasma generating surfaces of the electrodes can also be modified with functional coatings for a variety of reasons.

Electrode surface coatings are generally applied by thermal spray or elecrodeposition methods and can provide benefits including:

1. Electrode erosion control,
2. Modification of plasma ignition or operating characteristics (eg. voltage),
3. Voltage stabilization during long term operation.

Plasma performance

Plasma gas

As is the case with most plasma devices, a variety of input gasses are possible. Stable discharges have been formed with a number of plasma gasses including oxygen, nitrogen, argon, helium, hydrogen, and mixtures thereof.

High density oxygen discharges may be particularly noteworthy. Due to the robustness of the devices and the possibility of including electrode protection coatings, oxygen can be directly used as the plasma forming gas with no need to include inert gas in the system. In contrast to some plasma devices with electrode surfaces which may be more sensitive to oxidation, linearized hollow cathode plasma devices are able to sustain high power oxygen plasmas for hundreds of hours of continuous processing.

Thus far, most of the use of this technology has focused on very high-throughput applications where dynamic deposition rates are maximized. Since coating deposition rates in these cases can be considered to be roughly proportional to gas flow and pumping levels, high plasma gas flow has often been utilized to increase coating rate while maintaining the required ratios between plasma and precursor gas densities.

Typical hollow cathode PECVD devices for use in high-rate inline coating applications may utilize plasma formation gas flows in the range of 500 to 4000 sccm per linear meter of plasma length.

Operating pressure

The pressure range in which linearized hollow cathode plasma devices are able to operate is another interesting characteristic of these devices. Stable plasma has been maintained through extremely wide pressure ranges without any device modifications.

Figure 2 shows the relatively stable voltage discharge curve as a linear hollow cathode device is operated with oxygen input and no pumping, as the process chamber pressure was increased from 5mTorr up to 1 Torr.

Data in the range of 5 to 50mTorr was removed from Figure 2 due to transient conditions while the turbomolecular pump valve was being actuated, however a similarly stable voltage trend occurs in those lower pressure ranges.

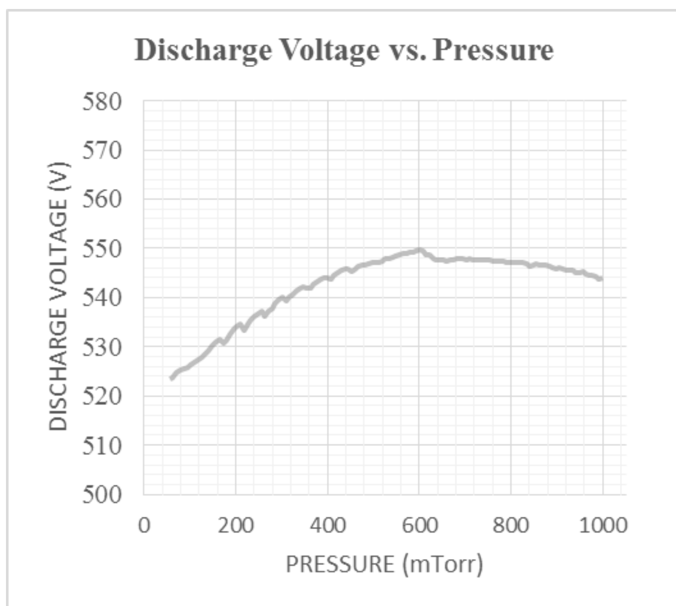

Figure 2: Voltage plot for a linear HC plasma discharge with pure oxygen feed gas and chamber pressure in the range of 50 to 1000 mTorr.

While most traditional optical coating materials are deposited by HC PECVD at pressures which are similar to standard PVD coating systems, higher pressure plasma discharges may be considered for materials with more specialized uses such as nanoparticle coatings. Depending upon the process and hardware configurations, more typical PECVD coatings may be deposited at pressures of 2 to 20mTorr and possibly up to 30 to 50mTorr. Above that upper pressure range, gas phase collisions may begin to increase and particle formation may begin.

The length of the plasma plumes extending from the electrode cavities is steadily reduced as chamber pressure rises, so most processing or coating at higher pressures may require reduction of the distances between the components of the system (electrodes, precursor outlets, and substrate).

Coating performance

Precursor material

With the wide variety of precursor possibilities that are available for PECVD use, it is impossible to fully quantify coating performance in this document.

A example result has been chosen using an interesting precursor named Trisilylamine [TSA] which can yield especially high performance for silicon-based coatings. TSA is a carbon-free precursor with molecular formula $N(SiH_3)_3$ and is expensive, but is also an extremely effective precursor that may be applicable to a variety of uses. The result that is shared here comes from tests where TSA has been used for optical coating depositions at AGC.

In testing to date with TSA precursor, dynamic deposition rates for optical quality SiO_2 with acceptable mechanical durability have been limited only by gas flow and pumping considerations. Even at coating rates above 500 nanometers*meters/minute, films showed properties that were comparable to PVD coatings that were produced at a deposition rate of approximately $1/10^{th}$ of the rates for the PECVD layers.

Material properties

Figure 3 shows the result of an FTIR examination of a silicon dioxide coating that was deposited using TSA precursor at a dynamic deposition rate of 590 nm*m/min.

Even at this extremely high deposition rate, coating properties were comparable to those of a sputtered film, with similar mechanical durability, minimal optical absorption, and a refractive index of approximately 1.47 at a wavelength of 632nm.

This coating was deposited onto a room-temperature substrate at a chamber pressure of 16mTorr, using a power density of 40kW per linear meter of plasma length. An oxygen input density of 2000sccm per meter of plasma length was utilized.

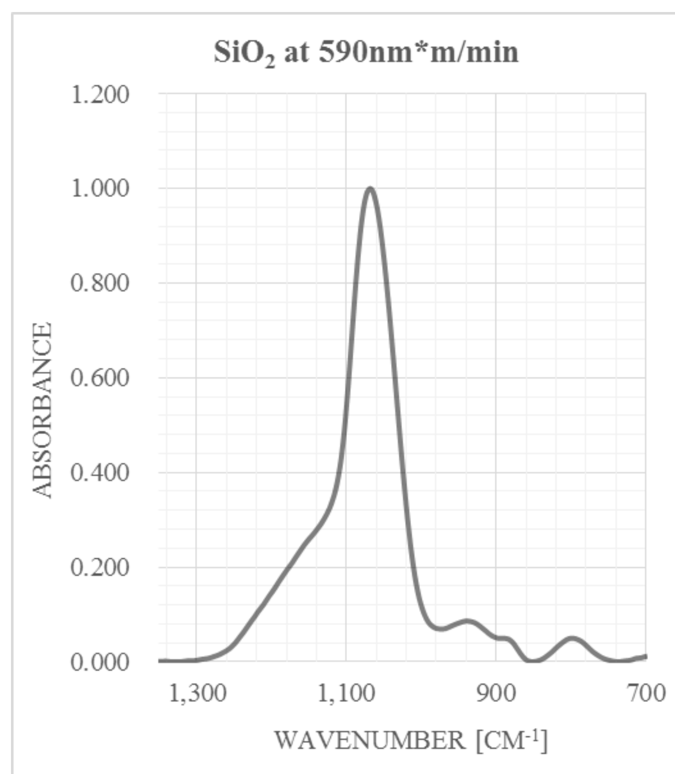

*Figure 3: FTIR result of an SiO_2 coating from TSA precursor deposited at a dynamic deposition rate of 590nm*m/min.*

The first thing to note in Figure 3 is the minimal carbon inclusion, which can of course be credited to the carbon-free precursor being used.

We can observe some level of –OH inclusion surrounding 926 cm^{-1}, which does tend to rise with such high PECVD coating rates but can be limited further if desired. Among other process modifications, increased input power is a powerful tool to reduce the level of this peak, which is also greatly reduced at coating rates which aren't so extremely high.

Even at this high deposition rate, this coating represents a good quality SiO2 film that is suitable for a variety of uses such as optical coatings or barrier layers.

Coating rates with carbon-containing precursors are often kept somewhat lower to avoid carbon inclusion, which can be observed not just in analysis methods like FTIR, but also in refractive index measurements and in reduced mechanical durability of the coatings. High quality PECVD films with low-cost carbon-containing precursors can typically be deposited at coating rates in the range of 100-300 nm*m/min, and at much higher rates if some residual carbon may be acceptable in the films.

Special applications

Hollow cathode PECVD has been benchmarked against competing PECVD devices and some specialized applications have emerged as particularly interesting for further development.

HC PECVD is well suited for applying coatings onto magnetic metal substrates because magnets are not required for the hollow cathode plasma formation. Alternative PECVD devices which require magnets below the substrate are not suitable for these applications. Even for plasma devices where magnets are not required below the substrate it may generally be preferable to avoid any magnet inclusion in the process chamber, as can be the case with this linear hollow cathode technology.

Also, HC PECVD provides some advantages for conductive coatings over PECVD processes that utilize antennas to transmit power (microwave PECVD for example). While the coating shields surrounding antennas may be rendered unusable after being coated with conductive materials, hollow cathode based plasma devices can operate normally after conductive materials have been deposited onto their shields.

Additionally, high pressure processes like the nanoparticle coatings mentioned previously can benefit greatly from the flexibility in operating conditions that HC PECVD can provide.

Conclusions

Linearized hollow cathode plasmas represent a novel tool for plasma processing and coating. They possess a variety of benefits over more traditional plasma technologies for both general high-rate coating use and for some specialized applications.

AGC/Interpane plans to expand the use of this technology further and hopes to work with new partners to include a wider range of applications across the vacuum coating world.