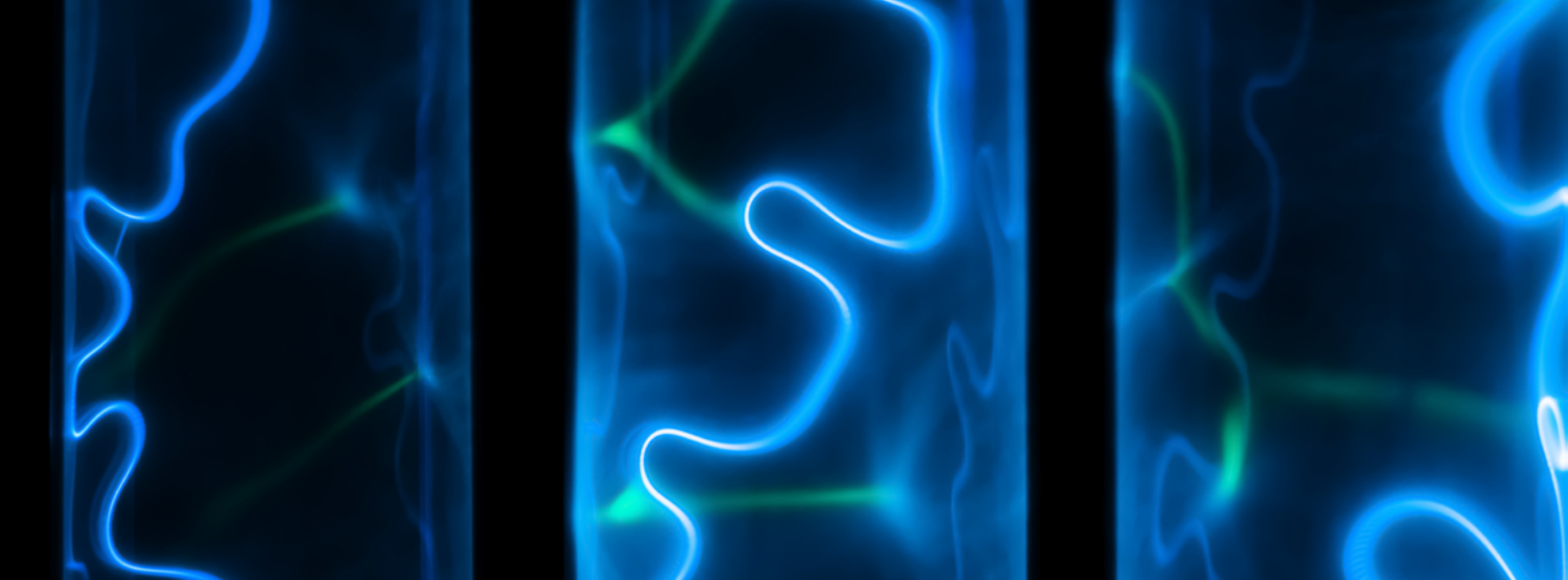


PAPER

OPTICAL EMISSION SPECTROSCOPY FOR PLASMA SYSTEMS



INTRO

OPTICAL EMISSION SPECTROSCOPY FOR PLASMA SYSTEMS

Thermal and nonthermal plasmas are used across a wide range of industrial, engineering, medical and research applications. For any plasma process, plasma composition is a critical parameter. Optical emission spectroscopy enables accurate, near-real-time monitoring of plasma both in chambers and on plasma-contacting substrates, facilitating inline process monitoring and optimization.

“Plasma” denotes a gas in which a significant proportion of the molecules have been ionized, producing a variety of excited atoms, ions, and molecules.

Electrons liberated from atoms and ions are highly energetic and can move freely throughout the plasma. These high-energy electrons can collide with neutral atoms and molecules, transferring some of their energy to them. As the neutral atoms and molecules relax back to their ground state, they emit photons of light. The color of the light that is emitted depends on the energy of the photons, which in turn depends on the energy difference between the excited state and the ground state of the neutral atoms and molecules. The presence of unbound charged particles affects the bulk electromagnetic properties of plasmas: they are electrically conductive and thus can be shaped and confined by magnetic fields.

Additionally, ionization means that plasmas can be extremely reactive, while high temperatures (and hence high particle velocities) in thermal plasmas are sufficient to cause the ablation of substrates.

Plasmas can be produced at a range of pressures and temperatures. Tuning these parameters and changing the chemical species present in plasma can dramatically affect plasma behavior and produce plasmas suitable for wide-ranging applications. Precise control of these parameters is crucial in order to maintain stable, reliable, and reproducible processes.

KEY PARAMETERS

In industry and research, plasmas can be broadly characterized in terms of pressure, temperature, and the chemical species present in the plasma.

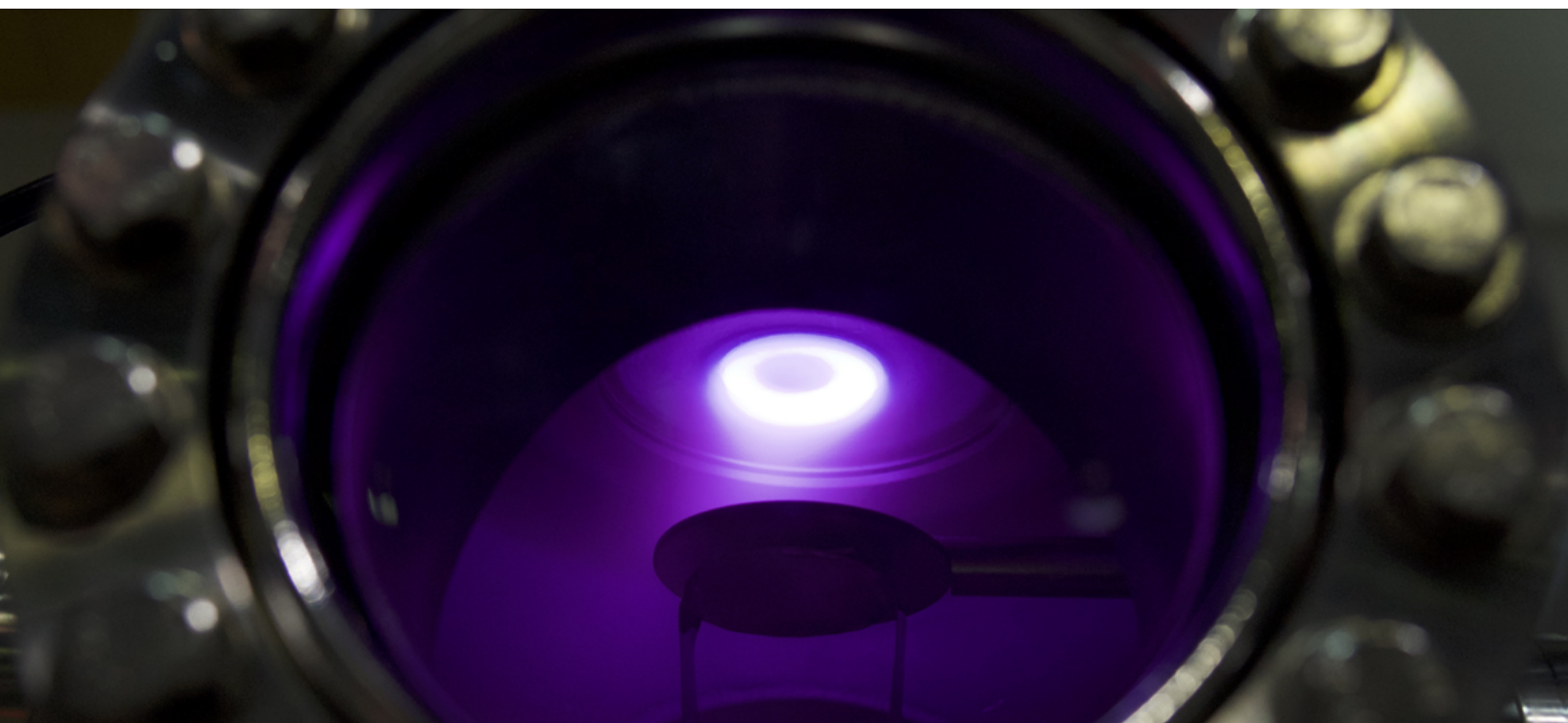
As with gases and other substances, plasma temperature can be measured in kelvin and relates directly to the thermal kinetic energy per particle. Critically, however, due to the difference in mass between ions and electrons, the effective temperature of the ions in plasma can differ from that of the electrons, sometimes significantly. In electromagnetically confined plasmas, energy is typically transferred much more efficiently to electrons than to ions, causing electron temperature to increase. Energy transfer from electrons to ions and from ions to the environment determines the temperature of the ions.

In nonthermal (or “cold”) plasmas, ions transfer heat rapidly to their surroundings before they are able to reach high temperatures. As a result, the majority of thermal energy in the plasma is stored within electrons rather than ions, resulting in an overall relatively low temperature. Nonthermal plasmas are often touch-safe and can be used in medical applications and in conjunction with heat-sensitive materials.¹

In contrast, thermal plasmas are those in which the ion temperature approaches the electron temperature. The particle energies in thermal plasmas are typically sufficient to ablate surfaces, granting them widespread application in etching, polishing and surface-texturing processes. Thermal plasmas have further applications in physical and chemical vapor deposition processes where they enable precise deposition of coatings.^{2,3}

Many applications of plasma are carried out under vacuum conditions for the primary reason that decreasing pressure reduces the rate of electron-ion recombination and reduces collisions with other molecules, thus increasing the mean free path of plasma particles. However, recent developments in plasma technology have enabled increasing applications of plasma at atmospheric pressure.

The chemical species present in the plasma are mainly dependent on the process gas used. However, the temperature and the pressure significantly alter the composition as well. As the color of the plasma is directly related to the composition, a variation in the chemical species will also have an effect on the color.



OPTICAL SPECTROSCOPY FOR PLASMA ANALYSIS

Plasma composition is a critical parameter in all types of plasma applications. In industry, engineering, and medicine, precise process control and reproducibility can only be ensured through in-depth characterization of molecular species in the plasma and on surfaces.

“**Optical emission spectroscopy**” is an umbrella term for techniques that measure optical absorption/emission spectra, i.e., the light being emitted when a sample is being excited. Optical emission spectroscopy is an important technique in plasma analysis, where it enables accurate non-contact characterization of the color of the plasma and thus the species present.

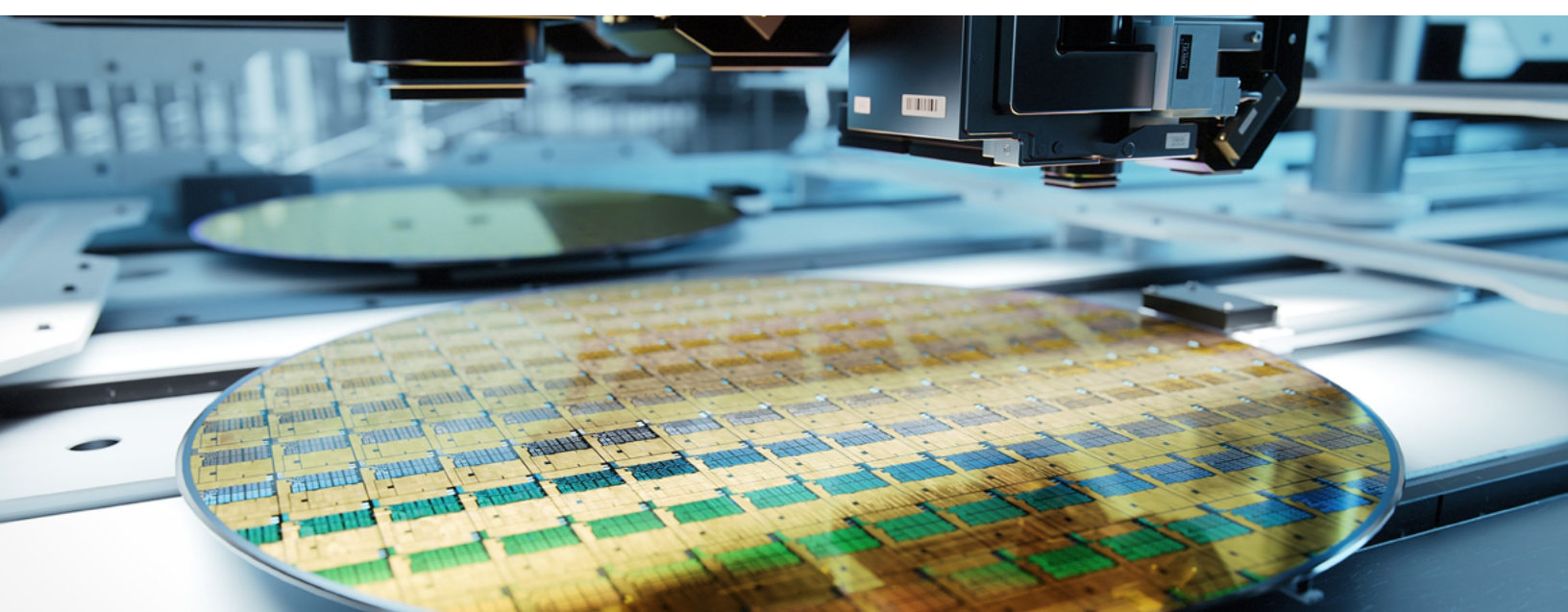
Crucially, optical spectroscopy is compatible with harsh thermal plasma environments and applications that are sensitive to contamination. In addition, optical spectroscopy provides near-real-time feedback, enabling inline process monitoring for fast, responsive process optimization in a wide range of plasma applications.

VACUUM PLASMA APPLICATIONS

One of plasma’s most common vacuum applications is the plasma etch process in semiconductor manufacturing.⁴ This is an application that involves the precisely controlled removal of material from a surface in order to develop patterns on silicon wafers. Plasma etching in semiconductor devices requires extremely precise monitoring of the reaction progress, also known as endpoint detection, and is also highly susceptible to contamination. These factors mean that plasma etching requires extremely accurate plasma analysis. Optical emission spectroscopy - typically across the near-infrared to near-ultraviolet regions of the spectrum - provides the necessary speed, stability and resolution for inline process control in plasma etch applications.

Vacuum plasma systems are also used for the deposition of coatings and thin films via various plasma-driven chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes, in particular in sputtering, plasma-enhanced chemical vapor deposition (PECVD), and ion beam deposition.

Such processes tend to involve harsh operating conditions due to high plasma energies and extremely reactive plasma species. Optical emission spectroscopy is vital for plasma analysis in such applications as it is a non-contact technique: using optical fibers enables accurate standoff measurements of the process environment.





ATMOSPHERIC PRESSURE PLASMA APPLICATIONS

Several applications are reported for nonthermal atmospheric pressure plasmas in medical applications as they are effective at sterilizing tools and tissues. They can also be tuned for other purposes, including genetic transfection, cell detachment, and wound healing.^{1,5,6}

Fiber optic spectrometers are particularly valuable in medical plasma applications, where disposable fiber optics offer low-cost disposable testing compatible with hygienic in vivo applications.⁷

Atmospheric plasmas are widely used for surface modification and finishing. Electrolytic plasma polishing (EPP) involves the production of atmospheric pressure plasmas in electrolytic baths for finishing metal surfaces, while the reactive atom plasma (RAP) process has been shown to be effective for the figuring of optical components.^{8,9} In these applications, optical emission spectroscopy provides a cost-effective and rapid plasma analysis solution suitable for inline analysis and process control.

Near real-time feedback means that optical emission spectroscopy plays a vital role in plasma analysis in a wide range of other atmospheric pressure plasma applications:

- Inductively coupled plasma mass spectrometry (ICP-OES) is a widely used technique for elemental analysis, in which atmospheric pressure plasma ionizes a sample prior to spectroscopic analysis.
- Plasma aerodynamics is a rapidly growing field that seeks to use plasmas to control aerodynamic processes. For example, for controlling laminar to turbulent transitions, reducing drag, and suppressing local heating.^{10,11}

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AVANTES OPTICAL SPECTROSCOPY SYSTEMS FOR PLASMA ANALYSIS

Optical emission spectroscopy is the ideal non-invasive measurement technique for plasma diagnostics in hostile plasma environments while preventing contamination.

However, plasmas are typically characterized by a large number of closely-spaced emission peaks. Separating these peaks requires an optical spectroscopy system with high spectral resolution. [Multichannel spectrometer systems](#) from Avantes provide extremely high spectral resolution for advanced plasma applications, even enabling the characterization of vibrational and rotational distribution functions of electronically excited molecules.

While CCD sensors have long been dominant in spectroscopy applications, newer devices such as the [AvaSpec-ULS4096CL-EVO](#) developed by Avantes achieve faster and more accurate performance using CMOS sensors. The AvaSpec-ULS4096CL-EVO provides integration times down to 9 μ s and up to 0.05 nm resolution within the range from 200 nm to 400 nm using a 3600-groove density grating, making it suitable for even the most demanding plasma analysis applications.

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