Hollow Cathode Plasma Sources for Plasma Enhanced ALD and PECVD:

Properties and Advantages

MEAglow

2018

Contents

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Introduction

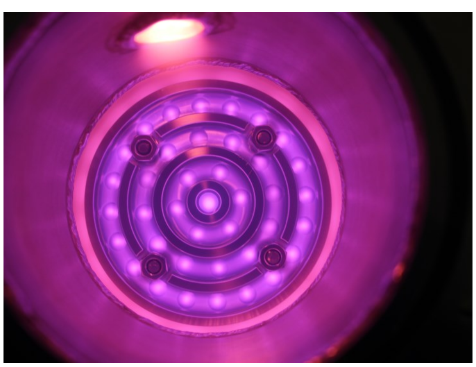
Hollow cathode plasma sources

Meaglow originally designed its range of hollow cathode plasma sources to overcome problems that old legacy sources have with the deposition of nitride materials. Since then these sources have shown a number of other positive attributes, particularly when used for plasma enhanced atomic layer deposition (ALD).

Older inductively coupled plasma (ICP) sources, widely used for many decades, were well suited for the deposition of relatively thick materials traditionally used in the semiconductor industry: in particular, silicon nitride and silicon oxide. However, in the last decade a new range of materials is being deposited with plasma based techniques, and deposition dimensions have been reduced to much thinner layers - often only a few nanometers. Oxygen contamination, identified for ICP sources as long ago as 1989 [1], not problematic for thick silicon oxide or even relatively thick silicon nitride layers, can be problematic for thinner silicon nitride layers and for the newer materials used.

Thin silicon nitride layers, grown by ICP plasma enhanced ALD, have been shown to have pinholes and lower density that seem to result in relatively high leakage currents [2,3]. Values of 141 nA/cm^2 at 2 MV/cm for a layer ~ 12 nm thick [3] are typical. This is about two orders of magnitude higher than the 1-2 nA/cm^2 more recently achieved with a hollow cathode plasma source [4] when measured at the same 2 MV/cm field strength for a film 10 nm thick. In the case of hollow cathode plasma enhanced ALD the layers are of a quality similar to LPCVD deposited material.

Figure 1: A Meaglow hollow cathode with air plasma..



Meaglow's hollow cathode plasma sources overcome the oxygen contamination problem, but also have the advantages of low plasma damage; high radical and electron density, leading to faster growth rates; improved crystallinity, and scalability. In this white paper we attempt to provide some basic background related to hollow cathode plasma sources, including some simple principles of operation and how they result in such benefits. For a more detailed understanding of hollow cathode operation we refer the reader to the reviews of Bardos [5], and Muhl and Perez [6].

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

What is a hollow cathode plasma source, and how does it work?

A hollow cathode (HC) plasma source is an all metal plasma source, in some respects similar to a parallel plate capacitively coupled plasma (CCP) source, as shown in figure 1 on the left, below. There are some review papers that provide more detail of their operation [5,6]. Here, only a very basic understanding is provided.

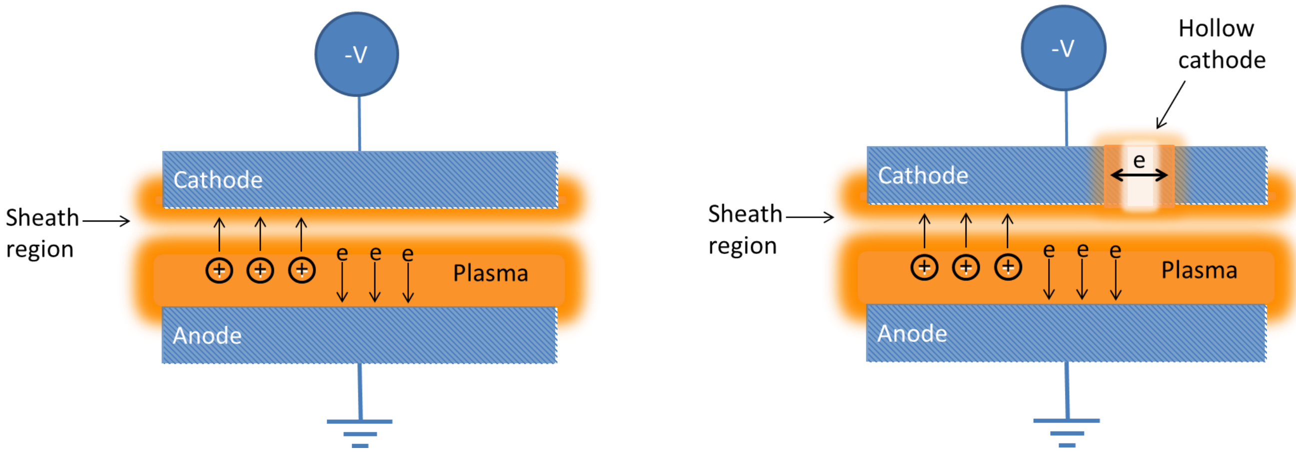


Figure 2: shows a parallel plate CCP source on the left and the same source on the right with a hollow cathode hole present in the cathode.

For the direct current (DC) case, a CCP source has a high voltage applied between a cathode and an anode to create a plasma. Near the cathode a sheath region occurs where most of the voltage potential is dropped. Electrons and ions are accelerated in this region.

Now, if a hole is present in the cathode that is about twice the diametre of the sheath width, electrons and ions become trapped in the hole and resonate in that region creating a high density (usually expressed by the electron density) plasma 2-3 orders of magnitude higher than can be achieved by a CCP. This is the hollow cathode effect. Radicals created by collision with the electrons and ions can escape, so that the hollow cathode is a very efficient producer of neutral radicals.

A similar effect happens under radiofrequency (RF) conditions: since ions are less reactive to an RF field than electrons, they separate spatially from the electrons creating a DC potential that establishes over a few RF cycles. Hence, in the RF case, the plasma itself acts as a virtual anode. Electrons emitted from the cathode that are trapped in the hollow cathode cavity resonate between the positively charged ion sheath and the cavity walls. In comparison to an inductively coupled plasma (ICP) source, the electron density is similar or slightly higher but there can also be much less contamination from the materials lining the plasma, especially when using gases that can cause reactive ion etching, such as hydride and halide gases.

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Reduced plasma damage

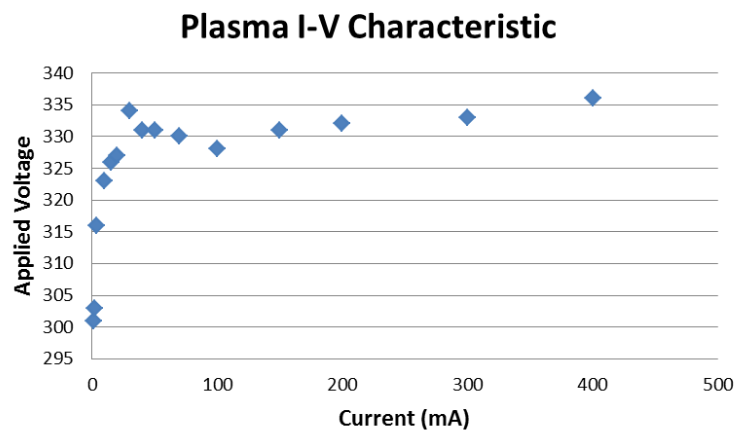


Figure 3: shows the DC I-V characteristic of a hollow cathode plasma source. For this particular plasma source, the hollow cathode effect occurs at an approximate current of 30 mA and higher.

The figure above shows the DC current-voltage characteristic of a hollow cathode plasma source. At low current a CCP plasma occurs between the cathode and an anode. With the CCP plasma the voltage increases continuously with current. Ions are accelerated by the voltage potential (to almost as high as the applied voltage) and can create considerable damage because of the excess kinetic energy they gain.

However, when the plasma strikes in the hollow cathode holes, the voltage drops, and further increases in current do not generate much of a voltage increase. Most of the increased power is absorbed as plasma current generated in the hollow cathode holes. In the holes themselves it is the local plasma potential that accelerates electrons and ions, and this plasma potential can be quite low, so that the ions generated in the hollow cathode have less energy to damage a substrate with.

Also, as shown in figure 2 on the right hand side, in the hollow cathode the electrons and ions are generated in the plane of the hollow cathode, which is often parallel to the substrate, and for the most part these charged species remain in the hollow cathode. Some damage may result from species generated by the residual CCP mode, however that becomes a minor part of the total flux available from the hollow cathode. In contrast, ICP sources operated under the same conditions accelerate a greater portion of ionic species toward the substrate. This can result in a degree of plasma damage that is evident as etching. For plasma assisted ALD, our customers who have replaced an ICP source

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Reduced plasma damage (continued)

with a hollow cathode source, and use the same deposition conditions, often see an increase in growth per cycle (GPC). This increase in GPC is particularly evident for materials that are susceptible to plasma damage, such as indium nitride [7], and may indicate a lower degree of plasma etching, a type of plasma damage. The table below shows some comparative results obtained from some of our customers for GPC values obtained initially with an ICP source and then with a replacement hollow cathode source using the same growth conditions.

Laboratory	Material	ICP GPC	Hollow Cathode GPC
National Taiwan University	Al_2O_3	1.0 Å/cycle	1.2 Å/cycle
US Naval Research Labs	InN	0.5 Å/cycle	1.0 Å/cycle
Bilkent University	AlN grown with NH_3 plasma	0.86 Å/cycle	1.02 Å/cycle
Bilkent University	AlN grown with N_2/H_2 plasma	0.55 Å/cycle	0.96 Å/cycle

Table 1: GPC values for ICP assisted ALD and using a hollow cathode plasma source replacement with the same conditions (Bilkent results are published in reference [8]).

In particular, for the case of indium nitride, the presence of free indium when doing plasma assisted ALD may be indicative of plasma damage since the nitrogen component is volatile and easily removed from the surface by high energy plasma species [7].

Comparatively, the hollow cathode plasma source appears to have less plasma damage than either CCP or ICP sources under many conditions.

High flux radical sources

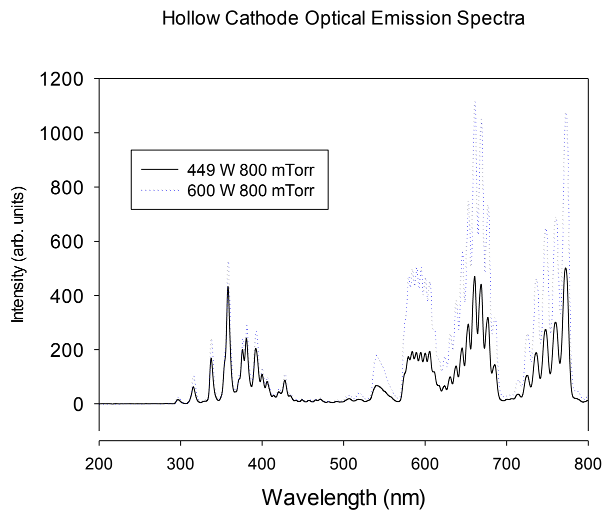


Figure 4: shows optical emission spectra for a hollow cathode plasma source with nitrogen gas [9].

While ions and electrons are trapped in the hollow cathode holes, they resonate there creating a higher density of ionized gas than can be achieved with a CCP source. Electron densities of up to 10^{13} cm^{-3} can be achieved under some conditions, that's two to three orders of magnitude higher than for a CCP source.

Figure 4 shows the OES (optical emission spectra) for a nitrogen plasma created by a hollow cathode. The spectra is taken with the spectrometer facing the plasma source directly. It is to be noted that despite the high level of ionization in the cathode holes, the OES spectra do not show ion peaks, but are dominated by emission from neutral molecular species. This doesn't mean that ions are not present, they must be in any plasma, however the production of neutral radicals is so efficient that signals from the high levels of ionized species are swamped by those of the neutral radicals. This indicates how efficient hollow cathodes are as radical sources.

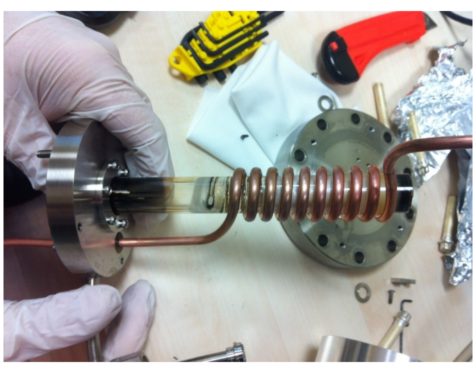
Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Reduced oxygen contamination

There are, of course, a number of well-known oxygen contamination sources for vacuum deposition: insufficient purity of source gases and background contaminants in the vacuum system being the two best known. These can be addressed with gas purifiers; by improving the vacuum system with the use of load locks; adequate attention to system leaks, and having a good quality pumping system. However, even after all these issues have been attended to, researchers have found that a lesser known third source of oxygen contamination can still result in percentage amounts of oxygen contamination in films.

For microwave plasma (MP) and ICP sources there can be quite severe oxygen contamination from plasma based etching of the dielectric liners used to contain the plasma. The release of parts per million of oxygen into the gas flow can result in percentage amounts of oxygen in a film since many materials '*getter*' oxygen. Though not widely realized, this has been a known problem for well over 25 years. As long ago as 1989 Johnson et. al. [1] reported 1% oxygen contamination in silicon (a material that is not a strong getter of oxygen) from a remote plasma source with a quartz lining. Replacing the quartz with alumina they were able to reduce the contamination. However, it was later found that even when using alumina tubes, materials that getter oxygen still had significant oxygen contamination [10].

Figure 4: Quartz lining of an ALD system's ICP plasma source, etched through over time.



For ALD, given the slow growth rates, the oxygen contamination from the dielectric liner can be considerably worse. What's more, though some of the contamination is due to ion bombardment of the dielectric windows used, for some gas plasmas, such as hydrogen, reactive ion etching of the liner can result in a greater amount of oxygen bearing species being released. Many plasma assisted ALD papers for the deposition of nitride materials show percentage amounts of oxygen contamination when using ICP plasma sources. Table 2, over page shows some examples.

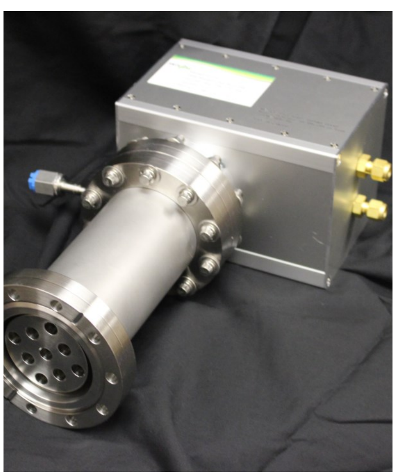
Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Reduced oxygen contamination (continued)

Table 2: examples of oxygen contamination in nitride films grown using ICP based plasma assisted ALD.

TiN ·5% and greater oxygen contamination, Microelectronic Engineering **86** (2009) 72. ·18% oxygen contamination, ECS Journal of Solid State Science and Technology **3** (2014) P253. ·20-30% oxygen contamination, J. Vac. Sci. Technol. A **31** (2013) 021503.
GdN ·5% oxygen contamination, J. Crystal Growth **338** (2012) 111.
NbN ·11% oxygen contamination, Supercond. Sci. Technol. **26** (2013) 025008.
VN ·2% oxygen contamination, Applied Physics Letters **102** (2013) 111910.
AlN ·3-35% oxygen contamination, Appl. Phys. Lett. **103** (2013) 082110. ·9% oxygen contamination, J. Crystal Growth **421** (2015) 45.
GaN ·12% oxygen contamination , Nanotechnology **26** (2015) 014002.
HFN ·5% oxygen contamination, J. Korean Phys. Soc. 56 (2010) 905.

Figure 5: One of the hollow cathode plasma sources supplied to the University of Texas, Dallas.



Hollow cathode results

Before the hollow cathode plasma source began to be taken up by the ALD community, Meaglow had already demonstrated oxygen levels as low as those obtained by MOCVD (metalorganic chemical vapour deposition) for GaN when using plasma assisted growth. Values down to $3x10^{16}cm^{-3}$ as measured by SIMS were obtained [11]. These results were very attractive for ALD researchers.

Bilkent university were the first to trial one of our hollow cathode plasma sources in place of an ICP source, taking their oxygen contamination from > 4% to approximately 0.1 % for GaN, with similar results for AlN [8]. The residual oxygen was probably from atmospheric exposure of the polycrystalline material. Other nitride materials have also benefitted, the improvement due to oxygen reduction in silicon nitride when using a hollow cathode was already mentioned in the introduction to this white paper. The technology is now well proven in terms of its ability to reduce oxygen contamination. Meaglow has a separate white paper discussing the oxygen contamination issue in more detail.

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Metal contamination from the cathode?

All plasma sources endure a degree of material sputtering or etching that can result in contamination. However, compared to microwave and ICP sources, and even CCP sources, this problem is easier to control for a hollow cathode plasma source, without the need for ultrahigh-vacuum conditions . As discussed in the previous section, the dielectric liners used for microwave and ICP sources can result in severe oxygen contamination (largely eliminated with hollow cathode sources) especially when using hydrogen or halide based gases. Hollow cathode sources are made from metals, which are generally more resistant to reactive ion etching than dielectric liners. There is also the possibility of tailoring materials to the process. For instance, for titanium nitride deposition many of our customers use a titanium hollow cathode, though we have also built stainless steel, molybdenum, Haynes alloy, and Inconel (for chlorine compatibility) hollow cathodes, with many other materials being possible.

In comparison to CCP sources, hollow cathodes use lower applied voltages, so the production of high energy ions, which can cause sputtering, is greatly reduced.

Of course, in the past hollow cathodes operating at extremely high currents were used as ion sources, so the concept of hollow cathodes that are low contamination plasma sources is not familiar to many people. Figure 6, adapted from reference [6], shows the lower current operating range of the hollow cathode plasma sources built by Meaglow, compared to the older ion sources.

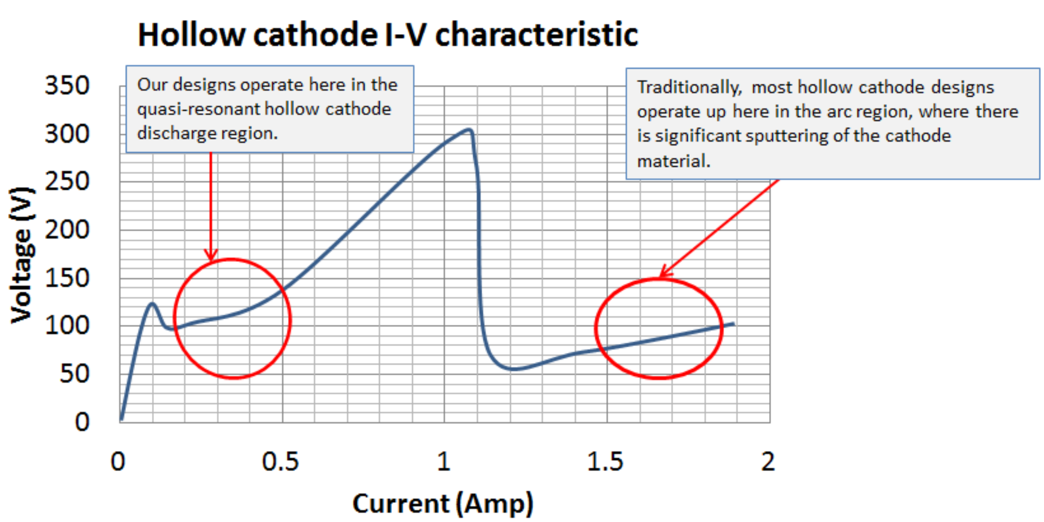


Figure 6: I-V characteristic of hollow cathode, adapted from reference [6], showing the lower current operating conditions of Meaglow's hollow cathode plasma sources.

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Metal contamination from the cathode (continued)?

Harder cathode metals, such as molybdenum, and the use of water cooling, reduce sputtering effects even more. Below, we show a SIMS (secondary ion mass spectroscopy) spectra obtained for an InGaN layer grown on GaN with a stainless steel hollow cathode plasma source. Fluorine is shown in the spectra because it acts as a reference for surface related contaminations unrelated to the growth process. The oxygen levels are approximately the same as achieved by higher temperature MOCVD film growth. Some iron is evident at the GaN-InGaN interface (at about 7000 Angstrom of depth) but in the bulk of the InGaN the iron signal is in the noise basement of the measurement, and therefore beyond the detection limit of the technique.

For this deposition process and material, the iron contamination was too low to be of concern, for other processes even lower levels might be required. Lower power operation and different materials compatible with the process can help in these instances.

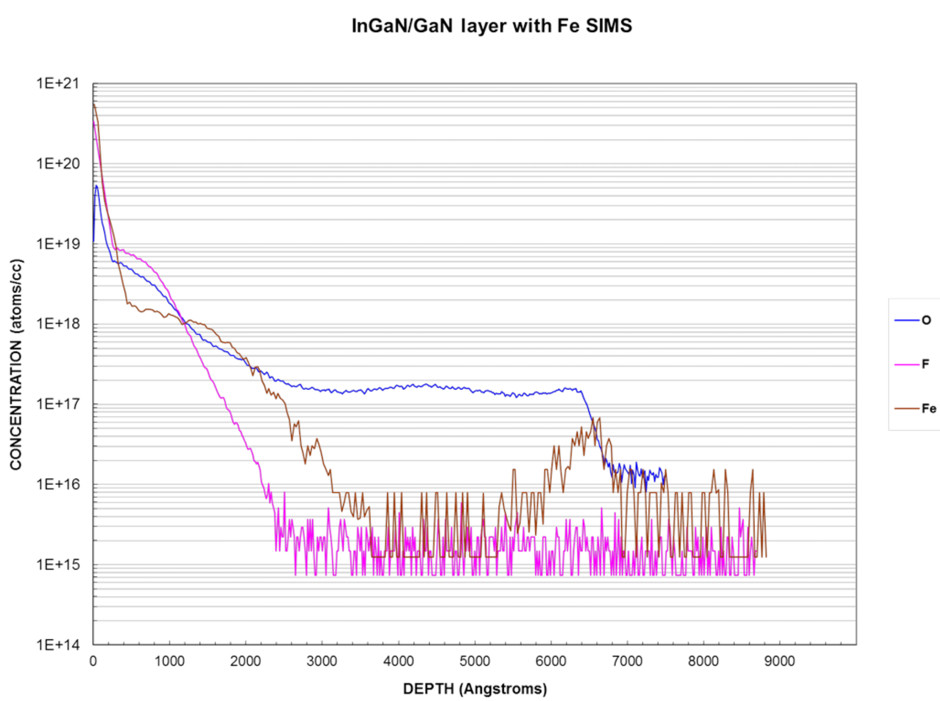


Figure 7: SIMS spectra for InGaN grown on GaN with a stainless steel hollow cathode plasma source.

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Deposition on the cathode and scalability

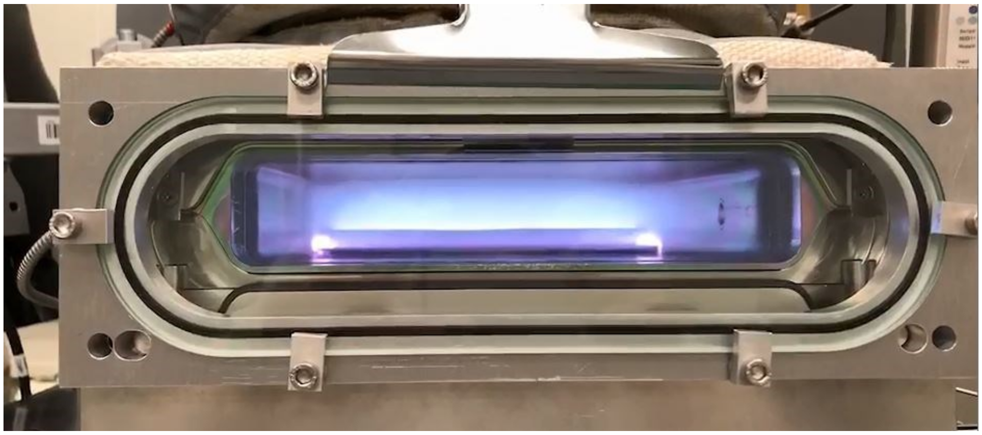


Figure 8: Meaglow ALD system fit with an 8” diametre hollow cathode plasma source.

ICP and microwave plasma sources can undergo catastrophic failure if there is metallic deposition on the dielectric windows used to contain the plasma. Such deposition can occur when there is a backflow of precursor material into those plasma sources. The problem with metallic deposition is that it blocks the high frequency electrical signal from entering the vacuum system through the dielectric, and will itself be heated by that electrical signal possibly causing the dielectric to crack and break vacuum.

This is why ICP sources tend to have small connection diametres for ALD systems: to maintain a relatively high gas flow from the plasma source so that the back flow of precursors is minimized.

In contrast, hollow cathode sources are all metal, so having metallic deposition on them is not an issue. The deposition of insulating materials is also not an issue when operating the sources at RF frequencies, since the RF will be transmitted through the dielectric insulating layer.

Because hollow cathode sources are largely immune to coating effects, the plasma source can be scaled to the same area as the substrate, as shown in the example of figure 8 above. This means that there is no longer a need to dilute the active species from a small area high density plasma source over a larger area. Hollow cathode plasma sources therefore allow a fundamental change in the guiding principles of ALD deposition equipment construction, and have the potential to increase growth rates considerably.

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

Finally

Some of the properties of the hollow cathode plasma sources are compared to other sources in the table below. For the thinner and newer materials deposited by the ALD community, the hollow cathode plasma source is the '*next generation*' solution to many old problems.

Contact Meaglow at info@meaglow.com for further information.

Table 3 - Comparison of general properties of Capacitively Coupled Plasma (CCP), Inductively Coupled Plasma (ICP), Microwave Plasma (MP) and Hollow Cathode Plasma Sources (HC).

Plasma Type	CCP	ICP	MP	HC
Plasma Density	Low	High ✓	High ✓	High ✓
Oxygen Contamination	Low ✓	High	High	Low ✓
Crystallinity	Average	Average	Average	Exceptional ✓
Plasma Damage	High	High	Low ✓	Low ✓
Growth Rates	Low	Medium	Medium	High ✓
Scalability	High ✓	Medium	Low	High ✓

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com

References:

[1] N. M. Johnson, J. Walker, C. M. Doland, K. Winer and R. A. Street, Appl. Phys. Lett. **54** (1989) 1872.

[2] J. Provine, P. Schindler, Y.Kim, S. P. Walch, H.-Ji. Kim, Ki.-H. Kim, and F. B. Prinz, AIP Advances **6** (2016) 065012.

[3] Y. Kim, J. Provine, S. P. Walch, J. Park, W. Phuthong, A. L. Dadlani, H.-J. Kim, P. Schindler, K. Kim and F.B. Prinz, ACS Appl. Mater. Interfaces **8** (2016) 17599.

[4] X. Meng, H. S. Kim, A. T. Lucero, S. M. Hwang, J. S. Lee, Y.-C. Byun, J. Kim, B. K. Hwang, X. Zhou, J. Young, and M. Telgenhoff, ACS Mater. Interfaces **10** (2018) 14116.

[5] L. Bardos, Surf. Coating Technol. **86** (1996) 648.

[6] S. Muhl and A. Perez, Thin Solid Films **579** (2015) 174.

[7] K. S. A. Butcher, D. Alexandrov, P. Terziyska, V. Georgiev, D. Georgieva and P. Binsted, Phys. Stat. Sol. A **209** (2012) 41.

[8] C. Ozgit-Akgun, E. Goldenberg, A. Kemal Okyay and N. Biyikli, J. Mater. Chem. C. **2** (2014) 2123.

[9] K. S. A. Butcher, B. W. Kemp, I. B. Hristov, P. Terziyska, P. W. Binsted and D. Alexandrov, Jap. J. Appl. Phys. **51** (2012) 01AF02.

[10] K. S. A. Butcher, Afifuddin, P. P.-T. Chen and T. L. Tansley, Phys. Stat. Sol. C **0** (2002) 156.

[11] K. S. A. Butcher, D. Alexandrov, P. Terziyska, V. Georgiev and D. Georgieva, Phys. Stat. Sol. C **9** (2012) 1070.

Customer and Meaglow journal papers for hollow cathode deposition are listed at the Meaglow website at

http://www.meaglow.com/publications/

Box 398, 2400 Nipigon Rd, Thunder Bay, Ontario, P7C 4W1, Canada +1 (807) 252-4391 info@meaglow.com