Electronics gases
Going green

By Paul Stockman, Technology Manager, The Linde Group

The electronics industry has, since the 1990s, depended greatly on the use of nitrogen trifluoride (NF_3) for its process chamber cleaning needs. When initially introduced it provided a faster way of cleaning a chamber than previous methods using sulfur hexafluoride (SF_6), tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6). In the past six years, however, we've seen a change in attitudes towards NF_3 and its predecessors thanks to the growing understanding of NF_3's environmental impact.

From the declaration by Michael Prather in 2008 that NF_3 is *the* Greenhouse Gas missing from Kyoto, and the report from the Scripps Institute showing the increase in measured NF_3 concentrations in the upper atmosphere, followed by its addition to the UNFCCC agreement in 2011, the world has seen growing momentum around the movement to significantly reduce NF_3 emissions. With the commercial availability of fluorine (F_2), a faster, lower cost and simpler method of cleaning manufacturing chambers that has zero global warming potential (GWP) compared to NF_3's 17,200 GWP100 rating is now available.

Linde has been the industry leader driving the move from NF_3 to F_2 in the electronics industry and has pioneered safe and reliable fluorine manufacturing systems and delivery techniques. Due to its advantageous chemical properties, F_2 reduces cost for electronics manufacturers, lessens their environmental impact, and creates major process efficiencies not available with NF_3.

Environmental impact

To minimise NF_3 process emissions, most manufacturers have installed high performance scrubbing systems. However, there still exists the risk of emissions during the whole production, transportation and use lifecycle. In 2008, Linde Electronics was quoted within the pages of **gas**world saying, "You can mitigate something with a high global warming potential but if your alternative has zero global warming potential, it is fundamentally better." Supporting F_2 in the semiconductor and other electronics manufacturing industries is Linde Electronics delivering on that message.

NF_3 has a GWP 17,200 times greater than carbon dioxide (CO_2). Molecular F_2 has no GWP value and with it being a very reactive molecule, there is very low concentration of the gas in exhaust streams, making it much more straightforward to abate. F_2 can also be generated on-demand and onsite from anhydrous HF and then consumed and abated at the same site, thus eliminating much of the risk of undesired emissions and lowering the total carbon footprint associated with the manufacturing, transport and disposal of NF_3 cylinders.

Across the entire value chain, in moving our customers to F_2 processes, Linde has eliminated 35,000 tonnes of CO_2 from the cleaning gas supply chain per year. However, the benefits of moving to F_2 go beyond its reduced environmental impact to

Global Warming Potential of Greenhouse Gases (100 year GWP kg CO_2 eq)	F_2	NF_3	SF_6
	0	17,200	22,800

business process and operational cost, two areas that must remain core concerns in the competitive electronics industry.

Cost

On a molecule basis, F_2 price can be very competitive with NF_3, particularly at the large scales used for chamber cleaning in a large 300mm wafer fab.

There is also a reduction in the mass of gas required – 80kg of F_2 delivers the same amount of F-atoms as 100kg of NF_3. You are not buying and transporting N atoms, which play no role in the cleaning process and in fact hinder the efficiency of the cleaning process.

Fluorine can also help improve factory productivity (thus lowering overall manufacturing costs) due to its up to 5x faster cleaning rate.

Process benefits

Fluorine allows for significant throughput improvements over NF_3 in many cleaning processes. The NF_3-based cleaning process typically uses a remote plasma source (RPS) to activate NF_3 but the F-N bond requires more energy to break than the simpler F-F bond and thus for a given RPS unit, higher flows of F_2 can be used compared to NF_3 which allows for shorter cleaning times.

Alternatively, for the same flow of F molecules, significantly lower power can be used with F_2 thus helping reduce power costs and also improving the reliability of the RPS units.

It has also been observed that the temperature of the reaction chamber typically increases during cleaning with NF_3. This is not unexpected – the recombination mechanism for NF_3 can release significant amounts of heat energy but also more energy is required by the RPS unit to activate the same number of F atoms, and some of this power is dissipated as heat in the plasma. For a high temperature deposition process this effect may not be particularly significant, but for the newer low temperature process, accurate control of the process temperature is critical. Consequently, with NF_3, additional recovery time may be required before subsequent wafers can be processed.

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It is also possible in many cases to carry out the chamber cleaning with F_2 *without* the need for an RPS unit. The RPS unit is typically only present on the process tool because it is required for the cleaning step using NF_3. Most plasma deposition processes use an in-situ method to generate the plasma and this same system can be used with F_2, with no obvious adverse effects on the chamber hardware, thus simplifying the process tool.

In some cases the cleaning can also be carried out thermally without the use of plasma. All these benefits help reduce the amount of time the process tool is unavailable for production, thus improving overall productivity and helping to lower costs.

A call to action

Linde Electronics has pioneered the use of molecular fluorine as a replacement for high GWP fluorinated cleaning or etching gases, such as NF_3 and SF_6, which are routinely used in the manufacture of semiconductors and flat panel displays. It can also be used to replace chlorine trifluoride (ClF_3) for similar cleaning applications,

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which, whilst not a greenhouse gas, can be hazardous to handle.

In order to fully realise all the benefits that F_2 can provide, some optimisation of the process may be required – and it is likely that for each OEM, unique process optimisation will be required to deliver the best results. This can be due to a number of factors – gas flow uniformity, plasma density, chamber pressure and temperature, for example.

However, whilst it may not be as simple as replacing one gas with another, the benefits that can be gained are significant. By implementing F_2 on the tools studied at a typical 300mm memory customer, tool availability improved by three weeks per year and there was a reduction in the mass of gas consumed by more than 2.5 tonnes, along with significant reductions in both power consumption and CO_2 equivalent emissions when the whole lifecycle of NF_3 is considered.

Due to the multiple significant benefits associated with the industry transition from NF_3 to F_2, Linde Electronics remains committed to continue innovating in this area. There are now more than 30 Linde installations of fluorine cleaning processes globally across the semiconductor, display and photovoltaics (PV) industries, covering a wide range of OEM platforms and process types. We'll continue to expand that number and look for new ways of creating cost, environmental and process improvements within the electronics industry, while offering them a greener alternative. gw