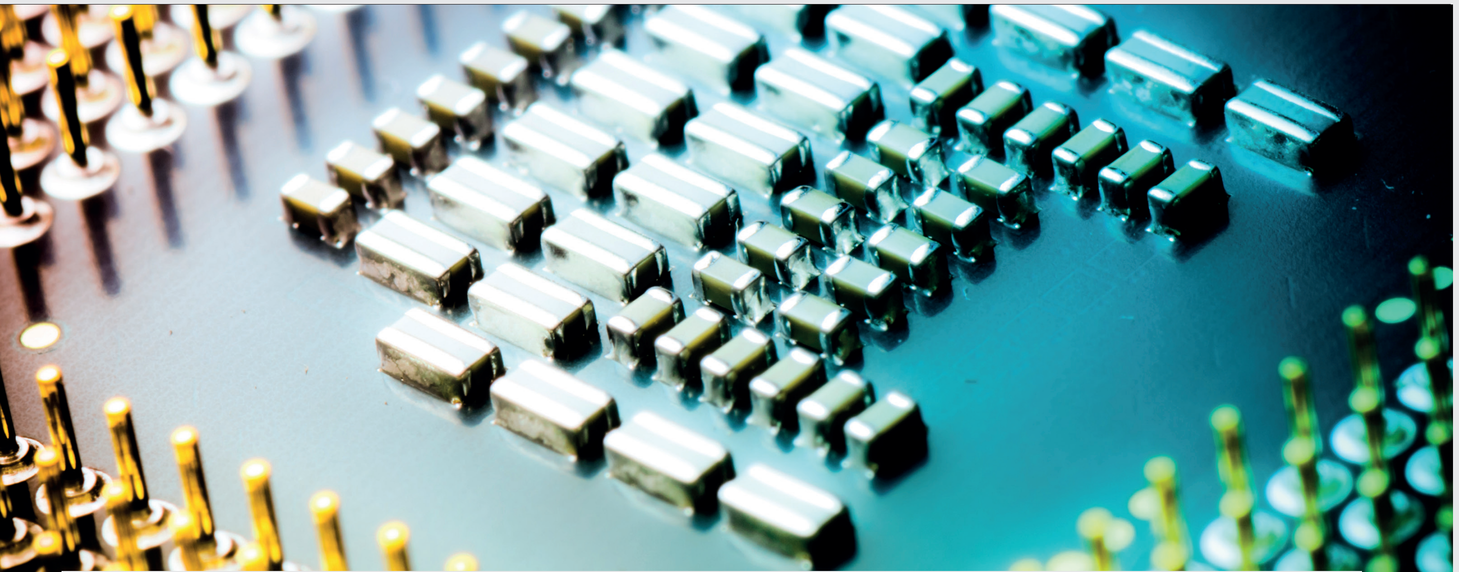
SPECIALTY GAS ZONE



Creating a semiconductor and the gases that make it happen

By Dr. Paul Stockman, Head of Market Development, Linde Electronics

Gases have been a key enabler of the electronics industry since the first commercial transistors and integrated circuits were produced in the mid-twentieth century. Properties unique to gases have made them the desired materials to build ever more complex devices: easy to transport and store; easy to dispense with precision and accuracy; and most importantly, easier to control desired chemical reactions at the molecular level.

At the core of almost all electronic devices are semiconductors. These are materials that have electrical conducting properties lying between conductors, which allow electrons to freely move, and insulators, which prevent the movement of electrons. The most familiar semiconductor material is elemental silicon, and by adding small amounts of other elements and/or placing it in an electric field, we can regulate the number of electrons moving at any time.

Electronics are built up from semiconductor devices – capacitors, diodes, and transistors – just like the simple breadboard circuits we may have built in science lab, but thousands of times smaller in scale. And just like those simple circuits, these electronics have not only semiconductors, but also conducting wires, with insulators surrounding all the working devices to ensure the electrons move where the circuit engineers intend them.

While some electronics achieve an incredible level of complexity – the latest computer chips are made using more than 1,000 steps and have more than 10 billion individual transistors, all connected by nano-scale wires in intricate, 3D levels of design – they all are made using mostly simple, building block-like processes in use for over 50 years, and are built and shaped using mostly gas materials.

In this article, we'll introduce six primary processes and some of the important gases that are used to enable them.

Electronics processing

Electronic devices are fabricated on an initial substrate. Often the substrate serves as a first electrical insulator for the device. Other times this substrate is temporary or sacrificial, and is removed after the fabrication is complete.

In addition to the silicon wafers commonly used for semiconductor chips and solar cells, other materials like sapphire, gallium arsenide, and silicon carbide can be used for making power regulating chips and LEDs. For display screens, thin pieces of glass as large as 10m^2 are used.

Nearly all electronics processing involving gases takes place inside metal-walled reactors, or chambers, which allow the process chemistry to be precisely controlled. These chambers can be the size of a few 5cm diameter wafers used to make specialised power semiconductors, or large enough to accommodate the pieces of glass used to make television display screens.

Typically, the chambers are held at reduced pressure to eliminate atmospheric contamination of the gas-phase chemical reactions, and to remove surplus chemical reactants or products from the chamber. Temperature control is also important. The substrates usually rest on top of a horizontal surface that can be heated or cooled to the desired temperature. Helium or other gases can be flowed from the surface to aid in the temperature control. Here are the primary processes used in creating computer chips and some of the principle gases used:

1. Deposition is the process that creates the materials found inside electronic devices: the conductors, semiconductors, and insulators. Typically, two gas-phase reactants are flowed into the process chamber while the substrate is heated to an elevated temperature favourable to the desired reaction, which results in a thin film product produced directly on top of the preceding layer. The reaction can be further activated by using an argon or helium plasma.

Many different gases are used in deposition steps, and these are obviously chosen as the precursors to the desired thin film product. Some gases like ammonia and silane have been used since the beginning of semiconductor fabrication. Others have come into use later, and some have been developed specifically for use in electronics.

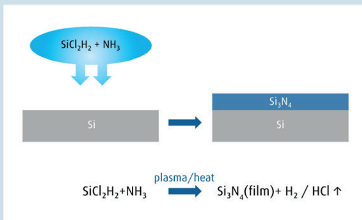
2. Photolithography is the process that forms the shapes of the devices and is key to the miniaturisation of microchips. The lithography tool – called a scanner – acts like a slide projector: it takes the light from a source to transfer an image from a master pattern, etched in a piece of glass, onto the substrate that is covered with light-sensitive chemical films. This image is the pattern that will form the minute circuitry of the microchip. Subsequent wet chemical steps are used to develop the pattern and remove either the exposed or non-exposed portion of the chemical film.

Importantly, the light sources most used for patterning are based upon gas-phase lasers, which use small amounts of fluorine, chlorine, hydrogen chloride, argon, and xenon mixed with a majority balance of neon. Photolithography is the largest application for neon. Carbon dioxide is also used as a process aid to reduce defects in the images. A new form of photolithography will use an excited tin vapour to create the light. Because the tin can deposit upon the expensive optics, large amounts of hydrogen are used to react with the tin and remove it as tin hydride (SnH_4) through the vacuum system.

3. Etching is the process used to selectively remove materials and usually follows photolithography as the way to permanently realise the pattern and shape made in the lithographic process. Etchant gases are activated in argon plasmas above the substrate and then react with one material at the surface preferentially to another. The reaction products are also gases and are →

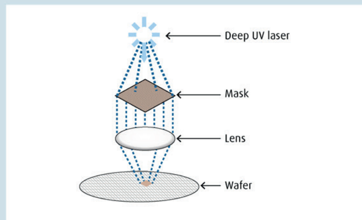
Processes and Gases Used

Deposition



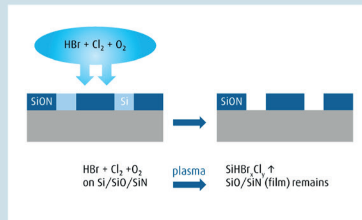
Nitrogen gases: NH_3, N_2O
Silicon gases: SiH_4, Si_2H_6, TCS, HCDS, TMS
Oxygen: O_2
Tungsten hexafluoride: WF_6
Germane: GeH_4

Lithography



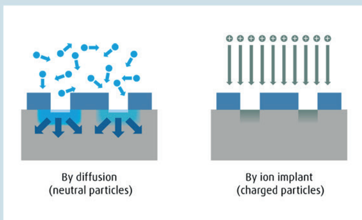
Laser gases: 95+% Ne, with Ar, Kr, and F_2
Carbon dioxide: CO_2
Hydrogen: H_2

Etching



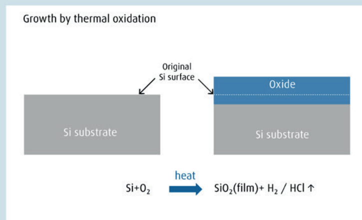
Fluorocarbons: $C_xH_yF_z$ CF_4, C_2F_6, C_3F_8, C_4F_8, C_5F_8, C_4F_6, CHF_3, CH_2F_2, CH_3F, C_2HF_5
Sulfur hexafluoride: SF_6
Halides: HCl, Cl_2, HF, F_2, HBr, ClF_3, XeF_2
Oxygen: O_2

Doping



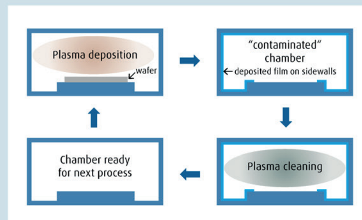
Hydrides: AsH_3, BF_3, B_2H_6, PH_3, GeH_4, Ge_2H_6

Annealing



Oxygen: O_2
Hydrogen: H_2
Argon: Ar

Chamber Cleaning



Nitrogen trifluoride: NF_3
Other fluoride gases: CF_4, C_2F_6, C_4F_8, ClF_3, SF_6
Chloride gases: HCl, Cl_2
Fluorine: F_2

removed through the vacuum system.

Most etchant gases are carbon-based and contain fluorine or other halogen atoms. The exact composition of the fluorocarbon helps to determine the selectivity to its target thin film. When excited in the plasma, these activated species are highly-reactive to the target material on the substrate surface. Fragments of these fluorocarbons also deposit on other areas of the device in fabrication and serve as a protective layer. Oxygen is also sometimes used.

4. **Doping** is the process that helps to modify the conductivity of semiconducting materials. By adding atoms of these materials into a previously deposited semiconductor material, the circuit engineer can determine the exact conditions at which the semiconductor layer will conduct electrons. The doping atoms can be added either by allowing gases to react on the surface and diffuse into a heated substrate or by plasma activation where an electric field is used to accelerate them into the substrate.

Gases used for doping include arsine (AsH_3), phosphine (PH_3), and the boron gases boron trifluoride (BF_3) and diborane (B_2H_2). Arsine and phosphine are particularly toxic and are often stored and used from safe-dispense containers, which prevents leaks of these materials by limiting the effective pressure to lower than atmospheric. Diborane is a thermally unstable molecule that will slowly decompose. This can be controlled by storing it at refrigerated temperatures and mixing it with hydrogen. Germanium is added to silicon thin films to change its conductance by slightly disrupting the order of the silicon crystal structure.

5. **Annealing** is another process used to modify the composition of an existing thin film. Most often conducted at elevated pressure and temperature, oxygen or hydrogen is reacted with the existing layer to create a new oxide or hydride layer on the surface. In other applications, the substrate with added thin film layers is heated and cooled so that the top-most thin film can form a crystalline phase.

> "Most important of these chamber cleaning gases is nitrogen trifluoride"

Argon is used when making the silicon ingots from which semiconductor and solar wafers are cut. This is because nitrogen will react with silicon at its melting temperature of 1414ºC.

6. **Chamber cleaning** is an important process to keep chambers in working condition. Excess of chemical reactants and products deposit not only on the substrate, but also on the chamber walls and other equipment inside the process chamber. Because of the sensitive dimensions of electronic devices, even small particles produced from these excess materials can ruin devices under fabrication. In between process steps, halide gases are plasma activated to react with and remove the excess materials, like an etching step for the entire inside of the process chamber.

Most important of these chamber cleaning gases is nitrogen trifluoride (NF_3), which is synthesized almost exclusively for use in electronics manufacturing. Global production now exceeds 27,000 tons. Fluorine (F_2) can also be used as a chamber cleaning gas and can be generated onsite.

Supply

Process gases in electronics manufacturing are divided into two categories for purposes of supply. Bulk gases – nitrogen, oxygen, argon, helium, hydrogen, and carbon dioxide – are six gases that are both used in large amounts and commonly sourced from industrial supply chains. These are normally stored in tanks or ISO containers to ensure adequate supply.

Electronic special gases, commonly referred to as ESGs, are all other gases and number over a hundred in pure and specialty mixtures. These can be supplied in sizes from small lecture bottles to ISO containers, depending upon the process demand. All of these require additional levels of purification and quality control well beyond that of other industrial processes.

Interestingly, though seldom a direct process gas, nitrogen is the most important gas used in electronics fabrication, in terms of the number of uses, the amount used, and the spend per year. Nitrogen is used to inert and purge most areas of the process flow, including large amounts to purge the vacuum systems and waste abatement systems. Because of the volumes used, most large semiconductor and display fabs use on-site nitrogen generators to provide reliable and economical sources of nitrogen. While it can be produced to very high levels of purity by the generators, nitrogen along with other bulk atmospheric gases are further purified to levels below 1 parts-per-billion (ppb) impurities before being distributed to the customer facility.

Conclusion

Since the start of electronic device manufacturing, gases have enabled essential processes and ever more complex designs and products. Gas manufacturers and providers have grown with the industry to expand production, provide new materials, and reach extreme levels of purity and quality control.

The Linde Group exemplifies the broad portfolio of products and deep commitment through the development and investment necessary to be a partner in this industry. Linde Engineering is the global leader in designing and building plants to produce the key bulk gases used in electronics fabrication, including on-site SPECTRA® nitrogen generators specifically designed for electronics manufacturers. Linde Gas provides a network of global and local gas production resources, from helium production on five continents, to fleets of bulk gas delivery, to high-purity ESG plants to make the most demanding of products. gw