Enabling Electronics Manufacturing: Etching Relies on Electronic Special Gases

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

for Silicon Semiconductor China

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 evermore 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.

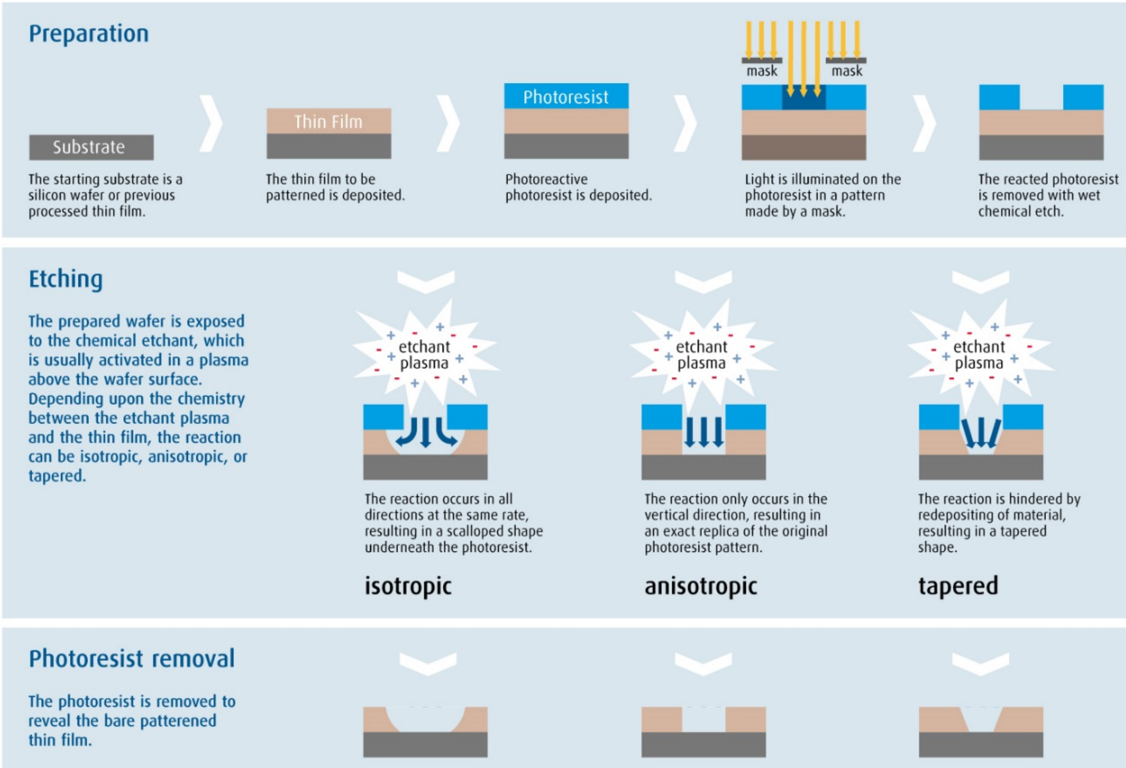
Selective gas-phase etching—that is removing part of a single material in a particular shape—is one of the enabling processes for electronics manufacturing. In this article, we introduce how simple gas molecules are used to chemically cut materials into precise shapes at nano-scale dimensions.

BASELINE PROCESS: REACTIVE ION ETCHING

Electronics manufacturing uses both wet and dry etching, but for different processes, much like using course- and fine-toothed saws to make different size and different quality cuts. In wet etching, aqueous solutions of acids or bases are used to quickly remove large amounts of material, or to completely remove a particular material. Dry etching uses plasma-activated etchant gases, usually containing halogen atoms, to selectively remove a portion of a material with greater precision and accuracy than wet etching can achieve. It is the dry etching process, often referred to as reactive ion etching or RIE, we describe here.

Electronic devices are composed of many individual circuit elements like transistors and capacitors. Each of these elements is built from different materials in three-dimensional forms by a sequence of discrete steps of material deposition, patterning, and etching. Most of these steps are conducted in an ultra-clean, high-vacuum chamber to eliminate atmospheric contamination and improve the reactions.

- **Preparation:** The usual sequence of fabrication starts with bare substrate like a silicon wafer for semiconductors, a glass pane for displays, and sapphire wafers for LED lighting. A thin film of the first desired material is deposited. Then, using photolithography, a pattern is made on top of the thin film with a sacrificial, light-sensitive material commonly called photoresist.
- **Etching:** Relative to wet etching, dry etching is much slower because of the reduced density of gases vs liquids. Dry etch rates are improved by activating the etchant gas in a plasma discharge in which there are positive and negative ions created from the neutral starting gas. The plasma is contained by electric fields, and the reactive ions are directed toward the prepared substrate. The etchant gas reacts selectively with the thin film, and the reaction products, which are also gases, are removed from the reaction chamber by the vacuum pump.
- **Photoresist removal:** The photoresist is removed by oxidizing at high temperature followed by wet etching.



Etch Profiles

Depending upon the chemistry between the plasma etchant gas and the thin film, different physical profiles will result.

- **Isotropic:** When the reaction occurs equally in all directions, the etch undercuts the photoresist, resulting in a scalloped shape.
- **Anisotropic:** When the reaction occurs only in the direction perpendicular to the substrate, the pattern is exactly replicated. This is generally the preferred profile, and halocarbon etchants are often used for etching because a certain amount of the etching reaction products will deposit on the vertical sides of the etch cut protecting against lateral etching.
- **Tapered:** The reaction can be hindered by too much side-wall deposition, resulting in a tapered shape.

While usually an anisotropic profile is the desired outcome, sometimes the more complex isotropic or tapered shapes are helpful for how the finished circuit element will function.

Criteria

Electronics manufacturing uses hundreds of different types of thin film materials. Selecting the best etch gas must balance several different criteria. Here are some of the most important ones.

- **Etch rate:** Time is money and especially in electronics manufacturing where individual fabrication tools can cost millions of dollars. All other criteria being equal, the fastest etch rate will improve the utilization of the tool.

- **Profile:** As discussed above, the shape of the etched feature is important to the device function.
- **Selectivity:** In order to be effective, the etch gas must react with the thin film much faster than patterned photoresist, underlying substrate, or previously patterned thin films.
- **Uniformity:** Because the devices are made at a very small scale, any variation in their shape will affect their performance.

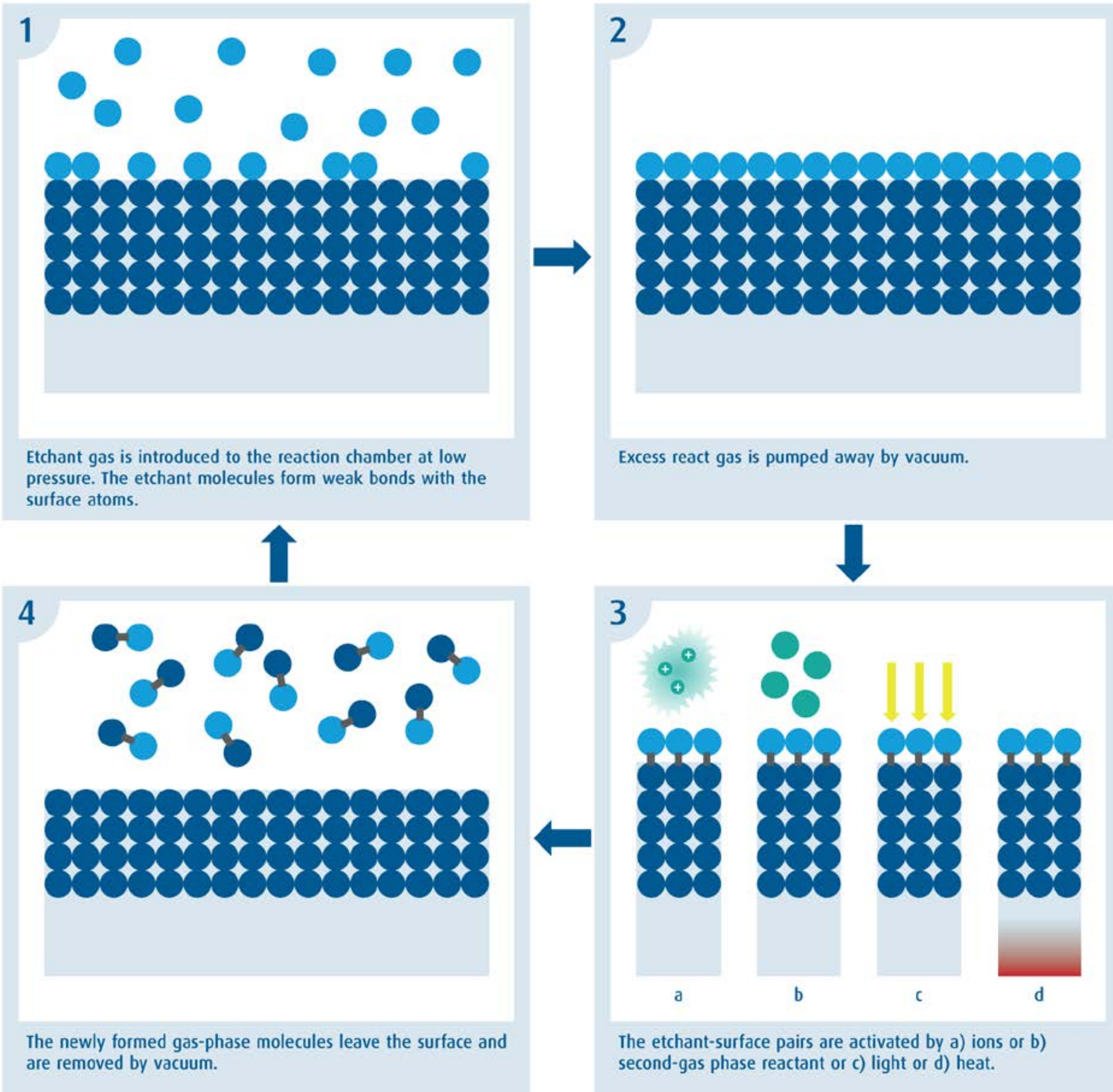
In order to optimize all these criteria, often mixtures of etchants and other gases like oxygen, argon, and hydrogen are blended at the tool in differing proportions to create processes, or recipes, which are proprietary to individual manufacturers. In the tables below, we show some of the etchant chemistries used in semiconductor and display manufacturing for common thin films.

Thin Film Material	Etchant Gas
Silicon	$CF_4/C_2F_6/SF_6/HBr/Cl_2$
Silicon oxide/ Silicon nitride	$SF_6/CF_4/CHF_3/NF_3/CH_2$
Titanium	Cl_2/CF_4
Aluminium	$Cl_2/BCl_3/HBr$
Photoresist	HCl/Cl_2

ATOMIC LAYER PRECISION: ATOMIC LAYER ETCHING

For more than 10 years now, atomic layer deposition (ALD) has been used in high-volume semiconductor manufacturing, allowing chip producers to precisely deposit single atomic layers of complex materials. Now, the complementary etching process is entering commercialization.

Atomic layer etching (ALE) is accomplished by using two half reactions. First, a reactant etchant is introduced to the process chamber as a gas at very low pressure. Van der Waals (weak-bond) forces bind a monolayer of etchant molecules to the wafer surface, and the remainder of the etchant gas is removed by vacuum pumps. Then, in a second reaction, the etchant-surface molecule pairs are activated. The activation can take various forms: reactive ion bombardment, a second gas-phase chemical reactant, heat, or light. The activated pairs then form a new molecule, which is a gas and leaves the surface. The net reaction is the removal of one monolayer of the surface thin film.



Because only one molecular layer has physical contact with the surface, the reaction is self-limiting. The sequence is repeated to remove additional layers of the surface thin film, and can result in either isotropic or anisotropic etching depending upon the nature of the chemistry and activation method. While offering greater control, ALE by its nature is a very slow process compared to bulk gas-phase etching, and therefore is only used for processes with complex shapes and single-nanometer dimensions.

Today, ALE finds commercial use for the critical metallization layers of advanced logic. In the near future, it is forecast to also be used for smoothing line-edge roughness of EUV patterned features and also with nanowire or gate-all-around (GAA) transistors which appear in technology roadmaps below the 5 nm node.

Market

Almost all etchant gases are manufactured on industrial scales for non-electronic applications. Fluorocarbons (C_xF_y) are commonly used as refrigerants. Chlorine (Cl_2), hydrogen bromide (HBr), and boron tetrachloride (BCl_3) are all used in large quantities as chemical intermediates. And sulfur hexafluoride (SF_6) is used as an electrical insulator for high-voltage switches. Only nitrogen trifluoride (NF_3) is made almost exclusively for use in electronics manufacturing. All of these are manufactured in China for industrial purposes, and capability is developing for electronic grade materials.

Purity distinguishes the quality of material used in electronics manufacturing versus industrial applications. Refining these gases using distillation and absorption, the purity is increased to 99.99% pure or better. Purification and analysis is critical because any impurities in these gases will come in direct contact with the semiconductor wafer or display glass in process. It is the responsibility of the material supplier to ensure uniform purification and analysis from source material, which may have multiple, global origins.

Depending upon the usage requirement, etchant gases can be supplied in a variety of containers, ranging from small cylinders holding only a few hundred grams to ISO containers that can supply up to 10 tons in a single package.

The size of the current global market for electronic etching gases is 4 billion RMB. Growth is driven both by number of devices like smart phones and televisions sold, which increases the area of substrates processed, and by the complexity of the devices, which increases the number of etch steps required.

Today's leading-edge logic chips require over 150 different etch processes. Recently, memory chips have changed in order to increase the density of information that can be stored. Now, the 3D NAND designs have many storage circuits stacked vertically on a single wafer, and the critical etch processes need to make high-profile holes and trenches through hundreds of layers of thin-films at a time. The etch process takes several hours and consumes relatively larger amounts of etch gases.

SUMMARY

Making complex nano-scale devices requires precision processes. By selecting the right etchant gas or mixture of etchant gases, along with the optimization of other parameters, electronics manufacturers can continue shrinking device scales and increasing device complexity.

Linde provides the complete portfolio of etchant gases for all application sectors in electronics. Linde combines multiple raw material suppliers with its own investments and proprietary technology for purification and packaging. Diversity of source and investment in technology is the way Linde ensures the most robust supply chains of critical materials for its electronics customers.