Less is Moore

Electronic etchant gases selectively remove materials to reveal nano-scale circuits

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Electronics manufacturing is a highly complex sequence of adding and subtracting material, with the resulting sum yielding circuits sometimes less than one hundred atoms wide. For over 50 years, Moore's Law has driven an industry to make smaller devices on larger scales.

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

Process

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.

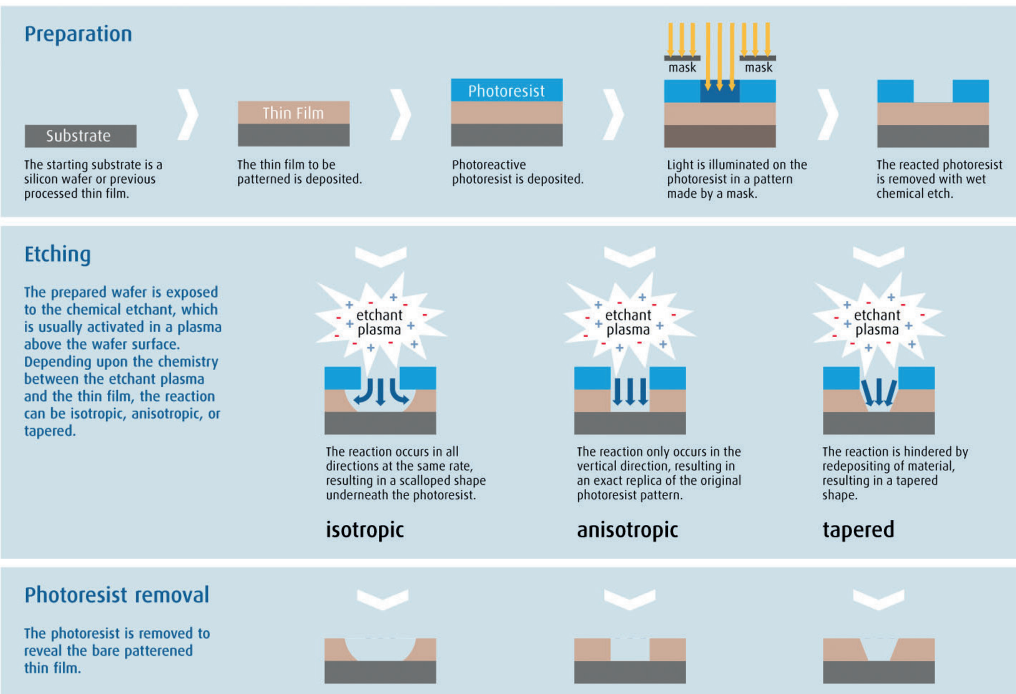
In wet etching, aqueous solutions of acids or bases are used to quickly remove large amounts of material, or to completely remove a particular material. Dry etching uses plasma-activated etchant gases, usually containing halogen atoms, to selectively remove a portion of a material with greater precision and accuracy than wet etching can achieve. It is the dry etching process 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 a 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 (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, some of which are described here:

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 either patterned photoresist or 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.

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

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.

Market

Almost all etchant gases are manufactured on industrial scales for non-electronic applications.

Fluorocarbons (CxFy) 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.

Purity distinguishes the quality of material used in electronics manufacturing vs industrial applications. Refining these gases using distillation and absorption, the purity is increased to 99.99% or better.

The size of the current market for electronic etching gases is $550m. Growth is driven both by number of devices like smartphones 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 computer 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 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. The company 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.