Gas Plasma—A Dry Process For Cleaning & Surface Treatment

By Lou Rigali

Everyone is familiar with some form of gas plasma or glow discharge. The neon bulb is an example of a low-temperature gas plasma. The sun is a high-temperature gas plasma. Lightning is a high-energy electrical discharge that produces a glow or plasma. While all similar, these forms of plasma differ in many important details. An explanation can be as extensive as a doctoral thesis, involving chemistry and physics, but even a simplified description can provide meaningful information.

Plasma is a state of matter—a so-called fourth state, along with gases, liquids and solids. An ion is a gas atom that has become charged by losing or gaining an electron. When a significant, but low, fraction of the gas is ionized, the plasma formed is not in thermal equilibrium, and the temperature of the gas is only about 30–50 degrees above ambient, while the electrons are much hotter. A neon light is an example of this kind of plasma. The sun is an example of a high-temperature plasma, where the gas is all ionized and the gases and electrons are both at a very high temperature.

Typically, a low-temperature plasma is formed under vacuum conditions ranging from 100–1000 mTorr, although there are a number of publications that describe an atmospheric process (not a corona or dielectric discharge).[1] The energy to dissociate the gas can be either DC voltage or radio frequency from several thousand Hz, up to microwave frequencies of 10 GHz. It can be argued that the chemistry of the plasma is the same, independent of the power source; however, each method of dissociation has its merits and disadvantages.

In addition to ions, a plasma contains free radicals, which are atomic and molecular species in excited energy states. Many of these species can react chemically or physically under relatively mild conditions. For instance, paper that will "burn" or oxidize rapidly at about 800 °C will undergo the same reaction at about 30–60 °C.

The types and nature of the species formed will depend on the gases used. The most important active agent is atomic oxygen in an oxygen plasma. This is a free radical, and will react with all organic material to form CO_2 and H_2O. When argon is used as a gas, an argon ion can be accelerated in a field and has enough energy to break carbon-to-carbon bonds, or to displace by sputtering other elements on a surface. Whichever gases are used, the reaction is at the surface and material is removed on the molecular level at rates of Ångstroms per sec or min.

The first commercial application of gas plasma was for ashing animal tissue. The technique was used to remove the organic matrix and leave the inorganic residue for subsequent analysis. In this way, the analyst could detect trace amounts of elements in plant leaves, human hair and animal tissue. Even now, plasma-ashing techniques are used to screen for the presence of asbestos in lung tissue. What began as an analytical technique for the chemist, soon grew into a billion-dollar business for making semiconductor devices.

Plasma, however, is not only used for the fabrication of wafers. It is used for a variety of applications in different industries. There is merit in reviewing the various applications in order to obtain a better understanding of the process and its benefits. Terminology for a specific technology may differ significantly from one industry to another, even though the processes may be similar. What a wafer fabrication engineer refers to as *resist stripping*, an engineer in another field will call *cleaning*.

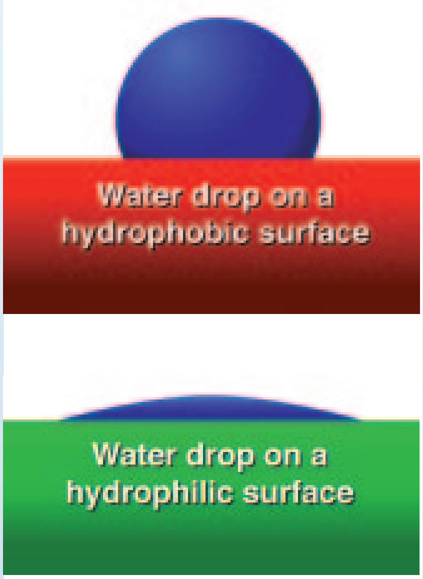

Fig. 1

Semiconductor Applications Wafer Fabrication

There are many terms used to describe the plasma process. It is often difficult to define these terms, because the same term can apply to more than one process—and vice versa. In the semiconductor industry, the terms *ashing*, *stripping* and *etching* can all mean the removal of photoresist from a wafer. Removing metal and oxides is usually referred to as an etching process. Thin organic and inorganic films, such as nitrides, can be deposited on wafers (and other surfaces). Most applications involve making significant changes in the surface, extending several microns into the surface.

Packaging & Assembly

Unlike the wafer fab, most of the applications in this section involve the first few hundred Ångstroms of the surface. The topography of the surface is not drastically changed, and most applications involve improving adhesion. Adhesion to a surface is usually good if the surface has high

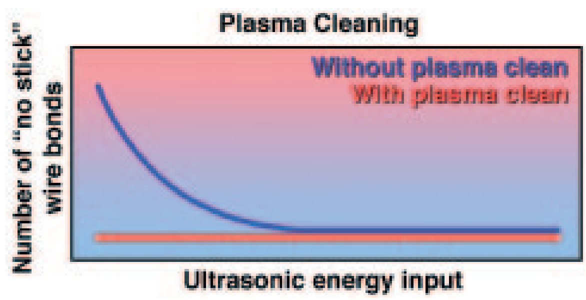

Fig. 2

surface energy. Terms such as cleaning, ablation, treatment or roughening generally describe the sample process.

A convenient way to measure surface energy is by measuring the contact angle of a deionized water droplet (see Fig. 1). When the contact angle is small, the surface energy is large and the unactivated surfaces are called *hydrophobic*. Good adhesion can be obtained when the contact angle is less than 10 degrees.

Die Bonding

Plasma cleaning/treatment of substrates will always improve the adhesion of the epoxy and provide a better bond between the die and the substrate, as shown in Fig 2. The better bond provides better heat dissipation. Studies have also shown that there is less delamination at the die with those samples that have been plasma treated.[2]

Wire Bonding

Electron spectroscopy for chemical analysis (ESCA) has shown that the presence of carbon on a surface will limit the quality of the wire bond.[3] The relative level of carbon contamination on a copper surface, for example, can be determined from the ratio of the area of the carbon (C) and copper (Cu) peaks in ESCA. Because water drop measurements are much easier to perform, it is good to know that the measured ESC C/Cu ratios correlate extremely well with water drop contact angles measured on the same surface (see Fig. 3).

Bonding pads on the substrate are also subject to various and inconsistent levels of contamination. One source of contamination on the die surface is fluorine ion, most likely left as a residue on the wafer or die during the fab process.[4] While the presence of this contamination may not show wire bond degradation immediately, there is evidence showing correlation of the presence of this element and bond failure resulting from the migration of fluorine, causing embrittlement of the wire.[5] Removal of this contaminant may require the use of argon bombardment. This is an important application of plasma (*i.e.*, the removal of trace amounts of impurities, such as inorganic ions, by the use of argon).

Encapsulation

In this process, we are asking the molding compound to provide, in addition to all of the other important required properties, good adhesion to a number of different surfaces. Depending on the type of package, the molding compound must adhere to the substrate material, solder mask, die and the metal bond pads. There are many applications that involve the bonding of one material to another—plastic to plastic, metal to plastic, etc. In each of these bonding operations, plasma improves the quality of the bond, as shown by the testing and measurement done in the study by Herard (Fig. 4).[6]

Marking

The replacement of organic solvent-based inks with aqueous-based inks does not provide the same consistency of adhesion. Even heat or hydrogen flame treatment produces inconsistent adhesion. Again, plasma-treated surfaces always provide a better surface. Some situations will show better results than others because of the nature of the ink, the encapsulant and the marking process. Plasma treatment ensures uniformity of the process, and decreases the variability of the results. Printing or marking on many different types of surfaces is also improved, especially with the use of aqueous-based inks.

Fluxless Soldering

A patented process by MCNC, using plasma, has been shown to give good welding results with typical lead and gold solder formulations, without the use of flux, and therefore without the requirement of a flux removal step.[7]

Non-semiconductor Applications

Removal of Vacuum Grease From Machined Copper & Stainless Steel Parts

Manufacture of very sophisticated medical diagnostic equipment that operates under vacuum conditions requires that the machined metal subassemblies that go into the product must be absolutely clean from contamination, in particular, but not limited to carbon. In addition, many of these same machined parts must be replaced periodically. The wet cleaning process that was used included the use of acetone and water. The disadvantages were that there was always

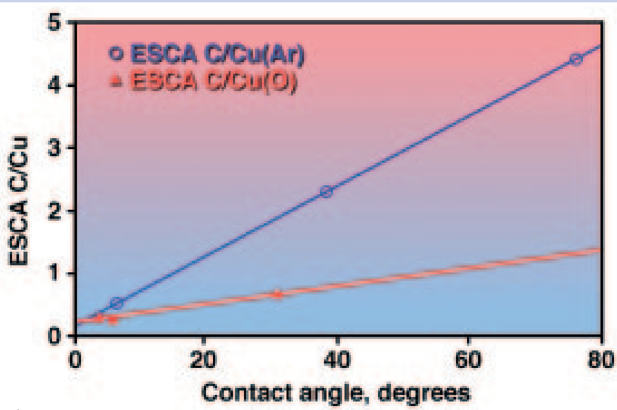

Fig. 3

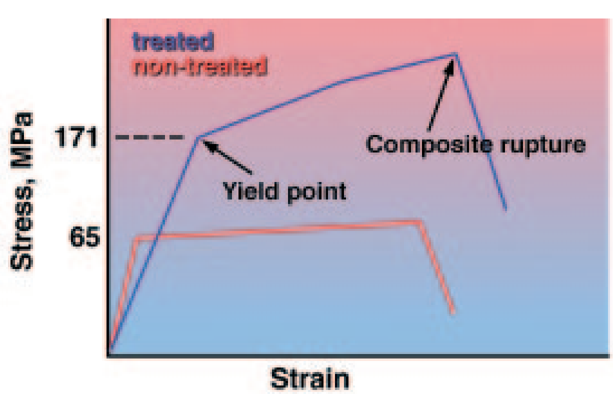

Fig. 4

some residue of the solvent that compromised the vacuum; a company directive required that, wherever possible, the use of all organic solvents be eliminated.

A specific cleaning process was developed using O_2/CF_4 plasma in a batch plasma system (March PX-2400). The test samples were contaminated by taking a finger smear of vacuum grease and spreading it on the parts. No attempt was made to measure the amount of contamination, but it would appear that it was about 1000 times greater than would normally occur during actual use. Process time varied, as one would suspect, as a result of the indeterminate levels of contamination, from about 10–30 min.

There are many other applications that are outside the semiconductor industry. From the examples provided here, one can project the use of plasma into many other fields, such as:

- Medical—treatment of catheters
- Environmental—low-temperature combustion of toxic agents
- Manufacturing—removal of machine oils from various parts
- Plastic—treatment of films to improve surface properties
- Disc Media—improve the uniformity of deposited thin films
- Film—micro-via etching[8]

Equipment Choices

One can select either manual batch, automated batch or fully automated processes. Plasma systems have been developed to meet most requirements—from small development tools costing less than $10,000, to automated systems costing about $250,000.

Today, the plasma process can be integrated into almost any assembly and high-throughput line. The only obstacle is the reluctance to add a new (25-year-old technology) process to the line. P&SF

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About the Author

Lou Rigali is a graduate of Northeastern University in Boston, worked as a chemist for several years and then entered into product marketing with Varian Associates. He started in plasma technology in the late ’60s with Tracerlab (LFE) as a product manager. Lou began working with March Instruments in 1982.