Wafer Bonding

Improved Water Vapor Delivery for Direct Hydrophilic/Hydrophobic Bonding

“Wafer Bonding” refers to the ability to bond mirror-polished, flat, clean wafers without adhesives or external forces. A wide range of applications use wafer bonding techniques to bond both similar and dissimilar material wafers (Figure 1).

![Figure 1: Wafer Bonding Application Illustration. Source: Yole Développement](http://www.semiconductor-today.com/news_items/2011/MAY/WAFERBONDING_200511.html)

For wafer bonding to be effective the bonding interface must be:

1. Flat
2. Clean
3. Particle free
4. Bubble free

Even optically flat wafers will have surface roughness in Angstroms (Å) that will generate gaps between two wafers. For a stable bond to form, wafer surfaces must become polarized. Water enables polarization on each surface. The water molecules act as a bridge to bring two non-flat surfaces into contact. Hydrogen bonds—formed from either the silanol groups (hydroxyl terminations) of the hydrophilic wafers or through dangling hydrogen bonds on hydrophobic surfaces—allow joining of the wafers through Van der Waals forces. The water molecules can fill gaps of up to 10 Å between the wafers. (Figure 2)
Wafer bonding is used to fabricate hydrophilic and hydrophobic wafers. In a hydrophilic process, the wafer surfaces have an affinity to water and readily adsorb water molecules. These surfaces are termed “wetted”. A hydrophobic process creates an aversion to water and the water is pulled into droplets on the surface. These surfaces are termed “dewetted”.

TABLE I: Comparison of hydrophilic and hydrophobic bonding processes.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Hydrophilic Bonding Process</th>
<th>Hydrophobic Bonding Process</th>
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<tr>
<td>Pre-bond hydration</td>
<td>SiO2 terminates in Si dangling hydroxyl bonds that react with water</td>
<td>Generates dangling Si bonds with water molecules</td>
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<tr>
<td>Heating (2000C)</td>
<td>Hydrogen bond bridging develops between OH groups</td>
<td>Bonding bridges formed through OH groups</td>
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<tr>
<td>Post-Bond (&gt;300C)</td>
<td>Hydrogen bonds are replaced with Si-O-Si bonds</td>
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<tr>
<td>Annealing (~1000C)</td>
<td>Bonds achieve full strength</td>
<td>Si-O-Si bonds formed</td>
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<tr>
<td>Post Process (500C)</td>
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<td>Si-O-Si bonds convert to Si-Si</td>
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Applied Microengineering reported improved bond strength through the use of wet oxygen during the bonding process. After several other process steps, they pumped down to base vacuum, back filled with wet oxygen, evacuated again, bonded the wafers and then post annealed at 200°C. The figure below shows the improvement in wafer bond strength after exposing the surface to moisture versus and dry process. Bond strength increased by 2.5 times. This may be due to the ability of the water to fill gaps between the bonding surfaces.

It is assumed these bond strength improvement is from better gap filling. It takes 44 molecules to fill a 10 Å gap between two silicon wafers. If the bonding surfaces are saturated with silanol groups, they contain 36 water molecules. At least 8 water molecules are needed for bonding. The injection of water molecules before the bonding step, but after vacuum will be useful. These extra water molecules should be retained through bridging created by Van der Waals forces previously mentioned. [2] The excess water and gas is then evacuated to allow for completion of the oxide bond. Removal of carbon contamination is also critical. Water is known to preferentially displace hydrocarbons from silicon surfaces. [3]
Water Vapor Delivery to Enable Wafer Bonding

The bonding of hydrophilic and hydrophobic wafers can be improved through the use of water. Controlled delivery of pure water vapor into vacuum is challenging. Direct flow control is difficult due to the enormous expansion from water to gas: 1 gram of water expands to 1,244 cc of gas at room temperature and atmospheric pressure. For vacuum applications this factor can be 1,000,000 to 1. Because of this, water vapor is commonly delivered through a bubbler with a carrier gas or by directly pulling vapor off the head space of an ampoule.

Water bubblers add water vapor based on the partial pressure of the water relative to that of the carrier gas. Unfortunately, bubblers have problems with contamination and bacterial growth, as well as variability with temperature, pressure and fill level. To remove residual oxygen and nitrogen in the water, the DI water in the bubbler must be degassed before use. Most problematic is the violent boiling that can occur if the bubbler is directly exposed to vacuum.

Microdroplets are another serious problem when using bubblers because they can be entrained, increasing variability in the delivered water and making the actual volume delivered neither controlled nor repeatable. Further, microdroplets lead to entrainment of ion contamination and particulates, and cold spots occur where microdroplets land, leading to non-uniformity and warpage.

Ampoules have all the same problems as bubblers except they eliminate a carrier gas. This allows higher concentrations of water vapor, but does not prevent any of the contamination and water droplet entrainment issues.

Because of these known changes, a new water vapor delivery method has been developed that uses a specialized membrane for purifying and delivering water vapor directly into vacuum processes. The membrane selectively allows water into a carrier gas or a vacuum process while excluding other components due to differences in permeation rates.

Referred to as pervaporation, this separation techniques employs the membrane as partitioning phase. In the process, a driving force, usually pressure or concentration gradient, is generated across the membrane and the selective component(s) preferentially pass to the other side as the permeate.

By selection of a non-porous ionic perfluoropolymer membrane, water vapor crosses through the membrane, but particles, micro-droplets, volatile gases, and other opposite charged species are excluded. Other contaminants in the water source cannot permeate across the membrane. Similarly, because the membrane is highly selective it prevents most carrier gases or vacuum from crossing over into the water source. A barrier is created to separate the liquid water from directly contacting the process conditions.

For oxide films to work properly, controlled film thickness and uniformity are critical. The membrane process solves many of the challenges for direct delivery of water vapor by completely changing the way water molecules make the transition from liquid to gas phase. Where bubblers and vaporizers depend on water molecules overcoming the surface tension and water molecule binding energies, RASIRC products are based on a hydrophilic membrane that uses the ion charge of the membrane to separate each water droplet into its molecular components. The energy required to enter the membrane is equal to the heat of vaporization. Transfer across the membrane is restricted to single and small channel transfer rates. Once molecules cross the wall of the membrane, they are energized and ready to enter the gas phase based solely on the vapor pressure curve that
relates to the water temperature. Using the membrane as the phase separator prevents water droplets from permeating the membrane and ensures very smooth and consistent flow.

For wafer bonding applications, chamber volumes are typically less than 10 liters. Working with a 1 Torr pressure, the mass of water needed to coat the chamber, 4 wafers surfaces, and fill the chamber from base vacuum is less than 0.004 grams (4.5 cc at STP) of water. This amount can easily be delivered in a controlled fashion with a RASIRC membrane vaporizer.

**Conclusion**

Wafer bonding must overcome gaps between the two wafer surfaces. The addition of water vapor immediately before bonding can increase bond strength when compared to dry bonding by providing a gap filling material. RASIRC has developed a simple membrane vaporizer to allow for the direct doping of low levels of water vapor. This provides direct injection into the vacuum system without water droplets, particles, and other gas contaminants resulting in a high integrity bond.

**References**

