SVC Topics

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Water & Water Vapor

Water vapor often presents a major variable in physical vapor deposition (PVD) processing, and is generally the most common contaminant in a good vacuum-processing system. Water and water vapor in the vacuum system increase the pump-down time and can increase the contamination level during the deposition process to an unacceptable level. In the extreme, gas cooling during rapid pumping can actually cause water condensation and "rain" in the vacuum chamber during pump-down. Figure 1 shows the water molecule and the hydrogen bonding of water molecules to form liquid water.

In the water molecule, two hydrogen atoms are covalently bonded to an oxygen atom with a configuration as shown in Fig. 1a. The diameter of the water molecule (O^{2-}) is about 2.64 Å. In liquid water, the water molecules are bonded by a special type of polarization bond called the hydrogen bridge. In this bond, the small hydrogen nucleus is attracted to the unshared electron in the adjacent water molecule, as shown in Fig. 1b. This bonding accounts for the high boiling temperature and the heat of vaporization of water.

Water vapor (and solvent vapors) is much more difficult to pump away than gas molecules, because the water vapor molecule has a long "residence time" on a surface compared to a gas molecule. Table 1 shows the residence time of molecules on various surfaces at various temperatures. Therefore, if many adsorption-desorption events are necessary for the water molecules to reach a vacuum pump and be removed, the time to reduce the partial pressure of water vapor in the chamber will be long. Figure 2 shows the pump-down time for water vapor in a vacuum chamber, starting with dry surfaces and wet surfaces. Note that it can take hours to reduce the level of water vapor in the system if the surfaces start out wet. If there is liquid water in the system, the partial pressure of water vapor in the system will remain at about 20 Torr until the water has all vaporized. If there is rapid evaporation, evaporative cooling can cool the water and even form ice, which will further increase the time to rid the system of water.

The surface morphology of materials in the vacuum chamber also affects the removal rate of the water. If the surfaces are porous, water is retained in the pores and capillaries much longer than it would be on a smooth surface. A common source of surface porosity in PVD processing is film buildup on chamber surfaces and fixturing. Removal of water vapor, therefore, becomes more difficult the longer the time since the surfaces were cleaned. Also, roughening the surfaces, such as abrasive cleaning or grit blasting, will increase the retention of water on the surfaces.

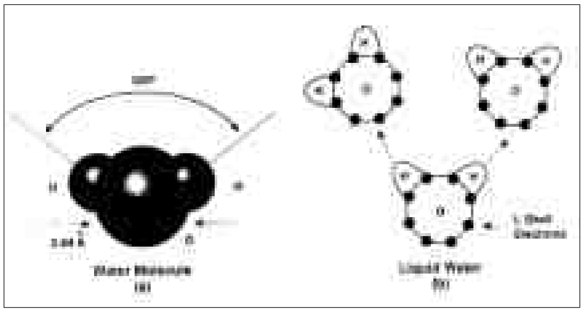

Fig. 1—The water molecule and the bonding of H_2O molecules to form liquid water.

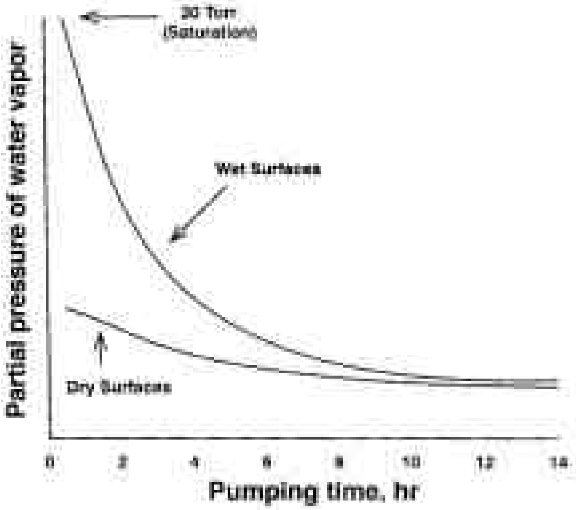

Fig. 2—Examples of pumpdown curves for water vapor, starting with dry surfaces and wet surfaces. The saturation (100% relative humidity) vapor pressure of water at room temperature is about 20 Torr.

If the partial pressure of the water vapor in the system is high, compression-type vacuum pumps, such as the oil-sealed mechanical vane pump, will compress the water vapor to above its saturation vapor pressure (20 Torr at room temperature) and condense water in the pump. This water will mix with the oil and cause the oil to "froth," reducing the pump efficiency and causing vane-wear. Removing the water from the oil can take appreciable pumping time. Mechanical pumps are usually fitted with "ballast valves" that allow the dilution of the moist air from the vacuum chamber with dry gas from an external source. This increases the pumping load, but can reduce the pump-down time by eliminating water in the oil. It is important that the gas into the ballast valve be dry—

Table 1
Residence Times of Gases & Vapors on Various Surfaces

System	Desorption Energy	Residence Time, calculated		
		77 K (LN2)	22°C	450°C
Gas-surface	—		10^{-12} s	
H_2O on H_2O	0.5 eV/molecule	10^{15} s	10^{-5} s	10^{-9} s
H_2O on metal oxide	1		10^{5} s	10^{-5} s
H_2 on Mo	1.7		10^{17} s	1 s

Table 2
Equilibrium Vapor Pressure of Water

Temperature, °C	Vapor Pressure, Torr
-183	1.4×10^{-22}
-100	1.1×10^{-5}
0	4.58
20	17.54
50	92.5
100	760
250	29,817

moist gas will only exacerbate the pumping problem.

Turbopumps have a low pumping speed for water vapor because of the many surface adsorption-desorption events necessary for the water molecule to pass through the pump. Some turbopumps have heated stages to increase their pumping speed for water vapor. Some hybrid turbopumps have a cryopumping stage to pump water vapor rapidly. Cryopumps have a high pumping speed for water vapor, but if there is a lot of water vapor, the pumps have to be "regenerated" often to remove the accumulated water. Diffusion pumps will pump water vapor rapidly.

Crowding of fixturing in the chamber reduces the conductance (increases the number of adsorption-desorption events) of water vapor to the vacuum pumps. Cryopanels (Meissner traps) in the processing chamber allow rapid pumping of water vapor by cryocondensation, when they are designed such that the conductance to the cold surface is high (few adsorption-desorption events). Table 2 shows the vapor pressure of water as a function of temperature. In order to reduce the vapor pressure of the water to a low level, it must be cooled to well below freezing. Cryocondensation surfaces generally operate at about -150°C and are cooled by hydrocarbon refrigerants. At that temperature, the water vapor pressure is an inconsequential 10^{15} Torr. The thermal conductivity of frost is rather poor, so as the frost layer thickens, the ability to cool the surface decreases to the point that the cryocondensation surface must be regenerated by heating and "defrosting" the surface. Care must be taken that heat produced during processing does not heat the surface of the frost, causing water vapor to be returned to the processing environment. This often means that the cold surface must be shielded from the source of process heat.

The best procedure for minimizing and controlling water vapor (or solvents) in the vacuum chamber is to minimize its introduction in the first place. This can be done by:

1. Backfilling the vacuum system with a dry gas,
2. Minimizing the time the system is open to the ambient,
3. Maintaining a flow of dry gas through the chamber while it is open,
4. Keeping the chamber walls and surfaces warm to prevent condensation,
5. Wiping down the vacuum surfaces with anhydrous alcohol,
6. Drying and warming the fixtures and substrates before they are introduced into the deposition chamber, and
7. Controlling the humidity in the processing environment.

Large volumes of dry gas for backfilling and flushing can be obtained from the vaporization of liquid nitrogen (LN$_2$), usually from above the LN$_2$ in a tank (1 liter of LN$_2$ gives about 650 liters [stp] of dry gas), by compression and expansion of air, or by using high-volume air dryers. The relative humidity in the processing environment can be regulated by drying the air by refrigeration, heating it to the desired temperature, and introducing water vapor to the desired level using nebulizers that spray a fine mist into the air. It is useful to keep a record of the relative humidity in the processing environment. Often high humidity can be correlated with abnormal pump-down times or other processing problems.

When introducing substrate materials that can absorb moisture, such as polymers or porous materials, the history of the material can be an important variable in the amount of water vapor released in the deposition chamber. If the material has been processed or stored in a moist environment, it may contain appreciably more water than if processed and stored in a dry environment. In order to have a reproducible process, the history of these materials must be controlled, and perhaps the materials outgassed (vacuum dried) before they are introduced into the deposition chamber. In some applications, water vapor and other volatile materials may be sealed in the bulk material by using a dense basecoat.

In some cases, the design of the system or chamber can be optimized for handling water vapor. For example, in some web-coating machines, the web material is unwound in a separately pumped vacuum chamber before it is introduced into the deposition chamber. This isolates the deposition chamber from most of the water vapor released during the unrolling operation. The unrolling chamber can accommodate large-area cryocondensation surface to pump the released vapors.

Removing water vapor from surfaces during pump-down can best be done using a plasma. Surfaces in contact with the plasma are subjected to low-energy ion bombardment ("ion scrubbing"), which desorbs the water from the surface. It is important that the desorbed water vapor be removed during this plasma cleaning. This can be done by cryopumping or flushing.

In many cases, removing water vapor is like pumping against a virtual leak. The rate of removal is not determined by the pump speed, but rather by the ability of the water vapor to get to the pump. **P&SF**