Water vapour Cryo-pumping in coating applications

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Version 1.09 – 17/9/02

Introduction

Water is the dominant species in most vacuum systems (ref Mattox). It can form as much as 97% of the gas remaining in the vacuum (ref. Schneider, Hjorvarsson et al, 1999). We will discuss here why this is, what effects it has in coating applications and what you can do about it.

We aim to provide an understanding of: -
   a) Why water vapour cryo-pumping is essential for removal of water from a vacuum
   b) How water vapour cryo-pumping removes water and why it is much more effective than other types of secondary pumping (e.g., turbo molecular pumps, diffusion pumps, or helium cryo-pumping).
   c) What advantages and benefits users experience with efficient removal of water from their vacuum systems.

What is a vacuum?

We think of a vacuum as an'empty' space, but even a good vacuum contains a large number of atoms or molecules that can interfere with your processes. For example at the relatively good vacuum levels of 1×10^{-6} mBar there are around 10^{18} particles (atoms or molecules) per m^3. This is a huge number of particles and nothing like our imagined 'empty' space. Even so our vacuum processes work very well, so how is this possible when our vacuum is nothing like 'empty'?

Vacuum is normally used in a process for one (or both) of two reasons (ref. Mattox): -

   a) To stop or slow contamination of a process
   b) To allow particles involved in a process to gain (or keep) sufficient energy (otherwise lost in collisions).

It is the first of these that residual water has strong influence on. Water can become bound into the coating as Oxygen, Hydrogen, or -OH groups. It will react easily with many metals. It can also be dissociated into species such as O, H, or -OH by plasmas or energetic species such as ions, electrons or photons. Once generated the Hydrogen in particular can be difficult to remove from the vacuum chamber (many secondary pumps pump Hydrogen poorly ref chambers p 61). The primary source of hydrogen within a vacuum originates from water vapour, both atmospheric and from out gassing of the substrate and chamber walls. Schneider, Anders at al (1999) saw Hydrogen

concentrations up to 10% in what were expected to be relatively Hydrogen free plasmas. This caused significant contamination in Alumina films they were depositing.

Why water remains in vacuum

Schematic of a water molecule

H⁺

O

H⁺
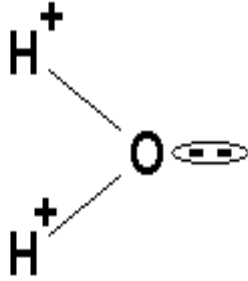
Water is unusual in that its molecules are highly polar. Both hydrogen atoms are on one side of the molecule, the electrons that were originally on the hydrogen are strongly attracted to the oxygen. As shown in the schematic this leaves the positive Hydrogen nuclei (now each sharing an electron with the Oxygen) at one end and the Oxygen (now having gained extra electrons from the Hydrogen) at the other.

Schematic of water adsorbing on a surface
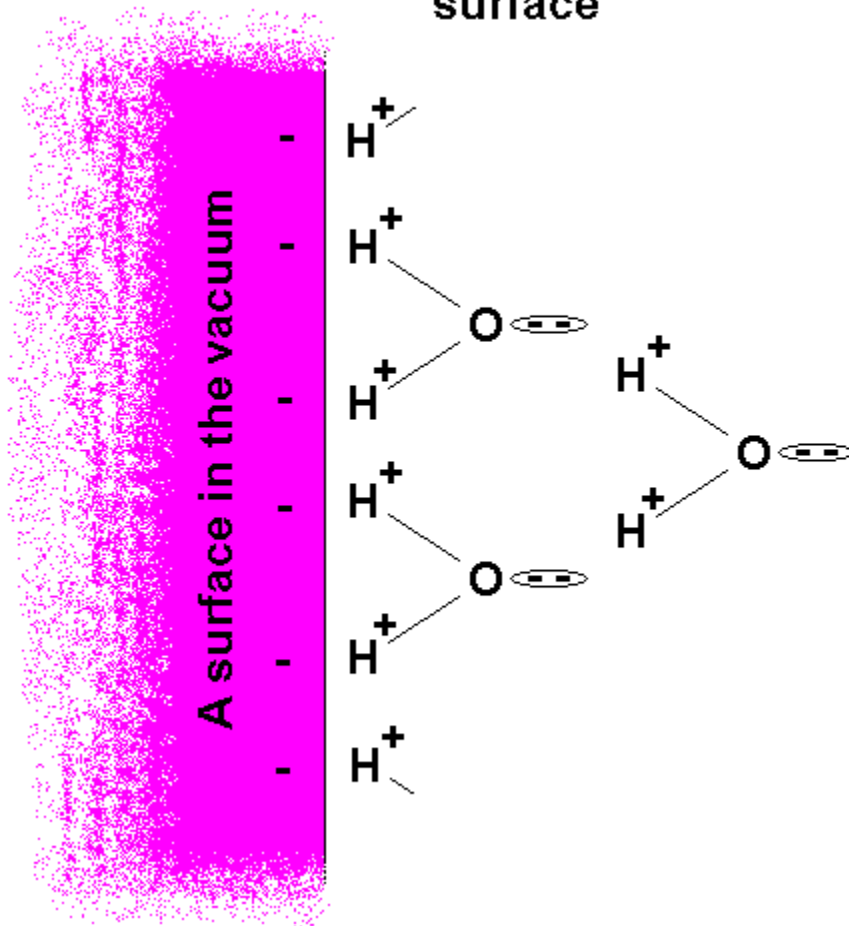
As a water molecule approaches any surface in the vacuum the positively charged end attracts the electrons of atoms in the surface. These electrons are not free to leave the surface but they can drift towards the surface. This attraction binds the water molecule to the surface. Other water molecules can then bind to those already on the surface. These layers can get several molecules thick.

If the water bound tightly there wouldn't be a problem since it would stay there. If it bound weakly similarly wouldn't be a problem as the water would rapidly escape the surface and be pumped away. Unfortunately for vacuum applications the water is bound so that the water comes off at a high enough rate to cause problems but no so fast that we can feasibly wait for it to be pumped away.

Having escaped from the chamber walls the water molecules typically hit another wall where they stick and the whole process repeats itself. It will have to undergo numerous collisions with the walls before it arrives at the vacuum pump and is removed from the chamber (ref. Mattox.).

Coating arrival rates

Most vacuum processes are surface treatments where either material is deposited or removed. Here we discuss coating processes although many of the effects of water contamination apply.

A typical coating process deposits material at between 0.1nm/s and 10nm/s. A typical atom is around 0.3nm diameter. So our typical coating process has atoms arriving at the substrate at a rate of 0.3 - 30 atom layers/second.

Gas arrival rates

How long does your surface stay clean?

Mono-layer formation time (s) vs Pressure (mBar)
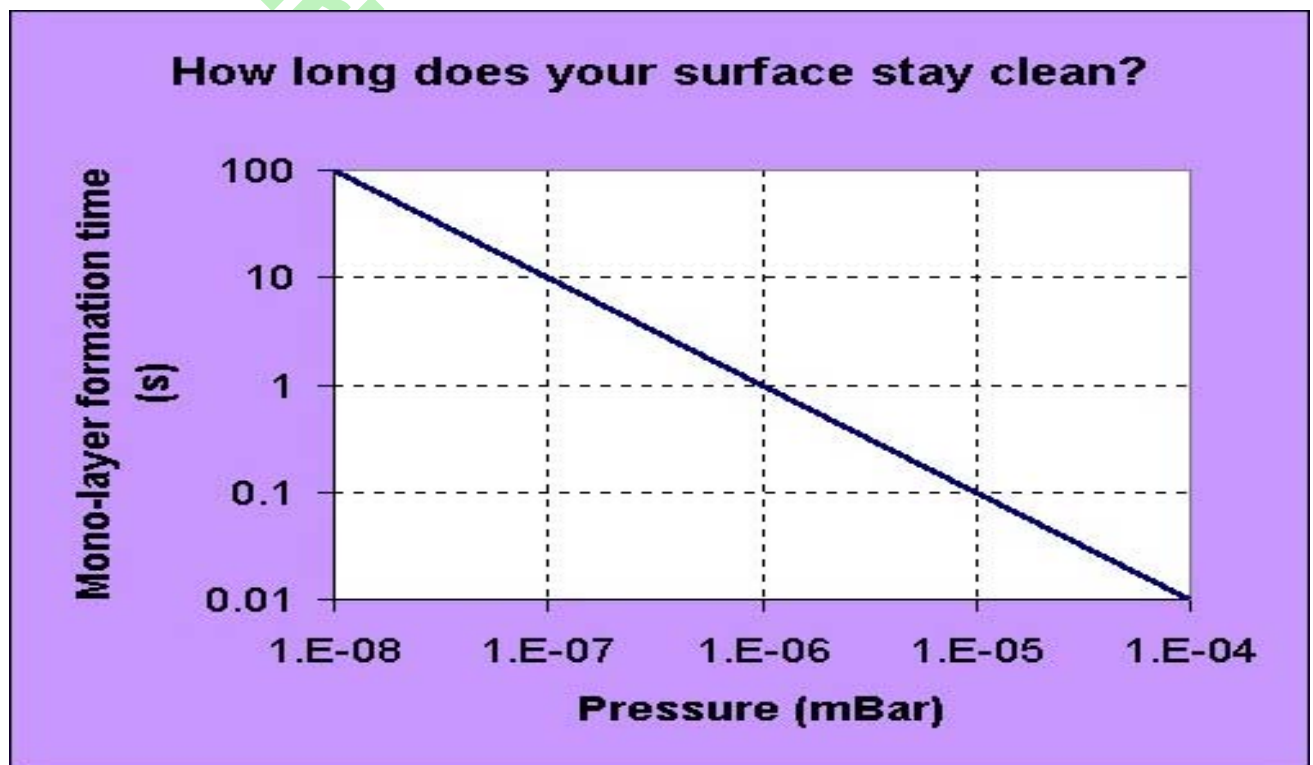
If we assume that every arriving atom sticks to a surface we can calculate the useful parameter the *monolayer formation time* (ref chambers p3). That is if we have a clean surface how long will it take it get a complete coverage of atoms, one layer thick. As you can see in the figure the times are extremely short. At our nominal vacuum of 1×10^{-6} mBar we have a monolayer formation time of around 1 second.

Base pressure required for a for pure coating

So at a base pressure of 1 x 10-6 mBar we've estimated a monolayer formation time of around 1 second. We've also estimated that a typical coating process uses a coating arrival rate of between 0.3 - 30 atom layers/second. So in the worst case we are taking 3 seconds to deposit a layer of the atoms we want (the coating material) and only 1 second to form a complete atomic layer of impurities. If the impurities (in this case water) react with the coating material we're obviously not going to get a pure coating. So for example a coating of the highly reactive metal titanium made under these conditions would be badly contaminated with oxide and hydroxide from the water vapour. In well designed processes an extreme situation like this would be avoided but even small concentrations of water or water products (-OH, H) can have significant effects.

Ishibashi et al show that a water pressure of 2×10^{-5} Torr during sputtering has significant effects on both the resistivity and etching properties of the conducting transparent oxide ITO. Also on ITO, Lee at al found changes in the crystal structure (sizes and lattice constant) and electrical properties as they varied the base pressure between 2.5×10^{-7} Torr and 2×10^{-5} Torr, for films deposited at 5 nm/s by sputtering.

Schneider, Anders et al found that both arc evaporated and sputtered Alumina films could contain significant amounts of hydroxides and that the background water pressure caused this. They believe that this causes the wide range of refractive indices and chemical stability reported for thin film alumina. The same group (Schneider, K. Larsson, et al) later found alterations in the mechanical properties of Alumina thin films caused by the water vapour in the vacuum.

Schneider Hjorvarsson et al also found significant OH content in sputtered Strontium Titanate films (up to 8%). This material is of interest for electronic device applications because it has a large dielectric constant and high breakdown strength. This incorporated OH reduced the dielectric constant.

Cryo-coils for pumping water

If we want to remove water from our vacuum chambers there are two options: -

   a) Remove it from the walls and surfaces of the chamber
   b) Pump it quickly from the vacuum.

The only way to quickly remove water from the walls and surfaces of the chamber is to have those wall and surfaces clean and polished and then to bake them. This is standard practice for ultra-high vacuum (UHV) chambers. It is not practical for most coating processes. In coating machines the build up of coating material on the chamber walls and furniture increases the amount of absorbed water and significantly increases pump out times. The walls and furniture must be regularly cleaned. Then the solution used on most vacuum coating machines vacuum is simply to wait for an acceptable vacuum. If you wait long enough then the bound water 'outgases' sufficiently from the walls to allow a reasonable vacuum to be reached. Depending on the size and cleanliness of the

vacuum chamber this will take from tens of minutes to several hours. This is not a cost effective strategy as vacuum coating equipment is relatively expensive and must sit idle while we wait for a suitable vacuum to be reached.

The other way is to pump the water quickly from the vacuum. In the vacuums we're discussing the behaviour of the gas is governed by molecular flow. Our everyday experience is of viscous flow. Under molecular flow each atom or molecule is completely independent of the others around it. This means that you cannot 'suck' the gas into the pump as happens at normal atmospheric pressures (i.e., with viscous flow). All the pump can do is wait until any given gas molecule/atom arrives in the pump and then trap it. This means the pumping speed in a vacuum is proportional to the area of the pump, the bigger the pumping area the more likely any given gas molecule/atom is to arrive in the pump and so the faster the pumping speed.

It also means that if we place our pump down a tube or behind any fittings (cold traps, flange adaptors, gate valves, etc.,) then the gas molecules/atoms are even less likely to arrive at the pump and so the pumping speed is reduced. Formally this is calculated as: -

$$1/S' = 1/S + 1/C$$

Where

> S' is the effective pumping speed in the chamber
> S is the pumping speed of the pump
> C is the conductance of the fittings linking the pump to the chamber

So pumping speed in a vacuum is limited by how quickly the gas to be pumped arrives at the pump i.e., on the area of the pump and where it is placed. The 'rule of thumb' number typically used is 10 l/s/cm^2, that is for every cm^2 of pumping surface, gas will arrive at a rate of 10 l/s (this is for Nitrogen, for water the figure is actually a little higher but for simplicity we'll use 10 l/s/cm^2 throughout) (ref. Chambers *et al*, p 40). Theoretically the maximum water pumping speed by a cryogenic surface is 16.4 l/s/cm^2 this figure is often quoted and used by some pump manufacturers caution should always therefore be exercised when calculating pumping requirements.

Typical vacuum pumps on a deposition chamber might have pumping ports anywhere between 10cm and 50cm diameter. These have surface areas of 80 and 2000 cm2, so we can expect maximum pumping speeds of 800 to 20,000 l/s. A 50cm diameter oil diffusion pump will have a rated pumping speed of around 12,000 l/s (ref BOC Edwards catalogue 2001/2 or Leybold catalogue 2001/2). A 50cm cold baffle to fit this has a conductance of 12,000 l/s (ref Leybold catalogue 2001/2). A 50cm vacuum valve has a conductance of 37,000 l/s (ref Boyarsky *et al*). The effective pumping speed S' in the vacuum chamber is then

$$\frac{1}{S'} = \frac{1}{12,000} + \frac{1}{12,000} + \frac{1}{37,000} .$$

This gives an effective pumping speed of $S' = 5,000$ l/s.

SCHEMATIC OF VACUUM COATER

(note placement of water vapour cryo-pump in chamber while the vacuum pump must be fitted externally)

Water vapour cryo-pump

Valve

Vacuum pump
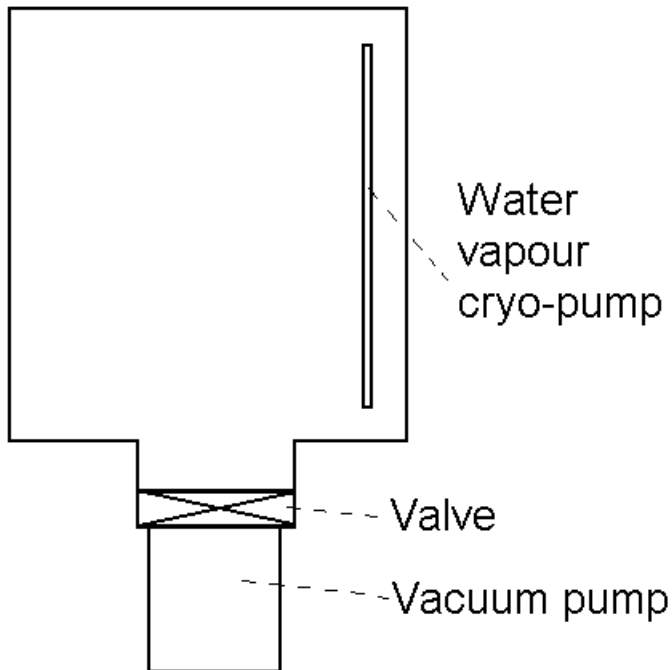
Water will freeze out on a cold surface so a cost effective way to get a lot of pumping area for water is to use a cold surface as a pump i.e., a water vapour cryopump (ref. Boyarsky *et al*). Usually this surface is a coil. A typical coil is 40m of 15.7mm copper tubing, this gives around 20,000 cm^2 of area, which will pump water at around 200,000 l/s. This water vapour cryo-pumping coil can be placed inside the vacuum chamber, and does not have to be bolted on externally. This is a crucial difference because the pumping speed of the coil is not then limited by the conductance of the hole and fittings onto which we bolt it.

To summarize the previous paragraphs fitting a large diffusion pump will give a pumping speed in the chamber of 5,000 l/s. A water vapour cryopump can easily provide 200,000 l/s. That is a factor of 40 difference. We need to keep the secondary pump (turbo molecular pump, diffusion pump, or helium cryopump) to pump all the non-water species but a for the predominant water species huge increases in pumping speed can be achieved by adding a water vapour cryopump.

Tubomolecular pumps, because this type of pump construction leads it to have a large surface area it is particularly inefficient at pumping water vapour, which tends become

attached to the internal surfaces of the pump. Therefore the effective water vapour pumping speed of turbomolecular pumps is considerably lower than the anticipated speed based upon flange size.

Cost saving

A quick pay back calculation gives a useful indication of how cost effective it can be to add a Cryo-coil water pump to your vacuum process.

If our vacuum machine costs £500,000 and this is written off over 5 years then we have costs of

Write off costs	= £500,000/5	= £100,000
Interest at 4%	= 0.04 x 500,000	= £20,000/year
	TOTAL	= £120,000/year

Working an 8 hour shift, 5 days/week, for 50 weeks/year gives costs of = £120,000 / (8 x 5 x 50) = £60/hour. Allowing for manpower at 2 x £20/hour = £40/hour gives a total cost of £100/hour

So if the water vapour cryopump saves 3 hours/day (estimated as 30 minutes per cycle with 6 cycles per day), this is a cost saving of £300/day = 300 x 5 x 50 = £75,000 per year. On a capital cost of £20,000 for the water vapour cryopump this is a payback period of 3.5 months. This neglects the increase in production capacity of 3 hours/day. The payback time is therefore very impressive and easily justified in accounting terms.

Practical benefits

Whether waiting for a swap over point between pumps or a start pressure for your process then this will be achieved more rapidly when a water vapour cryopump is used.

The welding institute found that they could swap over to the diffusion pump 30 minutes earlier using a water vapour cryopump. They also found that having swapped to the diffusion pump better vacuum levels were achieved more quickly.

EB2 Pumpdown curves.
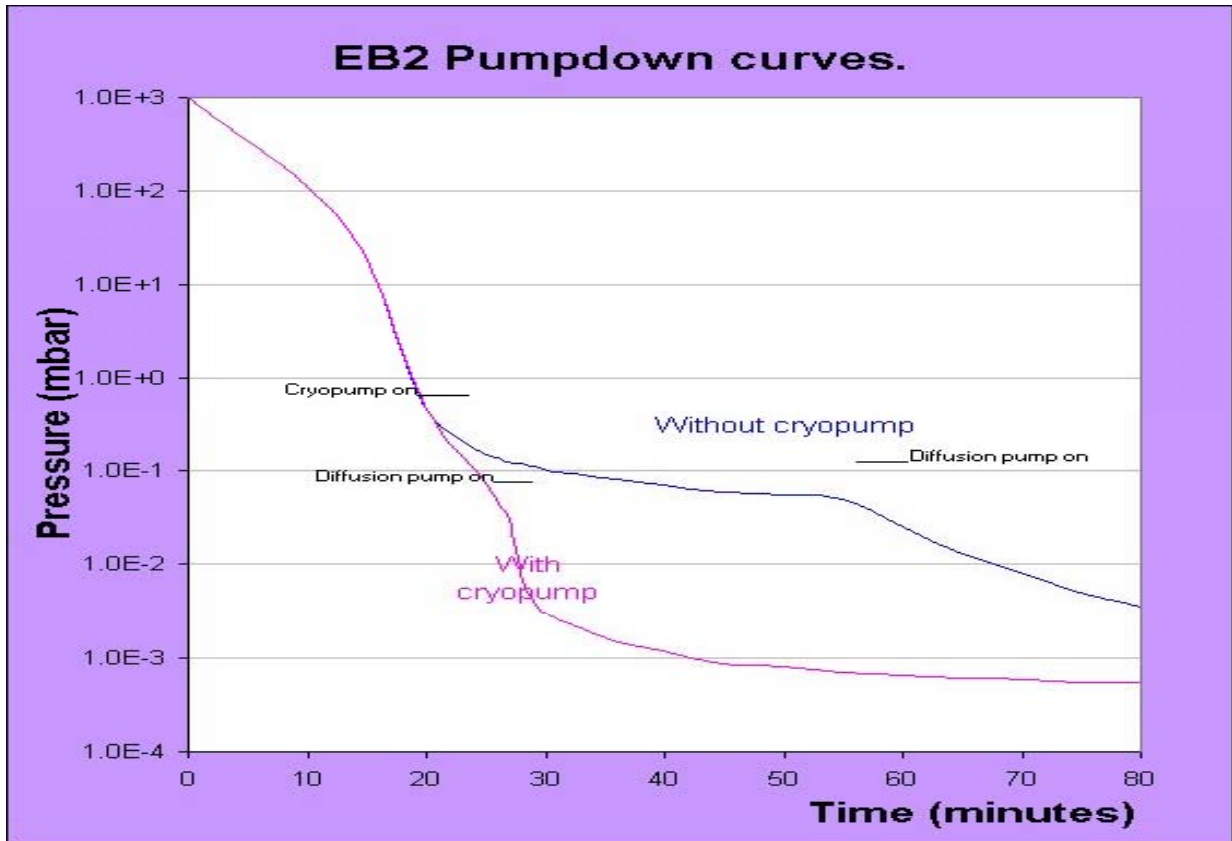
Film quality can also be influenced by the film impurities caused by background water. The use of a water vapour cryopump can help in two ways

1. More reproducible film quality (as the background water level is not varying)
2. Purer coatings as background water levels are reduced.
3. Faster processing which is simply integrated into standard vacuum processes.

Ion Bond Limited a manufacturer of hard coatings systems for decorative and industrial use have experienced the following results for sputtered arc hard coatings of TiN, deposition rates are typically 0.016 to 0.03 micron / minute. During repeated processing the contamination of the chamber and its fittings contributes to a significant lengthening of the process.

Chamber state	Cryopump * used	Pump down (min)
Clean	No	30
Dirty	No	45 – 60
Clean	Yes	15
Dirty	Yes	25 – 30

Ion Bond report greater process reproducibility and higher quality films (colour and mechanical strength) when Cryopumping is employed.

Conclusions

- Water is the single biggest contaminant in most vacuum coating systems
- Pumping speed in a vacuum is limited by how quickly the gas to be pumped arrives at the pump i.e., on the area of the pump and where it is placed.
- A water vapour cryopump is the most effective way of removing this water. This is because it
    - Can have very large surface areas compared to other pumps and so gives much larger pumping speeds
    - Can be placed directly into the vacuum chamber rather mounted on the side via fittings which limit the conductance to the pump
- Contamination of thin films by background water in the deposition vacuum has been shown to alter the mechanical, electrical, optical and chemical properties of the thin films. Improvements in coating quality/reproducibility can therefore be expected with a water vapour cryopump.
- Significant time savings can be expected with a water vapour cryopump
- Impressive pay back times of 8 months or less can be demonstrated.

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