Vacuum

Pumping by chemical means

Sputter-ion and sublimation pumps form a complementary pair that, by transforming gases to the solid phase within the vacuum chamber, can routinely reach pressures as low as 10^{-11} torr.

Theodore Tom

The need for a vacuum environment has been encountered by more and more fields over the years. In high-energy accelerators, extraneous molecules would attenuate the beam of particles being accelerated. In mass spectrometers, atmospheric gases would mask the sample being analyzed. In thin-film production, impurities would affect the electrical properties of the film being deposited. Similar considerations arise in the fields of space simulation, surface physics, thermonuclear research, pollution detection and control, analytical instrumentation and many others.

A vacuum can be generated by two kinds of methods. One is to remove physically all the gas to the outside of the chamber. This method is the basis for mechanical pumps, which operate from atmospheric pressure to 10^{-3} torr and below, and momentum-transfer pumps, such as the commercially available turbomolecular pumps. The second means is chemically to change the gas to a solid inside the chamber. Such a change in phase is accomplished by sputter-ion and sublimation pumps. Because these pumps are relatively new and unfamiliar, I shall describe the several processes through which pumping occurs within both sputter-ion and sublimation pumps and discuss their advantages.

Often the sputter-ion and sublimation pumps are used hand-in-hand, because the ability of the former to pump inert gases complements the rapid pumping of the active gases by the latter. Both are most effective as a final stage for pumpdowns from atmospheric pressure and operation at low pressures; oil diffusion pumps (see box) and turbomolecular pumps should be used for long-term, high-pressure operation (above 10^{-5} torr). Pumps based on a chemical change in phase require little maintenance, because they have no moving parts, make no noise and maintain a vacuum even in a power failure, providing the chamber has no leaks. Each is essentially a black box with a switch: By a mere flip of the switch, one can produce a vacuum environment in a relatively short time. Those problems that do develop can be minimized through knowledgeable design and operational procedure. A final advantage of this type of pump is that it provides a clean environment free from oil and hydrocarbon backstreaming.

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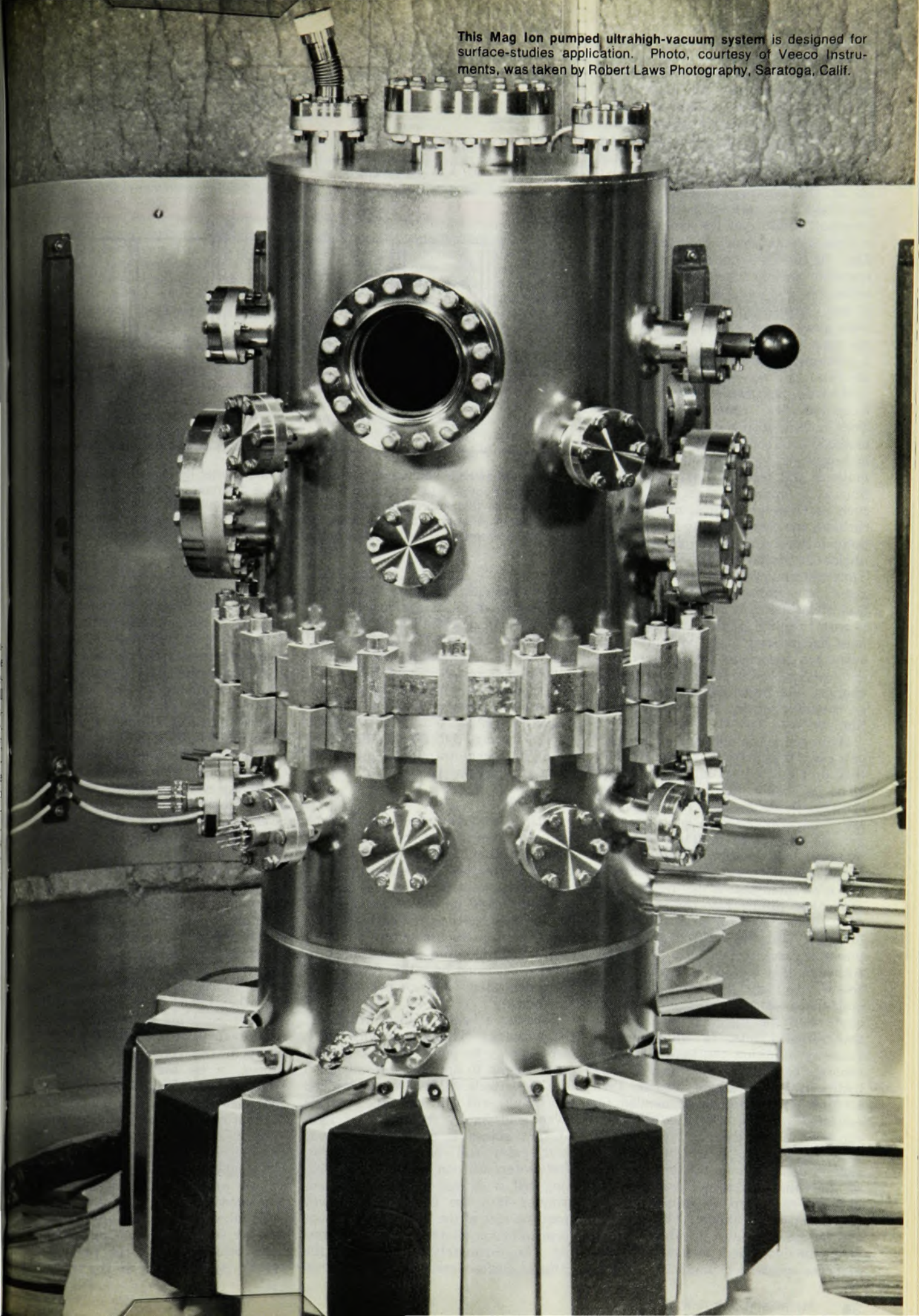
The Penning discharge

The basis for the sputter-ion pump is the Penning cold-cathode discharge, illustrated in figure 1. Two flat cathodes sandwich a cellular anode structure. When a high voltage is applied to the anode at pressures in the range of 10^{-3} torr, electrons produced by cosmic rays or some other random event will immediately go to the anode. On the way they will collide with gas molecules and ionize them. The ions will be attracted to the cathode and a discharge ensues. As the pressure is lowered, the discharge extinguishes itself, because the number of electrons produced by collision decreases with the collision frequency. Electron drain to the anode then exceeds electron production, and the discharge goes out. However, if an axial magnetic field is applied in the direction shown in figure 1, the resulting radial force prevents the majority of electrons from reaching the anode. Electrons now spiral around the magnetic field, oscillating back and forth from cathode to cathode, causing more and more ionizing collisions, which in turn produce more electrons. Quickly an electron space charge is established with a density approaching 10^{-10} per cm^3. This density can be maintained even at very low pressures.[1] We have found in our laboratory that the Penning discharge will not be extinguished even at pressures below 10^{-12} torr.

The Penning discharge results in a chain of processes that can be exploited to remove particles from the gas phase, as depicted by the four steps of figure 1. First, a gas molecule is ionized (figure 1a). The resulting ion is accelerated by the electric field and bombards one of the cathodes. In the conventional ion pump these cathodes are

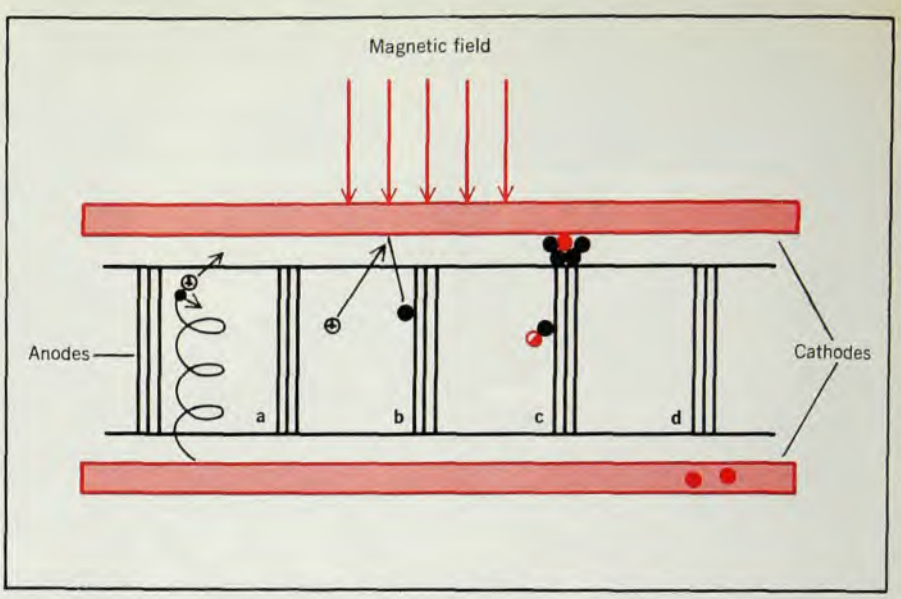


This Mag Ion pumped ultrahigh-vacuum system is designed for surface-studies application. Photo, courtesy of Veeco Instruments, was taken by Robert Laws Photography, Saratoga, Calif.

made from titanium. When the energetic ion strikes the cathode, it "sputters" or ejects a titanium atom (figure 1b). The number of atoms sputtered at an angle θ with the normal varies as cosine θ, so that most atoms will end up at the opposite cathode. These particles then get resputtered and eventually end up at the anode surface to form a continuously replenished thin film. If the film consists of a reactive material such as titanium, active gas molecules that come into contact with it are chemisorbed (figure 1c). The inert gases, however, do not react and are mainly pumped by cathode burial, a process that is described below (figure 1d).

Most of the gases in the earth's atmosphere are chemically reactive. They include nitrogen, oxygen, carbon monoxide, carbon dioxide, water vapor, hydrogen and light hydrocarbons. The majority will readily react with a thin film of titanium to form compounds such as titanium oxides, nitrides and carbides that are stable up to very high temperatures. For example, titanium nitride is stable up to 3000 deg C. Thus the pumping of these reactive gases is permanent and irreversible. Gas molecules that do not react readily with titanium, such as the hydrocarbons and heavier, more complex molecules, are dissociated into smaller fragments ("cracked") by the intense discharge. The fragments are then readily chemisorbed by the reactive thin film.

Hydrogen is the only one of the reactive gases that presents a problem, and this problem arises only if hydrogen alone is being pumped. Hydrogen sputters poorly because its mass is so low. If other, heavier gas molecules are not present to do the sputtering, hydrogen will not be chemisorbed in significant amounts. However, hydrogen is so small that it can readily penetrate and diffuse into the solid cathode. This injection and subsequent diffusion into the solid is the major pumping mechanism for hydrogen. Although this method is a very effective way to pump hydrogen, it has several shortcomings. One problem occurs when the injection rate exceeds the diffusion rate, in which case a runaway condition can take place. In general, continuous pumping of pure hydrogen at pressures higher than 1×10^{-5} torr is not recommended for extended periods. Another difficulty can arise in long-term hydrogen pumping: The entrance of hydrogen into titanium causes a nonuniform expansion of the solid. In some instances, the cathode can warp so severly that it shorts out to the anode. This problem can be circumvented by proper design of the anode-cathode element. In general, the sputter-ion pump is a very effective device for pumping hydrogen if one is aware of its limitations. For example, it can pump a continuous inlet of hydrogen at 1×10^{-6} torr for 50 000 hours before its pumping speed falls off to 60% of its initial value. The pump can then be rejuvenated by a high-temperature bakeout to allow the hydrogen to diffuse out of the cathode solid. During the rejuvenation, the hydrogen driven out must be evacuated by an auxiliary pump.



Penning cold-cathode discharge is the basis of the sputter-ion pump. Electrons (small black circles) spiral in the magnetic field and ionize gas molecules (a). Ions (+) sputter titanium atoms (black circles) from the cathode (b). Titanium forms a film on the anode and combines with gas molecules (half-open circles c). Inert-gas atoms (colored circles) are pumped by means of the ion-burial process (d). Figure 1

Inert gases

Entirely different processes must be used to pump inert gases such as argon, helium, neon, krypton and xenon. Titanium has no affinity for these inert gases, so that they cannot be chemisorbed on the anode surfaces. Nor do they react at the cathode. Instead, inert gases are pumped mainly by injection into the cathode and subsequent occlusion by a thin film that is being deposited. This process is called "ion burial."

Consider a beam of ions arriving at the cathode. Those ions with sufficient energy to penetrate but insufficient energy to sputter are embedded in the cathode. However, continued sputtering will uncover the surface layers and finally re-emit these ions. At first glance it appears that these inert gases will never be pumped. Fortunately the ion beam in the Penning cell is so well focussed that ions straying into the fringe areas, away from the axis of the cell, simply do not have sufficient energy to cause sputtering. Approximately 10 to 20% of the cathode surface area is not subject to sputtering. These surfaces will receive a continuous deposit of material sputtered from the opposite cathode. It is in these areas that most of the inert gases are irreversibly pumped.[2] Some inert gases are also pumped at the anode. Pumping at the anode may possibly take place for high-energy neutral particles through impact and occlusion by the depositing thin film. High-energy neutrals can result from charge-transfer processes or from back scattering of incident ions at the cathode. (This pumping at the anode has been proposed as a major pumping mechanism for inert gases in the sputter-ion pump.[3])

The pumping rate for inert gases has been found to be substantially below the pumping rate for active gases. For example, the pumping speed for argon is only about 1% the speed of air. This speed is adequate in most pumpdown situations, because there is only 1% of argon in the atmospheric gases. On the other hand, when large quantities of inert gases are involved, or when a continuous inlet of inert gases must be pumped, the conventional ion pump proves to be unstable. It develops large pressure fluctuations because of the re-emission of inert gases. These fluctuations are periodic in nature, with an amplitude and period that depend on the level of operating pressure. This problem arises even when one pumps against an air leak, although argon constitutes only 1% of air.

To alleviate the inert-gas problem, a number of innovative developments have been made in the past several years. Among these is the triode ion

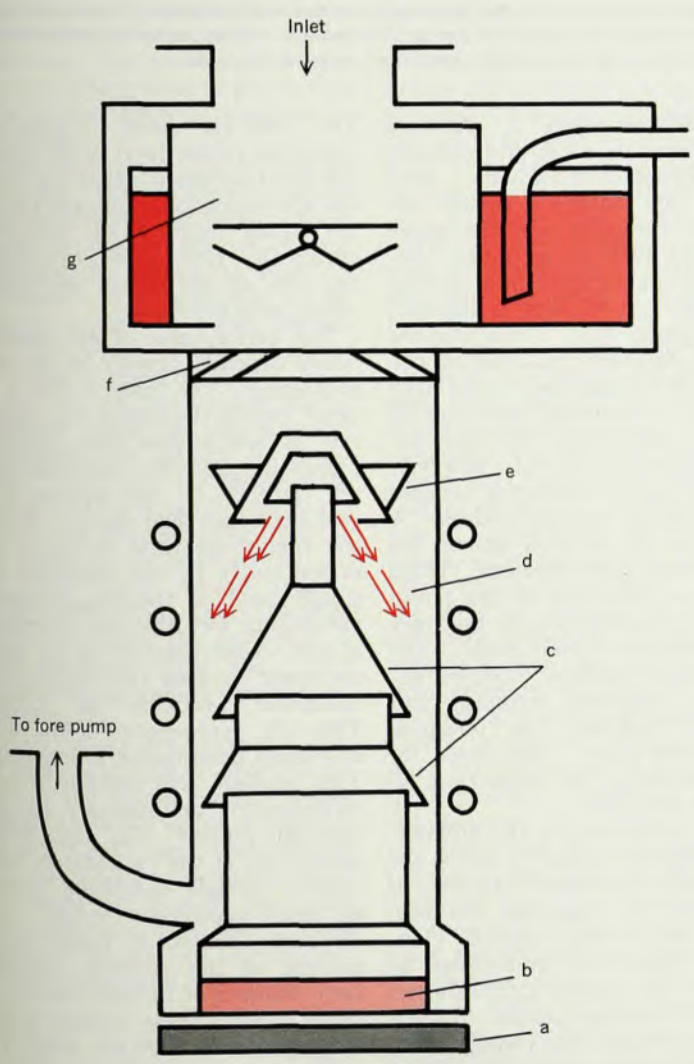
Diffusion pumps

Over the past ten or fifteen years, modifications of the diffusion pump have doubled its pumping speed and reduced backstreaming of pump fluids by four or five orders of magnitude. These improvements result from redesign of some basic pump features and from development of new pump fluids with lower vapor pressures.

The accompanying figure illustrates a diffusion pump with some recent modifications. The basic components are

- a heater (a) that vaporizes the pump fluid (b)
- one or several nozzles (c) that deflect the vapor stream down and out toward the cold pump walls
- the high-speed, low-pressure jet stream (d) that sweeps gas molecules from the inlet toward the fore-pump
- a cold cap (e) that intercepts backstreaming pump fluid at its primary source, the top nozzle
- water-cooled baffles (f)
- a cold trap (g)

The combination of cold cap, baffles and cold trap are needlessly redundant.[1] When he replaced the full ("oppedes the pumping speed. Marsbed Hablanian has shown that, especially with the new pump fluids, the baffles and cold trap are needlessly redundant.[1] When he replaced the full ("optical") baffles with partial baffles (see the figure), he found little or no increase in backstreaming but a substantial increase in speed. Other experiments have indicated that the standard cold cap does not prevent all backstreaming. One remaining source of backstreaming is evaporation from pump fluid that drips off the cold cap. Thus a disk was attached to the cap, as shown in the figure, to reduce backstreaming by 99%.



With these modifications and with liquid nitrogen in the trap, the pumping speed is 50% of the available speed, or twice the speed attained ten years ago. The backstreaming rate corresponds to formation of a monolayer of hydrocarbon molecules on the surface of a bell-jar system over a period of one year. Contamination at this low rate is just as likely to come from rubber gaskets or inadequate cleaning.[2] The ultimate vacuum obtained with a trapless diffusion pump has been lowered to 10^{-9} torr, trapless, and still lower pressures can be reached with properly trapped systems.

Another new diffusion-pump design is based on an enlargement of the section directly under the inlet flange.[3] This innovation increases the space available for pumping action and makes room for more gas molecules to flow into the pump. Of course this modification had to be accompanied by other changes in order to improve the performance of the pump as a whole. For example, the baffle was enlarged and the lower stage nozzles were designed for higher pumping speeds, to keep pace with the increased pumping speed created by the enlarged inlet. At the same time, the overall pump dimensions were unchanged so that the pump would be compatible with standard vacuum flanges.

Diffusion pumps play a different role from sputter-ion and sublimation pumps. The latter are preferred for isolated systems, such as accelerators, that must be maintained at high vacuum over a long period of time. They are also best for systems where cleanliness is so important that one cannot tolerate the risk of an accident. Diffusion pumps can more easily handle large quantities of gas. They can pump continuously, in a steady-state situation even at inlet pressures as high as 10^{-3} torr, whereas sputter-ion and sublimation pumps cannot go above 10^{-6} torr. Diffusion pumps may thus be preferred for systems that must be pumped often.

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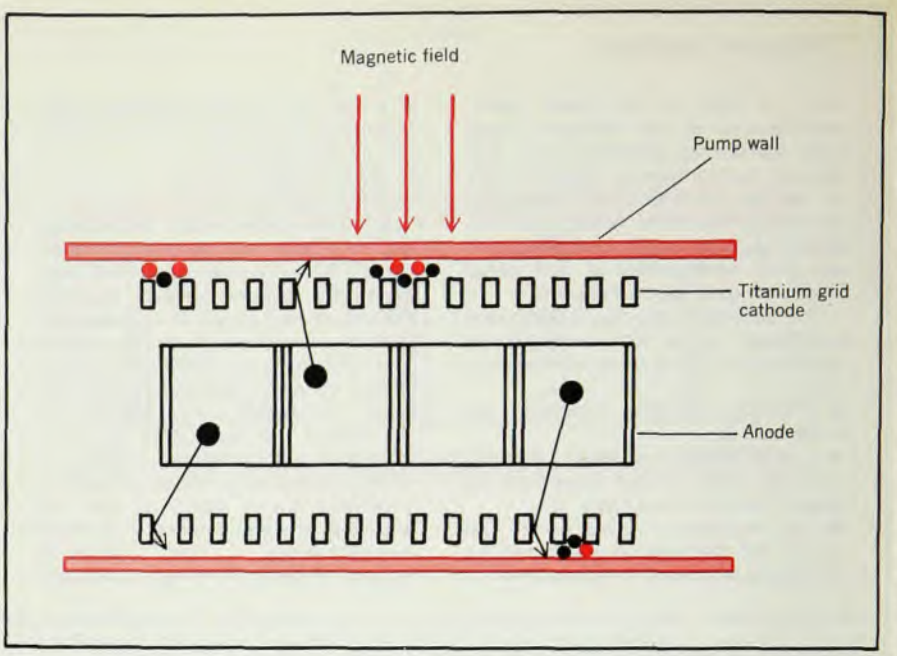
References

1. M. H. Hablanian, J. Vac. Sci. and Technol. **6**, 265 (1968).
2. M. H. Hablanian, *Proceedings* of the Ninth Annual Symposium of the Amer. Vac. Soc., Nov 1962, Los Angeles.
3. M. H. Hablanian, Transactions of the *Vacuum Metallurgy Conference*, Amer. Vac. Soc. (1966).



In the triode-ion pump, a titanium grid replaces the solid cathode. Sputtering rate is increased by the angular impact of the gas molecules. Inert-gas ions (black circles) and the titanium atoms (colored circles) are buried on the pump wall. Figure 2

pump[4] shown in figure 2. Here, a semitransparent titanium grid replaces the conventional solid cathode. Also, a negative high voltage is usually applied to the cathodes, and the anode and the pump walls are grounded. Because of the semitransparent structure, a continuous flux of ions is directed toward the pump wall. These ions are decelerated after they pass the cathode and arrive at the wall target with little or no energy. Therefore, these ions do little or no sputtering. The ions impinging on the grid cathode, however, cause a high rate of sputtering because they are incident at large angles. A large number of titanium atoms are ejected in the forward direction. These atoms form a thin film on the pump wall, which physically covers the inert gas ion previously driven there. The triode stabilizes inert-gas pumping except during long-term pumping and significantly improves the pumping speed for inert gases. The speed for argon, for example, can range from 25 to 30% of the air speed.

Another development is the differential sputtering ion pump,[5] in which one of the titanium cathodes in figure 2 is replaced with a tantalum cathode. Tantalum has a very desirable characteristic: When it is bombarded by ions arriving at angular incidence, its sputter yield increases rapidly. Thus a thin film is formed more rapidly at all areas of the cathode where ions are incident with insufficient energy to sputter, and more rapid pumping of inert gases by ion burial results. This device has been found to pump inert gases stably for the life of the pump. The inert-gas speed is significantly improved to the level of 25 to 30% of the rated air speed. Both the differential sputtering ion pump and the triode ion pump improve the pumping of chemically inert gases by increasing the rate of ion burial, and both are widely used in industry.

The performance of any sputter-ion pump depends directly on the rate of sputtering: The faster a film of sputtered ions is deposited, the faster the rate at which that film "getters" or pumps the gas. The sputtering rate itself depends on the number of ions generated and their energy. However, the energy spectrum of ions is determined solely by the particular power supply used, so the rate of sputtering varies only with the rate of production of ions. Unfortunately, as the pressure decreases so does the number of gas molecules available for ionization. Thus the performance of the sputter-ion pump deteriorates at low pressure. This problem was recently solved by incorporating an auxiliary ion source into the pump.[6] The ion source replaces one of the cathodes of figure 1 with a cathode composite containing an easily vaporizable metal.[6] As the discharge strikes, it causes localized heating of the cathode, releasing a large number of metallic atoms in the vapor phase. These metallic atoms are ionized by the electron space charge and accelerated to bombard the cathodes. The additional ions increase the sputtering and therefore the pumping. The cathode composite is designed to increase sputtering by positioning some target surfaces for angular

ion incidence. Thus the inert-gas pumping is improved in the same way as in the triode and the differential sputtering ion pump.

Leakage currents

All these devices are very effective in producing a vacuum environment that requires little or no maintenance. Occasionally, some problems will develop after long-term operation. One such problem is leakage current. Resistive leakage results when a conducting path is formed across ceramic insulators. This type of leakage is rare, because most ion-pump elements have shielded insulators with re-entrant grooves to prevent formation of a conducting path. In the event that a conducting path is formed, the insulators must be replaced. A more common type of leakage current is caused by field emission. The electric field is intensified by whisker growth, for which the Penning discharge is notorious, or by surface irregularities that result from continuous bombardment of electrodes by ions. Sometimes the electric field can be magnified by as much as two orders of magnitude. The existence of strong fields causes a depression of the surface potential barrier, allowing electrons to tunnel through.

One can detect this type of leakage current with the Fowler–Nordheim plot. A straight line in a Fowler–Nordheim plot of voltage against current indicates that the leakage is caused by field emission. A simpler way to detect field emission is to reverse the polarity of the anode–cathode element: Field emission current should then disappear, but resistive leakage should be identical regardless of polarity. Field emission can usually be eliminated by "hi-potting" the anode–cathode element. Hi-potting is simply the application of a voltage higher than the normal operating voltage of the ion pump. This high voltage usually burns off the emitting tips. Another method is to operate the ion pump in the glow discharge range, about 10^{-3} torr. Discharge scrubbing can also destroy emitting tips.

Aside from these problems, the sputter-ion pump is usually trouble free for the life of the pump, which ranges from 20 000 to 50 000 hours of continuous use at 1×10^{-6} torr. Especially in cases of low-pressure operation, sputter-ion pumps can operate for years with few problems; they have proved themselves in applications such as analytical instruments and high-energy accelerators.

In addition to sputter-ion pumps, other types of ion pumps exist that derive their major pumping action from sublimation rather than sputtering. One is the Orbitron,[7] which injects electrons into a cylindrical electrostatic field and collects them at the anode, which is made of titanium and is located at the center of the cylinder. The electrons hitting the anode cause it to heat to its sublimation temperature. The sublimed titanium is deposited on the cylinder walls and forms a reactive getter surface. Another device is the Electro Ion pump,[8] which uses four cylindrical grids to orbit electrons around to cause ionization. Contact heating[9] is used to sublime titanium to form a getter surface. Neither of these devices, however, generates as much ionization as a magnetically confined discharge; ion-pumping is therefore minor compared to sublimation pumping in these pumps.

Sublimation pumps

Ion pumps are often complemented by sublimation pumps to form an integral system. Sublimation pumping takes place when a getter film is generated by thermally heating a chemically reactive metal such as titanium to its sublimation temperature. The sublimed titanium will form a continuously renewed thin film that, when cooled to near room temperature or below, pumps through the process of chemisorption. Various sublimation methods may be used to generate a thin film. One of the most economical is resistance heating. Usually the source is a filament made from a reactive metal or alloy.[10] When several hundred watts are applied to the filament, the source sublimes at a rate varying from 0 to 250 milligrams per hour. At these rates, deposition surfaces can be designed to yield pumping speeds for most active gases of the order of several thousand liters per sec. Most commercially available resistance-heated sublimators have about 1 to 2 grams of usable titanium. Depending on the rate of sublimation, each filament will last from several hours to several weeks before it must be replaced.

Efforts to increase the sublimator life have resulted in devices that achieve sublimation through electron bombardment. A tungsten filament is set next to a titanium target. When a potential of several thousand volts is applied to the target, it will collect a large number of electrons emitted by the filament. Depending on the size of the target and the power applied, sublimation rates may be as high as 1 gram per hour. At these rates, pumping speeds of several hundred thousand liters per sec can be achieved. Electron-bombardment sublimators can have as much as 100 grams of usable titanium. Depending on the rate of sublimation, these sublimators can last for years, far longer than resistance-heated sublimators. Other sublimation devices utilize contact heating and radiation heating[11] to generate a thin

film. However, these methods are not very efficient, and consequently they require substantially higher power than either the resistance-heated or the electron-bombardment type of sublimator at the same sublimation rate.

A sublimed titanium thin film has a very high sorption rate for most of the chemically reactive gases such as nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide and water vapor. The pumping is stable and irreversible in most cases; hydrogen is the only exception. Hydrogen pumping is irreversible only when the surface temperature is not raised, for then the hydrogen sorbed at a lower temperature will diffuse out. At a given sublimation rate, the sorption rate depends directly on the deposition surface area. It is therefore simpler to talk about the pumping speed per unit surface area. The pumping speed for nitrogen, for example, varies from about 15 liters per sec per square inch of getter surface at 1×10^{-6} torr to about 77 liters per sec per square inch at 1×10^{-10} torr and below. The sorption rate depends on pressure, because the availability of pumping sites (titanium atoms) on the surface varies with the pressure. At low pressures, gas molecules arrive at the surface and see essentially a monolayer of titanium atoms, all of which are available for pumping. Thus the sticking probability is high. At higher pressures, gas molecules impinge at high rates. The surface is saturated more quickly, so that at any given instant the gas particles see only a fraction of a monolayer.

One can derive an equation relating the rate of saturation of vacant sites (titanium atoms), the rate of replenishment of vacant sites (titanium-sublimation rate), and the rate of impingement of molecules at the surface (a function of pressure). This equation allows one to adjust the sublimation rate for maximum effective use of titanium for a given performance requirement. At pressures below 10^{-7} torr, continuous sublimation is not required. Most sublimators are equipped with cycle timers to allow the sublimator to be turned on and off cyclically. The on-time is usually set equal to the time needed to deposit a monolayer of titanium atoms, and the off-time is the time it takes to saturate approximately one half the sites in a monolayer. This procedure allows optimum use of titanium for performance and long life.

Another method to enhance effective use of titanium is to cool the getter surface to a lower temperature. The lower the surface temperature, the higher the sticking probability. For example, the intrinsic surface pumping speed can be increased tenfold if we cool the getter surface to liquid-nitro-

gen temperature (77 K) instead of room temperature. However, the speed cannot exceed 77 liters per sec per square inch of getter surface for nitrogen, because this speed represents the maximum rate of gas arrival at the surface.

Sublimation pumps effectively remove most active gases but are completely ineffective against inert gases and gases with complex molecular structure, such as the hydrocarbons. On the other hand, sputter-ion pumps are not very effective for pumping large active gas loads (because sputtering is an expensive way to generate a thin film and the film is not easily controlled), but they are effective for pumping inert gases and hydrocarbons. A natural response is to combine the two pumping methods. The combined system is capable of pumping at the speed of hundreds of thousands of liters per sec and reaching ultimate pressures below 10^{-12} torr. The function of the ion pump is to pump the inert gases and to crack the complex active gases. The dissociated products are then readily chemisorbed by the sublimed thin film. This combination is so effective that a system whose capacity is several thousand liters per sec can repeatedly pump a 200-liter volume from atmospheric pressure down to 10^{-7} torr in less than five minutes. (Cryosorption, mechanical roughing or a combination of the two is generally used to reduce the pressure from atmospheric to 10^{-3} torr.) Ultimate pressures of 10^{-11} torr are routinely achieved in bakeable systems.

References

1. W. J. Lange, J. Vac. Sci. and Technol. **7**, 228 (1970).
2. K. Kawasaki, T. Sugita, I. Kohno, J. Watanabe, N. Hayashi, J. Appl. Phys. **35**, 479 (1964).
3. R. L. Jepsen, *Proceedings* of the Fourth International Vacuum Congress, 1968, page 317.
4. W. M. Brubaker, Trans. 6th Amer. Vac. Soc. Symp., Pergamon, London (1960), page 302.
5. T. Tom, B. D. James, J. Vac. Sci. and Technol. **6**, 304 (1969).
6. T. Tom, J. Vac. Sci. and Technol. **9**, 383, (1972).
7. R. A. Douglas, J. Zabritski, R. G. Herb, Rev. Sci. Instr. **36**, 1 (1965).
8. D. R. Denison, D. G. Bills, *Abstracts* of the 13th Amer. Vac. Soc. Symp., Herbick and Held, Pittsburgh (1966), page 15.
9. K. A. Warren, D. R. Denison, D. G. Bills, *Abstracts* of the 13th Amer. Vac. Soc. Symp., Herbick and Held, Pittsburgh (1966), page 17.
10. C. F. Brothers, T. Tom, D. F. Munro, Trans. 10th Amer. Vac. Soc. Symp. Macmillan, New York (1963), page 202.
11. D. J. Harra, T. W. Snouse, J. Vac. Sci. and Technol. **9**, 552 (1972). □