Essence of UHV Technology in Surface Processing Systems

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Key Words: Vacuum engineering, Desposition technique, Media coating, Surface engineering

ABSTRACT

Around 1950, scientific technology for preparation and measurement of ultra high vacuum was born in Canada and the United States. Today, along with the development of manufacturing industries for semiconductor devices, flat panel displays, magnetic and opto magnetic memory devices, etc., newly designed efficient production systems are required or proposed, let us say, every other month. Many of those surface device production systems require UHV partially or throughout multi-step processing. Designing a high quality, dynamic, UHV system and its careful operation is often the key for obtaining good results. Engineering issues here should be based on scientific understanding of interaction between gaseous molecules and physico-chemical structure of the specific surface. Control of gaseous plasma often needs specific accumulation of experience with regards to interactions between plasma and surfaces of inner assembly and wall of the UHV chamber. Rather recent participation of organic material for display devices adds new challenging targets in UHV technology. High volume production of consumer products has pushed efficient and improved design for dynamic UHV systems.

INTRODUCTION

Physically or theoretically the simplest surface processing UHV system was for Molecular Beam Epitaxy (MBE), originated by A.Y. Cho and J.R. Arthur, Jr. at Bell Lab. (1968) and developed at Physical Electronics Co. by Arthur et al. (Figure 1).

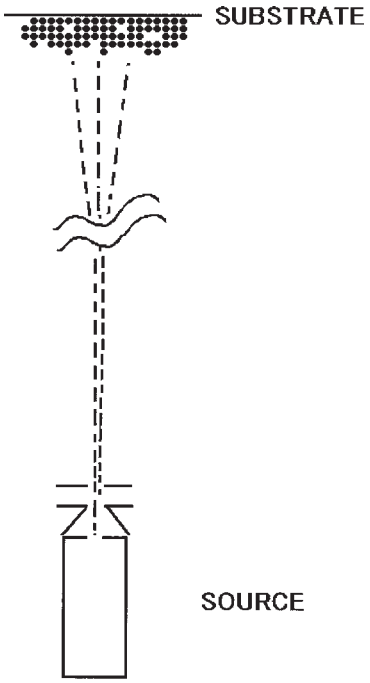

Figure 1: MBE

Kinetic behavior of elemental atoms or molecules in UHV space at quasi-stationary thermal environment is well calculated by using established gas dynamics. Atom level cleaning of substrate surface has been required to obtain reasonably good samples for further study.

Leo Esaki at IBM originated multi-layered thin film electronics (1970's) by using a multi-source MBE system; computer process control was developed for obtaining designed and required precision. For electronics, photonics, photo-electronics and magnet-electronics devices manufacturing today multi-layered film structure formation is a conventional practice. Thickness of each film is ranging from less than 1 nm to 100 nm.

Magnetic random access memory is recently under R&D by using physical vapor deposition for formation of multi-layer of several metallic thin films (Figure 2). UHV environment is preferable for metal film formation, and tantalum layer formation in UHV was apparently a critical process (Figure 3).

By using synthesized Trimethlgallium, $(CH_3)_3Ga$ or Triethylgallium, $(C_2H_5)_3Ga$ and Arsine, (AsH_3) compound molecular vapor (chemical vapor) alternatively, which should be thermally dissociated on the substrate surface, J. Nishizawa at ERATO Lab (1981-86) at Tohoku University made monolayer by monolayer Ga-As-Ga-As… perfect crystalline surface. The laboratory transferred knowledge and technology to an industrial company. The company has developed LED products for red and green lights that we see today worldwide, together with blue lighting LED (GaN), developed in late '90s. LED family is expected to replace ordinary lamps because of electrical energy savings.

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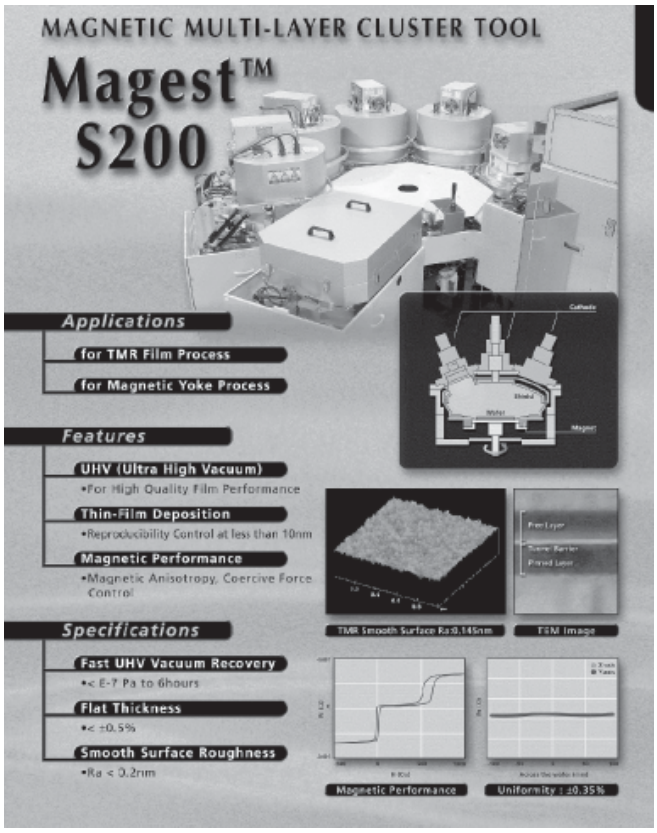

Figure 2: Magnetic Multi-layer Cluster Tool

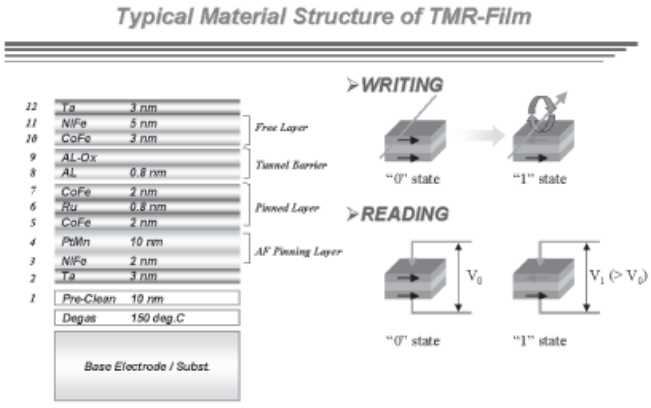

Figure 3: Typical Material Structure of TMR-Film

Monolayer by monolayer deposition using chemical vapors is being developed extensively for the semi-conductor industry categorized as Atomic Layer Deposition (ALD).

Chemical Vapor Deposition (CVD) is applicable, at least in principle, to large area substrate with sufficient uniformity and less difficulty on micro-fabricated three dimensionally shaped surface: suitable compound chemical vapors should be backfilled for dissociative chemical reaction on the surface to put monolayer deposit; vapor feeding and scavenging of the used vapors should be very precisely and quickly controlled to get rid of any trace of contamination; programmed short time-interval unit processing will be repeatable for monolayer by monolayer formation, (CVD-ALD).

For reactive material processing, requirement for UHV comes from requirement for extremely clean or pure environment throughout a sequence of critical processing. Classical UHV stands for ultra high vacuum measured by a total pressure vacuum gauge. CVD and other multistep multilayer thin film formation process require that vacuum environment should be completely free from contaminating species of atoms, molecules and other particles, which is called Ultra Clean environment rather than UHV. Ultra Clean environment require analytical instrument for sensing contaminants. Use of UHV residual gas analyzer is one way for the sensing but at present still insufficient in many cases.

So-called PVD Hard Coating on cutting tools and decorative coatings on durable commodity items appeared in the early 1970's, which was based on ion plating process originated by Don Mattox in the mid 1960's. Other plasma processing, diffused arc and sputtering have widened process capability for expanding variety of products. When ULVAC (Hayashi) first commercialized ion-plating in Japan the late 1960's, nitrides (TiN, CrN) were chosen in consideration of reliability and reproducibility in vacuum processing. If we feed hydrocarbon vapor in plasma, unidentifiable hydrocarbon molecules will be born in plasma which eventually stick and pile up on the vacuum chamber wall. Such contaminants coming back, desorbed, give rise to change plasma components. This was an example telling us surface engineering to prepare physico-chemically stable and identifiable inside wall surface of a vacuum system is often a prerequisite. Optimum thickness of the hard coatings has been proven to a few micrometer ranges in most cases, indicating that the processing margin is not as stringent as it should be for MBE and ALD where atom to atom or monolayer structure is an issue. The hard or decorative coatings, however, are often complicated in accommodation to meet with wide range of feedback information from the market. In other words, design of thick films of a variety of structures have been made. Color sensitivity is an example. Anti-erosion, anti-corrosion property combined with hardness and tenacity is obtainable by changing processing parameter, namely by an integrated processing which results in either mixed zone or multi-layers, of the interface.

Almost defect free TiN coating was applied on high field magnets installed in a huge electron storage ring for producing monochromatic soft x-ray and other beams. The storage ring should be operated at extremely high vacuum. The TiN coated (by using hollow cathodes discharge) layer worked well for the otherwise terribly outgassing rare earth magnet.

Surface engineering for formation of surface (boundary) layer in vacuum should be based on arrangement of atoms or molecules especially at the boundary, regardless of PVD or CVD. Then we will rely on data and pictures obtained by using surface analysis instruments for which maintaining ultra-high vacuum environment is a key.

It is a trend of today's Semiconductor Solid Device (SSD) manufacturing and Flat Panel Display (FPD) production industries that unit surface processing be integrated as much as possible. Both SSD and FPD require multi-layer stacked thin (~nm range) films, and each boundary must be kept ultra-clean between successive film processing. Figures 4, 5 and 6 illustrate typical equipment usable for formation of thin films in SSD and FPD industries. UHV technology is one of the keys for successive thin film formation processes in consideration of productivity, which will be discussed elsewhere.

Figure 4: Multi-layer thin film coating system for SSD

Well engineered use of UHV technology for preparation of bulk material, namely substrate for product, source material for deposition, pure gases and vapors for processing are also required in addition to surface engineering of UHV chamber and structural members. Epitaxial growth technology has been used for preparation of perfect crystalline atom arrangement of Si, Ge-Si, Ga-As, etc. defect free surfaces.

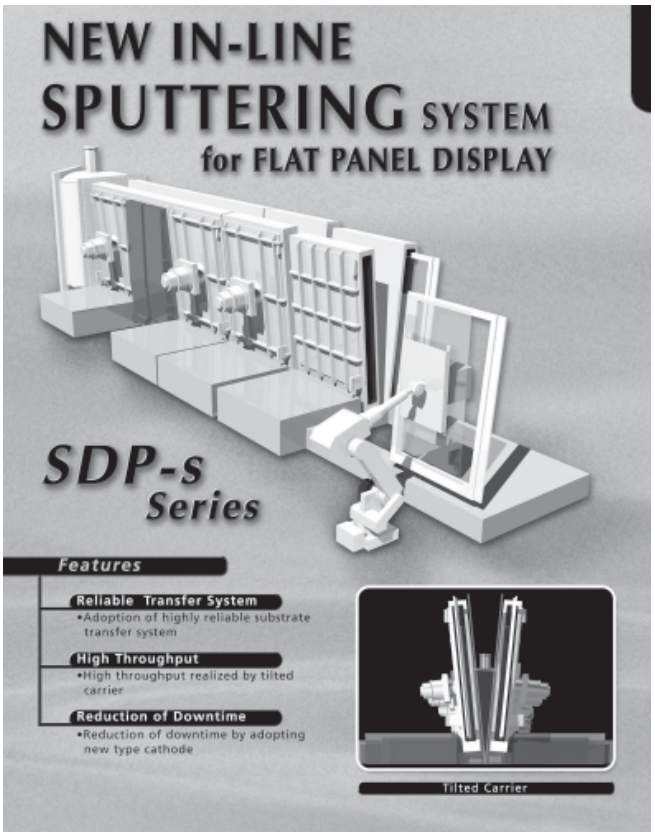

Figure 5: In-line sputtering system for large display panel coating (conceptual)

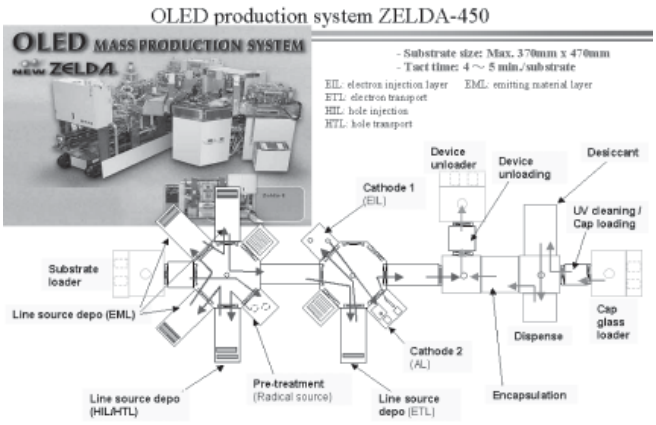

Figure 6: OLED Production System

Preparation of hyper-pure aluminum for semi-conductor surface devices usable for computer it was necessary to make it free from radioactive substance, namely U, Th, Pb, etc. Zone refining process in sufficiently clean vacuum environment has been suitable.

In situ vacuum distillation purification for providing organic substance for OLED is required to keep reasonable yield. At present purity level of a complex organic substance is reportedly 99.5, which may need further improvement.

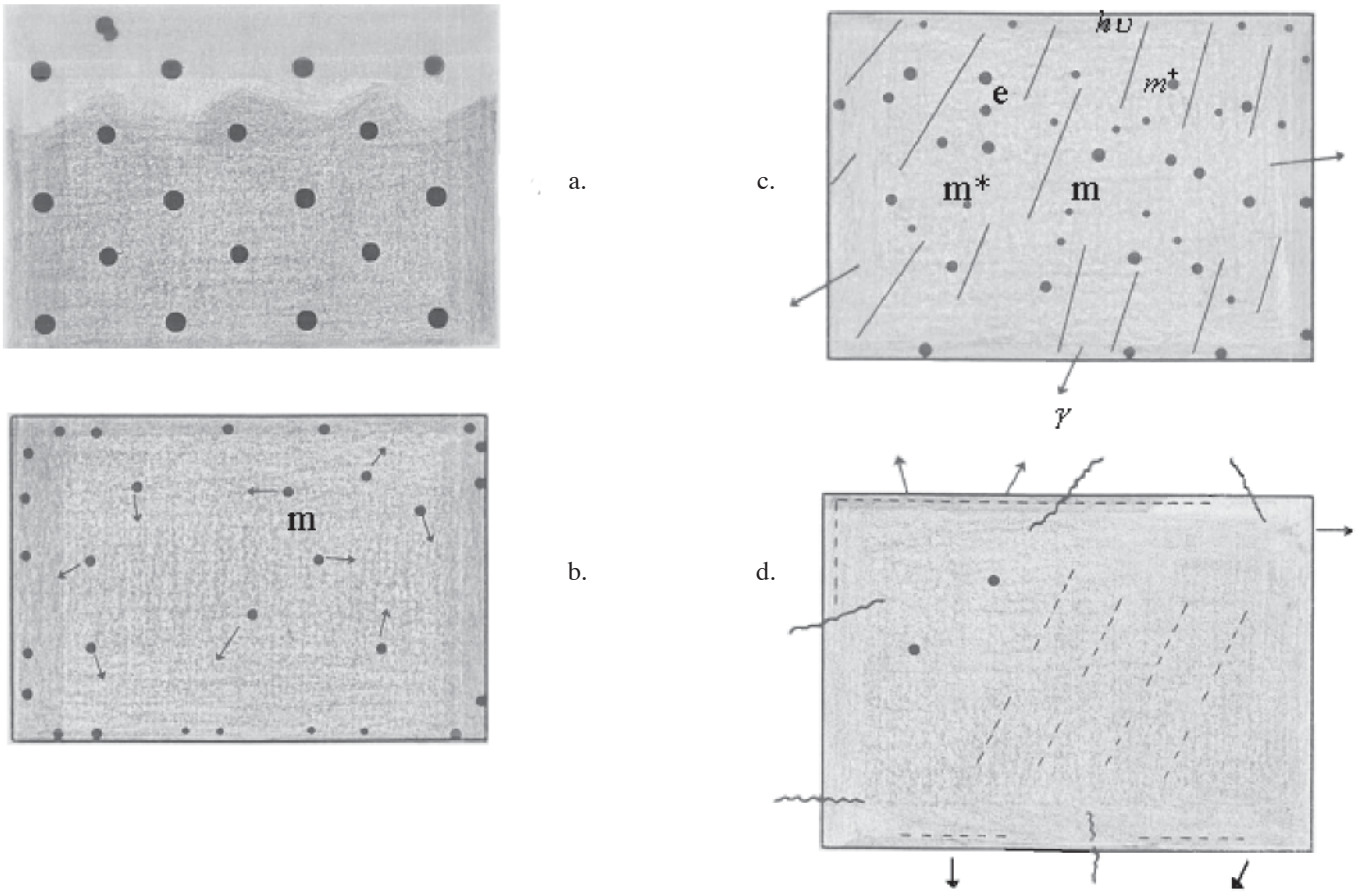

Figure 7: Typical particle energy in vacuum: a. near field vacuum mK ≤ 5ev; b. thermal vacuum molecular dynamic and thermally radiant zone ~300k~0.3ev; c. low energy plasma vacuum ~10ev~ ≤ 100ev; d. high energy particle vaccum 1 Mev~40Tev Hadroon Lepton (Gluon)

WHAT SORT OF VACUUM

Categorically there are four vacuum spaces (see Figure 7). Near field vacuum, thermal vacuum, normal plasma vacuum and high-energy particles vacuum. Average energy range of particles flying in each vacuum should be ≤ 5ev, ≤ 0.3ev, ≤ 100ev and ≤ 40Tev, respectively.

Nuclear fusion plasma today is made in a vacuum chamber, but uses a very pure plasma (≥ 10 KeV). Surface scientists and surface analysis instrument engineers are working with near field vacuum. Bulk materials processing, including earth environmental technology, deals mostly with thermal vacuum. Material surface processors generally use knowledge of near field, thermal vacuum and the low energy normal plasma vacuum.

Historical and present state of UHV and extreme high vacuum (EHV) science and R&D technology are described in excellent articles by P. A. Radhead, J. P. Hobson and H. F. Dylla published in special issue JVSTA Vol. 21, No. 5 supplement. UHV technology in surface processing systems has taken advantage of the science and R&D technology. Industrial application, however, is diversified, and lots of specific materials are involved with economically complicated compromises necessary. Industrially the UHV technology is a part of Ultra Clean Technology (UCT) wherein any materials and processing should remain extremely pure and clean. Evacuation with measurement to UHV is the first step to UHT processing. I will, however, discuss the basics of molecular dynamics in UHV systems first.

MOLECULAR TRAVELER

Molecular mean free path in UHV space is larger than 10 km (at 10^{-6}Pa at room temperature). Molecules or atoms leaving, desorbed from surface, fly straight to a target surface directly in sight, therefore evacuation of an empty UHV chamber is to capture or provide sinks (pump) for those molecules coming from the surface in lin-of-sight.

Molecules desorbed or outgassed from a portion of the chamber surface usually experience many collisions with other portion of the chamber and evacuation tube connected to the chamber. Each collision is actually an energy exchange transfer process between the surface and the colliding mol-

ecule; that is an adsorption-desorption process. We still do not possess a good instrument to observe and pursue a particular molecule in such exchange process.[1] We can, however, pursue statistically in case of monolayer sorption which will be typical for the UHV situation.

SOJOURN TIME

Statistical balance between arriving and desorbed molecules (Figure 8) is expressed in Equation 1.

$$\langle \upsilon \rangle \cdot S = \sigma \cdot \frac{1}{\langle \tau \rangle}$$

Equation 1

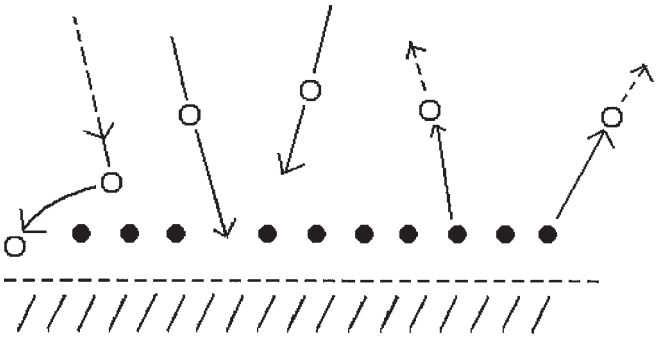

Figure 8: Adsorption and desorption

where ν is number of arriving molecules per unit time (second) and unit surface (cm^2). σ is number density of adsorbed molecules per unit surface (cm^2). τ is the sojourn time of an adsorbed molecule on the surface. S is so-called sticking probability.[2] ‹ › means average of sufficient number of events. ‹τ› can be roughly expressed as Equation 2 in classical statistics.

$$\langle \tau \rangle = \tau_o \exp\left(\frac{E_d}{RT}\right)$$

Equation 2

We may have an image that $\tau_0=1/f_0$; f_0 is frequency of oscillation of surface atom of the substrate, typically between $10^{-12} \sim 10^{-14}$ sec. E_d is the activation energy for the desorption (cal/mole) and RT is the gas constant and temperature of the adsorbed system. If we prefer expression for a single adatom, we may replace E_d/(RT) to $\epsilon_d/(k_BT)$. Dealing with a single particle, however, we would perhaps better go to quantum statistics, which is still out of the scope for vacuum people. We can find a number of articles illustrating electron microscopy pictures of surfaces and atomic, molecular arrangement computer models calculated by quantum statistical treatment or Monte Carlo assembly.

Average sojourn time calculated by using experimentally observed desorption energy is surprisingly long with large E_d (Table 1). We will then understand that the major reason we have to wait hours to reach desirable UHV is because of the long sojourn time.

Table 1: Rough estimation of the sojourn time*

$\tau = \tau_0 e^{E/RT}$ ($\tau_0 = 10^{-13}$ sec)

E, cal/mole	t = 22°C	t = 100°C	t = 500°C	t = 1000°C
100	1.2×10^{-13}	1.2×10^{-13}	—	—
1,500	1.2×10^{-12}	1×10^{-12}	—	—
3,500	4×10^{-11}	2.4×10^{-11}	1×10^{-12}	—
4,000	1×10^{-10}	5.5×10^{-11}	1.5×10^{-12}	5×10^{-13}
10,000	3×10^{-6}	7.2×10^{-7}	7×10^{-11}	5×10^{-12}
20,000	1×10^{2}	5	5×10^{-8}	3×10^{-10}
30,000	4×10^{9}	4.3×10^{7}	4×10^{-5}	2×10^{-6}
40,000	1×10^{17}	2.6×10^{14}	3×10^{-2}	9×10^{-7}
147,000	$\sim 10^{97}$	$\sim 10^{87}$	$\sim 10^{30}$	$\sim 10^{20}$

**Logically an adatom already on the adsorbed state would have spent the equal time before we start counting (observation); therefore total residence time is two times as large as the sojourn time in this table, that is, however, negligible if we consider accuracy of τ_0 and E_d.*

[1] Well known STM, AFM, MFM etc., and near field photonic microscopy for large organic molecules and clusters are advancing to collect images of moving (surface migrating) particles.

[2] Logically the sticking probability here should also be averaged, namely be better expressed as ‹S›.

Adsorption of water vapor or organic large molecule proceeds in less than a minute after a vacuum chamber is exposed to atmosphere. Flying molecule in vacuum space has a velocity $v \approx (3k_BT/m)^{1/2}$, that is usually in the range of 100 m/sec to 1.5 km/sec for nitrogen, oxygen… hydrogen molecules in thermal vacuum. Therefore a space travel time for one flight of a molecule in a high vacuum chamber is normally in msec range. Surface migration drift velocity of an adatom is typically estimated to be mm/sec to mm/min.

We know number density of molecules is quite large, approximately 10^7/cm^3 at 10^{-6} Pascal at room temperature, and monolayer molecule will be counted around 10^{14}/cm^2; therefore a statistical treatment is still reasonable, though mean free path of a molecular flight is actually the mean distance, ‹d›, from one point to another point separated by space.[3]

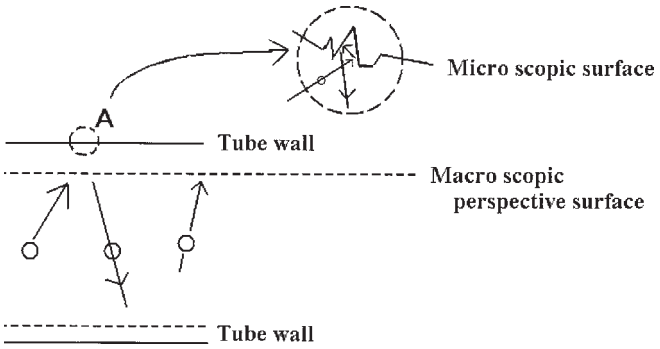

Figure 9: Gaseous molecules are affected by micro geometrical surface.

It is essential here for a vacuum processor to understand that the flying time ‹d›/v is dependent on chamber size, but Ed or ‹τ› represents physico-chemical nature, property of interaction between the adatoms and the substrate surface (atoms), which is independent of chamber size. In other words, desorption of an adatom proceeds independent of degree of VHV or UHV in space, while population change of adatoms on the substrate represent balance of incoming adatoms and desorbing adatoms per unit time.

Figures 10 and 11 are a speculative model of microscopic surface to illustrate near field potential zone. Typical binding energy, shown on the center horizontal line, represent necessary energy for a bound atom or molecule to leave the surface. In some cases the desorption needs additional energys (shown with the dotted curve).

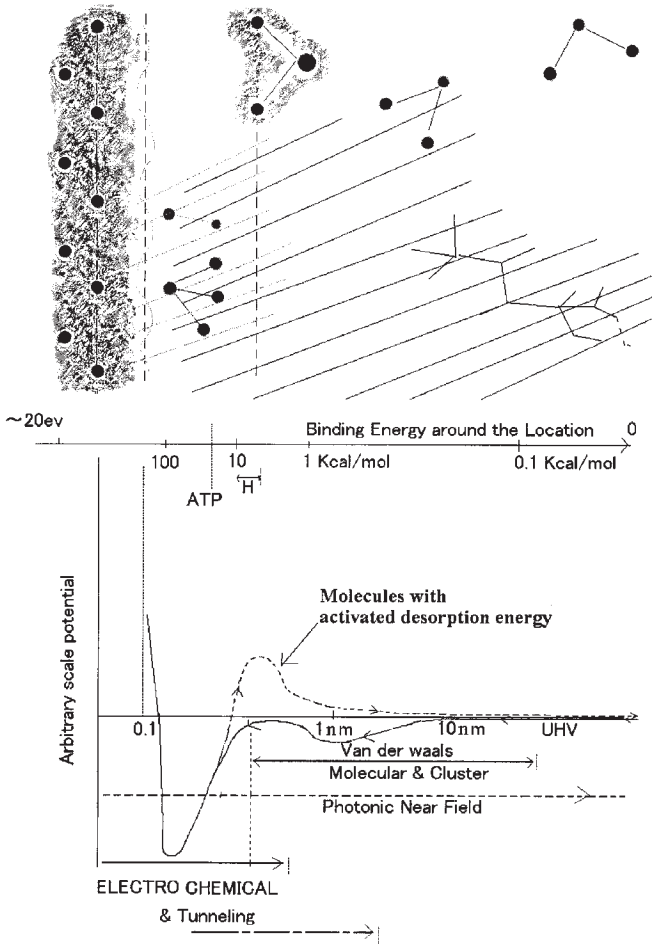

Figure 10: Speculative model of micro surface by a vacuum engineer.

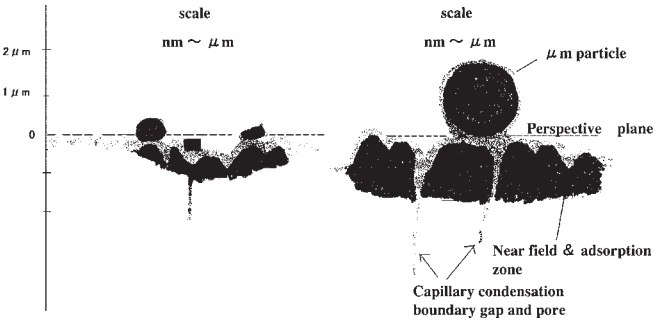

Figure 11: Surface (molecular & thick layer) crossectional, typical vacuum chamber wall

[3] ‹d›=4V/(βA), where V and A represent chamber volume and perspective, apparent surface area respectively. β represents surface roughness factor which is real (true microscopic) surface area/perspective surface area.

[4] Adsorption kinetics of water vapor in a vacuum chamber is discussed by Y. Tuzi et al., VACUUM, Vol. 47, No. 6–8, pp. 705-708, 1996 PERGAMON.

MEASUREMENT OF UHV

The most precise UHV total pressure gauge available today is the Axtron gauge (Figure 12). The ionization gauge tells density of molecules in a specific partial zone in the ion generating space. Ions generated in the zone have specific energy which is detectable by a connected energy analyzer. Stray ions with different energy and stray electrons, sources of intrinsic noise, are not allowed to reach the ion collector. Axtron gauge connected to a plasma processing chamber was immune to stray electrons from plasma. Axtron works in the range 10^{-3}Pa to 10^{-11}Pa total pressure. Because of the sorption sojourn time mentioned, any type of vacuum gauges tube-connected to a process chamber need to be calibrated in-situ for precise matching to a specific process. Such calibration is, however, not always reliable for a process analysis. In industrial processing using complicated UCT processing, a UHV total pressure gauge is usable for monitoring vacuum chamber and system. For intrinsically clean system-like particle accelerators, analytical systems etc. UHV total pressure gauges, including cold cathode gauges are useful. For some process monitoring, mostly quadrupole gas and vapor analyzers have been developed. However, the sorption phenomena has to be considered, especially for time lag of information in changing environment. Tube wall irradiated by ions, electrons and hot neutral particles give different time lag depending on species of adsorbed vapor. It is highly desirable for vacuum people to have suitable in-situ surface sensor for specific processing.

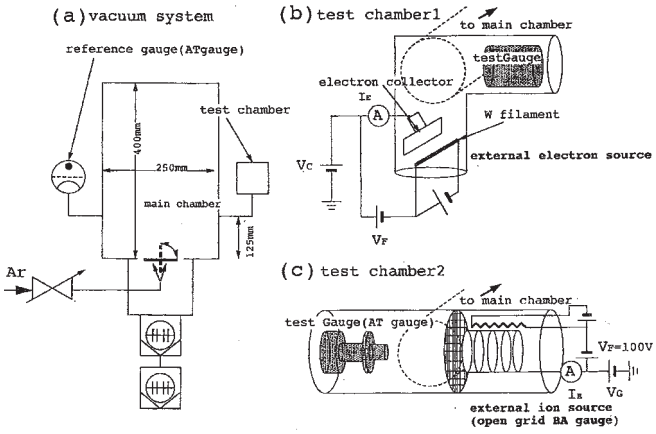

Figure 12: Schematic view of the experimental apparatus. a) Vacuum system for the experiment. b) Test chamber for the measurement of the effect of the external electron source. c) Test chamber for the measurement of the effect of the ion source that is made from a B-A gauge without the top electrode of the grid and the ion collector. Details of the Axtron (AT) gauge are published by H. Akimichi et al., VACUUM, vol. 47, No. 6–8, pp. 561–565, 1996.

The operating condition of the test gauges

	B -A gauge	Extractor gauge	AT gauge
grid potential	150 V	220 V	110V
filament potential	25 V	100 V	10
electron current	0.5 mA	1.6 mA	1 mA
reflector potential		205 V	
V_{BE}/ V_{BA}			67 V/300V
ion collector potential	0V	0V	0V
sensitivity factor(Pa^{-1})	0.15	0.06	0.023

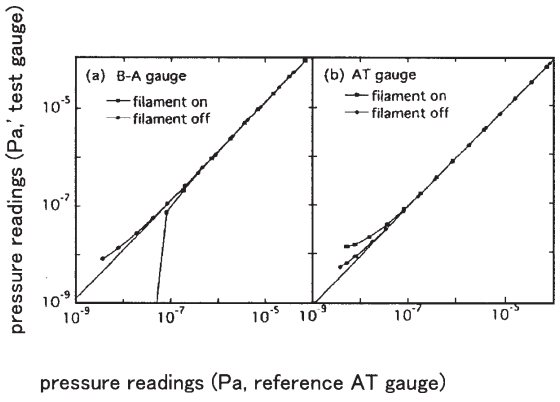

Figure 13: The effect of electrons emitted from the grounded filament of the external electron source. The pressure readings of the test gauges versus those of the reference AT gauges are plotted. a) The pressure readings of the B-A gauge showed very low pressure when filament of the electron source was lighting. b) The pressure readings of the AT gauge showed no sign of the disturbance (reference Figure 12).

EVACUATION, PUMPING

Well baked, outgassed vacuum gauge performs as a sink of gases and vapors (pump), while the gauge tube wall is cooling down. Practically, Helium is the only exceptional gas with regard to adsorption phenomena. The fresh tube wall continues to catch and adsorb vapors. This process is explained in Figure 10, Table 1, etc. The higher the vacuum the longer the required time to reach an equilibrium condition.

Inert gases usually reach the equilibrium quickly, unless ions and radicals are generated with rather high ionizing current. Ions and radicals can be active at a surface to cause change of atomic arrangement of substrate surface atoms. It is then possible for them to be embedded and result in a shallow yet not easily desorbable layer. Dynamic evacuation process is also understandable when considering the sojourn time.

PLASMA VACUUM

Industrial plasma processing utilize lots of ions, radicals, electrons, photons, and electrically neutral particles, generated by recombination in the plasma. Those particles arriving at surfaces surrounding the plasma cause both useful and detrimental reaction. In-situ plasma cleaning of a vacuum chamber is useful. While damaging well prepared structure and composition of the chamber is detrimental. T. Ohmi proved incoming particles from RF plasma with (kinetic?) energy less than 5ev is usable for damage free cleaning in case of silicon wafers. 5ev is close to hydrogen bond energy.

Chemical reaction of atomic hydrogen on oxygen covered tungsten filament in incandescent light bulbs, so called water cycle, was proven by I. Langmuir in 1920's. Light bulbs today are backfilled with inert gas that is functional as protective gas. LED today is provided with dense protective thin film against atmospheric air containing water vapor.

Inert gas blanket over a damage free surface seems preferable if it works in a vacuum process chamber. Some ingenious design, perhaps for each specific application, should be developed.

Protection of the plasma container wall has long been under development in nuclear fusion plasma systems. Actually protection was for fusion plasma from contaminants emission from the container wall. Shaping and confinement of plasma by using magnetic field has been tried for many, many years. Industrial application of knowledge of the plasma generation has been developed by T. Uchida at ULVAC. His system was named Neutral Loop Discharge (NLD) plasma system (Figure 14). High density and low temperature doughnut plasma can be easily produced along a magnetic neutral circular loop formed previously in vacuum chamber, by appling rf electric field along the neutral loop. The NLD system has proven to be marvelously effective for nearby substrate surface processing, partly because the NLD is operable in clean high vacuum ($\leq 10^{-2}$Pa); The chamber wall will be cleaned by bombarding neutral radicals and kinetically energetic neutrals. Recombination of ions and electrons proceeds quickly. Control of the bombarding particle energy is a next issue for energy sensitive applications.

VACUUM SEAL

Necessity in industry for rather frequent maintenance either scheduled or unscheduled prefer elastomer seal to metal seal because of reliability, operating cost etc. elastomer vacuum seal are, however, the largest source of gas and vapor in an empty industrial UHV chamber (Figures 15, 16, and 17).

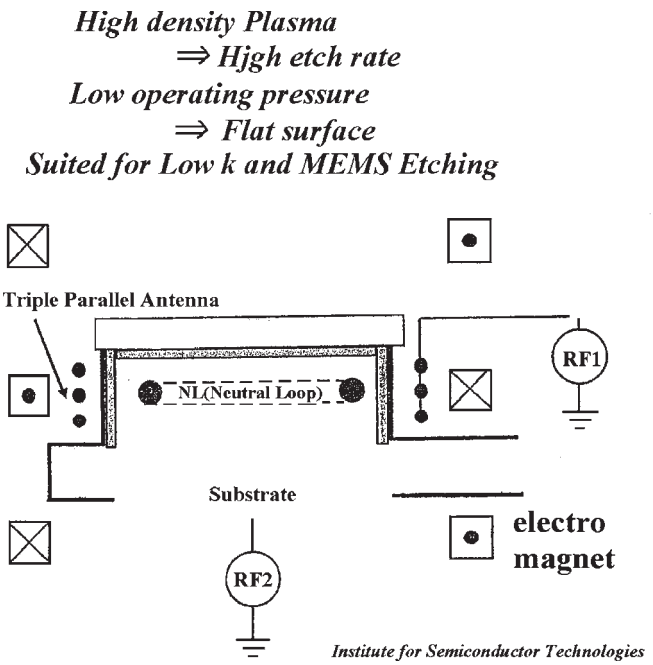

Figure 14. The NLD, conceptual

Figure 15 is data taken for comparison of base pressure reached by using four different sealing methods. The basic pressure values are taken after over hundreds of hours of continued evacuation namely at quasi-stationary condition. Outgassing rates of a high quality elastomer are obtained by using other test system and illustrated in Figure 16. Elastomers exposed to atmosphere adsorb gases to various degrees. From industrial systems point of view, the more important could be the sojourn time. Outgassed molecule, typically H_2O, require long time to pass through the channel as illustrated in Figure 17. The average time required for a molecule to pass through the channel should be approximately $\beta \bullet S \langle\tau\rangle \bullet \langle\varsigma\rangle$, neglecting $\langle d/v \rangle$.

Where β:Real (micro) surface area/perspective surface area
S: Sticking probability
$\langle\tau\rangle$: Average sojourn time
$\langle\varsigma\rangle$: Average number of collisions with the channel wall for a molecule to come out to UHV spece.

The β is estimated to be less than 1.3 for a polished surface. $\langle\varsigma\rangle$ can be calculated from the geometrical shape of the channel, $\langle\varsigma\rangle$ is roughly $1/2(L/2d)^2$.

We should remember that the sojourn time is not a matter to be considered in case of an exactly stationary molecular flow state.[5] In non-stationary state, however, like during evacuation of UHV chamber in high vacuum region, $\langle\tau\rangle$ plays a tremendous role.

[5] Pump speed values shown in commercial catalogue are measured at stationary flow condition. Dynamic evacuation process is more of the sojourn time issue.

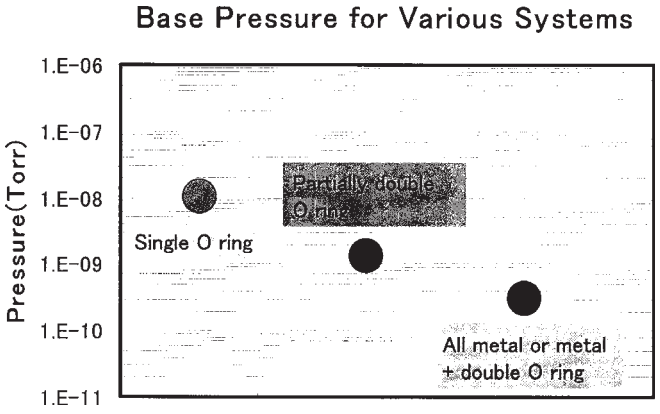

Figure 15: Practically attainable vacuum with flexible seal

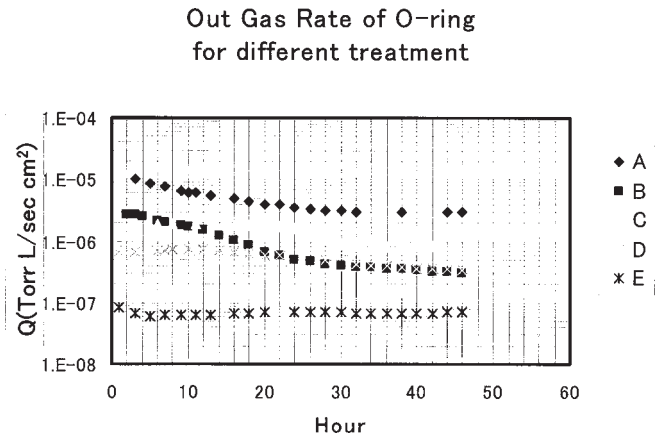

Figure 16: Rate versus pumping hour. A) No treatment B) Out gassing at 120C, 10^{-3} (Torr) for 10 hours C) Boiling for five hours D) Out gassing at 130C, 10^{-7} (Torr) for 6 hours E) C+D

DISTRIBUTED PUMPING

Distributed pumping by using gettering metals and alloys of Ti, Zr, etc. has been a common practice in high energy accelerators. The getters catch stray wandering gas molecules, water molecules, and small hydrocarbon molecules, etc. Similar design was adopted by using cryo-pumping surface for an ion-implantation system (Figure 18). In the latter case catching organic molecules generated on the ion bombarded substrate and diffused back along the ion beam track zone. The cryopanel is not designed to catch hydrogen, which would be the last residual gas in extremely high vacuum system like storage ring where hydrogen is believed to come out from structural metal alloy members. High-density alumina or ceramic is practically immune to hydrogen diffusion, while traces of Helium diffusion is possible. The model implantation system was very good for highly uniform implantation (Figure 19), but industry often prefer easy maintenance and high volume production to low contaminations.

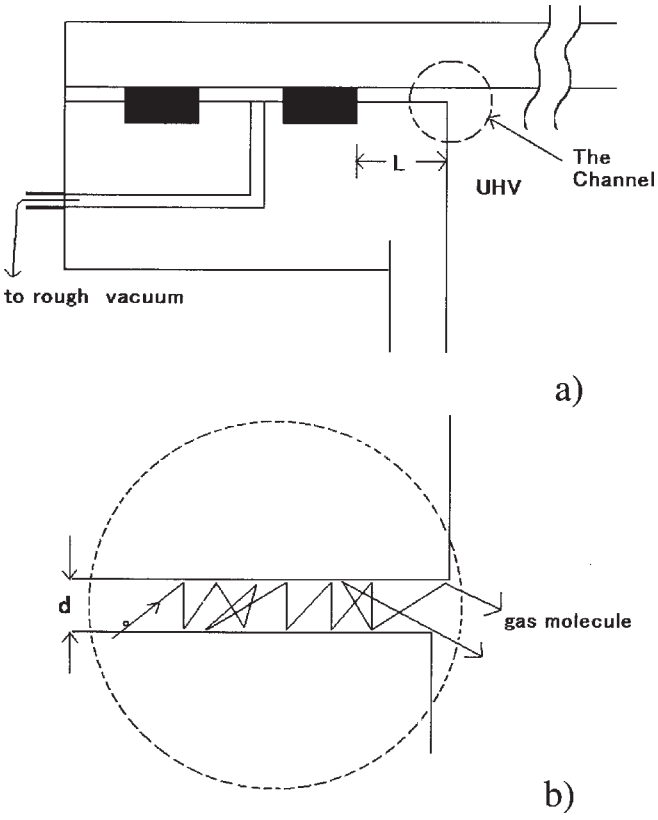

Figure 17: Molecular flow through the channel

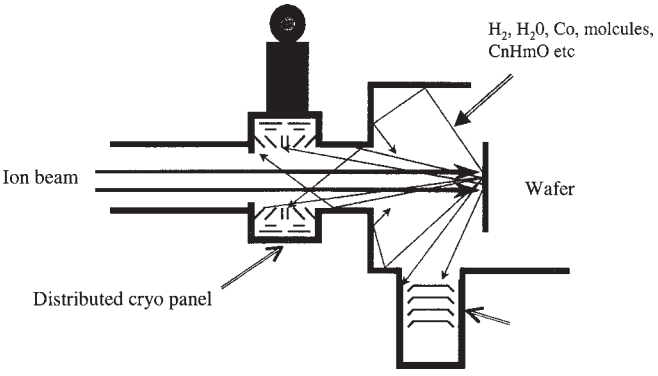

Figure 18: Effective capture by distributed pumping

NANO-PARTICLES

Small populations of nano-particles, condensed matter consist of assembled atoms or molecules and usually of ~ 10 to 10^6 atoms, plays a significant role in thin surface film processing. Nano-particles show catalytic behavior in surface processing. Surface migration of relevant atoms, and molecules should be taken into account along with incoming atoms and molecules that are colliding with surface nano-particles; this subject is definitely worthwhile to discuss, but I will put details of that out of the scope in this presentation.

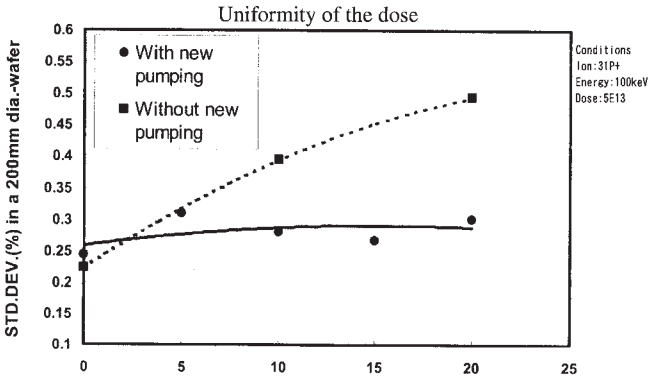

Figure 19: Comparison of the resulting implantation, the new uses distributed pumping.

NOTE 1

This being a technological review paper, the author would like to summarize the basic concept in dynamic (to get UHV quickly after each exposure to rough vacuum or atmospheric pressure) surface processing systems; as described in the following items.

1. Control of the sojourn time.
2. Minimize narrow channels and holes.
3. Purification of materials to be exposed in/on the surface.
4. Confine plasma, avoid hitting the surface.
5. Informative measurement near the surface.
6. Scavenging used gas/vapors quickly.
7. Reliability and reproducibility of mechatronics by using advanced computers; remote control.

NOTE 2

As a background in writing this paper, the author tried to introduce what has been developed in Japan with UHV technology for vacuum coating industry. In that context, the author must admit there will be many other works relevant to the subject accomplished in North America, Europe and other industrially advanced countries. Ongoing effort by the SVC in transnational and networking activity in the field of UHV and UCT Technology would be highly appreciated.