Atomic Layer Injection

ALI-1000

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ALI-1000

ALI-1000 is a versatile tool for the deposition of macromolecules and nanoparticles from solution in high and ultra-high vacuum (UHV) environments.

A variety of techniques exist for the growth of atomic and molecular layers where solids, liquids (solutions) or gases can be used as sources. Working with solutions instead of solids has the advantage that the material to be deposited does not need be heated. It is perfectly stable, so that fragmentation or hydrolization does not take place.
Electrospray and drop casting are the two most frequently used techniques using liquid sources. However, both have certain limitations.
In *Electrospray* a solution is passed through a capillary to which a high voltage is applied. The charging of the liquid causes it to break apart at the end of the capillary, creating a fine spray of highly charged microdroplets. These then travel through a pressure gradient toward the sample, reducing in size as the solvent evaporates and resulting in the deposition of the solute on the sample. This technique allows introducing a substance from atmospheric pressure directly into ultra-high vacuum conditions. The disadvantage of electrospray as a deposition technique is that it is only applicable to polar solutions and requires a relatively large sample volume (>1ml). Furthermore, the required differential pumping system (vacuum pumps, valves, gauges) is expensive and requires high maintenance.

Dropcasting, on the other hand, takes place under controlled atmospheric conditions, outside the vacuum system. A drop of solution is deposited on the sample surface and can then be homogeneously distributed over the sample by different mechanical methods. Once the solvent has evaporated, the sample is inserted in the vacuum chamber for study. The technique has the disadvantage of not always yielding a homogeneous coating. The main problem, however, is that the sample unavoidably becomes contaminated, because it is prepared outside the vacuum system.

Liquid solution injection, the technique used in ALI-1000, overcomes these problems. In ALI a pulse valve is used to inject a very small amount of solution into UHV. The solvent quickly evaporates, while the solute travels through the vacuum, assisted by gravity and the pressure gradient. The pressure in the chamber increases with each pulse but rapidly recovers, as with a virtual leak.
The advantages of this technique are that it can be used with all kinds of solutions, both polar and apolar, and the only factors to consider are the geometry of the system, the pressure in the pulse valve, and the concentration of the solution. Since there is no heating involved, ALI is also compatible with biological samples.

ALI-1000 can easily be incorporated into any running vacuum system through a standard DN40CF flange.

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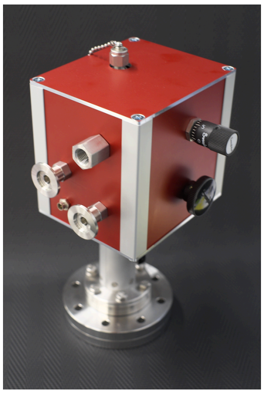
Components

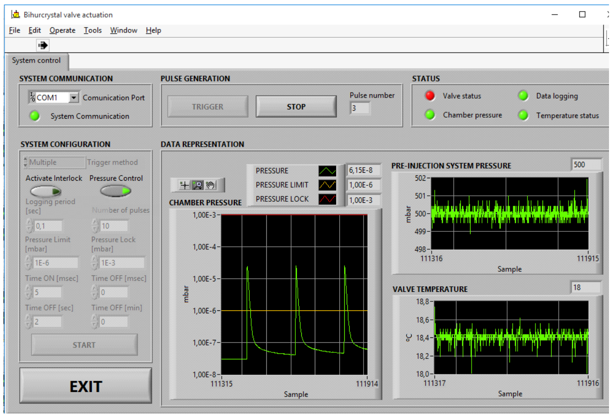
The core component of the ALI Deposition System (*ALI-DS001*) is a **pulse valve**. When the coil in the valve is energized, the magnetic field produced in the coil moves the valve's plunger from closed to open position against the action of a spring, allowing flow through the valve, and injection of the solution (or gas) into the vacuum chamber. ALI's pulse valve features include

- Pulses of down to 1 ms with high reproducibility.
- Leakage rate: 10^{-7}mbar·l·s^{-1}
- Working temperature range: 4-105ºC (4-80ºC recommended)



The pulse valve is connected to the **pre-injection system**, through which the solution to be injected and a carrier gas are introduced. The pre-injection system includes flow valves and a gauge to control the carrier gas flow and pressure.

The ALI Software & Electronics Package (*ALI-SE001*) includes the software, electronics and the necessary drivers (Windows v. 7, 8, or 10; 32 or 64 bit). The **control and data-acquisition software** consists of a single window from which the user may easily control the injection process (pulse duration, number of pulses, etc), as well as keep track of and create a log of the system's status (pressure in chamber and pre-injection system, pressure/temperature in valve, etc). The control software also incorporates safety features in order to preserve the vacuum and avoid overload in the system's vacuum pumps.



The GUI (Graphical User Interface) shows the pulse-injection controls and a graph interface in a single window.

ALI can be used in three modes of operation:

- *Single/Manual*. A single injection pulse with an open-time defined by the user.
- *Single/External*. A single injection pulse triggered externally by a 5V TTL signal via a BNC connector.
- *Multiple*: A series of injection pulses with activation time and pulse frequency defined by the user.

The ALI **electronics** provides the following functions:

- Powering the pulse valve
- Powering the vacuum gauges
- Generating pulses in the pulse valve
- Acquiring data on pressure, temperature and valve activity
- Safety mechanism to avoid pump overload
- Connecting to the PC through the control software

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Principle of Operation

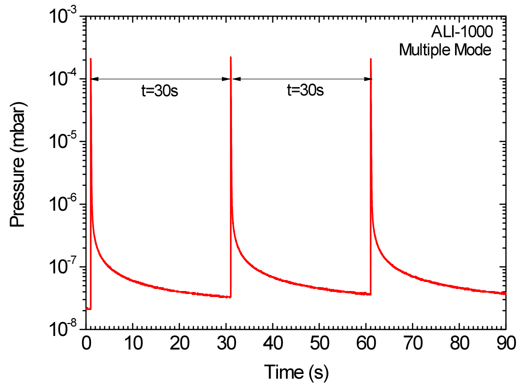
Injection of gases and liquids into UHV conditions inevitably affects the vacuum system's pressure.

When a *gas* is introduced into a UHV system, the system's pressure first rises sharply due to the sudden expansion of the gas upon entering the chamber, and then recovers exponentially, as shown in the graph to the right for an injection in multiple mode.

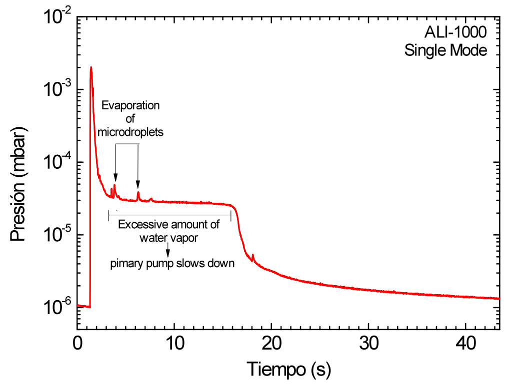
The case of *liquids* is somewhat different: when injected into a UHV system, a liquid forms a spray that immediately begins to evaporate, causing a sharp rise in pressure. The large amount of vapor in the chamber makes the pumping slow down, causing the plateau in the pressure graph on the right. Once the water vapor has been pumped from the system, the pressure continues to recover exponentially.

ALI is mainly used to inject liquid solutions into UHV (though injection of gases is also possible). The solute is the material to be deposited on the sample. The solution is first introduced in the valve via the pre-injection system. After this, an inert carrier gas is introduced up to the desired pressure. The carrier gas pressure affects the spray geometry during injection, and avoids contamination of the sample.

As it is injected from the valve, the solution forms a spray of microdrops. As the drops travel towards the sample, the solvent evaporates, and the solute travels on and is deposited on the sample, forming a layer that can be subsequently analyzed.



Different pulses of air in *multiple mode*. Time between pulses was 30s and pulse duration was 5ms. The pressure in the valve was 1000mbar. The pressure recovers practically instantaneously after each injection.



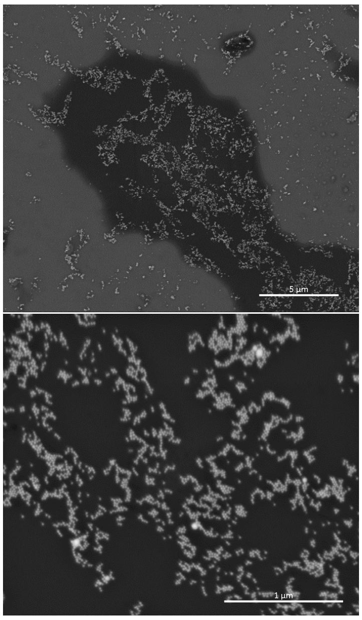
Single pulse of Milli-Q water. Pulse duration was 50ms and pressure in valve was 1000 mbar. Once the excessive amount of vapor is pumped from the system, the pressure continues to decrease exponentially.

Applications

Nanoparticles

ALI allows the deposition of nanoparticles produced ex-situ, in UHV environment, thanks to its injection system.

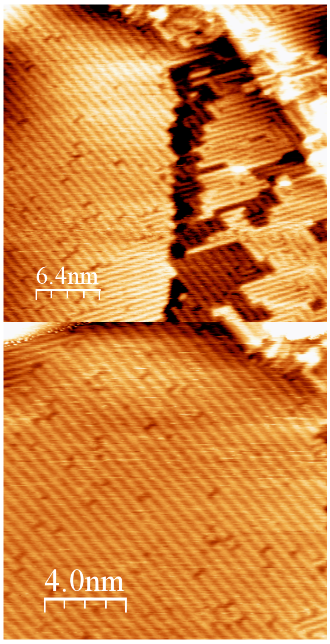
The figure on the right shows two scanning electron microscopy (STM) images of gold nanoparticles on a Si wafer. These were obtained after injection of a gold nanoparticle colloid with a density of 1012 particles/ml, at 1000mbar. The zoom image shows the nanoparticles with an average size of about 20nm.



Images courtesy of J.M. Sobrado from Centro de Astrobiología (INTA-CSIC), Madrid, Spain

ATP on Cu (110)

Adenosine triphosphate (ATP) is a nucleoside considered to be the molecular unit of energy currency within the cell.
ATP is related to ribonucleotides, the polymerization of which produces ribonucleic acid, an essential element in the flux of genetic information. Its evaporation in UHV is a difficult task because the molecule degrades when heated. ALI is an ideal alternative to deposit ATP in vacuum conditions, since it does not involve any temperature treatment.
STM images show ATP deposited on Cu(110). Molecules form ordered islands on the copper terraces.



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Technical Specifications

Carrier gas	Argon (recommended)
Pressure of carrier gas	25 mbar (water vapor pressure) up to atmospheric pressure
Carrier gas regulation	Double-stage pressure regulator at carrier gas cylinder outlet, and needle valve in pre-injection system. Pressure monitored by a direct gauge (0.1 to 1100 mbar)
Carrier gas connection	stainless steel ¼" double-ferrule fittings
Pulse duration	1 ms up to 10 min
Pulse Frequency	1000 Hz – 0.006 Hz
Max. Volume Solution	1 ml
Solution Molarity	< 5mM (depending on valve diameter)
Primary pump requirements	Dry pump with gas-ballast (5<S<7) m^3/h and <$5x10^{-2}$mbar base pressure
Secondary pump requirements	Turbomolecular pump (250l/s or better, depending on volume of chamber)
Pre-injection pump requirements	Dry pump with gas-ballast (base pressure < 7 mbar)
Communication	USB
External control	TTL
External signal out	220V/0.1A