Laboratory Demo

Thin film growth of $YBa_2Cu_3O_{7\_s}$ with pulsed laser deposition technique

Equipment: CALAS deposition chamber with Lambda 200 eximer laser

Task description

A. Discuss and choose the deposition regime for YBCO thin film fabrication. Substantiate your selection of the substrate material, laser energy density, substrate temperature, background oxygen pressure, cooling-down sequence.

B. Acquaint yourself with the computer-aided laser ablation system (CALAS). Consider the possibilities and advantages of the computer control of the basic deposition parameters.

C. Deposit a YBCO thin film in the chosen regime using CALAS system. Pay attention to such peculiarities as laser energy density measurement, target surface polishing, ablation plume size, substrate gluing and heating, etc.

D. Discuss the properties of the obtained films on the basis of subsequent T_c-measurements, optical microscopy observation and X-ray diffraction characterization.

Content:

1. Basic description of the laser ablation deposition technique

Laser ablation deposition technique is based on the explosion that occurs on the surface of a bulk material when it is hit by the photons of a pulsed laser. A suitable laser for this purpose is an excimer laser filled with krypton and fluorine as laser gases and neon as buffer gas. An excimer laser with this gas mixture has a wave-length of 248 nm. The average energy of a single pulse is 400-700 mJ and the duration time is about 25-30 ns all depending on the chamber size of the laser.

Ablation of $YBa_2Cu_3O_{7-x}$ (YBCO) bulk material or some other related material usually requires an energy density above 15 mJ/mm^2 This means that the needed power density of a single pulse is 600 kW/mm^2 or more. When a photon pulse gets absorbed by a bulk material there will be a dramatically increase of the temperature on the surface of that bulk material. Only a few atom layers close to the surface will absorb the momentum of the photons. Hence, the absorption can therefore be regarded as a skin phenomenon. Because of the extremely high energy density and short duration time of a single laser pulse, the bulk material will not be able to distribute the absorbed momentum on the surface to the interior of itself and the reaction will instead be that the material in the skin region will be thrown out into the surroundings.

The intensity of a laser pulse and the momentum of a single photon (the wave-length of the laser light) affects the result of the ablation process. The majority of the photons in a single laser pulse has to be absorbed by the bulk material. This means that the used laser wave-length must match the e-m radiation absorption coefficient of the bulk material. An increase of the power density will, of course, increase the number of absorbed photons.

If the surrounding pressure is low enough, the transferred momentum from the laser beam photons to the bulk material will force the material in the skin region to eject perpendicular from the bulk surface in a plume shaped material cloud containing atoms, molecules, clusters and ions. The perpendicular ejection of the ablated cloud is very important for the geometrical arrangements of a laser ablation deposition chamber (Fig. 1). Sometimes, specially if the laser beam is intensity heterogeneous or the power density is too small, so called target boulders will be a part of the ablated cloud. These boulders are big particles that have not been smashed.

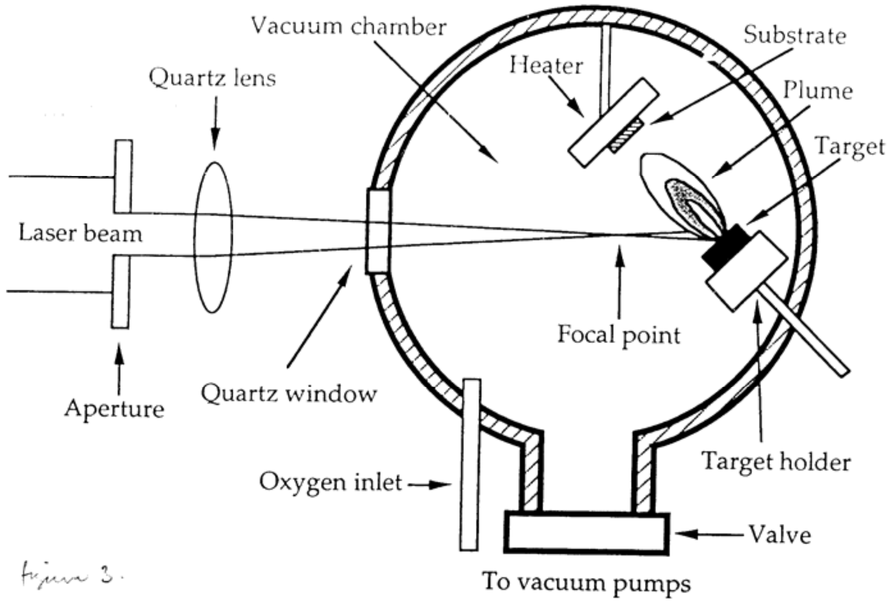

Figure 1. A schematic drawing of a laser ablation deposition system. The quartz lens and window are used for the laser beam since they have high transparency in the UV-region of light. The substrate is thermally anchored to a heater in order to provide the condensing material of the ablated cloud with energy so that an epitaxial film might be formed on the substrate. Some deposition processes require additional oxygen. A deposition chamber has therefore an inlet where oxygen can be admitted. Note that the ablated material cloud, i.e. the plume, is ejecting perpendicular to the target surface even though the laser beam hits the target at a 45° incidence angle.

If a substrate is located in a proper position with respect to the ablated cloud, it will condense on the substrate and form a thin film. When a crystalline grown film is wanted, it is necessary to have a hot substrate with a matching lattice structure. The condensing material components use the surface energy of the hot substrate to move around and find their most favorable lattice sites. A simple way to look upon this is to consider the substrate as a crystalline template for the growing film. However, if the laser pulse frequency is too fast, there will not be enough time for a growing film to settle in its correct stoichiometric form. Many growing materials also need time to react with the oxygen gas that most ablation processes have present as a background atmosphere. The needed time between the pulses is called the relaxation time of the growth process.

The temperature that the substrate should have during the growth process is also related to the different phases that a condensing material can form. Another thing that can affect the used growth temperature of the film is the substrate material, however its influence is usually much smaller than the specific properties of the condensing material.

2. How to obtain a hot substrate surface

The heating of the substrate is in fact the process condition that is hardest to arrange. There are in principle two different ways to obtain a hot substrate, One is to place the substrate on a hot surface and clamp it with thin sheet-metal pieces or glue it with some heat conducting material. In this first case the heat transfer is done by the conductivity of electrons and phonons inside a solid body. The second method is radiation balance, which is done by putting a substrate in a hot cavity and thereby forcing the substrate into radiation equilibrium with its surroundings. The two different methods have their drawbacks.

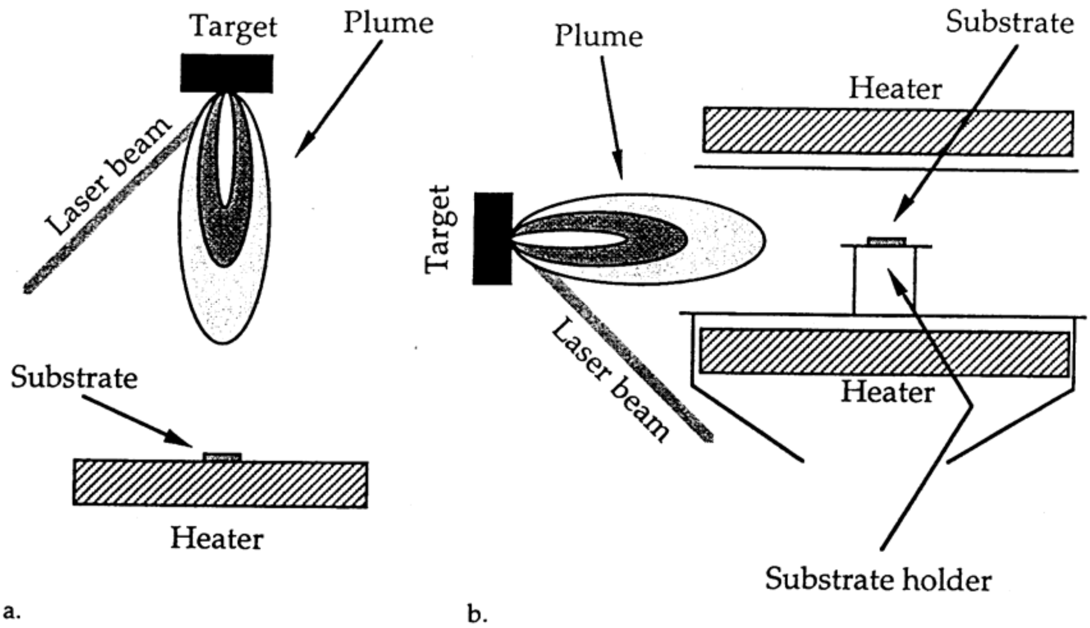

Figure 2a. A schematic drawing of a substrate heated through direct contact heat transfer. The deposition geometry is of on-axis type. In b) the substrate is heated through radiation balance at off-axis deposition geometry. The substrate holder, which can rotate, is made of thin wires so that the substrate is not shadowed during deposition. Double sided depositions are possible in this case.

In the case of gluing the substrate, which is normally done with silver paste, a good thermal contact during deposition usually goes together with a strongly fixed substrate when the deposition is finished. The reason for this is that when silver paste gets heated above 700 °C, it reacts with both substrate and heater and forms an interface that is stronger than the substrate. Small substrates of 5x5 mm^2 size and maybe 10x10 mm^2 can with some effort be removed from the heater by a from the side applied shear stress of a knife or some other tool. Substrates bigger than that usually break when they are removed.

Clamping requires both a flat heater surface and a flat back side of the substrate. If the thermal contact alters in the heater-substrate interface, the temperature on the substrate surface also alters which means that the growth conditions of a film is heterogeneous. A trick that can be used in order to improve the thermal contact is to have a thin metal foil of silver or gold between the heater and the substrate, however the foil might react with the back side of the substrate due to the heating, Remaining metal foil might cause problems later on if the substrate should be processed. The advantage with both these above described heating methods and the reason why they are the most used ones are that the ablation plume has easy access to the substrate surface and the substrate orientation can be either of on-axis or off-axis geometry (Fig. 2).

Radiation heating is the far best heating method, because it is a method without any physical contact and leaves the substrate untouched. The big problem in this case is to have a hot surrounding and at the same time let the ablation plume reach the substrate surface without heating the target and its holder. The openings of the hot cavity for the plume and the laser beam have to be arranged in such a way that both the back and front sides of the substrate are facing the hot surfaces of the cavity. This means that off-axis geometry is the preferable orientation, since temperature variations will otherwise occur on the substrate (Fig. 2b). Another draw back of off-axis deposition is that if the substrate is not rotating there will be a thickness gradient with a thicker film closer to the target.

3. The importance of a clean substrate surface

A YBCO thin film has a typical thickness of 10-300 nm with a well oriented crystalline structure. All the different kinds of substrates that can serve as epitaxial templates need to have smooth surfaces otherwise the growth template effect will be partly or completely suppressed. The substrates are because of this mechanically and chemically polished so that the roughness over a distance of 0.4 mm is less than 4 nm. However these flat surfaces are hydrophilic, i.e. they have an affinity for water. Water is an excellent solvent for different salts and organic substances. This is exactly what water vapor from the human body contains so if a substrate is close to a human the water layer on the surface will contain salts and organic substances. Other kinds of contaminations can of course appear. Remaining polishing powder and substrate dust can be left on the surface if it is not rinsed in proper solvents after the polishing process is finished. As mentioned above the substrates must be hot during deposition and therefore they are often glued with silver paste to a heater in order to have good thermal contact. During the heating to deposition temperature the silver can be a source of contamination, since it might evaporate from the heater surface and end up on the substrate surface. When the oxygen is admitted into the chamber the organic substances will be burned away and that is good, but the salts will react with the substrate surface and create local defects in the crystal lattice. Local defects on a substrate surface, whether they are small particles lying on the surface or defects in the crystal lattice will cause defects in a growing YBCO film.

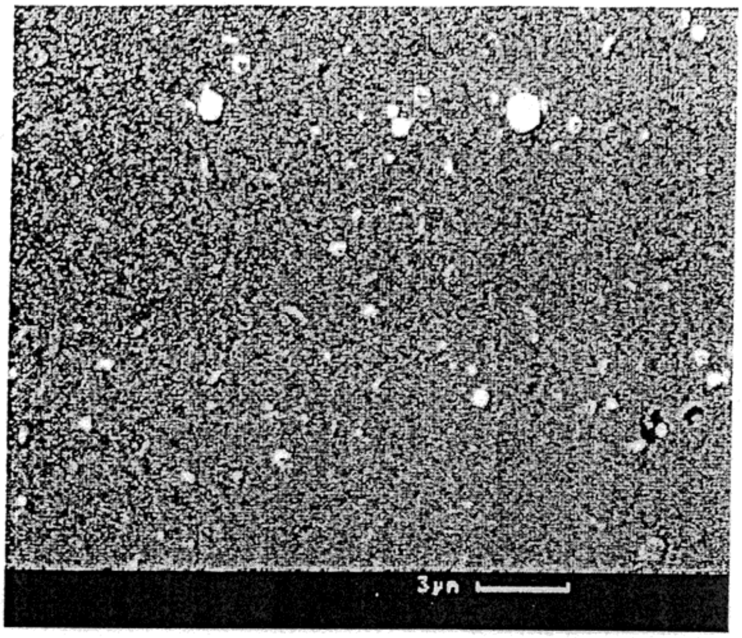

Figure 3. A YBCO thin film that has copper oxide boulders imbedded. Particles that have their origin from the target can also be seen (Courtesy of E. Olsson).

There are two possible sources for stoichiometric film defects that have their origin from the ablation process itself. First, the substrate has to be located in a true stoichiometric volume of the ablated cloud to avoid this problem. Further, the probability that an atom stays where it lands on the surface of the growing film is called the sticking coefficient. If these coefficients are different for the different atoms in a growing film structure, the film will of course grow non-stoichiometrically. The over represented atoms usually form islands in an imbedding stoichiometric film. The most common defect in a YBCO thin film, that is caused by non-stoichiometric growth, is copper oxide boulders (Fig. 3).

The choice of the substrate material is mainly determined by the crystal lattice matching with YBCO. A good matching is necessary to initiate epitaxial growth. The parameters of the most suitable and commonly used substrates for deposition of YBCO thin films are summarized in Table 1.

4. Laser ablation of c-axis oriented YBCO films and the necessary presence of additional oxygen

A laser ablation system for high temperature superconductors consists of several parts that emerge into one complete deposition unit for YBCO and related materials (Fig. 1 and Fig. 6). The laser pulse travels first through a 12x4 mm^2 aperture so that only the central part of the beam passes, i.e. it is only the intensity homogeneous part of the beam that is used for the ablation process. Then the beam is focused by a quartz lens and continues through a quartz window into a vacuum chamber. Inside the chamber the beam hits a target at a 45° incidence angle and a 3.0-3.5 mm^2 spot is projected on the target all depending on which lens-target distance that is chosen. The projection on the target is done behind the focal point of the lens. When the beam has entered the chamber, the intensity of a single pulse should be at least 45-50 mJ, which gives a spot energy density of 15-17 mJ/mm If YBCO is about to be ablated, the maximum repetition rate of the laser is 10 Hz, since, as mentioned above, a certain relaxation time is needed for the condensation and the epitaxial growth process.

Substrate material	Structure	Lattice constant [Å]	Dielectric constant at 300 [K]	Loss tangent at 300 [K]	Thermal expansion coeff. [K^{-1}]
STO	cubic	a=3.905	300	≈2 x 10^{-2} at 10 [MHz]	9 x 10^{-6}
YSZ	cubic	a=5.125	27	-	8 x 10^{-6}
MgO	cubic	a=4.203	8.1	≈9 x 10^{-3} at 10 [GHz]	8 x 10^{-6}
LAO	cubic	a=3.831	≈24	≈3 x 10^{-4} at 10 [MHz]	10^{-5}
	rhomboedric	a=5.377 α=60.13°			
NGO	orthorhombic	a=5.426 b=5.496 c=7.707	20	≈3 x 10^{-3} at 1 [MHz]	1.1 x 10^{-5}
	perovskite cell	a,c=3.863 b=3.854			
YBCO	orthorhombic	a=3.82 b=3.89 c=11.68			

Table 1. Lattice structures and constants of some materials that can serve as epitaxial templates for the YBCO superconductor. On MgO, YSZ, rhomboedric LAO and orthorhombic NGO substrates YBCO grows with 45° in-plane rotation angle. A few other important electrical and thermal parameters are also given. The information about the substrates are data from different substrate manufacturers.

A deposition process starts with the pump down routine of the chamber to vacuum state (< 10^{-5} mbar) and after that the substrate is heated to the deposition temperature (Table 2). The substrate is fixed by silver paste to a heater, which is an on-axis type of heater. The heater is located at a distance of about 50 mm from the target so that the center of the ablated material cloud will hit the center of the substrate. When the deposition temperature is reached, the chamber is filled with 200 mbar of oxygen and left at this status for 2 minutes. During this process step, organic contaminations on the

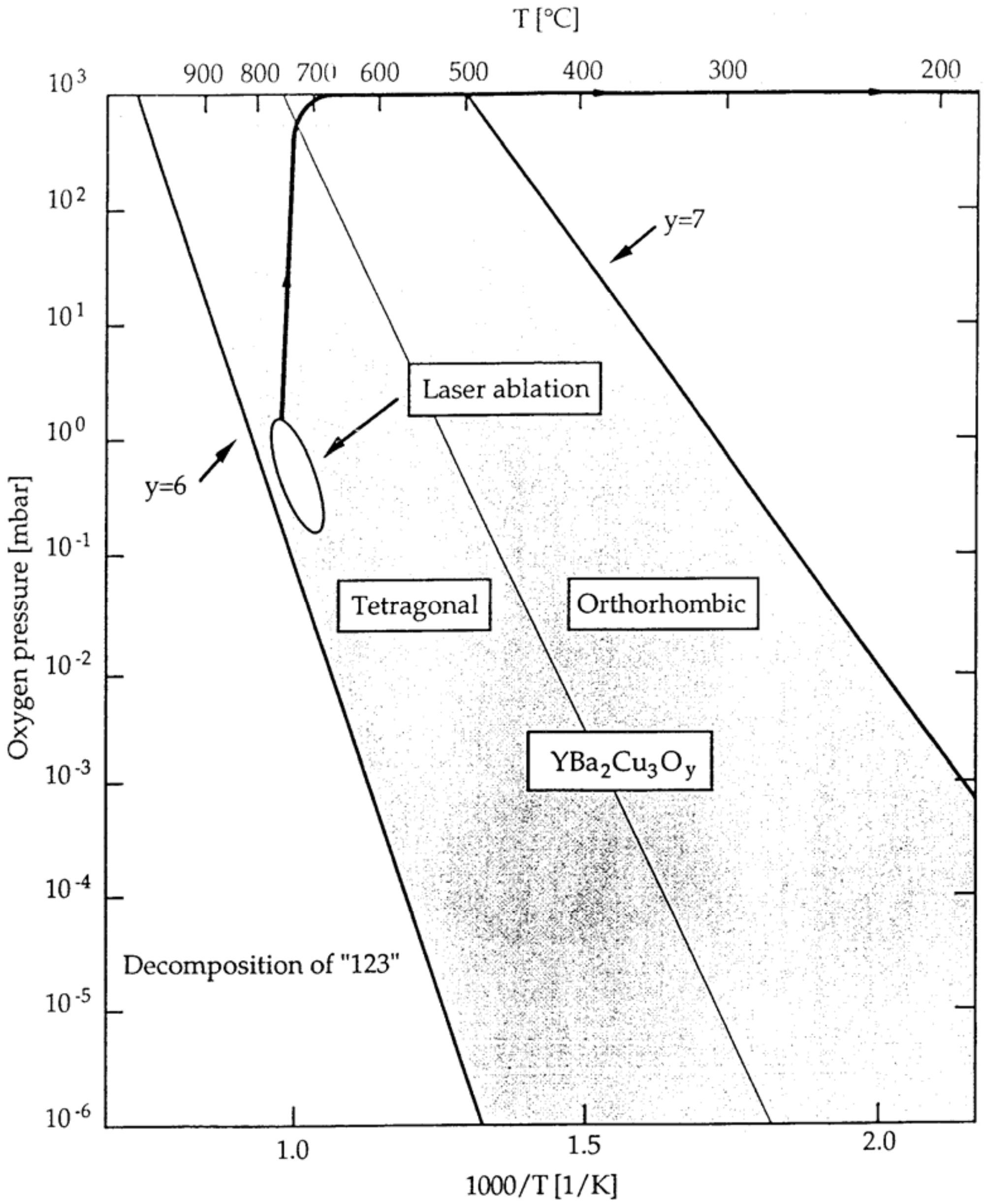

Figure 4. Phase diagram of YBCO. A schematic survey of the laser ablation growth domain and the following oxidation cycle that phase transfers the YBCO from tetragonal to orthorhombic structure is inserted in the diagram.

Materials that are frequently used together with YBCO are a number of electrically insulating and lattice matching materials like STO, YSZ, CeO_2, MgO and PGO. They are often used as buffer layers between the substrate and the YBCO or just as pure electrically insulating layers between two YBCO layers. These materials and YBCO have approximately the same deposition parameters. They have all in common that they need an oxygen pressure present during the deposition and about the same energy density and repetition rate settings of the laser.

5. A computer assisted laser ablation system with a multitarget carousel head

The laser ablation deposition technique allows discrete growth of thin films, since the average growth rate of an ablated material is about 1/2 Å per pulse. This property makes laser ablation suitable as deposition method when multilayer thin films of different composition should be made. A laser ablation system with several target holders mounted on a rotating carousel can be used to support the process for making these kinds of structures. When the carousel rotates, each target holder will be in firing position of the laser beam one time each revolution. A couple of position sensors and an electronic device that contains a programmed firing sequence can easily determine if the laser should fire or not on a specific target. A master computer, which is the interface towards the user, can be set up to program the electronic device of the target carousel and at the same time also be used to control the laser, a heater regulator, gas flow meters, a vacuum valve control unit, pressure gauges and other equipment that is needed to run the laser ablation system in a computer controlled mode. Such a deposition system will be very flexible, since the performance of the system is just a matter of how the algorithms of the software are written.

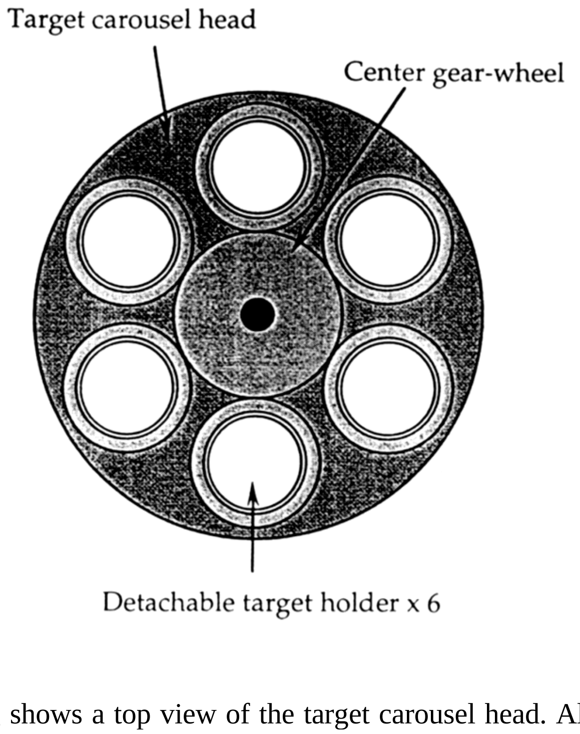

Figure 5. The drawing shows a top view of the target carousel head. All six target holders are separated by a 60° angle. Note that the center gear-wheel and the target holders have confined rotation through their mechanical connection.

The laser ablation target device can operate in two different deposition modes; the single target deposition mode and the multitarget deposition mode. The specific mechanical construction of the target carousel is that it is based on two electric motors, which gives the target carousel the necessary freedom of movement for positioning and continuous rotation of the target holders (Fig. 5). A DC-motor is connected to a center gear-wheel on top of the carousel head by a vacuum feedthrough. All six target holders, which are suspended by bearings and detachable from the carousel, are connected to the center gear-wheel. When the center gear-wheel turns, all target holders will rotate synchronously with it. In that way it is possible to rotate one individual target when the laser fires. A servo motor is connected to a second feedthrough, which allows the target carousel head to rotate. The servo motor can operate in two modes. In one mode it can operate as a positioning motor and thereby put any arbitrary target holder in the firing position of the laser beam. This is the single target deposition mode of the system. The other is the continuous rotating mode with adjustable speed. Hence, this is the multitarget deposition mode, and it will make the target holders pass by the firing position on parade when the carousel head is rotating.

The multitarget device can be completely controlled by the master computer through the communication and parameter settings of the DC-motor speed, servo motor speed and positioning, firing sequence memory and excimer laser. However, a computer assisted laser ablation system also needs other external supporting slave equipment to be able to run a complete deposition cycle (Fig. 6). A unit that runs close to the excimer laser is the pulse counter. The computer can generate free frequencies from 1-50 Hz for the single target deposition mode. When the multitarget deposition mode is executed, the laser is trigged by the firing sequence memory. The pulse counter keeps track of the number of pulses that should be fired by the laser and turns it off when the correct number of pulses has been fired. The vacuum valve control, which can either be operated in manual or remote mode, has the option to control 16 valves or shutters and at the same time independently read their position status (open or closed). Other units that the computer uses together with the valve control during a film deposition to keep the chamber pressure at a certain value are the gas flow unit and the pressure gauges. To be able to set the chamber at the condition of deposition atmosphere, the computer can run a sub-program that pumps down the system from atmosphere pressure to high vacuum and after that sets the system in bypass pumping mode, i.e. the turbo pump pumps on the chamber through a narrow line. At this pump status, the computer can open the two mass flow meters that are connected to the system; one for oxygen and the other for an additional gas if that is required. The interesting pressure range of deposition is 0.05-1.5 mbar. An accurate capacitance manometer reads the deposition pressure. This manometer tells the computer the present pressure in the chamber and the computer sets the mass flow values so that the pressure is kept at a constant level. The chamber is very pressure inert, i.e. it means that the pressure does not change much in time. Only small adjustments of the mass flow from the computer side are needed to keep the pressure constant. One more thing is needed for a complete control of the deposition process and that is the temperature control of the substrate heater. A heater regulator with its own CPU communicates with the master computer as a slave CPU and it can thereby run its own programs once the master computer has downloaded the necessary parameters. A thermocouple is hooked up to the heater and this is

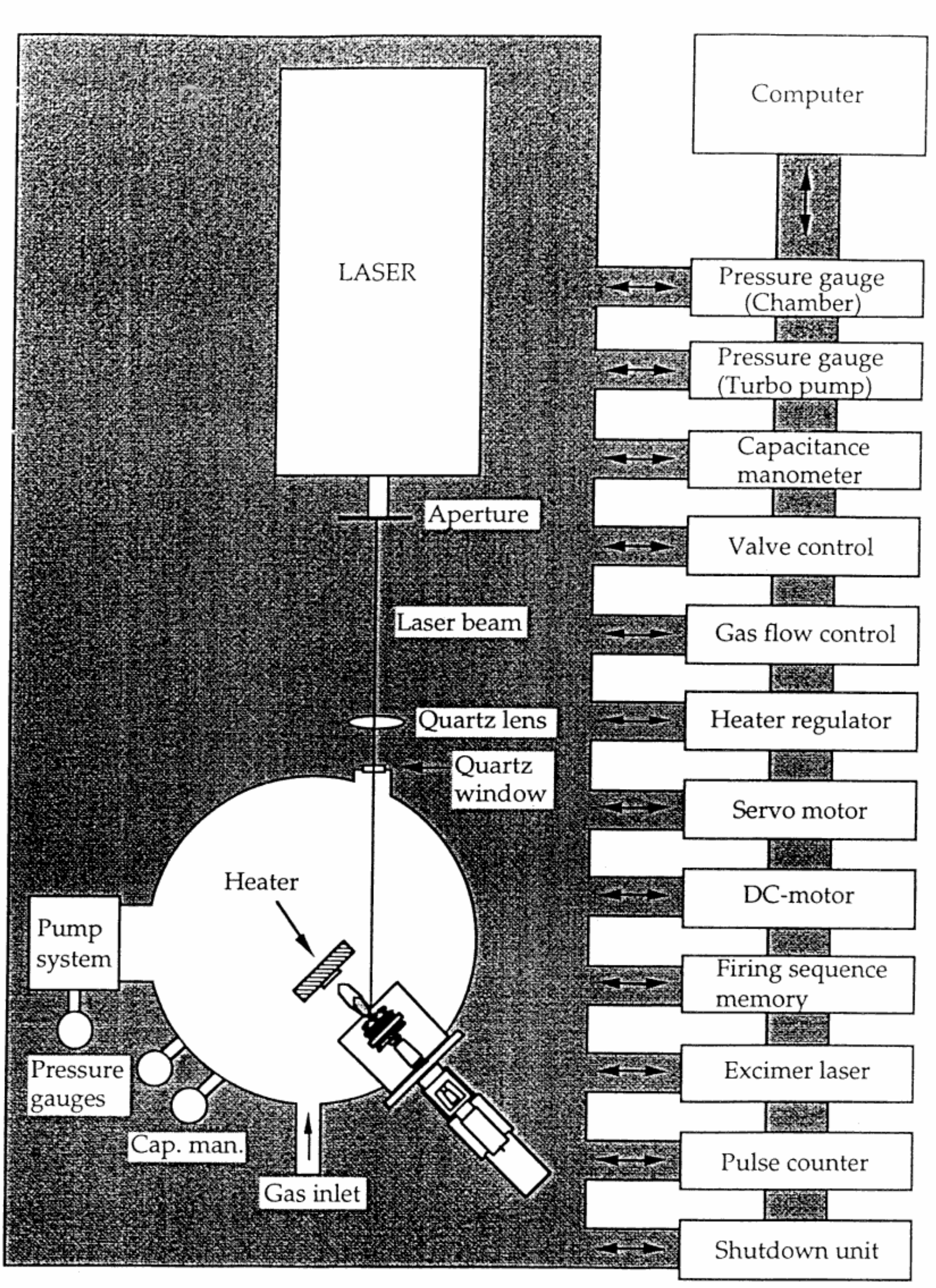

Figure 6. The drawing shows a schematic view of the computer assisted laser ablation system. The connections with the horizontal double headed arrows indicate that each external slave electronic device can communicate with the part of the deposition system that it has been appointed to control, while the vertical connection from computer to shut down unit indicates that the computer is the master of the whole deposition system. This means that the computer just gives orders to the external slave electronics, which they execute.

the feed back loop of the regulating circuit. The output of the regulator is connected to a thyristor which in its turn is connected to a transformer with secondary outputs of 20 or 40 V. This transformer feeds the heater. The shut down unit is simply a device that turns off the heater and closes the gas lines as a safety precaution if the computer program gets stuck.

References

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