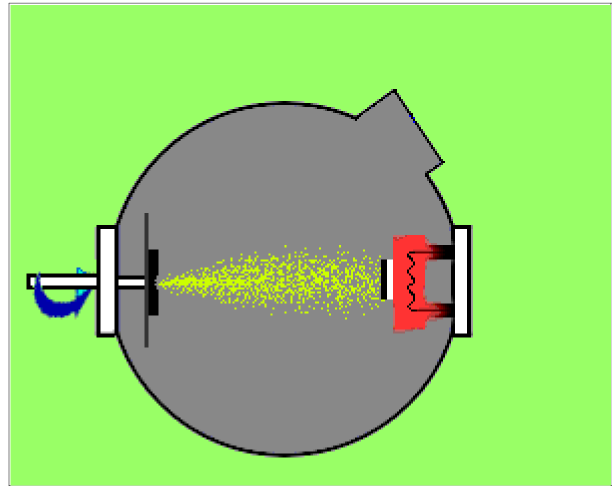
Pulsed Laser Deposition and Epitaxy

The PLD method of thin film growth involves evaporation of a solid target in an Ultra High Vacuum chamber by means of short and high energy laser pulses.

What's PLD?

Introduction



Laser is a powerful tool in many applications. It is especially useful in material processing. Thanks to it's narrow frequency bandwidth, coherence and high power density this instrument is used in many scientific research works and experiments. Often the light beam is intense enough to vaporize the hardest and most heat resistant materials. Besides, due to its high precision, reliability and spatial resolution, it is widely used in material processing industry. For example: machining of the thin film, modification of materials, heat treatment, welding and micro-patterning. Apart from these, polycomponent materials can be ablated and deposited onto substrate to form stoichiometric thin films. This Procedure is called Pulsed Laser Deposition (PLD).

In general, the method of pulsed laser deposition is simple. Only few parameters need to be controlled during the process. Targets used in PLD are small compared with other targets used in other sputtering techniques. It is quite easy to produce multi-layer film composed of two or more materials. Besides, by controlling the number of pulses, a fine control of film thickness can be achieved. Thus a fast response in exploiting new material system is a unique feature of PLD among other deposition methods. The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited films. This is the result of an extremely high heating rate of the target surface (10^8 K/s) due to pulsed laser irradiation. It leads to the congruent evaporation of the target irrespective to the evaporating point of the constituent elements or compounds of the target. And because of the high heating rate of the ablated materials, laser deposition of crystalline film demands a much lower temperature than other mentioned film growth techniques. For this reason the semiconductor and the underlying integrated circuit can refrain from thermal degradation.

In spite of mentioned advantages of PLD, some shortcomings have been identified in use of this deposition technique. One of the major problems is the splashing or the particulates deposition on the film. The physical mechanisms leading to splashing include the surface boiling, expulsion of the liquid layer by shock wave recoil pressure and exfoliation. The size of particulates may be as large as a few microns. Such particulates will greatly affect the growth of the subsequent layers as well as the electrical properties of the film and should be eliminated. Another problem is the narrow angular distribution of the ablated species, which is generated by the adiabatic expansion of laser produced plasma plume and the pitting of the target surface. These features limit the use of PLD in producing a large area uniform thin film, and PLD has not been full deployed in industry. Recently remedial measures, such as inserting a shadow mask to block off the particulates and rotating both target and substrate in order to produce a larger uniform film, have been developed to minimize some of the PLD problems.

Historical development of the pulsed laser deposition

Albert Einstein postulated the stimulated emission process in as early as 1916. The first optical maser using a rod of ruby as the lasing medium was, however, constructed in 1960 by Theodore H. Maiman at Hughes Research Laboratories, a lapse of 44 years. Using laser to ablate material has to be traced back to 1962 when Breech and Cross, used ruby laser to vaporize and excite atoms from a solid surface. Three years later, Smith and Turner used ruby laser to deposit thin films. This marked the very beginning of the development of the pulsed laser deposition technique.

The creation of the first technological installations for laser deposition and epitaxy should be attribute to the beginning of 80's, when there were the real preconditions for manufacturing and investigation of quantum structures on the basis of super thin films. There already existed rather powerful and productive infrared lasers on neodymium glass and JAG. Few research groups (mostly in former USSR) have achieved remarkable results on manufacturing of thin-film structures using laser technology. Among them the group of researchers of Institute of Applied Physics (Moldavian Academy of Sciences, Kishinev) with Prof. S. L. Pyskin in head, in which the author of this page began his research activity. Already in time we managed to receive thin epitaxial films of AIIIBV semiconductor materials on silicon (see the list of our Publications). The investigation of laser deposition process, including methods of spectroscopy with temporary and spatial resolution was simultaneously conducted. We have called our method - Laser Vacuum Epitaxy by analogy with MBE. Laser - was a source of evaporation, Vacuum - the process occurs in Ultra High Vacuum, and Epitaxy - as the monocrystaline structures were manufactured.

Rapid development of laser technology, however, enhanced the competitiveness of PLD in following decade. The lasers having a higher repetition rate than the early ruby lasers made the thin film growth possible. Subsequently, reliable electronic Q-switches laser became available for generation of very short optical pulses. For this reason PLD can be used to achieve congruent evaporation of the target and to deposit stoichiometric thin films. The absorption depth is shallower for UV radiation. Subsequent development led to laser with high efficient harmonic generator and excimer lasers delivering UV radiation. From then on, non-thermal laser ablation of the target material became highly efficient.

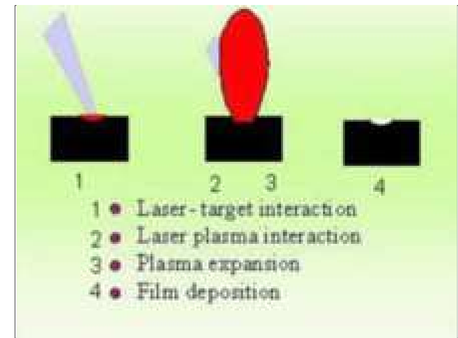
Pulsed laser deposition as a film growth technique has attained its reputed fame and has attracted wide spread interest after it has been used successfully to grow high-temperature Tc superconducting films in 1987. During the late decade, pulsed laser deposition has been employed to fabricate crystalline thin films with epitaxy quality. Ceramic oxide, nitride films, metallic multilayers, and various superlattices grown by PLD have been demonstrated. Recently, using PLD to synthesis buckminster fullerness and nanopowers have also been reported. Production-related issues concerning reproducibility, large-area scale-up and multiple-level have begun to be addressed. It may start up another era of thin film fabrication in industry.

Mechanisms of pulsed laser deposition

The principle of pulsed laser deposition, in contrast to the simplicity of the system set-up, is a very complex physical phenomenon. It does not only involve the physical process of the laser-material interaction of the impact of high-power pulsed radiation on solid target, but also the formation plasma plume with high energetic species and even the transfer of the ablated material through the plasma plume onto the heated substrate surface. Thus the thin film formation process in PLD generally can be divided into the following four stages.

1. Laser radiation interaction with the target

2. Dynamic of the ablation materials
3. Deposition of the ablation materials with the substrate
4. Nucleation and growth of a thin film on the substrate surface

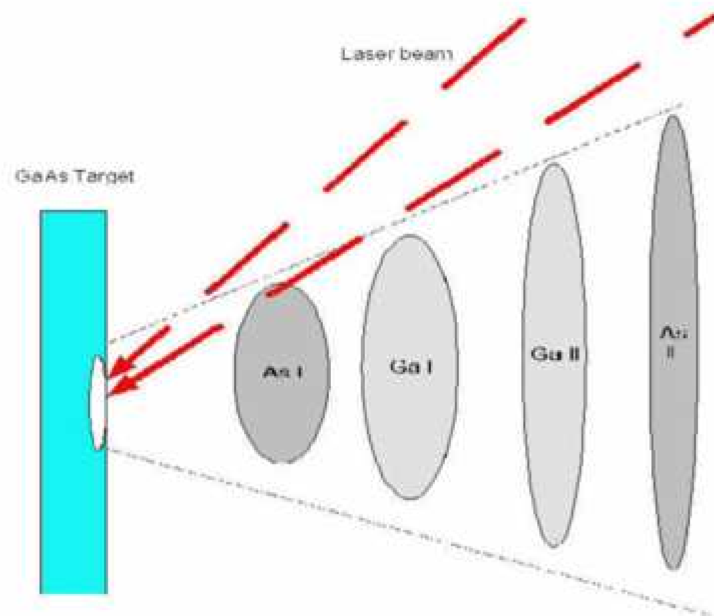


Each stage in PLD is critical to the formation of quality epitaxial crystalline, stoichiometric, uniform and small surface roughness thin film.

In the first stage, the laser beam is focused onto the surface of the target. At sufficiently high flux densities and short pulse duration, all elements in the target are rapidly heated up to their evaporation temperature. Materials are dissociated from the target surface and ablated out with stoichiometry as in the target. The instantaneous ablation rate is highly dependent on the fluences of the laser shining on the target. The ablation mechanisms involve many complex physical phenomena such as collisional, thermal, and electronic excitation, exfoliation and hydrodynamics.

During the second stage the emitted materials tend to move towards the substrate according to the laws of gas-dynamic and show the forward peaking phenomenon. R. K. Singh reported that the spatial thickness varied as a function of cos q. The spot size of the laser and the plasma temperature have significant effects on the deposited film uniformity. The target-to-substrate distance is another parameter that governs the angular spread of the ablated materials. Hanabusa also found that a mask placed close to the substrate could reduce the spreading.

The third stage is important to determine the quality of thin film. The ejected high-energy species impinge onto the substrate surface and may induce various type of damage to the substrate. The mechanism of the interaction is illustrated in the following figure. These energetic species sputter some of the surface atoms and a collision region is formed between the incident flow and the sputtered atoms. Film grows after a thermalized region is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the rate of particles supplied by the sputtering, thermal equilibrium condition can be reached quickly and film grows on the substrate surface at the expenses of the direct flow of the ablation particles and the thermal equilibrium obtained.



Nucleation-and-growth of crystalline films depends on many factors such as the density, energy, ionization degree, and the type of the condensing material, as well as the temperature and the physico-chemical properties of the substrate. The two main thermodynamic parameters for the growth mechanism are the substrate temperature T and the supersaturation Dm. They can be related by the following equation

$$Dm = kT \ln(R/R_e)$$

where k is the Boltzmann constant, R is the actual deposition rate, and R_e is the equilibrium value at the temperature T.

The nucleation process depends on the interfacial energies between the three phases present - substrate, the condensing material and the vapor. The minimum-energy shape of a nucleus is like a cap. The critical size of the nucleus depending on the driving force, i.e. the deposition rate and the substrate temperature. For the large nuclei, a characteristic of small supersaturation, they create isolate patches (islands) of the film on the substrate which subsequently grow and coalesce together. As the supersaturation increases, the critical nucleus shrinks until its height reaches on atomic diameter and its shape is that of a two-dimensional layer. For large supersaturation, the layer-by-layer nucleation will happen for incompletely wetted foreign substrates.

The crystalline film growth depends on the surface mobility of the adatom (vapour atoms). Normally, the adatom will diffuse through several atomic distances before sticking to a stable position within the newly formed film. The surface temperature of the substrate determines the adatom's surface diffusion ability. High temperature favours rapid and defect free crystal growth, whereas low temperature or large supersaturation crystal growth may be overwhelmed by energetic particle impingement, resulting in disordered or even amorphous structures.

Metev and Veiko suggested that the N_{99}, the mean thickness at which the growing, thin and discontinuous film reaches continuity is given by the formula

$$N_{99} = A(1/R)^{1/3} \exp(-1/T),$$

where R is the deposition rate (supersaturation related) and T is the temperature of the substrate and A is a constant related to the materials.

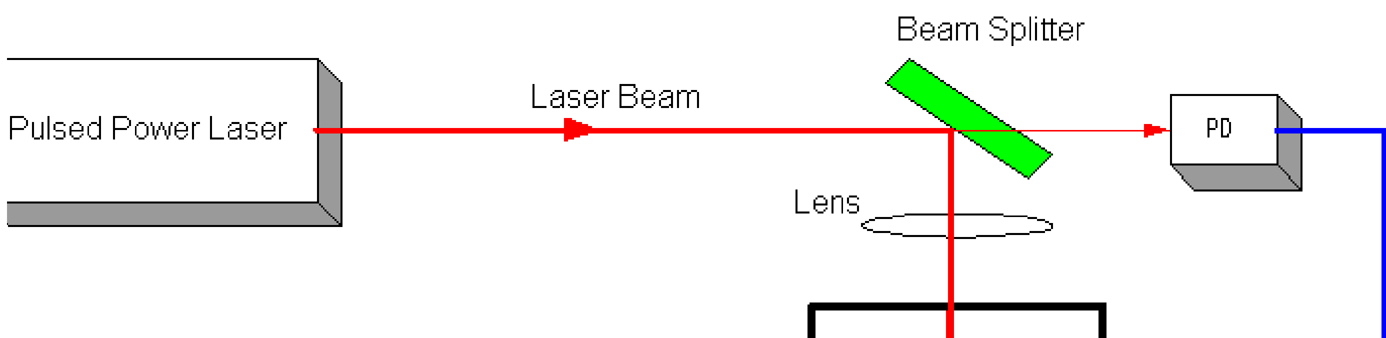
In the PLD process, due to the short laser pulsed duration (~10 ns) and hence the small temporal spread (<=10 ms) of the ablated materials, the deposition rate can be enormous (~10 mm/s). Consequently a layer-by-layer nucleation is favoured and ultra-thin and smooth film can be produced. In addition the rapid deposition of the energetic ablation species helps to raise the substrate surface temperature. In this respect PLD tends to demand a lower substrate temperature for crystalline film growth.

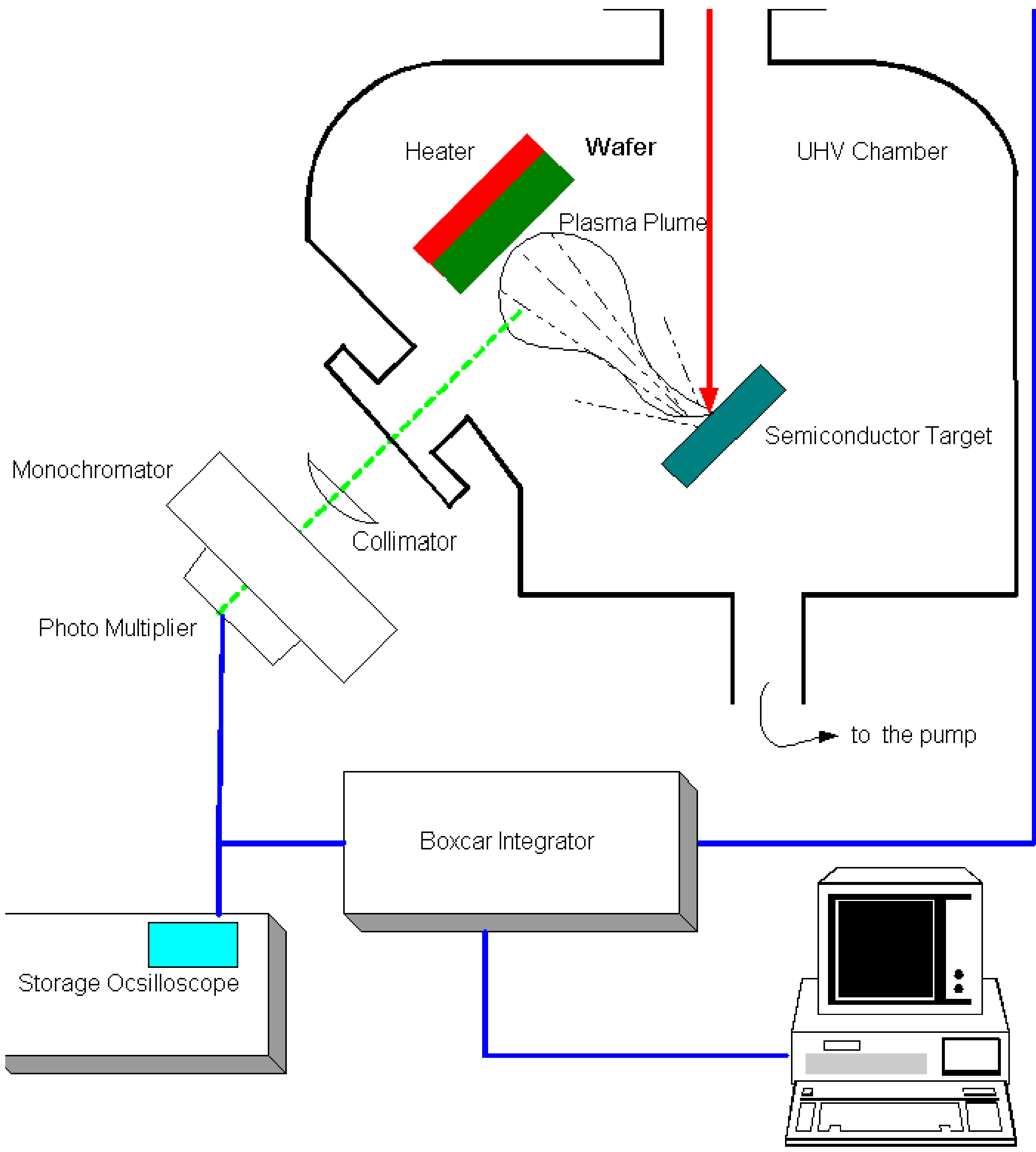
Spectroscopic Investigation of Semiconductor Target Evaporation by Laser Irradiation

Target -GaAs, $q = 10^9$ W/cm^2, distance $d = 5$ mm

Material	Spectral lines (nm)	Time delay (μs)	Clusters velocity (cm/s)
Ga I	403.29 417.21	0.8	1.1×10^6
As I	540.81	0.95	1.0×10^6
Ga II	626.17	0.57	1.3×10^6
As II	617.05	0.40	1.4×10^6

Experimental Setup Block Diagram

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Wafer
UHV Chamber
Plasma Plume
Semiconductor Target
Monochromator
Collimator
Photo Multiplier
to the pump
Boxcar Integrator
Storage Ocsilloscope

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