

# **Fundamentals of Pulsed Laser Deposition**

## **First age (1975-1995)**

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The method of dielectric and semiconductor thin films deposition by evaporation of initial targets using laser radiation has started to develop right after powerful lasers creation. Progress in laser technology, understanding of processes of laser radiation interaction with substance, and condensation of the formed plasma plume, have created a basis for the further development of pulsed laser deposition (PLD). It is necessary to list the following PLD advantages:

1. Removal of the evaporator (laser) from processing chamber will reduce a danger of pollution of growing layer because of evaporating elements;
2. The high power density of laser radiation on the target surface will allow the evaporation and deposition of any possible materials;
3. The short pulse duration (usually less than 10 ns) will allow the creation of the stoichiometric condensate close by a substrate;
4. High energy of laser plasma plume will make possible the reduction of epitaxial growth temperature and then will allow the formation of very sophisticated hetero-structures.

These advantages may expand considerably a number of materials and their combinations (in particular, hetero-structures) that could be manufactured using PLD in comparison with others modern epitaxial techniques.

Pulse solid-state lasers based on Nd-glass or JAG ( $\lambda = 1.06 \mu\text{m}$ ), operating in free generation mode ( $\tau = 1 \text{ ms}$ ), and in Q-switching mode ( $\tau = 10 \text{ ns}$ ) were mostly used as the main component of PLD technique. According to existing that time understanding of laser radiation interaction with metals and semiconductors with  $E_g < h\nu$  (where  $\nu$  - is a laser radiation frequency in Hz) , the processes occurring on a surface of a material under the influence of a laser millisecond pulse, essentially differ from the processes caused by the pulse with duration of an order 10 ns and less.

At low intensity of laser radiation the quantity of the evaporated substance mostly depends on the material heat conductivity, than from its latent evaporation warmth. When the radiation power density  $q$  is increased up to critical value  $q_c$  the heat is allocated so quickly that it has no time to be taken away any more because of heat conductivity. The latent evaporation warmth becomes the dominating mechanism.

For millisecond laser pulse duration the typical values of  $q_c = 10^6 - 10^7$  W/cm<sup>2</sup>. Evaporation in this mode can be considered as an event occurring at normal temperature of boiling with the constant tap of the evaporated substance from a surface. In the laser plume produced by such long pulse, the liquid phase (drops) and products of target destruction (splinters) are presented. Typical values of the substance mass which have been taken away from a laser spot in this mode (at  $E = 10$  J) could reach several mg. The resulting crater on the target surface could have a depth from one to several mm.

This behaviour, of course, influences the quality of produced layers and consequently it is no wonder, that the free generation mode practically at once has been rejected by researchers of PLD.

For the laser operating in Q-switching mode it's easy to make the power density on a target of about  $10^9$  W/cm<sup>2</sup>. In this case we have evaporation model at which dynamics of all processes are defined by absorption of laser radiation by resulting plasma plume. Increase of plume temperature leads to that the radiant heat conductivity starts to play an essential role along with the electronic heat conductivity. Therefore the depth of a layer heated by the laser pulse under the target surface could exceed the depth of penetration of laser radiation. In this layer during very short time ions receive a considerable energy that is much more than evaporation warmth of a material. Then this overheated layer operates as explosive. The shock wave with considerable energy penetrates the target that leads to the substance evaporation in the returning wave.

For semiconductors with  $E_g < h\nu$ , obviously, some other mechanism of destruction could realized. As in this case the radiation absorption coefficient is much less than for metals, the initial stage could be photo-desorption in thin (an order of several mono-layers) layer of a target substance. Then there is an intensive multi-photon ionization and a warming up of the formed laser plume which finally

lead to explosion over a surface and to evaporation of its substance in the returning wave. Overheated layer on a target surface in this case is not formed. The main part of target mass is taken away in the returning wave and makes in a nanosecond mode ( $E = 1 \text{ J}$ )  $10^{-5} - 10^{-6} \text{ g}$ . Drops are practically absent in a scattering laser plume.

The structure, composition, and parameters of plasma plume particles scattering in vacuum, represent the big interest as they basically define epitaxial process. The analysis of electrical probe measurements has shown that power distribution of ions essentially depends on laser radiation power density and not on target material. The great part of ions possesses energy in the range 50 -1000 eV. The power spectrum of neutral particles was defined by registration of atoms emission, by resonant absorption, and by others methods. According to data received during our experiments in spectral diagnostics of laser plume with high time resolution, it may conclude that the difference in scattering speeds of ions and neutral particles was insignificant. Hence, the real power spectrum of particles that composed the laser plume has less wide strip with the maximum around 100 eV.

The processes arising at the interaction of products of laser erosion with a substrate surface have a great interest. It was shown, that under action of high energy ions ( $E > 10 \text{ eV}$ ), there was a sputtering of a substrate surface. The thickness of a layer sputtered by single pulse for various materials was experimentally measured, and the dispersion maximum corresponds to the ratio of the bombarding and bombarded particles masses, close to unit. Depending on parameters of incident and sputtered streams their interaction will vary.

According to experimental PLD data, the following mechanism of epitaxial film formation was suggested. First, high energy ions arrive on a substrate and sputter a part of superficial atoms. As a result of interaction of the incident stream with the atoms which have been sputtered out from a surface, the impact area with the raised temperature and high particles concentration can be formed. This area will block for a while the direct penetration of an incident stream on a substrate.

In this case the film growth begins after formation of the thermalized region which will be a source of condensed particles. Condensation rate will increase with time and since the moment, when it will exceed the rate of incident stream the thermalized region will start to break up. After its definitive decomposition the film growth occurs from the direct stream only in which the particles energy

decreases by approximately to 10 eV. In the case of less dense or shorter incident plasma streams the thermalized region probably is not formed. Processes of condensation and defect formation in the growing film will run in parallel until the particles energy does not become less than the defect formation threshold. Thus, in the case of thermalized region formation over substrate surface the film growth occurs from particles with smaller energy and corresponds to more equilibrium conditions.

The explanation of epitaxy mechanisms in PLD is a most important and difficult problem. It is known, that the most perfect epitaxial films turn out at the step-layer mode of growth. Realization of three-dimensional and island-based mechanisms of growth in PLD can sharply worsen its advantages in comparison with other epitaxial methods. The possible reasons leading to the transition from step-layer mechanism to growth from the separate centers could be: residual pollution of substrate surfaces, mobility restriction of ad-atoms on a surface, influence of lattices parameters mismatch at hetero-epitaxy.

The behavior of doping impurity during PLD of semiconductors is also unclear. Firstly, many widely used in crystal growth impurities have the sticking factor close to zero at substrate temperatures used in PLD. As an example it can be chosen Zn at doping of gallium arsenide. Secondly, the impurity can segregate on a surface and, in the presence of strong chemical interaction with growing film components, to form chemical compounds. Such behavior could be observed for tellurium which can form on a surface the compound GaTe. Thirdly, there are kinetic restrictions on possible embedding of impurity atoms into a growing film. The given phenomenon takes place for most doping impurities used in PLD. For example, in gallium arsenide epitaxy such behavior is typical for tin on a growth surface. Both effects, impurity segregation on surfaces and kinetic restrictions on impurity embedding will complicate realization of PLD advantages, such as creation of sharp profiles of impurity distribution or super lattices formation.

One of the effects leading to conductivity compensation of the doping impurity during PLD is an effect of radiating defects generation where the basic carriers will be localized. It was shown, that the bombardment of gallium arsenide epitaxial layers by an intensive stream of low energy particles, produced by laser material ablation of As, C, Si, and Te, leads to conductivity indemnification at the depth of about  $10^{-5}$  cm. This is almost two orders of magnitude more than the

thickness of a layer in which the generation of primary radiating defects (vacancies) occurred because of particles having energy around 10 eV and incident from plasma plume. The increase in temperature of substrate will accelerates the indemnification, and apparently, the effect is based on diffusion of mobile defects from a narrow zone of generation deep into the semiconductor.

The PLD possibility for different semiconductor materials was confirmed by numerous research works.