U.P.B. Sci. Bull., Series A, Vol. 79, Iss. 2, 2017 ISSN 1223-7027

STUDY OF THE PULSED LASER DEPOSITION PHENOMENA BY MEANS OF COMSOL MULTIPHYSICS

Alexandru COCEAN[1], Iuliana COCEAN[1], Silviu GURLUI[1],
and Felicia IACOMI[1]

In this paper, thin films behavior obtained by Pulsed Laser Deposition (PLD) have been analyzed by means COMSOL Multiphysics, taking into account various experimental parameters: laser fluence, laser pulse width, laser wavelength, the temperature achieved during ablation, the target material type, the temperature of the support, the distance between target and support, etc. The obtained results are in very good agreement with the experimental. Moreover, the current model may be easily furthermore applied to any other film deposition technique by changing parameters values as needed in the experiments

Keywords: laser ablation, PLD, COMSOL

1. Introduction

Film pulsed laser deposition, when different laser parameters are varied, results in a thickness according to the given deposition conditions. (Pulsed laser deposition when different laser parameters are varied leads to a thickness of the film according to the given deposition conditions). [1-4]. When a certain layer thickness is required, many tests should be conducted before achieving it. In order to reduce the number of tests, a deposition simulation could offer an estimation regarding dependence between laser parameters – such as energy, pulse width, wavelength, distance between target and support, target material and film thickness deposited after a number of shots. Estimating the parameters that could lead to the purposed results is the aim of our work presented herein. A simulation based on the finite element analysis is purposed and conducted in COMSOL Multiphysics software, based on the analysis of Physical phenomena and processes. This is a complementary method that reduces the number of experiments estimating parameters and work conditions. The simulation is used also to estimate values that cannot be experimentally determined, this being the case with temperatures achieved in laser ablation.

At the COMSOL Conference from 2007, E. Rogers and E. Gutierrez-Miravete presented in their paper an analysis of the laser heat treatment process of steel using analytical methods, a finite difference numerical method and the finite

---

[1] Alexandru Ioan Cuza" University of Iasi, Faculty of Physics, 11 Carol I Bld. 700506 Iasi, Romania

element method in COMSOL, but only for two-dimensional models [16]. However, the authors do not provide any specific information about the work and results in COMSOL, referring only to the new software as to a perspective for creating new models. In 2010, G. Poulain et al. present in their paper [11] the simulation of laser heating for silicon solar cells using heat transfer in solids in a two dimensional model. The same, M. Rühl et al. use a two dimensional model for heat and mass transfer simulation in COMSOL [12]. The two dimensional model for heat transfer in solids was considered by the authors as being sufficient for the symmetrical geometries. Yet, a two dimensional model is not satisfactorily for the laser heating, heat transfer and film deposition simulation. All these processes involved in a pulsed laser deposition are in volume and either they are applied to a symmetrical body or to an asymmetrical one, the heat transfer, the free molecular flow and the film deposition must be simulated in a three dimensional model.

Furthermore, the other important issue that needs to be addressed in a pulsed laser deposition analysis with finite element is coupling the heat transfer in solids and free molecular flow modes.

The main achievement of this paper is the setup of a general three dimensional model for pulsed laser deposition simulation in COMSOL, using two coupled modules, “Heat Transfer in Solids” and “Free Molecular Flow”. Once the three dimensional model in COMSOL for laser pulsed deposition was setup, it makes it usable as a template for any particular study for various pulsed laser irradiation parameters, materials and other specific conditions by only changing parameters and selecting different materials from COMSOL library.

Direct experimental measurements of temperature are not known yet during pulsed laser irradiation because of the very short heating time (nanoseconds order). In order to validate the model in COMSOL we choose to compare the results from the simulation with experimental data from different papers that offer information about plasma generation under the same laser irradiation conditions (energy, pulse width, frequency), heating depth of the material, deposited film thickness. As the temperature during pulsed laser irradiation is a parameter that cannot be measured, a model that allows its estimation is very important, enabling us to predict ablation and even chemical reactions based on levels of temperature achieved.

The numerical model that we added in COMSOL is based on the M. Stafe’s et al. papers regarding theoretical and experimental work on pulsed laser ablation [1,5]. S. Gurlui et al. and G. Dascalu et al. contributions to plasma of ablation study [2,6,7] are the papers that provided the experimental information used as parameters and to compare the results of the simulation presented herein. The influence of various parameters such as laser fluence/energy, laser pulse width, laser wavelength, the temperature of the support and the distance between target and support as parameters for the simulation based on those reported in the cited papers can be varied using the parametric sweep option. For the simulation presented within this paper, a variation of the energy was used, but a parametric sweep can be added for any of the other parameters. Regarding material type, it can be changed in the same model by selecting a new one from the Material Library of COMSOL. The temperature achieved in the simulation is compared with the experimental information related to the plasma generation.

The silver target was virtually irradiated with a pulsed laser and the film deposition is simulated as a free molecular flow. The free molecular flow was used because the laser irradiation conducts to temperatures as high as for material ablation when plasma or vapors are formed. Shortly after that, plasma is transformed into gas phase and deposits on the support. [5–10]. The results are presented as graphics and tables.

The variables observed in the herein study refer to the temperature achieved during laser irradiation, its evolution in time and distribution on surface and in target depth for the pulsed laser irradiation simulation and the thickness of the film deposited in time on the support.

2. Theoretical approach: COMSOL Multiphysics

The simulation presented herein is based on two models. The first model uses Heat Transfer in Solids mode and the aim is to determine the temperature during pulsed laser irradiation of a silver target and takes into account laser parameters (energy, pulse width, spot size), and material parameters that are specific for heat transfer calculation, as per COMSOL library. The second model corresponds to the film deposition on a support based on the vapors pressure, average temperatures achieved on the target, the distance between the target and the support, the number of pulses and material constants and parameters (silver density and molecular mass). For this second model, the Free Molecular Flow mode was used in COMSOL. The two models represent together the virtual pulsed laser deposition. The support material is not taken into account in the second model, but it is supposed to be made of silica glass or silicon that does not react with the silver nanoparticles that will deposit on it.

2.1 Model for Pulsed Laser Irradiation Heating

The model consists of a cylinder as target with 26 mm diameter and 13 mm height and silver is added as material from the COMSOL database that includes material thermal dependent specific constants and parameters. COMSOL provides thermal dependent functions for each of the parameters and constants, e.g. density, thermal conductivity, heat capacity at constant pressure, for each material, for different temperature ranges. However, the said functions are only for up to a maximum temperature, e.g. 1235 K for Silver, and for higher temperatures that are expected for the laser power amounts, an extrapolation based on “nearest function” was chosen in COMSOL. In other words, the software will use the parameters and material constants calculated based on the functions that are implemented in the program up to the temperature of 1235 K and will extrapolate using the nearest function for the temperatures exceeding 1235 K.

The mesh was set up as it follows: extremely fine in the spot - with a maximum element size of 0.508 mm and a minimum element size of 0.00508 mm, coarse for the remaining top surface - with maximum element size 3.81 mm and minimum element size 0.711 mm, and normal for the remaining geometry – with a maximum element size of 2.6 mm and a minimum element size of 0.468 mm.

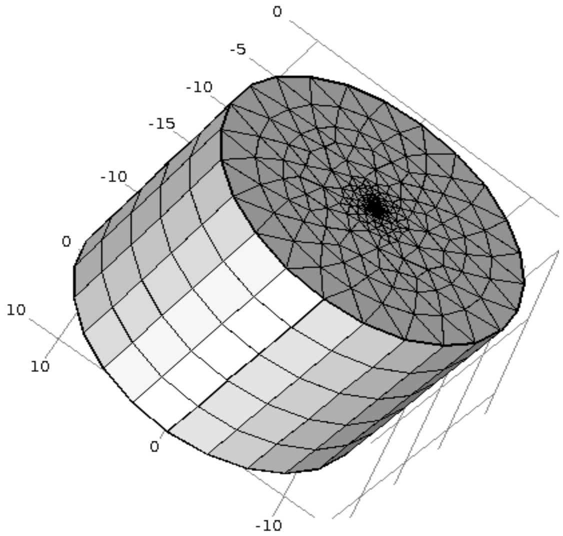


Fig. 1 Geometry and mesh of the irradiated target

The study selected is a time-depended one. Domain and border conditions are selected as per model requirements. The target is irradiated with a pulsed laser of 50 mJ, 100mJ and 150 mJ energy (using a parametric sweep), 10 ns pulse width, 532 nm wavelength, 10 Hz frequency and the spot of 100 μm diameter as per laser parameters usually achieved in LOASL Laboratory from Faculty of Physics/ “Alexandru Ioan Cuza” University of Iasi. [6]. The COMSOL module used for the laser irradiation is Heat Transfer in Solids. This module simulates only the material heating and the results offer information about temperature achieved, i.e. information if there are conditions for ablation.

The modeling for the pulsed laser ablation is based on the heat – transfer equation (1), assuming that laser irradiation is the material heating, melting and vaporization:

$$\rho(T)C_p(T)\frac{\delta T}{\delta t} = \Delta[k(T)\nabla T] + Q \qquad (1) \qquad [1], [11\text{-}12]$$

where:
ρ(T) = material density; C_p (T) = heat capacity
T = temperature (K); t =time; K = thermal conductivity
Q = heat source in volume due to absorbed laser power

The COMSOL module Heat Transfer in Solids has already implemented the heat – transfer equation (1), but the heat source Q must be defined. In our study, the heat source is the laser power that is absorbed and then transferred in all volume of the domain by conduction.

$$Q = \big(1 - R(T)\big)\alpha(T)P_{in}(x,y,t)I(z) \qquad (2) \qquad [1], [11]$$

where:
α(T) = absorption coefficient of the material
R(T) = reflectivity coefficient of the material
P_{in} = incident laser power, the laser power on the target surface
I(z) = relative intensity based on Beer – Lambert law:
$I(z) = exp(-\alpha(T)|z|)$ (3)

I(z) reflects laser intensity attenuation due to absorption coefficient α(T) along target thickness, i.e. z-coordinate.

The incident laser irradiation has a Gaussian distribution in time and space on the target surface, i.e. the spot shape.

$$P_{in}(x,y,t) = P_0 exp\left\{-3.5\cdot\left(\frac{t-\tau}{\tau}\right)^2\right\} exp\left\{-\frac{(x-x_0)^2}{2\cdot r^2} - \frac{(y-y_0)^2}{2\cdot r^2}\right\}$$

, for a circular spot shape (4a)

$$P_{in}(x,y,t) = P_0 exp\left\{-3.5\cdot\left(\frac{t-\tau}{\tau}\right)^2\right\} exp\left\{-\frac{(x-x_0)^2}{2\cdot \sigma_x^2} - \frac{(y-y_0)^2}{2\cdot \sigma_y^2}\right\}$$

, for an eliptical spot shape (4b)

For a general use of the model, we chose the formula (4b) that becomes (4a) when simply make $\sigma_x = \sigma_y$.

P_0 = peak power of the laser beam
t_0 = time shift
τ = pulse time width
r = beam radius at half height (FWHM - full width at half maximum)
σ_x and σ_y = pulse x and y respectively standard deviation

The absorption and reflectivity coefficients are calculated based on the laser wavelength and refractive index [11]:

$$\alpha_{(T)} = \frac{4\pi {k_{(T)}}^2}{\lambda} \qquad (5)$$

$$R_{(T)} = \frac{\left(n_{(T)}-1\right)^2 + {k_{(T)}}^2}{\left(n_{(T)}+1\right)^2 + {k_{(T)}}^2} \qquad (6)$$

The effective beam area is $\pi r^2/2$, formula also used by ISO 21254 [11], [13].

The very high absorption coefficient in case of metals leads to a very low absorption depth. The depth absorption is given by δ [m] =1/α. [1] (7)

The thermal penetration depth is defined by the equation

$$\delta_{th} = \sqrt{\frac{k\cdot\tau}{\rho\cdot C_p}} \text{ [4]} \tag{8}$$

The ablated height is given by the relation h = max(δ, δ_{th}) [1] (9)

The boundary conditions are adiabatic (thermal insulation) for the bottom and side areas: $\acute{n}(k_{th}\nabla T) = 0$, where $\acute{n}$ is the vector normal to the surface and k_{th} is the thermal conductivity. The heat flux is considered normal to the top surface with boundary conditions including thermal radiation and heat transfer to the ambient room: $\acute{n}(k_{th}\nabla T) = Q_0 + h(T_{ext} - T)$, where h and T_{ext} are the heat transfer coefficient and the external temperature respectively. The formulae for heat flux are included in COMSOL software and only boundary conditions need to be selected for each area of the geometrical system.

In the heat – transfer equation (1), the temperature dependence of the material properties covers all the temperature range, hence all the phases, by extrapolating with “nearest function” based on the polynomial functions from COMSOL materials library. Latent heat is not considered in this model.

Although the influence of the ablation plasma on the ablation process was not separately treated in this model, it is considered in the heat - transfer equation (1). The simulation is a continuous heat exchange process that considers the temperature achieved on the target surface, including the temperature of the ablated plasma after 10 ns and the heat is transferred from the heated surface with temperatures as high as for plasma into the thickness of materials. After 0.1 s representing the pulse repetition time (the frequency is 10 Hz), the temperature mitigates back to the initial temperature of 293 K, and there is no thermal effect of the first pulse on the second pulse.

2.2 Film Deposition

The module in COMSOL used to simulate the film deposition is Free Molecular Flow. The high temperatures achieved during pulsed laser irradiation with the energies of 50 mJ, 100 mJ and 150 mJ, conduct to vaporization and plasma formation that transforms back into vapors before hitting the support, followed by solidification and deposition as a thin film [8]. The Free Molecular Flow mode is the best assumption because the simulation is based on a stochastic model and, for this particular case when the target is a monoatomic material, the ablated particles, i.e. ions, atoms, clusters have the same molar mass.

A geometry representing a cylinder is chosen with the base diameter of 26 mm in accordance with the target and support diameter and 15 mm height as distance between target and support. The materials added are silver for the upper surface (simulates the target) and silica glass for the support. The mesh is extremely fine for the deposition surface and coarse for the remaining geometry.

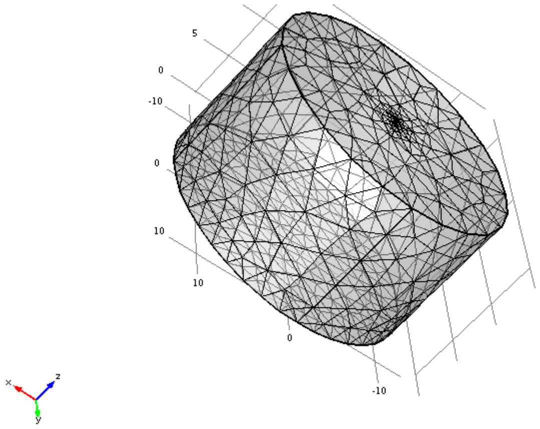


Fig. 2 Geometry and mesh for the deposition system

The temperature of the target is the average temperature achieved during pulsed laser irradiation and the temperature of the support is the room temperature (293.15 K). Other parameters used for this simulation are the silver molar mass of 0.108 kg/mol and silver density of 10490 kg/m^3.

The film thickness variation in time is given by the equation: $\frac{dh_{film}}{dt} = \frac{M_n G}{N_A \rho_{film}}$ (10) where: h_{film}, M_n, G, N_A, ρ_{film} are the film thickness, molecular weight, incident molecular flux, Avogadro number, Silver density. The incident molecular flux, G [1/m^2·s] is the incoming flux at the surface, defined as the number of molecules dN crossing a unit surface in one direction during a unit of time.[17, 18]

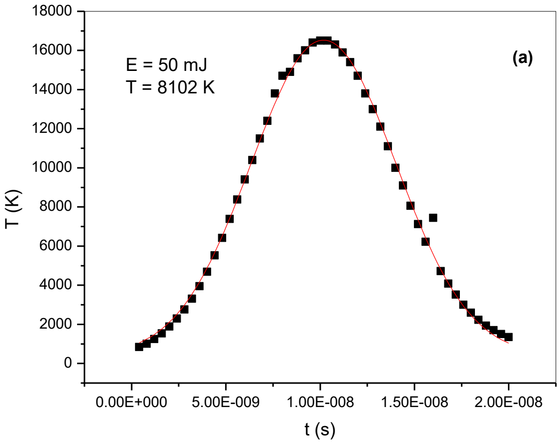
After integration of equation (10), a time linear dependence of film thickness is observed. The reservoir of particles that will deposit is the spot target where the temperature after laser irradiation enhances enough for silver vaporization. The spot target is of 100 μm diameter. The reservoir pressure considered is the pressure of silver vapor at vaporization temperature 100 kPa [12]. The incident molecular flux, number density and pressure are calculated based on the formulae already implemented by COMSOL software.

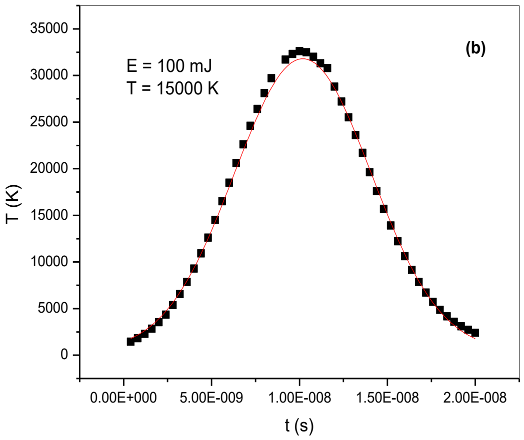
3. Results

3.1 Pulsed Laser Irradiation Heating Results

The temperatures of 10^{4}K order, achieved in this simulation, indicate condition of silver ablation in spot center (silver vaporization point being 2435 K). The literature indicates plasma formation at similar laser irradiation conditions [6] and temperatures resulted in the simulation are in accordance with expected plasma temperatures (10^4K order) [5]. The temperature variation in thickness shows that there are vaporization conditions on about 10μm in accordance with experimental data [5].

The time step to store solutions of pulse width divided by 25 (time step = τ/25, where τ is the pulse width) will provide 50 solutions for temperature during a time equal to 2τ (two times pulse width). The 50 solutions of temperatures are represented in a time-dependent graphic that results in a Gaussian like curve as in the Fig.3a-c





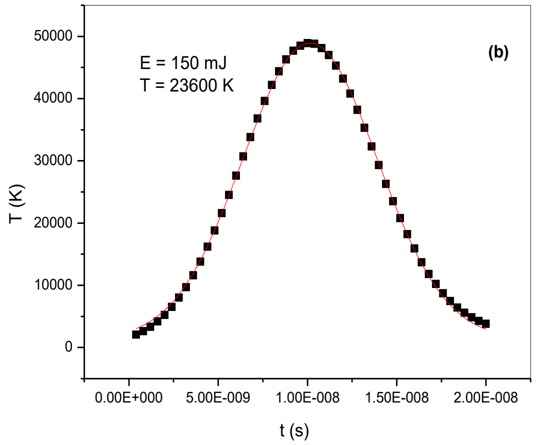


Fig.3 a-c – Temperature-time profiles at various laser energy. The mean obtained temperatures are the following: 8103 K (50 mJ), 15000 K (100 mJ) and 23600 K (150 mJ).

Average temperature calculation is based on the formula: $T_{AV} = \frac{1}{2\tau}\int_0^{2\tau} T(t)dt$, where τ is the pulse width, T is the temperature in Kelvin and t is the time. The integral represents the area under the Gaussian curve and it is listed in Table 1 for each of the laser energies.

3.2 Film Deposition Results

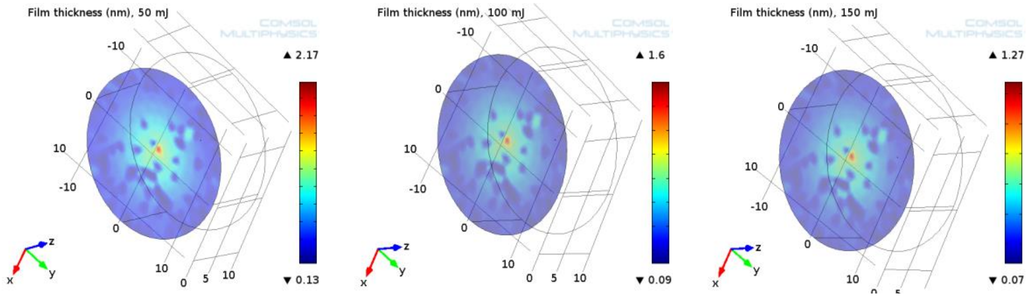
The simulation results are in accordance with the experimental film thickness in similar conditions. The results are listed in Table 1.

Table 1

Physical properties of PLD thin films

Energy (mJ)	Average Temperature (K)	Thickness of the deposited film (nm)
50 mJ	8102 K	2.17 nm
100 mJ	1.5E+4 K	1.60 nm
150 mJ	2.36E+4 K	1.27 nm

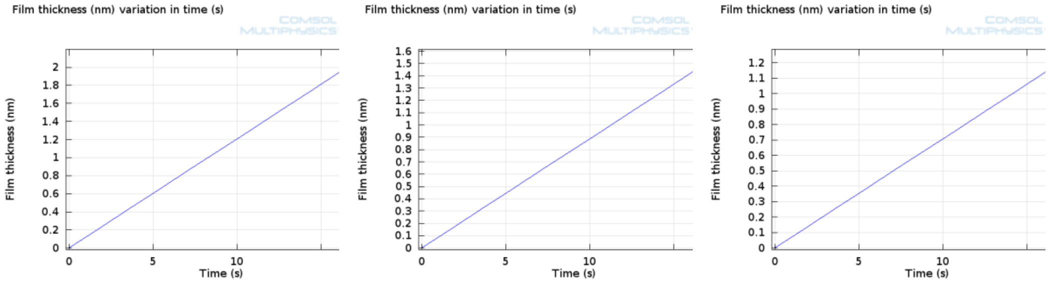
The thickness of the film deposited shows variation with the laser energy in a way that the film deposited is thinner when the energy is higher, in accordance with the literature [15]. A 3D plot (Fig. 4 a, b, c) shows the non-uniformity of the deposited material and the beginning film formation after 18000 pulses as reported in literature [3].



(a) Film thickness, E = 50 mJ (b) Film thickness, E = 100 mJ (c) Film thickness, E = 150 mJ

Fig.4 Film thickness deposited when different laser energies are used

The thickness variation of the deposited material in time is represented in Fig. 5 a, b, c and it is of a linear shape as expected based on equation (10).



(a) Film thickness variation in time, E = 50 mJ (b) Film thickness variation in time, E = 100 mJ ©Film thickness variation in time, E= 150 mJ

Fig. 5. Film thickness variation in time in the point of coordinates x = -0.5 mm, y= -0.05 mm, z= 0 mm

The 1D plots is a point graph, representing thickness of the deposition in a point of coordinates x = - 0.5 mm, y = - 0.005 mm, z = 0 mm and it represents the point with the highest deposition rate. The deposition is based on a stochastic model.

4. Conclusion

The irradiation model presented herein proves to be in accordance with the experimental data. The formula and conditions that we added to the existing COMSOL model conducted to an operational and reliable simulation that can offer reliable information about laser irradiation heating, temperature, plasma formation, evaporation and ablation conditions and film deposition. The pulsed laser ablation model and the deposition model can be improved adding and changing the already existing modeling that COMSOL provides. We are going to develop a more complex model using ablation rate, plasma temperature variation in time as well as other parameters and formula that will provide a better way to estimating the film deposition phenomena.

REFERENCES

[1]. *M. Stafe, C. Negutu, N. N. Puscas, I. M. Popescu*, Pulsed laser ablation of solids, Rom. Rep. Phys. 62(4) (2010) 758-770

[2]. *G. Dascalu, O. Pompilian, B. Chazallon, V. Nica, O. F. Caltun, S. Gurlui, C. Focsa*, Rare earth doped cobalt ferrite thin films deposited by PLD, Applied Physics A, 110 (4), pp.: 915-922 (2013)

[3]. *J. H. Bechtel*, Heating of solid targets with laser pulses, J. Appl.Phys. 46(4) (1975) 1585-1593.

[4]. *S.R. Franklin, R.K. Thareja*, Simplified model to account for dependence of ablation parameters on temperature and phase of the ablated material, Appl. Surf. Sci. 222(1-4) (2004) 293-306.

[5]. *M. Stafe, I. Vladoiu, C. Negutu, I.M. Popescu*, Experimental investigation of the nanosecond laser ablation rate of aluminum, Rom. Rep. Phys. 60(3) (2008) 789-796.

[6]. *S. Gurlui, M. Sanduloviciu, M. Strat, G. Strat, C. Mihesan, M. Ziskind, C. Focsa*, Dynamic space charge structures in high fluence laser ablation plumes, J. Optoelectron. Adv. M. 8(1) (2006) 148-151.

[7]. *S. Gurlui, M. Agop, P. Nica, M. Ziskind, C. Focsa*, Experimental and theoretical investigations of a laser produced aluminum plasma, Phys. Rev. E 78(2) (2008) 026405 part 2.

[8]. *Viorel Pop, Ionel Chicinaş, Nicolaie Jumate*, Fizica materialelor. Metode experimentale, (Physics of materials. Experimental methods), Presa Universitară Clujeană, 2001, ISBN 973-610-036-7 (in Romanian)

[9]. *M. Ohring* (2001). Materials Science of Thin Films (2nd ed.). Boston: Academic Press. ISBN 9780125249751.

[10]. *K. Seshan,* ed. (2012). Handbook of Thin Film Deposition (3rd ed.). Amsterdam: Elsevier. ISBN 978-1-4377-7873-1

[11]. *G. Poulain, D. Blanc, A. Kaminski, B. Semmache, M. Lemiti*, Modeling of Laser Processing for Advanced Silicon Solar Cells, COMSOL Conference 2010 Paris

[12]. *M. Rühl, G. Dietrich, E. Pflug, S. Brau and A. Leson* , Heat and Mass Transfer in Reactive Multilayer System (RMS), COMSOL Conference 2012 Milan

[13]. ISO 21254-2:2011, Lasers and laser-related equipment – Test methods for laser-induced damage threshold – Part 2: Threshold determination; ISO 21254-3:2011, Lasers and laser-related equipment – Test methods for laser-induced damage threshold – Part 3: Assurance of laser power (energy) handling cap abilities.

[14]. *Stull, D.,* in American Institute of Physics Handbook, Third Edition, Gray, D.E., Ed., McGraw Hill, New York, 1972.

[15]. *P. J. Beltramo, C. L. Bodarky, H. M. Ky*d, Design and Control Using Stochastic Models of Deposition Reactors, Senior Design Reports (CBE), University of Pennsylvania Scholarly Commons, Department of Chemical & Biomolecular Engineering (4-14-2009)

[16]. *E. Rogers, E. Gutierrez-Miravete*, An Analysis of the Thermal Effects of Focused Laser Beams on Steel, Proceedings of the COMSOL Conference 2007, Boston

[17]. *Dmitry Garanin*, Molecular theory of ideal gases, Statistical Thermodynamics, October 1, 2012

[18]. *Gerd M. Rosenblatt*, Effect of incident flux on surface concentrations and condensation coefficients when growth and vaporization involve mobile surface species, Published by the American Institute of Physics, doi: 10.1063/1.432010