SUMMARY OF THE PhD THESIS

Inverse pulsed laser deposition

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I. Introduction

The earliest success of *pulsed laser deposition* (*PLD*) dates back to the 1980's, when high critical temperature superconductors (e.g. yttrium barium copper oxide, YBCO) were deposited for the first time in thin film form using this technique. PLD employs high-energy laser pulses which are focused on the surface of a rotating target, and the transferred energy converts the topmost layer(s) of the irradiated target surface into plasma phase. In the common (*on-axis*) PLD arrangement, a substrate is placed parallel to the target, facing its ablated surface. During the expansion of the plasma plume, either in vacuum or a low-pressure gas atmosphere, the plasma species deposit on the surface of the substrate as a thin film. The plasma species may also interact with the background atmosphere, in this case the process is called reactive PLD.

The key element of the success of this method is that PLD films deposited in vacuum preserve the stoichiometry of the target material. Further advantages of this technique are its flexibility and versatility, the relatively inexpensive experimental apparatus and the decent running and maintenance costs. Another benefit worth mentioning is that several properties of the deposited films can easily and accurately be tuned via the process parameters.

By the turn of the millennium, these advantages made PLD a widely used laboratory technique, aiming especially the development of new materials. However, PLD could not yet emerge in industry, mostly due to the co-deposition of micrometer scaled solid and molten particles (called particulates) that locally degrade the properties of the PLD films. To overcome this drawback, several ideas were proposed: starting with as simple as using optimal laser parameters; filtering the particulates by mechanical shutters or electromagnetic fields; or the rearrangement of the target and the substrate positions. Unfortunately, these solutions were not satisfactory enough, or some of them decreased the deposition rate of the film itself drastically. Moreover, in most PLD arrangements, the inhomogeneous spatial material distribution within the plasma plume lead to unwanted effects, *e.g.* lateral variation in the thickness and the chemical composition of the films.

It is a well-known phenomenon that during PLD, material also deposits on surfaces facing the dominant direction of the plasma plume expansion (*e.g.* on the target surface). Despite being generally known, our research group was the first who deliberately used this process for growing thin film in a novel target-substrate arrangement. In this geometry, called *inverse pulsed laser deposition* (IPLD), the substrate lies in, or slightly above the plane of the target surface, and its normal points to the dominant direction of the plasma plume expansion. In the present dissertation this modified PLD arrangement is studied comprehensively.

II. Objectives

Preliminary results of our research group showed that the IPLD technique can represent an alternative to the traditional PLD technique by preserving its simplicity, flexibility, and versatility maintaining or even increasing the deposition rate of the film, while producing films of better surface morphology without expensive or complex instrumentation.

My main aim was to study how film growth proceeds in the IPLD arrangement. I grew films of different materials (*e.g.* metals, oxides, and non-metallic elements) in IPLD geometry. As a first step, I determined the lateral thickness distribution of IPLD films, the lateral variation of the deposition rate, and the pressure dependence of these features. Since the major goal of my project was to improve the surface characteristics of the grown films, morphological studies played a vital part of my research.

In the inverse geometry, the substrate is placed in the target plane, so the rotational mechanism of the target can also be used to rotate the substrate, and therefore to homogenize the properties of the growing films. This promising idea motivated me to develop and investigate an IPLD-configuration in which homogeneous thin films can be grown, while keeping the advantages of the original IPLD arrangement.

As a conclusion of my work, I propose a model for IPLD film growth based on the tendencies describing the lateral variation of the deposition rate and its pressure dependence.

III. Materials and methods

I deposited thin layers of carbon nitride, amorphous carbon, titanium, and titanium oxide on silicon substrates by IPLD in 0.5–50 Pa gas atmospheres. I developed and used a target-multisubstrate holder which allowed the simultaneous growth of PLD, as well as static and co-rotating IPLD films. In the *static IPLD configuration*, the substrate is stationary with respect to the ablated spot; while in the *co-rotating IPLD* configuration the substrate is fixed to the target surface and rotates simultaneously with the target. The target was ablated by 248-nm KrF excimer laser pulses of 7–10 Jcm^{-2} fluences (*Lambda Physik EMG 150 TMSC*), with typical pulse length of ~22 ns.

Film thickness measurements were carried out by profilometry (*DEKTAK 8*) using step edges created between the film surface and the substrate by masking. The deposition rate of the films was derived by dividing the thickness values with the number of laser pulses used for the deposition.

The morphology of the deposited thin films was investigated by optical microscopy (*Nikon Labophot-2*), atomic force microscopy (*PSIA XE-100*), and

scanning electron microscopy (*Hitachi S4700*). Optical and AFM micrographs allowed me to determine the number density and size distribution of particulates in the 10 nm–100 μm size domain. I studied the nanostructure of the films by high-resolution AFM and scanning electron microscopy. SEM images were also used for fractal analysis. The homogeneity of the chemical composition of the deposited CN_x thin films was deduced by measuring the refractive index and the porosity of the layers by variable angle spectroscopic ellipsometry (*WOOLLAM M-2000F*).

IV. New scientific results

1.a I demonstrated that metal, metal oxide, and non-metallic thin films can be grown by inverse pulsed laser deposition (IPLD) in vacuum, as well as in inert or reactive gas atmosphere. [T1, T2]

1.b I showed via profilometric thickness measurements that the deposition rate of IPLD films grown on substrates fixed in the target plane and stationary with respect to the ablation spot (*i.e.* in the static IPLD configuration), decreases with increasing lateral distances from the laser spot. Through the example of Ti and amorphous carbon layers, I demonstrated that along the symmetry axes of the elliptic laser spot, the deposition rate of static IPLD films grown by non-reactive processes decreases in an exponential fashion within the 3.5–60 mm range, as measured from the centre of the laser spot. My investigations on CN_x and TiO_x static IPLD films revealed that the above mentioned exponential tendency remains unaffected when the interaction between the plasma species and the gas molecules is of mostly physical in nature (like in the case of CN_x). However, the exponential dependence is distorted if plasma species interact chemically with the gaseous environment (like TiO_x). [T1, T2]

1.c I showed that the deposition rate of metal (Ti), metal oxide (TiO_x) and non-metallic (amorphous carbon and CN_x) static IPLD films, grown in the 0.5–50 Pa pressure domain, varies in the 0.001–0.1 nm/pulse range at lateral distances between 3.5 mm and 60 mm with respect to the centre of the laser spot. Contrary to the decreasing trend of PLD, the average deposition rate of static IPLD films, referring to this 3.5–60 mm axial region, proved to increase with increasing ambient pressure. Moreover, it was demonstrated that the yield of the IPLD films grown at pressures of a few tens of Pa exceeds that of the simultaneously deposited PLD films. [T1, T2]

2.a I developed a modified IPLD geometry, called co-rotating IPLD configuration, in which the substrate is fixed onto the surface of the rotating target. It was proven that the co-rotating IPLD configuration is capable of homogenizing the film thickness. At 5 Pa background pressure, I deposited CN_x and Ti thin films on 10-mm diameter substrates with a relative thickness variation of 3.5% and 16%, respectively. In an

oxygen atmosphere of 5 Pa pressure, TiO_x layer with a lateral thickness variation of less than 10% was grown on a 25-mm diameter substrate. [T2, T3, T4]

2.b I revealed by ellipsometry that the lateral variation of the refractive index and porosity of 10-mm diameter co-rotating CN_x IPLD-films (grown at 5 Pa) is 1% and 16%, respectively. Thereby I showed that the co-rotating IPLD configuration may also be used to homogenize other physical and chemical properties of the layers, for example their chemical composition. [T3]

2.c Using the variation of deposition rate along the symmetry axes of static IPLD films as input, I derived numerically the radial variation of deposition rate on simultaneously grown co-rotating IPLD films. My model predicted the average film thickness of co-rotating CN_x IPLD layers grown at 5 Pa with 20% accuracy, while the absolute error between the measured and calculated lateral thickness variation was less than 3%. [T3]

3.a On the basis of optical and atomic force microscopic investigations, I demonstrated that smaller and fewer particulates can be found on IPLD grown CN_x and TiO_x films than on PLD ones grown under identical conditions. I also proved that the surface roughness of IPLD films is always lower than that of the corresponding PLD ones. [T5]

3.b I showed that when using 248-nm laser pulses of 7–10 Jcm^{-2} fluences, CN_x and TiO_x IPLD films of optimum surface morphology can be grown with reasonable deposition rates at 5–10 Pa nitrogen, and 5–20 Pa oxygen pressures, respectively. [T2, T5]

3.c By high-resolution atomic force microscopy I showed that the nanostructure of the particulate free regions of CN_x and TiO_x IPLD and PLD films, grown under identical conditions, is very similar. CN_x IPLD films grown in a nitrogen atmosphere of 5 Pa were found to build up of flat, elliptic grains having main dimensions of approx. 75 nm×150 nm×15 nm, while TiO_x IPLD films deposited in 10 Pa oxygen atmosphere, consisted of approx. 40-nm diameter nanograins, aggregated into a cauliflower-like structure. Evaluation of the SEM micrographs revealed that TiO_x IPLD films exhibited a fractal structure. [T5]

4.a I devised an empirical model describing the growth mechanism of IPLD films. My observations support that at least two processes play competitive roles in the inverse thin film growth. The first process dominates at lower pressures, when plasma species are mainly scattered in the KNUDSEN layer and land on the substrate surface after a few collisions. Therefore, the thickness distribution of the growing film reflects the symmetry of the plasma plume. The second process, which prevails at higher pressures, mostly involves plasma species scattered on the ambient gas atmosphere,

and due to the large number of collisions, thin films of circular symmetry is resulted even if the plasma species originate from an asymmetric plume. [T1, T6]

4.b Model calculations showed that the lateral and pressure dependence of the deposition rate, $z(r,p)$ of static CN_x IPLD films can be described as follows:

$$z(r,p) = \frac{z_o}{\left(\ell_{ref}^2 \cdot \left(\frac{p_{ref}}{p} \right)^{2/3} + r^2 \right)^{3/2}},$$

where z_o is a normalization factor, r is the radial distance from the laser spot, p is the background pressure, and $\ell_{ref} = 3{,}92$ cm and $p_{ref} = 1$ Pa are constants. [T7]

V. Publications

Publications in peer reviewed journals and a patent related to the thesis:

[T1] L. Égerházi, Zs. Geretovszky, and T. Szörényi:
Thickness distribution of carbon nitride films grown by inverse pulsed laser deposition,
Applied Surface Science, **247**, 182-187 (2005)

[T2] L. Égerházi, Zs. Geretovszky, and T. Szörényi :
Inverse pulsed laser deposition,
Applied Physics A – Materials Science and Processing, **93(3)**, 789–793 (2008)

[T3] L. Égerházi and Zs. Geretovszky:
Carbon nitride films of uniform thickness by inverse PLD,
Applied Surface Science, **253**, 8197-8200 (2007)

[T4] Zs. Geretovszky, T. Szörényi, and L. Égerházi:
Method and target-carrier arrangement for building uniform thickness homogenous coating made of plasma that produced by pulsed laser, as well as the coating,
Patent Application,
Patent numbers: WO2007036753-A1; HU200500911-A1

[T5] L. Égerházi, Zs. Geretovszky, T. Csákó, and T. Szörényi:
Atomic force microscopic characterization of films grown by inverse pulsed laser deposition,
Applied Surface Science, **253**, 173-176 (2006)

[T6] L. Égerházi, Zs. Geretovszky, and T. Szörényi:
On the orientation independence of inverse pulsed laser deposition,
Applied Surface Science, **252**, 4656-4660 (2006)

[T7] A. A. Morozov, Zs. Geretovszky, L. Égerházi, and T. Szörényi:
A point source analytical model of inverse pulsed laser deposition,
Applied Physics A – Materials Science and Processing, **93(3)**, 691–696 (2008)

Other publications in peer-reviewed journals:

[1] P. Petrik, T. Lohner, L. Égerházi, and Zs. Geretovszky:
Optical models for the ellipsometric characterization of carbon nitride layers prepared by pulsed laser deposition,
Applied Surface Science, **253**, 173-176 (2006)

[2] A. Buzás, L. Égerházi, Zs. Geretovszky:
High repetition rate PLD grown titanium oxide thin films,
Journal of Physics D – Applied Physics, **41(8)**, 085205 (2008)