Thin film deposition in nitrogen and argon background gases by pulsed laser ablation of molybenum, tungsten, carbon and boron-carbid target materials

Summary of PhD theses

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Introduction and scientific background

Production, application and research of thin films date back a rather long time. Nowadays, thin films are widespreadly applied as functional coatings that advantageously influence the properties of the substrate device due to the films's certain surface characteristics. Number of thin film deposition techniques have been developed in the last century, parallely with the improvement of electronics, vacuum- and measurement-technologies. Meanwhile, in the mid 20^{th} century the discovery of lasers initiated an exponentially growing research activity focusing on laser evaporation and deposition of thin films. Recently, Pulsed Laser Deposition (PLD) technique become one of the most versatile and hence dominant method for lab-scale thin film preparation. Accordingly, using PLD numerous materials have already been deposited successfully supporting a largely diversified field of applications.

From the aspect of the present thesis, it is relevant to mention wear-resistant and hard-coatings, which are typically used in machine fabrication to increase the lifetime of CNC tools, for instance. For that purpose, both ceramics (e.g. SiC, SiN) and nitrides or carbides of refractory metals (e.g. TiN, TiC, WN) are widely used. Two of such materials (MoN_x, WN_x) have been prepared in form of thin films by PLD and were studied as a part of this thesis. As a result, advantages and possibilities offered by reactive PLD were demonstrated in comparison with CVD and conventional sputtering solutions. Besides, also an important application where refractory metal nitrides (WN_x, TiN_x, MoN_x) are preferred is the diffusion barrier layer of microelectronic layer-structures. In these structures the nitrides are used to separate conducting metals (Al, Cu) from dielectric layers (e.g. SiO_x), since the electrical resistivity of metal nitrides (WN_x, TiN_x, MoN_x) can be tuned by changing the nitrogen concentration of the deposits. This effect was also studied for MoN_x, WN_x and it is demonstrated in the first experimental part of the thesis.

Thin film sensors are increasingly used in microelectronics, where sensitive devices are made from materials of selective response to specific environmental changes. Either electrical resistivity, optical properties or temperature (due to reaction heat) of the sensor film may change due to certain ambiental shifts. Making the gas-sensor thin films (e.g. WO_3, SnO_2, TiO_2) porously nanostructured, the increased effective surface area improves the sensitivity of the device. Investigation of pulsed laser depostion of nanoporous tungsten- and carbon-based thin films have been carried out and related results were incorporated into the present thesis, as well. The experience obtained, may contribute to the development of gas-sensing thin film applications.

Carbon has several allotropes, which results in manifold structural and hence physical properties of carbon-based thin films. Most attractive material of that kind is diamond-like carbon (DLC) offering impressive features regarding surface quality, hardness and friction. These are beneficial for MEMS applications, as well as for wear-resistant coatings in magnetic storage disks. Carbon atoms in DLC thin films build up connections with each other by strong sp^3 hybrid chemical bonds. Formation of sp^3 hybrid states of carbon atoms requires high kinetic energies of particles involved in the film deposition. Therefore, laser plasmas induced by high intensity laser pulses show outstanding potential to prepare DLC thin films by PLD, due to energetic particles impinging onto the growing film surface. Results, concluded from experiments on carbon thin film depositions, are also presented in this thesis. PLD films were

prepared using glassy-carbon target material and were characterized with respect to their bonding characteristics and to their macroscopically appearing optical behaviour. The present thesis is also dedicated to demonstrate morphologic, topographic and porosity studies of carbon films. Film characteristics are affected by the mean size of the growing (nano)particles, which can be influenced – within a certain limit – by varying the PLD process parameters.

Whilst some of the applications require dense films built from small particles (atoms, ions), there are other fields where larger nanoparticle coagulation or even porous structure formation is desired. Considering single nanoparticles, due to the small dimensions their physical characteristics may significantly differ from that of the bulk equivalent having the same chemical composition. Importance of research and development of nanoporous materials is obvious, since they possess new macroscopic properties different from that of the conventional bulk materials that we are familiar with.

First studies of nanoparticle systems stem from Lord Rayleigh's colloidal experiments in the late 19th century (1871). In the following more than 100 years continuous evolution of scientific knowledge and technical expertise enabled the appearance of nanotechnology and its advance by sophisticated instrumentation. Thin films prepared by PLD technique have lateral dimensions several orders of magnitudes larger than that of their thicknesses, which typically fall deeply into the sub-micrometer range causing high surface to volume ratios. As a result, surface characteristics tend to dominate over volumetric ones. That is why, thin films are commonly considered as „bottom-up"-type products of the nanotechnology in a wider sense. Furthermore, in case of nanoporous thin films even the mechanisms of layer formation and the required characterisation methods are part of the apparatus utilized by the nanotechnology. Nanoparticles can be nucleated and grown due to condensation in the ablation plume in case of sufficiently high background pressures. Afterwards, using PLD geometry substrates can be applied to collect material clusters in order to form porous contiguous thin films. Apparently, preparation of nanoporous PLD thin films has much in common with contemporary nanotechnology.

Regarding atmospheric pressure laser ablation of graphite and tungsten targets, previous studies pointed out two dominant phases distinct both in time and manner. Evaporation occurring below the ablation threshold fluence leads to formation of nanoparticles having diameters about 20 nm or less. Besides, above the threshold fluence larger nanoparticles are also formed due to thermally activated laser ablation. Application of HOPG as target material results in nanoparticle formation of ~60 nm in the thermally activated phase. Consequently, above the threshold fluence the two component of nanoparticles compose a bimodal size distribution showing local maxima corresponding to different ablation mechanisms. In previous studies performed with tungsten target material the examined fluence and repetition rate range were not wide enough to demonstrate the local maximum of the size distribution at larger particles. The present thesis includes results on size distribution studies showing that previously unseen local maximum emerges when tungsten was ablated in an extended laser parameter regime. In addition a hard ceramic material (boron carbide, B_4C) was studied using the same method. Scope of those investigations was to uncover relations between the main laser parameters and the characteristics of the size distribution of the generated nanoparticles in the measured 7-133 nm diameter window.

Objectives

Experimental work appearing in the present thesis started in 2001 when available literature of molibdenum- and tungsten-nitride claimed that thin films from these materials had been prepared typically with different sputtering and CVD techniques. By the same time, reactive PLD method had already proven it's applicability and versatility in case of numerous materials. Due to their high intensity and short pulse-lengths excimer lasers became the most promissing light-sources for PLD experiments. Therefore, it was believed that it was worthwhile to carry out UV excimer laser promoted PLD fabrication of molybdenum- and tungsten-nitride thin films.

- It was aimed to find appropriate N_2 partial pressures and substrate temperatures for good quality molibdenum- and tungsten-nitride thin film deposition by PLD. Parameter sets allowing stoichiometric molibdenum- and tungsten-nitride thin film depositions was intended to be identified.
- The main purpose of the in-situ substrate heating was to investigate whether crystallinity of the deposits could be increased without post annealing. On the other hand, it was aimed to investigate the possibility of cracking- and delamination-free in-situ stress relaxation of the deposited films. These kinds of failures are well known phenomena when post annealing metal-nirtide and -oxide thin films.
- High hardness and wide range electrical resistivity of refractory metal nitride thin films are attracting features for mechanical and microelectronic applications, respectively. Therefore, efforts were directed to prepare MoN_x and WN_x thin PLD films with the goal of determining their hardness values and studying their electrical resistivities as a function of the main PLD parameters.
- Beside the fabrication of MoN_x and WN_x thin PLD films different material characterisation methods were planed to be performed in order to find relations between sample attributes and PLD parameters, allowing better understanding of the reactive PLD process. Another objective was to support the experimental approach by numerical calculations of the laser induced temperature profiles. The main goal of those calculations was to compare the calculated ratios of evaporation rates of molybdenum and tungsten with measured ones.

As the application, instrumentation and philosophy of nanotechnology is spreading year-by- year, interest in novel aspects of PLD technique has been increasing, leading to studies aiming the investigations of nanoporous thin PLD films. Being interested in the above mentioned aspect of PLD method, initial experiments were performed with tungsten and were evaluated with AFM and HR-SEM in order to collect data about pressure ranges and substrate-to-target distance, at which nanoporous layer could be deposited. Later, target material was changed to glassy carbon, since carbon does not form oxides in the films, so that non reactive PLD and compositionally simple deposits could have been aimed to be investigated.

- Applying higher background pressures, preparation of nanoporous carbon-based thin PLD films was aimed. Due to elevated pressure levels, thermalization of the ablation plume takes place at shorter distances. Therefore, substrate-to-target distances was planned to be significantly reduced compared to the commonly used distances (~50 mm). Two different excimer lasers (KrF: $\lambda = 248$ nm, and ArF: $\lambda = 193$ nm) were dedicated to carry out

comparative PLD experiments with the goal of pressure range investigations, where nanoporous carbon thin film deposition in Ar atmosphere could take place.

- Surface roughness, topographic and morphologic data were planned to be used to draw conclusions about the internal structure of the deposited carbon films. In addition, it was aimed to set up an ellipsometric effective-medium approximation model to obtain void to total volume ratios representing overall film nanoporosity.
- Carbon based thin films show manifold bond structures. Therefore, it was also aimed to determine the graphitic and diamond-like character of both ArF and KrF excimer laser PLD films deposited at different Ar background pressure. Consequently, both spectroscopic ellipsometric measurements, and Raman-spectroscopy of the films were planned to be carried out.

Nucleation and the subsequent condensation occuring in the ablation plume are basic mechanisms of the PLD process when nanoporous thin films are deposited. Both the cluster formation and the nanoparticle collisions strongly influence the size distribution of the nanoparticles building porous deposits. Atmospheric pressure ablation of graphite by excimer lasers and the subsequent nanoparticle formation have been studied in details focusing on the roles of different laser parameters (fluence, ablated spot area, repetition rate). However, similar investigations for tungsten or more complex compound materials have been barely worked out yet.

- Therefore, it was aimed to perform nanoparticle generation by atmospheric pressure excimer laser ablation and to determine in-situ the size distributions of the nanoparticles. Systematic variation of the fluence, and the repetition rate of the applied ArF excimer laser was intended to promote investigations with the goal of demonstrating different shape characteristics of the size distributions. Experiments were planned to focus on those laser parameters which allowed the evolution of bimodal distributions showing distinct local maxima at larger nanoparticles, too. After reproducing tungsten related results known from literature, an extended laser parameter regime was planned to work with, in order to do nanoparticle size distribution investigations at higher fluences and repetition rates.
- Assuming that the integrated total volume calculated from a measured size distribution is proportional to the quantity of the ablated material it was aimed to determine multishot ablation threshold fluence of B_4C target material for ArF ($\lambda = 193$ nm) excimer laser pulses. Since the multishot ablation threshold fluence for ArF excimer pulses had already been measured and published for tungsten, it was only planned to re-measure and check the known fluence value.
- It was also aimed to demonstrate the nitridation of the nanoparticles condensated from pulsed laser ablated tungsten and boron-carbide target materials in atmospheric pressure N_2 atmosphere. Therefore, XPS analysis of polidisperse nanoparticle deposits collected onto a Si substrate in N_2 and Ar background gases by an electrostatic precipitator were planned to be performed.

Methodology

Using reactive PLD, molybdenum- and tungsten-nitride thin films were deposited onto silicon wafers either at room temperature or at elevated temperatures, i.e. T = 250 and 500 °C. Metallic targets were ablated in low-pressure (1, 10 and 100 Pa) nitrogen atmosphere applying KrF excimer laser pulses (λ = 248 nm, Φ = 6.5 J/cm^2). Thereby, systematic measurement series were performed for both Mo and W targets. Temperature profiles formed during excimer laser irradiation, as well as an approximated thickness of evaporated surface layers were calculated numerically. Phase changes and temperature dependence of thermo-physical data have been taken into account. These calculations were used to compare the calculated average ratio of ablation rates of Mo and W targets with experimentally obtained deposition rated. Electrical resistivities of the prepared MoN_x and WN_x thin films were measured by four-point probe resistivity measurements. Hardness of the samples was characterized by performing dynamic micro-indentation tests (micro-Vickers). Chemical composition data and film thicknesses were derived using Ruderford-backscattering spectrometry (RBS). Crystallinity of the as-coated thin films was measured by X-ray diffractometry (XRD). Scanning electron- and atomic force-microscopy (SEM and AFM) were used to visualize film surfaces at lower- and higher magnifications, respectively. High resolution AFM measurements provided topographic data, which were used to calculate surface roughness describing qualitatively thin film surfaces formed at different N_2 pressures.

Utilizing tungsten and glassy carbon targets thin films were deposited by PLD. In these experiments plume characteristics were systematically varied changing the pressure of the argon atmosphere in a wide range. In general, deposition rate decreases in case of increased pressure of the ambient gas, therefore unusually short 10–20 mm target-to-substrate distances were set to compensate plume losses. Glassy carbon target was ablated by laser pulses of different excimer lasers (KrF and ArF) leading to different energy of the plasma plumes, and hence carbon deposits showed rich structural and optical characteristics. Tungsten- and carbon-based thin films were investigated by AFM and HR-SEM. In case of carbon films spectroscopic ellipsometric measurements were performed, and then evaluated from two different perspectives. A Tauc-Lorentz-Sellmeier model was used to obtain film thickness, surface roughness, dispersion of the refractive index and the extinction coefficient, as well as the optical band gap data. Secondly, Effective Medium Approximation (EMA) model mixing the optical data of diamond, graphite-like carbon and void served with information about void to total volume ratio (porosity) and about the character of the carbon deposits. Raman spectroscopy was also applied to investigate the nature of carbon bonds.

Nanoparticles (NPs) were produced by ablating W and B_4C targets using ArF (193 nm) excimer laser pulses in atmospheric pressure N_2 ambient. Their size distributions were monitored – within a 7-133 nm size window – by a condensation particle counter, connected to a differential mobility analyzer. Laser repetition rate was varied between 1–50 Hz, while the fluence was systematically changed in the range of 0.5–15 J/cm^2, for both materials. Measured size distributions and calculated integrated volumes of the nanoparticles were interpreted with respect to the laser parameters set. Polydisperse nanoparticles were deposited in N_2 and Ar atmospheres using an electrostatic precipitator. Chemical composition of the deposits was studied by X-ray photoelectron spectroscopy (XPS).

Theses

Thesis 1.

It was found that PLD process using KrF excimer pulses (λ = 248 nm, FWHM: 30 ns) and N_2 ambient can be sucessfuly applied to preapare MoN_x and WN_x thin films using Mo and W targets. The electrical resistivity of the films increase monotonously when increasing the N_2 pressure in the 1–100 Pa range. It was pointed out, that electrical resistivities of the deposited films varies over several orders of magnitudes. Wide range of elecrical resistivities were recorded between $2\times10^2 - 4\times10^4$ μΩcm and $2\times10^2 - 10^7$ μΩcm for MoN_x and WN_x, respectively. Increasing nitridation level, as well as the less dense grainy microstructure were also found as important contributions to the elevated electrical resistivities. **[S1]**

Thesis 2.

Optimal deposition conditions for Mo_2N and W_2N KrF-PLD thin films having beneficial film characteristics were established. RBS investigations indicated stoichiometric Mo_2N and W_2N copositions when N_2 pressure was set to P = 10 Pa and substrates were in-situ heated to T = 250 and 500 ºC. XRD measurements revealed microcrystalline structure of the films. Crystallinity of those as-coated films were superior to that of Mo_2N and W_2N as-coated films deposited by other sputtering techniquies. Using AFM and HR-SEM microscopy it was concluded that film surfaces, grown at 500 ºC did not show the traces of mechanical stress induced cracks occuring commonly due to ex-situ post annealing of sputtered WN_x films. **[S1]**

Thesis 3.

The ratio of the evaporation rate of W and Mo was found by numerical calculation of the temparature profiles to be v_W/v_{Mo} = 2.5. This was in good agreement with the average ratios of the deposition rates obtained from RBS data (v_W/v_{Mo} = 1.8, 2.1, and 2.4, at 1 Pa, 10 Pa and 100 Pa nitrogen pressure, respectively). It was demonstrated by microhardness measurements that Mo_2N and W_2N films deposited at 10 Pa N_2 pressure onto substrates heated to T = 500 °C tempetature were slightly harder (26 and 36 GPa, respectively) than the sputtered films known from available literature. It was also pointed out that hardness values measured both on MoN_x and WN_x films deposited at 100 Pa were significantly lower than that of the samples prepared at 1 and 10 Pa. Using AFM it was shown that surface topographies of the 100 Pa films consist of larger clusters leading to less dense films. Those structural changes were found to be responsible for descended hardness values. **[S1]**

Thesis 4.

Using different excimer laser sources and glassy carbon target material, placed 20 mm from Si substrates, allowed PLD of carbon-based thin films. Analyzing HR-SEM images it was concluded that KrF-PLD samples show nanostructured deposits when argon pressures of 10–100 Pa were applied. Surfaces of ArF-PLD samples were found exhibiting rather different, less grainy morphologies in the whole examined 10^{-3}–20 Pa pressure range. According to ellipsometric results it was also presented that surface roughness *(Ra)* is increasing from 1.5 nm to 40 nm with increasing argon pressure for KrF-PLD samples, while ArF-PLD sample surfeces show significantly smaller *Ra* values (1.1–5 nm). Furthermore, an effective medium approximation ellipsometric model was established and used to demonstrate an increasing void content in the films (porosity) as the pressure of background argon was increased. Void

to total volume ratios of carbon films increases from 0 to 70 and 60 % when increasing the argon pressure for KrF- and ArF-PLD, respectively. **[S2]**

Thesis 5.

Performing ellipsometric investigations the diamond-like or graphitic character of amorphous carbon films were characterised by the optical bandgap *(E_{gap})* and the features of the dispersion of refractive index. It was pointed out that either for KrF- or ArF-PLD samples the variations of E_{gap} as a function of argon pressure show non-monotonous courses. Three different regimes were identified, as follows. In the lowest pressure range E_{gap} decreases from 0.9 to 0.46 eV and from 1.5 to 4×10^{-3} eV in case of KrF- and ArF-PLD samples, respectively, indicating a change from diamond-like to graphitic character. At moderate argon pressures, an increase in E_{gap} up to 1.1 and 1.5 eV occurs for KrF- and ArF-PLD, respectively. This was attributed to growing cluster sizes with diamond-like behaviour. At the highest examined pressure levels for KrF- and ArF-PLD E_{gap} drops to 0.7 eV and stays around 1.5 eV, respectively. The pressure values belonging to low-, medium-, and high-pressure ranges were identified as 10^{-3}–5–50–100 Pa and 10^{-3}–2–10–20 Pa for KrF- and ArF-PLD, respectively. Appearance of grainy and porous structure was also indicated by the decrease in maximum values of refractive index *(n_{max})*, which changed between 2.7–1.5 and 2.7 – 1.7 measured on KrF- and ArF-PLD samples, respectively. **[S2]**

Thesis 6.

It was shown by XPS analysis of the polydisperse NPs formed during B_4C ablation by ArF excimer pulses (λ = 193 nm, f = 20 Hz, Φ = 3.4 J/cm^2) in atmospheric pressure N_2 gas, that successful nitridation of the ablated material took place. As a result, chemical composition of the deposited nanoparticles were B: 60 %, C: 10 %, and N: 30 %. Besides, lack of nitrid formation was shown by XPS, when ablating tungsten target in N_2 atmosphere (f = 20 Hz, Φ = 11.4 J/cm^2). Calculating integrated volumes from the size distributions of the produced nanoparticles as a function of the laser fluence, allowed to determine the multishot ablation threshold fluence *(Φ_{th})* of B_4C. This was found to be ~1.9 J/cm^2 for ArF excimer laser pulses. In addition, the multishot ablation threshold fluence of polycristalline tungsten was found to be 6 J/cm^2 for the same laser, which is in excellent accordance with literature data. **[S3]**

Thesis 7.

Varying the laser fluence *(Φ)* and repetition rate *(f)* of the ArF laser, which ablated B_4C target material in N_2 backround, size distributions of condensed nanoparticles were investigated. It was shown, that the characters of the distributions – in the monitored 7-133 nm diameter window – change to bimodal when Φ exceeds a repetition rate-dependent threshold value which is 6, 4, 2, and 1.4 J/cm^2 in case of f = 5, 10, 20, and 50 Hz, respectively. It was also pointed out that bimodal size distributions show local maxima at 25-30 nm of nanoparticle diameters. Application of higher Φ and f laser parameters allowed to measure bimodal distributions of nanoparticles condensated from tungsten vapour showing local maxima at ~20 nm when f was increased to 50 Hz and Φ was higher than 7 J/cm^2. **[S3]**

Peer-reviewed papers related to the theses

[S1]: *„Reactive pulsed laser deposition of thin molybdenum- and tungsten-nitride films”*
M. Bereznai, Z. Tóth, A.P. Caricato, M. Fernández, A. Luches, G. Majni, P. Mengucci, P.M. Nagy, A. Juhász, L. Nánai
Thin Solid Films 473(1) 2005 16-23

[S2]: *„Ellipsometric study of nanostructured carbon films deposited by pulsed laser deposition”*
M. Bereznai, J. Budai, I. Hanyecz, J. Kopniczky, M. Veres, M. Koós, Z. Tóth
Thin Solid Films 519(9) 2011 2989-2993

[S3]: *„Measurements of nanoparticle size distribution produced by laser ablation of tungsten and boron-carbide in N_2 ambient”*
M. Bereznai, P. Heszler, Z. Tóth, O. Wilhelmsson, M. Boman
Applied Surface Science 252 2006 4368-4372

Other papers published in peer-reviewed international journals

[S4]: *„Surface modifications induced by ns and sub-ps excimer laser pulses on titanium implant material”*
M.Bereznai, I. Pelsöczi, Z. Tóth, K. Turzó, M. Radnai, Z. Bor, A. Fazekas
Biomaterials 24(23) 2003 4197-4203

[S5]: *„Laser-induced etching of tungsten and fused silica in WF_6”*
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Applied Surface Science 208-209 2003 205-209

[S6]: *„Processing of transparent materials using visible nanosecond laser pulses”*
B. Hopp, T. Smausz, M. Bereznai
Applied Physics A 87(1) 2007 77-79

[S7]: *„Preparation of hydrogenated amorphous carbon films from polymers by nano- and femtosecond pulsed laser deposition”*
J. Budai, M. Bereznai, G. Szakács, E. Szilagyi, Zs. Tóth
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[S8]: **„***Three-dimensional focus manipulation by means of a birefringent plate”*
M. Erdélyi, M. Bereznai, G. Gajdátsy, Z. Bor
Optics Communications 281(19) 2008 4807-4811