PHD THESIS SYNOPSIS

Production of nanostructures on different metal and dielectric surfaces using laser-based methods

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1. INTRODUCTION

Nanostructured surfaces are defined as materials on which the arranged characteristic units have dimensions of about 1–100 nanometres. A nanometre is only a one-billionth part of a meter, a one hundred-thousandth part of the average width of a human hair, and only twenty times more than the diameter of the hydrogen atom. Nanoscience is destined to produce, manipulate and study such systems. The typical size of nanotextures falls between the size of atomic/molecular and macroscopic systems, which leads to several extraordinary and interesting features and phenomena. These include, but are not limited to the super-high hardness, or the superparamagnetism of metal nanoparticles, their exceptional catalytic properties, the interaction of light and photonic crystals with wavelength comparable lattice constant, the excitation of localized surface plasmons, the quantum confinement effect, etc. Generally, these extraordinary mechanical, optical, electromagnetic, and chemical attributes are mainly caused by the huge area to volume ratio of the nanoparticles, their small size leading to quantum effects, and the electrodynamic interactions between the nanosized elements.

Due to their exciting nature, nowadays there is an increasing demand towards effective, economical and high-quality micro- and nanomachining of different materials, in which lasers gained a remarkable role. With the use of laser-based methods, it is possible to control the size and the interaction of the building units on the patterned surface, with which the basic attributes of the material can also be modified. In case of laser-driven techniques, the applied "tool" is a light beam that is – unlike for example the expensive lithography masks or molding/embossing stamps – free from degradation, which is a notable advantage in comparison with conventional mechanical methods. Another privilege coming from the lack of the direct mechanical contact between the laser light and the sample is that the contamination of the processed area by the structuring tool is easy to avoid, which has great importance in the treatment of infection-sensitive medical, or biological targets, and when dealing with analytically pure samples as well. Besides that, the precise controllability of the laser parameters helps in reaching good reproducibility of the prepared formations.

My thesis concentrates on the construction, study and application of nanostructures on the surface of certain noble metals and dielectrics with the use of different pulsed laser techniques. The nanopatterned substrates are tested for two interesting, novel applications. The first is modifying the reflectivity properties of materials having high electrical conductivity (e.g. metals), while the second is the enhancement of the Raman signal of dyes or biomolecules due to the presence of nanostructures via the surface enhanced Raman scattering effect.

2. SCIENTIFIC BACKGROUND

The investigation of the micro- and nanostructuring of different surfaces is a research topic, which has several promising applications in multiple fields. For example in biological and life sciences, by properly manufactured topographies the cell growth and proliferation was accelerated, while in other experiments, the biocompatibility, and the level of osteointegration of medical implants was improved. In electronics, ultrafast switches were realized by the irradiation of isolator and semiconductor nanomaterials with ultrashort laser pulses. In addition, it is also possible to modify the adhesion properties of the surface in order to create hydrophobic, self-cleaning surfaces, or the adhesion and friction properties for tribological utilizations.

The improvement of the light trapping properties of materials having high electrical conductivity has great relevance in photovoltaic and light detection applications. It was observed that the interaction of certain metals with ultrashort laser pulses results in the permanent change of the optical properties of the laser illuminated surfaces. By the use of proper experimental conditions, the originally highly reflective materials can be transformed into practically perfect absorbers on a broad spectral range (from the near infrared to the near ultraviolet). The effect was successfully demonstrated for several metals like platina, wolfram, aluminium, steel, and titanium alloys. High resolution scanning electron microscopic images of the laser irradiated spots showed the presence of micro- and nanoscale formations with variable characteristics depending on the processed material and on the applied experimental conditions (fluence, ambient gas, pressure, etc.) as well. A number of physical processes can be responsible for the enhanced absorption like the scattering of the incident probe light on small surface non-uniformities, plasmonic absorption, inverse bremsstrahlung, or multiple reflections inside microcavities. The nanostructured, darkened metal surfaces can be exploited by broad areas of research and development, such as plasmonics, optoelectronics, metal colorization, engraving, manufacturing of antireflection coatings, solar light absorbers, broadband thermal sources, or improving the power conversion efficiencies in photovoltaic devices generally. The main benefit of the presented technique is that it does not require the application of special coatings prepared from materials which are different from the substrate, therefore the problems concerning the mechanical, thermal, electric, etc. matching of the different layers are avoidable.

Another important research field, in which nanostructures play a fundamental role, is the surface enhanced Raman spectroscopy (SERS). The conventional Raman spectroscopy is a well-known technique for the study of the rotational and vibrational levels of a molecular system via the inelastic scattering of the illuminating laser light. The Raman spectrum carries specific information about the chemical bonds and the symmetries of the investigated molecule, with which an unknown substance can be identified, or the concentrations of mixture compounds can be determined. In comparison with other spectroscopic techniques, the Raman spectroscopy allows fast, non-destructive investigation, and requires little preparation of the studied sample. However, a serious drawback of RS is that the total cross section of the Raman scattering process is rather low (generally the Raman signal is order of magnitudes lower than the intensity coming from elastic Rayleigh scattering), therefore the number of detectable molecules and concentrations are limited. The solution for this problem was the discovery of the surface enhanced Raman scattering (SERS) effect, which can be observed when the studied chemical substance is put on the rough surface of a conducting material. The surface plasmons of the system are excited by the laser photons of the Raman spectrometer, resulting in the significant increase of the induced electric field around the surface. The Raman intensity strongly depends on the magnitude of the developed electric near field, therefore high enhancement occurs in the measured signal. The key point of surface enhanced Raman scattering spectroscopy is to find the optimal conducting material and to form its surface on the ideal way by the use of adequate micro- and nanostructuring methods.

3. APPLIED METHODS

During my PhD work, I implemented different direct and indirect pulsed laser machining techniques in order to produce nanostructured surfaces. Direct laser irradiation is a rapid, simple, and relatively low-cost way for surface nanostructuring, which is based on the phenomenon of pulsed laser ablation. During the ablation process, photothermal and photochemical changes are induced in the irradiated sample due to the absorbed energy of the laser light, which result in the formation of regular or random micro-/nanostructures via melting, boiling, or plasma formation processes. However, only such target materials can be processed by direct irradiation, which have enough high absorption coefficient at the wavelength of the applied laser light. If this condition is not fulfilled, the required effect can only be reached through multiphoton absorption, which needs laser sources having ultrahigh power. This makes the precise laser machining of transparent targets complicated and energy-demanding. To resolve this issue, indirect techniques have been developed, where an absorber material having high absorption coefficient at the applied processing wavelength is irradiated through the transparent sample. During my experiments I used the Laser-Induced Backside Dry Etching (LIBDE) technique, where the absorber matter is a metal coating having a few tens of nanometres thickness, which is prepared by pulsed laser deposition or vacuum evaporation method on the transparent surface. According to the present theories, the absorption of the laser energy causes the rise of the temperature of the absorber film up to its melting, or even boiling point depending on the applied laser fluence. Because of the direct contact between the absorber layer and the transparent plate, and due to the good heat conduction properties of the absorber coating, heat is dissipated into the uppermost layers of the transparent sample causing phase transitions. Forces from the rapidly expanding metal vapour attack the melted surface, which leads to material removal and structurization.

During the experiments reviewed in my doctoral thesis, I analysed the constructed nanostructures by a broad range of surface investigation methods, including scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, profilometry, optical microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and reflective optical micro-spectrophotometry.

4. OBJECTIVES

The goal of my PhD work is to produce nanostructures on the surface of different metal (copper, silver and gold), and dielectric (fused silica and polyimide) substrates by direct and indirect pulsed laser methods. The laser machining of the targets is carried out with the use of several wavelengths (193, 355, 775 and 1064 nm), and pulse lengths (nanosecond, picosecond and femtosecond), with the variation of the applied laser fluence and the number of pulses in all cases. With advanced surface investigation techniques (atomic force microscopy, scanning electron microscopy and profilometry) I study and compare the effects of the foregoing laser parameters and the properties of the processed materials on the generated surface structure.

I propose to use the prepared nanopatterned substrates for two distinct purposes. The first is to form extensive low-reflectivity areas on the surface of materials having high electrical conductivity (metals) by pulsed laser irradiation. I acquire reflectivity spectra covering the spectral regions from the near-ultraviolet to the near-infrared on the laser treated surfaces in order to determine the appropriate irradiation and material parameters with which micro- and nanotextures showing the strongest light trapping effect can be created. In order to reveal the mechanism of the reflectivity decrease phenomenon, I will theoretically simulate the impact of a real surface structure on the total reflectivity by ray tracing method.

Afterwards I investigate another interesting application, in which the nanomachined surfaces are aimed to be used for surface enhanced Raman scattering spectroscopy. The SERS activity of the prepared formations are studied by Raman optical microscope. With the practical usefulness in view, my goal is to find a machining method and a proper substrate material with which the SERS active structures can be formed economically, with good reproducibility, on a relatively high area of the processed sample.

5. NEW SCIENTIFIC RESULTS

This thesis is focused on the production of nanostructures on different metal and dielectric surfaces with different direct and indirect pulsed laser machining methods. During the experiments the effect of various laser parameters on the nanostructure formation process and on the optical and plasmonic properties of the created structures were investigated comprehensively. The nanostructured materials were fabricated for two distinct purposes. Firstly, low-reflectivity surfaces was formed on the surface of different noble metals. Secondly, nanostructured substrates were constructed for application in surface enhanced Raman scattering spectroscopy.

My new scientific results are summarized hereinafter:

T1. Production of nanostructured metal surfaces having low reflectivity by ultrashort laser irradiation

I produced broadband low-reflective extensive metal surfaces by direct femtosecond laser scanning on the originally high-reflective surfaces of copper, silver and gold targets. [S1]

- Reflectivity measurements showed that the reflectivity of the processed samples decreases over the whole visible spectrum and reaches only 5% of the original reflectivity at 2000 mJ/cm^2 applied fluence and 100 pulses in case of all the investigated noble metals.
- With the use of scanning electron microscope, I compared the structured surfaces of the different metals, where the presence of two nanostructure types could be distinguished: on the surface of the irradiated silver sample sponge-like structures are formed consisting of frozen jets and nanodroplets having basically a few hundred nanometres linear dimensions, while in the cases of copper and gold a more or less similar, but less consistent basic structure is densely covered by mass of nanofibres having diameters of approximately a

few nanometres. The development of such foam-like structure types is due to the aggregation and back scattering of Cu and Au nanoparticles from the ablation plume. I proved that the characteristic size and shape of the created structures strongly depend on the applied fluence and on the number of laser irradiations. By careful adjustment of these parameters, the reflectivity of the processed metal surface can be controlled precisely.

T2. Production of nanostructured metal surfaces having low reflectivity by picosecond laser ablation using different processing wavelengths

I reached for the first time effective reduction in the reflectivity of copper, silver and gold surfaces by picosecond laser ablation using both UV (355 nm) and IR (1064 nm) wavelengths separately. [S2]

- My experiments showed that the wavelength of the applied laser source does not influence significantly the morphology of the produced surface structures and the achievable reflectivity decrement, therefore considering the technological aspects the fundamental infrared harmonic is preferable in practice.
- I found that the normalized reflectivity of the laser-treated areas drastically diminishes in a broad spectral range (from the near ultraviolet to the near infrared) with increasing laser fluence reaching lower than 3% in all cases above 3 J/cm^2 at 50 pulses on the average.
- By investigating the light scattering properties of the laser irradiated surfaces as the function of the applied fluence I discovered that the initial specular reflectivity of the surface is reduced due to the consecutive laser irradiations and above 3 J/cm^2 laser fluence a nearly ideal diffusely scattering surface with low total reflectivity is formed.
- My investigations with scanning electron microscope showed that molten structures are dominated on the processed surfaces, and the contribution of the filament-like structures in the picosecond case are less significant as compared to the femtosecond experiments at the same applied laser fluence.

T3. Simulation of the reflectivity properties of structured titanium surface by ray tracing technique

I proved first that multiple internal reflections, which are generated only by the changed morphology of the surface, have a considerable role in the drop of the reflectivity in case of a structured titanium surface produced by femtosecond laser ablation. [S3]

- I optimized the used simulation model regarding the applied geometry (number of cones on the surface and their disposition) together with the simulation parameters (number of the emitted rays and the size of the illuminated area). The calculated reflectivity of the structured surface was significantly lower than the reflectivity of the reference flat titanium plate and was only 6.7 percentage points higher than the results of the experimental measurements. This shows that the relatively simple and moderately computational time-consuming ray tracing method can be a promising technique for the theoretical estimation of the reflectivity value of microstructured surfaces.

T4. Fabrication of SERS active surfaces on fused silica substrate using laser-induced backside dry etching technique

I demonstrated for the first time that the Laser-Induced Backside Dry Etching (LIBDE) method can be used in itself to create nanostructures on the surface of a fused silica plate. I proved that these nanostructures prepared by LIBDE are able to trigger the surface enhanced Raman scattering effect, when coated by a silver thin film. [S4]

- My experiments proved that the intensities of the selected characteristic peaks of a R6G solution increase significantly in the Raman spectrum, when a silver film is applied, and a thicker layer produces higher enhancement in the investigated thickness range (10–40 nm).
- High resolution AFM images were taken from the specific areas of the etched holes and the R_a roughness parameters of the surfaces were determined. I proved that a rougher surface results in greater SERS signal in the investigated roughness range. This statement was underlined by modelling the near field electromagnetic properties of three similarly shaped structures having three different R_a values based on the measurements on the real surfaces.
- I compared the spectra of R6G on the best LIBDE treated surface covered with a 40 nm silver coating with the Klarite® commercially available SERS substrate under equal conditions. It was revealed that the surface structures created by LIBDE produce only ca. 20% lesser intense Raman peaks than Klarite® in case of the applied experimental circumstances.

T5. Creation of nanostructured surface on polyimide sample by excimer laser ablation for surface enhanced Raman spectroscopy

I verified that a nanostructured polyimide surface, which was fabricated by direct excimer laser irradiation and coated by a silver thin film can be used as a surface enhanced Raman scattering substrate. The produced SERS active surface was created with a simple and economical technique, on a relatively large area compared to the total irradiated zone, and in a reproducible way, which makes the applied technique possibly useful in practice. [S5]

- I discovered that the SERS activity of the irradiated areas prepared at higher laser fluences is higher in the investigated fluence range (40–80 mJ/cm^2).
- By taking a closer look by scanning electron microscope at the most appropriate parts of the irradiated spots with respect to SERS, I observed that besides conical microstructures the surface morphology is finely structured by redeposited micro- and nanofragments, which were backscattered from the plume during the ablation process. I concluded that the observed fine structure plays a central role in establishing the SERS effect.

6. PUBLICATIONS

6.1. Related publications in peer reviewed international journals:

[S1]: Hopp B., Smausz T., Csizmadia T., Vass Cs., Tápai Cs., Kiss B., Ehrhardt M., Lorenz P., Zimmer K.: *“Production of nanostructures on bulk metal samples by laser ablation for fabrication of low-reflective surfaces”*, Applied Physics A: Materials Science and Processing 113 (2), 291-296 (2013)
doi:10.1007/s00339-013-7913-y

[S2]: Csizmadia T., Smausz T., Tápai Cs., Kopniczky J., Wang X., Ehrhardt M., Lorenz P., Zimmer K., Orosz L., Varga E., Oszkó A., Hopp B.: *“Comparison of the production of nanostructures on bulk metal samples by picosecond laser ablation at two wavelengths for the fabrication of low-reflective surfaces”*, Journal of Laser Micro / Nanoengineering 10 (2), 110-118 (2015)
doi: 10.2961/jlmn.2015.02.0001

[S3]: Csizmadia T., Erdélyi M., Smausz T., Novák T., Hopp B.: *“Simulation of the Reflectivity Properties of Microstructured Titanium Surface by Ray Tracing Method”*, Journal of Laser Micro / Nanoengineering 10 (2), 210-215 (2015)
doi: 10.2961/jlmn.2015.02.0019

[S4]: Csizmadia T., Hopp B., Smausz T., Kopniczky J., Hanyecz I., Sipos Á., Csete M., Szabó G.: *“Possible application of laser-induced backside dry etching technique for fabrication of SERS substrate surfaces”*, Applied Surface Science 278, 234-240 (2013)
doi:10.1016/j.apsusc.2012.12.037

[S5]: Csizmadia T., Hopp B., Smausz T., Bengery Z., Kopniczky J., Hanyecz I., Szabó G.: *"Fabrication of SERS active surface on polyimide sample by excimer laser irradiation"*, Advances in Materials Science and Engineering 2014, 987286 (2014) doi:10.1155/2014/987286

6.2. Other publications in peer reviewed international journals

[S6]: Smausz T., Csizmadia T., Kresz N., Vass Cs., Márton Zs., Hopp B.: *"Influence on the laser induced backside dry etching of thickness and material of the absorber, laser spot size and multipulse irradiation"* Applied Surface Science 254, 1091-1095 (2007) doi:10.1016/j.apsusc.2007.08.068

[S7]: Hopp B., Smausz T., Csizmadia T., Budai J., Oszkó A., Szabó G.: *"Laser-induced backside dry etching: wavelength dependence"*, Journal of Physics D: Applied Physics 41, 175501 (2008)
doi:10.1088/0022-3727/41/17/175501

[S8]: Hopp B., Smausz T., Csizmadia T., Vass Cs., Csákó T., Szabó G.: *"Comparative study of different indirect laser-based methods developed for microprocessing of transparent materials"*, Journal of Laser Micro/Nanoengineering 5, 80-85 (2010)
doi:10.2961/jlmn.2010.01.0017

[S9]: Smausz T., Kecskeméti G., Csizmadia T., Benedek F., Hopp B.: *"Study on the applicability of polytetrafluoroethylene-silver composite thin films as sensor material"*, Applied Surface Science 278, 117-121 (2013)
doi:10.1016/j.apsusc.2013.01.051

[S10]: Zimmer K., Ehrhardt M., Lorenz P., Wang X., Vass Cs., Csizmadia T., Hopp B.: *"Reducing the incubation effects for rear side laser etching of fused silica"*, Applied Surface Science 302, 42-45 (2014)
doi:10.1016/j.apsusc.2014.01.115

[S11]: Lorenz P., Smausz T., Csizmadia T., Ehrhardt M., Zimmer K., Hopp B.: *"Shadowgraph studies of laser-assisted non-thermal structuring of thin layers on flexible substrates by shock-wave-induced delamination processes"*, Applied Surface Science 336, 43-47 (2014)
doi:10.1016/j.apsusc.2014.09.114

[S12]: Lorenz P., Klöppel M., Smausz T., Csizmadia T., Ehrhardt M., Zimmer K., Hopp B.: *"Time dependency of the laser-induced nanostructuring process of chromium layers with different thicknesses on fused silica"*, Applied Surface Science 336, 176-181 (2014)
doi:10.1016/j.apsusc.2014.10.130

[S13]: Lorenz P., Klöppel M., Smausz T., Csizmadia T., Ehrhardt M., Zimmer K., Hopp B.: *"Dynamics of the laser-induced nanostructuring of thin metal layers: Experiment and theory"*, Materials Research Express 2 (2), 026501 (2015)
doi:10.1088/2053-1591/2/2/026501

[S14]: Sansone G., Kuehn S., Dumergue M., Kahaly S., Lopez-Martens R., Tzallas P., Fule M., Csizmadia T., Varjú K., Charalambidis D., Osvay K., Calegari F., Devetta M., Frassetto F., Mansson E., Poletto L., Stagira S., Nisoli M., Rudawski P., L'Huillier A., Kalpouzos C.: *"The ELI-ALPS facility: the next generation of attosecond sources"* (submitted)

6.3. Conference posters, proceedings

1. Csizmadia T., Smausz T., Tápai Cs., Kopniczky J., Wang X., Ehrhardt M., Lorenz P., Zimmer K., Varga E., Oszkó A., Hopp B.: "Production of nanostructures on bulk metal samples by picosecond laser ablation at two wavelengths for fabrication of low-reflective surfaces"
LPM 2014: 15th International Symposium on Laser Precision Microfabrication
Vilnius, Lithuania, 2014.06.17. - 2014.06.20.

2. Csizmadia T., Erdélyi M., Smausz T., Hopp B.: "Simulation of the reflective properties of microstructured titanium surface by ray tracing method"
LPM 2014: 15th International Symposium on Laser Precision Microfabrication
Vilnius, Lithuania, 2014.06.17. - 2014.06.20.

3. Hopp B., Csizmadia T., Smausz T., Tápai Cs., Kopniczky J., Wang X., Ehrhardt M., Lorenz P., Zimmer K.: "Production of Low-Reflecting Surface Structure on Metal Films"
12th International Conference on Laser Ablation
Ischia, Italy, 2013.10.06. - 2013.10.11.

4. Csizmadia T., Bengery Zs., Kopniczky J., Hanyecz I., Hopp B.: "Fabrication of SERS active surface structures on rotating polyimide sample by excimer laser irradiation"
The European Conference on Lasers and Electro-Optics 2013
Munich, Germany, 2013.05.12. - 2012.05.16.

5. Csizmadia T., Hopp B., Smausz T., Hanyecz I., Kopniczky J., Szabó G.: "Application possibility of laser-induced backside dry etching technique for fabrication of SERS active surfaces"
E-MRS 2012 Spring Meeting: V: Laser materials processing for micro and nano applications
Strasbourg, France, 2012.05.14. - 2012.05.18.

6. Kecskeméti G., Smausz T., Csizmadia T., Benedek F., Hopp B.: "Study on the applicability of polytetrafluoroethylene-silver composite thin films as sensor material"
E-MRS 2012 Spring Meeting: V: Laser materials processing for micro and nano applications
Strasbourg, France, 2012.05.14. - 2012.05.18.

7. Csizmadia T., Smausz T., Vass Cs., Hopp B.: "Laser-induced backside dry etching of transparent materials having significantly different thermal parameters"
E-MRS 2010 Spring Meeting: R: Laser processing and diagnostics for micro and nano applications
Strasbourg, France, 2010.06.07. - 2010.06.11.

8. Papdi B., Csizmadia T., Vass Cs., Szabó G., Hopp B.: "Fabrication of micro-channels in fused silica using laser induced backside wet etching (LIBWE) method"
E-MRS 2010 Spring Meeting: R: Laser processing and diagnostics for micro and nano applications
Strasbourg, France, 2010.06.07. - 2010.06.11.

9. Hopp B., Smausz T., Csizmadia T., Vass Cs., Csákó T., Szabó G.: ”Comparative study of different indirect laser-based methods developed for microprocessing of transparent materials”
LAMP 2009: The 10th International Symposium on Laser Precision Microfabrication Kobe, Japan, 2010.06.29. - 2010.07.02.

10. Smausz T., Csizmadia T., Kresz N., Vass Cs., Márton Zs., Hopp B.: “Influence on the laser induced backside dry etching of thickness and material of the absorber, laser spot size and multipulse irradiation”
E-MRS 2007 Spring Meeting: P: Laser synthesis and processing of advanced materials Strasbourg, France, 2007.05.28. - 2007.06.01.