Raman spectroscopic and spectroscopic ellipsometric measurements on pulsed laser treated glassy carbon and silicon surfaces

Theses of PhD dissertation

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1. Introduction

Laser treatment of different materials is widely applied in industry and in science. Lasers are able to drill, cut and weld materials, furthermore, we can introduce structural changes of the material surface upon laser irradiation, for example hardening, crystallization or amorphization. The exploration of the physical background of these processes has been started long time ago. However, these fields are still intensively investigated nowadays, due to the versatility of materials and laser sources. There are many techniques which are able to follow the surface modification of the laser treated material. During my work I applied two complementary nondestructive methods, Raman-spectroscopy and spectroscopic ellipsometry. These two methods are based on two distinct physical phenomena. Due to this, with the simultaneous application of these methods, the structural changes of the material can be followed in a more accurate way.

Surface properties of materials, for example hardness, wetting and optical behavior can also be changed with pulsed laser treatments. During these modifications periodic surface structures may appear, which are commonly referred as LIPSS (Laser Induced Periodic Surface Structure). The physics behind the formation of these structure is still under investigation. Many experiments have been carried out to examine the effect of the pulse energy, pulse number, pulse duration on the properties of the developing surface structure. However, no systematic study can be found in the literature aiming at the investigation of pulse duration from few tens of femtosecond to the hundreds of picosecond range with the same laser at the same circumstances.

For better understanding of the physics behind the surface modification and the induced changes of the surface, it is necessary to follow the optical (e.g. reflection, absorption and refraction) changes during the laser pulse excitation. These parameters change in a transient

way during laser irradiation so the in-situ measurements of them provides useful information. For in-situ measurements the pump-probe technique is a commonly used method. During these experiments, the pump beam induce changes on the surface which can be followed by the probe beam. The limitation of these methods is the laser pulse duration. With femtosecond pulse duration the time resolution of the measurement can easily be pushed towards the sub-picosecond range. The optical parameters, i.e. complex refractive index modified during laser treatment, can be measured if we combine the pump-probe technique with the ellipsometry.

2. Aims

During my PhD work my aim was to examine the laser-matter interaction in ex-situ and in-situ ways as well. For this purpose, I used different pulsed lasers for the modification of glassy carbon and silicon surfaces. In the first part of my work, I examined the surface modification after pulsed laser treatment of glassy carbon with Raman-spectroscopy and spectroscopic ellipsometry. The aim of this work was to elaborate an evaluation method for the Raman-spectra which is able to separate the Raman-spectrum of the topmost layer of the treated samples from the Raman-spectrum of the substrate. To prove the correctness of the method I wanted to use the ellipsometric results as an independent method providing complementary information about the modified surfaces. I wanted to test the method and follow the structural changes on the surfaces treated by nanosecond or sub-picosecond UV and visible pulses.

In the second part of my work I generated periodic surface structures (LIPSS) on glassy carbon surface. For this purpose, I wanted to use infrared and UV laser pulses. The goal of this work was to investigate the effect of the pulse duration and the pulse number of the lasers for the properties of the periodic surface structures formation.

Besides, I wanted to determine the physical processes which take part on the LIPSS formation.

In the next part of my work I aimed at changing the previously used ex-situ ellipsometric measurement technique to an in-situ one. The goal of this work was to measure the transient optical changes of the material during the laser-matter interaction. For this purpose, I planned to build an ellipsometric setup in pump-probe arrangement. I wanted to use the setup with UV pump beam excitation and visible probing beam and measure the transient optical changes of silicon wafers.

3. Methods and results

In the first part of my results, I presented a new evaluation method for Raman spectroscopic measurements. With this method, it is possible to separate the Raman spectrum of thin surface layers from the substrate, if the two spectra are overlapped. This evaluation method is based on the fitting procedure of the measured Raman spectra. To validate the evaluation method I treated glassy carbon (GC) surfaces with nanosecond and sub-picosecond pulse duration Nd:YAG and excimer lasers, and used this method to evaluate the Raman spectroscopic measurements. First, I measured the Raman spectra of the intact GC and fitted with Gaussian functions. The parameters of these functions were fixed during the further steps of the procedure. After this I took the measured Raman spectra of the modified surfaces and fitted them with the combination of the fixed Gaussian functions and three new one. The fixed Gaussian functions were multiplied by a constant, which I named the weight factor. This value corresponds to the weakening of the Raman signal of the substrate which traverses the topmost modified layer. Since the weight factor is proportional to the absorption of both the excitation light and the Raman signal of the substrate while travelling through the modified layer, it provides information about the absorption and the thickness of the modified

layer. To check these properties the modified layer I carried out ellipsometric measurements on the samples as well. After the evaluation of the Raman spectra I compared the weight factor with the absorption parameters of the layer form the ellipsometric results and I found a good agreement between them. Based on this, I concluded that the elaborated evaluation method is capable of determining the Raman spectra of the topmost layer, even if the layer is transparent and the Raman signal of the substrate is overlapped with that.

In the second part of my results I used this evaluation method for the measured Raman spectra to get structural information about the topmost layer of GC modified by excimer and Nd:YAG laser pulses. From the Raman-spectra of the layer I determined the intensity ratio of the D and G peaks, the full width at half maximum of them, and the position of the G peak. I also determined the optical properties as the extinction, refraction coefficient and the thickness of the modified layer from the ellipsometric measurements. Since the wavelength of the lasers were divers, I interpreted the result as the function of the volumetric fluence, which is the product of the absorption coefficient and the fluence. This value corresponds to the volume in which the pulse energy is absorbed, and it was used successfully by my supervisors earlier in similar cases. I found that on the surface a thin modified layer appeared with thicknesses between 2 and 90 nm, after the laser treatment. The structure of the layers was similar to glassy carbon, but it was more disoriented. The evaluation of the Raman spectroscopic measurements revealed that the structure of the modified layer was close to the nanocrystalline graphite. In case of Nd:YAG treated samples, frozen droplets appeared on electronmicroscope (SEM) images, while such droplets could not be observed on the excimer laser treated samples. I explained this difference with the different ablation processes: with excimer laser treated samples the so called photochemical ablation takes place, but in the case of Nd:YAG laser the ablation happened in thermal way.

In the next part of my results, I studied a different aspect of the interaction of laser pulses and GC. I wanted to study the LIPSS generation with two different lasers. One of them was a Ti:Sapphire based CPA laser which provides pulses in the near-infrared region, and the other was a dye-KrF hybrid laser with pulses in the UV region. During my experiments I systematically varied the pulse number and duration to test whether the periodic structure appear on the surface or not. The formation of the periodic structure was studied by scanning electron microscopy by recording SEM images from the middle of the treated area. I made the Fast Fourier Transform analysis of the images to characterize the observed periodic structures quantitatively and qualitatively.

In the case of the Ti:Sapphire treatment I varied the pulse duration in order of magnitude steps between 35 fs and 200 ps. On samples which were treated with 30 ps or higher pulse durations the SEM images showed frozen droplets on the surface. Based on this information, I conclude that the thermalization time of the GC can be in the order of few picosecond. I observed sub-200 nm ripples on those samples which were treated with 35 fs – 2.4 ps pulse durations. If the pulse duration was longer than the thermalization time, the distance between the periodic structures was roughly the same as the laser wavelength. From this results I concluded that the physical effect behind the larger periodic structures can be the formation of capillary waves which appear in the molten surface layer during the treatment. For the treatment with 200 ps, SEM images were taken at the periphery of the treated area as well. While in the middle wavy like structures appeared with ~800 nm distances, at the periphery, where the local fluence of the laser pluses were less, ripple structure with few 100 nm distances was visible. In addition to this, the small ripples had a 3D fibrous structure. These results indicated that the local fluence in the treated area is important during the LIPSS formation. In all cases the

direction of the structures was parallel with the polarization of the laser pulses.

In the case of the dye-KrF laser treatment I varied the pulse duration between 250 fs and 2.1 ps. I also observed LIPSS formation with two different periodicities on the samples, but the two different kinds of ripples appeared in all cases independently from the pulse duration. One of them was parallel with the laser polarization direction and the characteristic distances were close to the wavelength of the laser pluses. The other one was perpendicular to the polarization direction and had a sub-100 nm periodicity.

In the next part of my results I presented the establishment of an imaging null-ellipsometer, which I designed and built to measure transient optical properties. The null-ellipsometer is the simplest ellipsometer, which is based on the nulling condition of the light reflected from the sample. For such a measurement the unpolarized light goes through a polarizer, a quarter wave plate, is reflected from the sample and passes through the second polarizer (analyzer). The nulling condition can be achieved with the alignment of the azimuth angles of the polarizer and analyzer. I elaborated a method for setting the nulling condition in a more accurate way. This method is based on the systematic scanning of the polarizer and analyzer angles resulting in an intensity map. To determine the ellipsometric angles (Ψ and Δ) I fitted with the map with exact expression describing theoretically the intensity distribution. To get information about the accuracy of the device, I measured the Ψ and Δ angles of two different thermally grown SiO_2 samples at all angles of incidence. Besides I measured the ellipsometric angles with a commercial Woollam M2000-F ellipsometer as well. Comparing the two measurements I found that the relative deviation of the null-ellipsometric measurements was less than 6% in Ψ and 1% in Δ.

In the last part of my results I presented an experimental and theoretical work related to the null-ellipsometric measurements done on silicon samples in pump-probe arrangement. During the experiments I used a dye-KrF eximer laser. The pump beam contained the 248 nm UV pulses and the probe beam was a small part of the seed pulses with 496 nm wavelength. The pulse duration of the pulses were 480 fs. I could determine the Ψ and Δ angles of the silicon samples between 2 and 146 ps delay after the excitation. To describe the transient changes of the ellipsometric angles I constructed a model that considers the free carrier and lattice temperature distribution of the samples by combining a gradient- and a Drude-model with the temperature dependent optical properties of Si. For this purpose, I programed a two temperature model in COMSOL Multiphysics. This program could provide the necessary information about the lattice temperature and the free carrier concentration distribution at different time instants after excitation. Based on these data, I could describe the Ψ and Δ changes of the silicon sample during the excitation.

4. Theses

T1. I developed an evaluation method for Raman-spectroscopic measurements which enables the determination of the Raman-signal of thin layers in such cases when the Raman-spectra of the substrate and layer overlap. The evaluation method is based on a fitting procedure allowing the separation of the Raman-signal of the layer and the substrate. The method does not only provide the spectrum of the layer, but it also results a parameter related to the absorption and thickness of the film, which I named as weight factor. To validate the method, I performed Raman-spectroscopic measurements on pulsed laser treated samples and measured the absorption and thickness of the treated samples using ellipsometry. The excellent correlation I found between the weight factor and the ellipsometric data approved the correctness of the evaluation method.

T2. I modified glassy carbon surfaces with sub-picosecond and nanosecond pulse duration excimer lasers and nanosecond pulse duration Nd:YAG laser. The Raman-spectroscopic measurements revealed that a thin layer is formed on the top of the treated samples. I used the evaluation method, which I demonstrated in my previous work, to determine the Raman-spectra of the surface layer. Based on the retrieved Raman-spectra, I demonstrated that the structure of the modified layer is close to the nanocrystalline graphite and with increasing volumetric fluence the layer is getting more amorphous. I measured the thickness of the modified layer with spectroscopic ellipsometry. In the case of the excimer laser treatment I found that the thickness increased with increasing volumetric fluence, but in case of the Nd:YAG laser treatment the thickness decreased. I attributed this different tendency to the different excitation processes occurring during the treatment with different photon energies. Based on electronmicroscope images, I proved that the surface of the Nd:YAG laser treated samples was melted, resulting in thermal ablation, against the photoablation expected to take place for the excimer laser treatment.

T3. I demonstrated periodic surface structure (LIPSS) formation on glassy carbon surfaces with ultrafast, Ti:Sapphire and dye-KrF laser treatment. In the case of Ti:Sapphire treatment LIPSS was orientated perpendicularly to the laser polarization. When varying the pulse duration, the periodicity of the structures changed between λ and $\lambda/5$. Based on electronmicroscope images, I concluded that longer pulse duration and larger local fluence is necessary for the formation of larger periodic structures. With Raman-spectroscopic measurements I showed that LIPSS is formed in a thin surface layer of which thickness is higher for the structures with higher periodicity. Based on these results, I concluded that structures with larger periodicity are formed when the top layer is melted during the process, which allows the appearance of capillary waves due to the interference of the incoming and the scattered light. For the dye-KrF laser treatment, I also showed LIPSS formation with periodicity close to the wavelength and $\lambda/(3.5)$. However, the orientation of the larger periodic structures was parallel with the polarization of the laser pulses in this case.

T4. I designed and built an imaging null-ellipsometer which works in pump-probe arrangement, with the purpose of measuring the transient optical changes of materials. I elaborated a measurement method to determine the accurate ellipsometric angles. When applying the method, an intensity map is recorded by systematically changing the angles of the polarizer and analyzer at fixed compensator angle. After fitting the maps, the ellipsometric angles can be determined. I validated the method and the setup using thermally grown SiO_2 samples.

T5. I performed pump-probe null-ellipsometric measurements on Si wafers. For the experiments I used sub-picosecond pump (λ = 248 nm) and probe (λ = 496 nm) beams and I determined the transient changes of the Ψ and Δ angles between 2 and 146 ps delays. For small delays the Ψ angle showed slight increase while the Δ angle decreased slightly. The Ψ reached the maximum value at 15 ps delay, and the

minimum value of the Δ was reached at 25 ps delay. At higher delays the ellipsometric angles returned to the original values. To model the changes of the ellipsometric angles, I programed a two temperature model, which provided information about the lattice temperature and the free carrier concentration distribution during the excitation. When applying these distribution in an ellipsometric model I could find good agreement between the model and the ellipsometric angles at 17 mJ/cm^2 fluence and with 4 ps relaxation time.

5. Publications related to the theses

[T1] **J. Csontos**, Z. Pápa, A. Gárdián, M. Füle, J. Budai, Z. Toth: *Spectroscopic ellipsometric and Raman spectroscopic investigations of pulsed laser treated glassy carbon surfaces*, Appl. Surf. Sci. 336 (2015) 343-348

[T2] **J. Csontos**, Z. Toth, Z. Pápa, J. Budai, B. Kiss, A. Börzsönyi, M. Füle: *Periodic structure formation and surface morphology evolution of glassy carbon surfaces applying 35-fs–200-ps laser pulses*, Appl. Phys. A 122 (2016) 593

[T3] **J. Csontos**, Z. Toth, Z. Pápa, B. Gábor, M. Füle, B. Gilicze, J. Budai: *Ultrafast in-situ null-ellipsometry for studying pulsed laser - Silicon surface interactions*, Appl. Surf. Sci. 421 (2017) 325-330

6. Other publications

[4] Z. Pápa, J. Budai, I. Hanyecz, **J. Csontos**, Z. Toth: *Depolarization correction method for ellipsometric measurements of large grain size zinc-oxide films,* Thin Solid Films 571 (2014) 562-566

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