Gold nano-wires and nano-layers at laser-induced nano-ripples on PET

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1. Introduction

Surface modification and structure formation at polymers are an important application of UV-radiation. Polymer surfaces can be modified, e.g. by deep UV-irradiation of an excimer lamp [1,2], light emitted by an atmospheric pressure plasma source [3,4] or by excimer laser beams [5–8].

Laser-induced modification can lead to the coloration of polymers [9]. Laser-pattern is employed for the production of planar nanostructures on polymer surfaces, it is possible to improve the parameters in polymer electronic memories [11]. Laser surface texturing is used also for the design and manufacturing of biomedical surfaces [12]. Surface modification of PET with excimer laser irradiation can influence the physical and biological properties used for medical devices [13]. Periodic surface structures can regulate the cellular adhesion behaviors on PET substrate [14]. Also excimer laser modification of polymer surfaces without pattern formation can influence adhesion, proliferation, morphology, viability or migration of cells seeded at such modified samples [15–18].

Surface exposure of polymer to plasma [19] or laser beam [20] can also affect the adhesion of consecutively deposited metal layer. The influence on adhesion of surface modification can be due to the change of surface morphology or chemistry and creation of oxygen atoms containing groups on polymer’s surface [19–22]. Nanostructured materials and metal nano-layers are being extensively studied in the field of microelectronics, such as sensors, actuators, photovoltaics, and polymeric displays [23–25].

Several studies have shown that the illumination of polymers by polarized UV laser beam induces self-organized ripple structure formation within a narrow fluence range well below the ablation threshold [26–30]. The properties of these periodic structures have been frequently studied since the first report about them [31]. The smallest features on polymers reported so far produced by our group by 157 nm F\textsubscript{2} laser irradiation of polyethyleneterephthalate [32].

The period of the ripples depends on the laser wavelength and on the angle of incidence of the radiation, and their direction is related to the direction of the laser beam polarization [33]. The spacing of the structures can be described by the relation:

\[ \Lambda = \frac{\lambda}{(n - \sin \theta)} \]  

**ABSTRACT**

Gold nano-layers were deposited onto laser irradiated polyethyleneterephthalate (PET) surfaces. For irradiation, we used the linearly polarized light of a pulsed 248 nm KrF and 157 nm F\textsubscript{2} laser, respectively. In a certain range of irradiation parameters, the irradiation resulted in the formation of coherent ripple patterns with a lateral periodicity in the order of the wavelength of the laser light and with a corrugation height of several 10 nm. The deposited layers were then prepared by sputtering. The layers were analyzed by atomic force microscopy (AFM), focused ion beam (FIB) cuts, scanning electron microscopy (SEM), and angular resolved X-ray induced photoelectron spectroscopy (ARXPS). Gold sputtering on KrF laser irradiated PET led to the formation of separated “nano-wires” at the ridges of the nano-patterns and not to a continuous metal layer, as we obtained in case of gold sputtering onto F\textsubscript{2} irradiated PET. The results of the XPS analysis indicated, that the KrF irradiation caused degradation on the ridge of the ripples, whereas no noticeable degradation occurred for F\textsubscript{2} laser treatment. We attribute the different growth mechanisms of the deposited gold layers mainly to the difference in surface chemical composition of laser irradiated PET with the two different lasers employed.

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where $\lambda$ is the lateral periodicity of the structures, $\lambda$ is the wavelength of the excitation laser light, $n$ is the effective refractive index of the material and $\theta$ is the angle of incidence of the laser beam [33].

These structures develop on the original material surface having small roughness, as a result of treatment with one laser beam with a uniform intensity distribution. It is known that the interference between the incoming and the surface scattered waves plays an important role in the structure formation [34]. The interference causes an inhomogeneous intensity distribution, which together with a feedback mechanism results in the enhancement of the modulation depth [28]. However, the whole mechanism is complex and different processes have been reported as responsible for ripple formation [32,35–38] such as thermal and non-thermal scissoring of polymer chains, amorphization of crystalline domains, local surface melting, photo-oxidation and material transport.

In this work we investigated the properties of gold coatings sputtered onto PET with ripples induced by $F_2$ and KrF laser irradiation, respectively. The surface morphology of the polymer surfaces with and without Au was assessed by atomic force microscopy (AFM) and by focused ion beam (FIB) cuts. The chemical composition of the surfaces was analyzed by angular resolved X-ray induced photoelectron spectroscopy (ARXPS). The differences in the metal layer morphology were attributed to the different morphologies of the ripples and the different chemical compositions of the surface after the laser treatment with the two different laser wavelengths.

2. Experimental

2.1. Polymer modification

For the experiments, we used oriented polyethyleneterephthalate (PET) foils with a thickness of 50 $\mu$m ($T_m \sim 260^\circ C$, $T_g \sim 80^\circ C$, supplied by Goodfellow Ltd., England). For irradiation of the PET samples we employed either the $F_2$ laser (Lambda Physik LPF 202, wavelength of 157 nm, pulse duration of 15 ns) or the KrF laser (Lambda Physik Compex, wavelength 248 nm, pulse duration of 20–40 ns). For the irradiation with the $F_2$ laser, the light was polarized linearly with a MgF$_2$ prism. For homogeneous illumination of the samples we used only the central part of the beam profile by means of an aperture (10 mm $\times$ 3.5 mm). We performed the irradiation at fluences well below the ablation threshold of PET at 157 nm (29.6 mJ/cm$^2$ [32]). The samples were mounted onto a translation stage and scanned at a speed of 14 $\mu$m/s. At a repetition rate of the laser of 11 Hz, each of the PET surface was irradiated with 5600 pulses. We carried out the experiments in a flow box purged with nitrogen at a pressure of 110 kPa. For the experiments with 6000 pulses per area. The experiments with the KrF laser were done in a flow box purged with nitrogen at a pressure of 110 kPa. For the experiments with the KrF laser, the light was polarized linearly with a MgF$_2$ prism. For homogeneous illumination of the samples we used again an aperture of 10 mm $\times$ 5 mm. The irradiation fluences were chosen well below the ablation threshold of PET at 248 nm (40 mJ/cm$^2$ [39]). The samples were mounted onto translation stage and scanned in a fixed position. PET samples were irradiated with 6000 pulses per area. The experiments with the KrF laser were done in ambient atmosphere.

2.2. Gold deposition

We deposited the gold layers from a gold target (99.999%) by diode sputtering (BAL-TEC SCD 050 equipment) onto pristine and irradiated PET. The time between the laser treatment of the polymer foils and the deposition of Au layers was several weeks, typically. The deposition was performed at room temperature with a deposition time 300 s and a current of 20 mA for $F_2$ laser and a deposition time 600 s (40 mA) for KrF laser, a total argon pressure of about 4 Pa, and an electrode distance of 50 mm. For control, the thicknesses of the gold layers were measured by means of an AFM on pieces of Si (1 1 1), which were coated simultaneously in the same set-up.

2.3. Analytical methods

The surface morphology was examined using an AFM. The AFM images were taken under ambient conditions on a Digital Instruments CP II set-up. The samples with an area of about 1 cm$^2$ were mounted on sample holders using double-sided adhesive tape. We used a small area scanner allowing to images an area up to 5 $\mu$m$^2$. The ‘tapping mode’ was chosen for the measurements to minimize damage to the samples surfaces. A Veeco oxide-sharpened P-doped silicon probe RTESPA-CP attached to a flexible micro-cantilever was used near its resonant frequency of 300 kHz. The scans were acquired at ambient atmosphere at a line scanning rate of 1 Hz. All surfaces were characterized both quantitatively by measuring the mean roughness ($R_m$) and semi-qualitatively via surface view plots. $R_m$ represents the arithmetic average of the deviations from the center plane of the sample. Four areas of each sample were scanned in order to obtain representative data.

FIB cuts were prepared with an adapted scanning electron microscope (FIB-SEM, 1540XB CrossBeam, Zeiss). The FIB cuts were made with a Ga ion beam at a current between 2 nA and 200 pA. After cutting with a current of 2 nA, the surfaces were polished at the lower ion current of 200 pA. The polishing procedure was performed to clean and flatten the investigated surfaces. Our soft polymer samples show a pronounced roughness due to interaction with the cutting ion beam, which can be only partially removed by the polishing procedure. In general, the quality of the polished cuts of the polymer samples was worse than for cuts of hard solid samples, as for instance polished cuts of SiO$_2$ films at Si surfaces shown in ref. [40]. The direct measurement of the layer thickness was done with a second scanning electron microscope (JSM-7500F, JEOL). The SEM images were taken under an angle of 54°. The influence of the investigation angle on the thickness measurement was automatically corrected by the SEM software. The averages thicknesses of the gold layers were similar to those obtained with on the control Si pieces mentioned above.

An Omicron Nanotechnology ESCAProbeP spectrometer was used to measure ARXPS spectra [38]. The analyzed areas had dimensions of 2 $\times$ 3 mm$^2$. The X-ray source provided monochromatic radiation of 1486.7 eV. The spectra were measured stepwise with a step in the binding energy of 0.05 eV at each of the six different sample positions with respect to the detector axis, which translated into different angles ranging from 0° to 80°. The spectra evaluation was carried out by using CasaXPS software. The composition of the various elements is given in at % disregarding hydrogen, which cannot be assessed by XPS.

3. Results and discussion

In a previous work, we showed that for $F_2$ laser irradiation with several thousand pulses a periodic ripple structure is formed at PET surface for the fluence range from 3.80 to 4.70 mJ/cm$^2$ [32]. In the case of KrF laser, periodic ripple structures were produced at the laser fluence between 4.2 and 18.8 mJ cm$^{-2}$. The laser-induced ripples had a fluence-independent width $\lambda$, which is given by formula (1), while the height of the structures differed and strongly depended on laser fluence employed. We performed our further experiments on samples with the most pronounced changes in surface morphology, i.e. with the highest ripple structures. In Fig. 1, we compare the morphology of $F_2$ (laser fluence 4.4 mJ/cm$^2$) and...
KrF (6.6 mJ/cm²) irradiated samples. The ripples formed under KrF laser exposure have larger width and height in comparison to the use of the F₂ laser. The periodicity of ripples, \( \Lambda \), was approx. 208 nm in case of KrF laser irradiation, while in the case of F₂ laser irradiation we obtained approx. 140 nm. The height of the ripple structure (top–bottom) was about 100 nm for KrF laser irradiated sample and about 15 nm for the F₂ laser irradiation.

We sputtered gold layers onto the ripple structures and studied their morphology. For comparison of the gold growth mechanism, we kept the gold-to-ripple height ratio constant. F₂ irradiated samples were sputtered with 50 nm thick Au layer, whereas KrF irradiated samples were covered with 200 nm thick Au layer. Fig. 1 shows morphology of sputtered gold layers on laser-induced ripples structures for both laser wavelengths. For both wavelengths, the ripple structure of the PET surface is transferred into the gold layers. The roughness values \( R_a \) were nearly identical for the surface with and without gold coating in both cases. However, for the F₂ laser irradiated samples it seems that the gold coated surface has a more pronounced granular structure than the uncoated ripple structure. Here one has to keep in mind that the AFM images show a convolution of the surface morphology with the geometry of the AFM tip. Therefore, small features and features with a high aspect ratio may not be feasible in the AFM images.

Supplementary to the AFM analysis, the samples were cut by FIB. The FIB cuts were then investigated with the SEM (Fig. 2). The gold sputtered onto the KrF laser-induced ripples is deposited in the form of “nano-wires”, which grow on the ridges of the ripples. The FIB cuts reveal that seems to be gaps between the individual wires and that the metal layer seems not to be continuous. Additionally, a kind of graining seems to be visible along the wires, but the FIB cut images suggest that these grains are connected. The morphology deposited on the F₂ laser-induced ripples is distinctly different. The gold is also deposited in the valleys of the ripple structure (see Fig. 2). The Au layers seem to partially smoothen out the ripple profile. The Au layers in general show cracks but they seem to be continuous and the cracks seem not to be directly related to the ripple pattern.

The chemical composition of the polymer surface can affect the growth morphology of gold layers on polymer surfaces [41]. Therefore, we analyzed KrF and F₂ irradiated PET with the ARXPS.
method [37]. By this method it was shown that the oxygen content in pristine PET is depth dependent, especially in first ten atomic layers [37]. This conclusion is explained by the reorientation of the polar groups in the surface layers and thus the oxygen content may be lower in comparison with theoretical value for pristine PET (29 at.%) [42].

The dependence of the oxygen concentration (at.%) derived by ARXPS on the angle of incidence of the XPS primary beam is shown in Fig. 3 for pristine PET, KrF and F₂ lasers irradiated PET, respectively. For pristine PET the oxygen content decreases from 25.5 at.% for an incidence angle of 0° to 19.5 at.% at an incidence angle of 80°. For F₂ laser irradiation, the oxygen content is about 18 at.% and is slightly decreasing to about 16 at.%, for KrF laser the O content increases from 28.5 to 33 at.%.

Because, the higher angles of incidence comply with smaller penetration depths, we conclude that the oxygen content remains nearly unchanged in the top ca 10 nm of the irradiated PET surface, which can be typically assessed by the XPS analysis. From this we conclude, that the ridges and the valleys of the F₂ laser-induced ripples have nearly similar chemical composition, at least regarding the oxygen content. The oxygen content in F₂ irradiated PET is lower than in pristine PET. While in the case of KrF laser irradiation the oxygen content is higher and towards the surface the oxygen content increases. From this we conclude, that in case of KrF the ridges of the ripple structure contain more oxygen groups than the areas at the valley, which are shielded at higher angles of incidence of the incident X-ray. The oxygen in the ridges is even higher than the oxygen content of pristine PET. This could be due to a thermal degradation (with oxidation) of the polymer at the ripple ridges during the irradiation process. The fact that the F₂ laser treated surface shows a lower oxygen content than the value for pristine PET may be related to orientation of the polar groups with a preferred direction inside the polymer [37,42] or by photochemical scission of the polymer chains in combination with preferential release of CO and CO₂ groups (Norrish type II reaction [43]).

Figs. 4 and 5 show detailed XPS spectra of the carbon C1s and the oxygen O1s for the angles 0° and 80°. The main peak in Fig. 4A at 284.7 eV can be associated to PET “bulk” carbon. Fig. 4B shows C1s spectrum for an incidence angle of angle 80°. The main peak position (a) at 290.1 eV is shifted with respect to a C1s peak in Fig. 4A, since the XPS set-up does not allow full surface charge compensation at these high angles. Here the primary X-ray beam is nearly parallel to the examined surface, thus the information originates from the top of the ridges predominately. While for F₂ laser irradiation mainly one carbon peak is visible in Fig. 4A and B, which associates to “bulk” carbon, the spectra for KrF irradiated samples show pronounced side peaks. The feature (b) in Fig. 4B has a similar position as “conductive” carbon originating from conjugated carbon bonds. It may be former from degradation of the polymer especially at the ridges of the KrF laser ripple structures. Fig. 5 shows detailed XPS spectra of the oxygen O1s peak of PET irradiated by a KrF or F₂ laser (incidence angles 0° (A) and 80° (B)). For an incidence angle of 0°, both spectra (for KrF and F₂ laser irradiation) are nearly identical, while in Fig. 5B – in the case of KrF laser irradiation – an additional “new” (b) peak is visible. It may also originate from oxygen in degraded polymer, especially on the top of the ripple structure.

Fig. 3. Dependence of the oxygen concentration (at.%) on the angle of incidence of the XPS primary beam for pristine PET (PET) and KrF (PET/KrF) and F₂ lasers (PET/F₂) irradiated PET.

Fig. 4. Carbon C1s XPS spectrum of PET irradiated by KrF and F₂ lasers (incidence angle of primary X-ray beam 0° (A) and 80° (B)). Peak (a) corresponds to PET “bulk” carbon, and peak (b) represents an additional carbon compound.
and peak (b) represents an additional oxygen compound.

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References

4. Conclusion
Krf laser irradiation of PET foils can induce the formation of nano-ripple structures with a periodicity of about 200 nm and a height of about 100 nm. Gold sputtering onto these PET surfaces leads to the formation of gold “nano-wires” at the ridges of the ripple structures. The gold layers seem to be non-continuous, with gaps between neighboring wires. The gold layer morphology is distinctly different for gold sputtered onto F2 laser-induced ripples, which are narrower and considerably shallower than the Krf laser-induced features. Here the layers are continuous showing only irregularly distributed cracks. From the XPS analysis we conclude that in the case of Krf irradiation, the exposure leads to degradation (oxidation) especially at the ridges of the ripple structures with an increased occurrence of oxygen containing groups. We suppose that this altered chemical composition induces an improved metal deposition on the tops of the structures rather than in the valleys between them. Together with shadowing effects, this may be the reason for the formation of gold wires rather than in the valleys between them. Together with shadowing effects, this may be the reason for the formation of gold wires rather than in the valleys between them.

For many of applications of PET, nano-patterned metal features are already frequently used. The gold nano-wires presented here could open up additional new application fields. Examples are or could be small magnetic domains, quantum dots, photonic crystal structures or nano-engineered surfaces for enhanced biocompatibility.

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Fig. 5. Oxygen O1s XPS spectrum of PET irradiated by Krf and F2 lasers (incidence angle of primary X-ray beam 0°.) (A) and 80°. (B). Peak (a) corresponds to PET “bulk” oxygen, and peak (b) represents an additional oxygen compound.