Tailoring of Silver Nanoparticle Size Distributions in Hydrogenated Amorphous Diamond-like Carbon Nanocomposite Thin Films by Direct Femtosecond Laser Interference Patterning

Aušrinė Jurkevičienė, Gerda Klimaitė, Tomas Tamulevičius*, Jacek Fiutowski, Horst-Günter Rubahn, Sigitas Tamulevičius

PhD student Aušrinė Jurkevičienė, Prof. Tomas Tamulevičius, Prof. Sigitas Tamulevičius
Institute of Materials Science, Kaunas University of Technology, K. Baršausko St. 59, LT-51423 Kaunas, Lithuania
E-mail: tomas.tamulevicius@ktu.lt

BSc student Gerda Klimaitė, Prof. Tomas Tamulevičius, Prof. Sigitas Tamulevičius
Department of Physics, Faculty of Mathematics and Natural Sciences, Kaunas University of Technology, Studentu St. 50, LT-51368 Kaunas, Lithuania

Assoc. Prof. Jacek Fiutowski, Prof. Horst Günter Rubahn
Mads Clausen Institute, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark

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Patterning of nanocomposites by conventional lithography processes is problematic due to the different physical properties of matrix and filler. Direct laser interference patterning (DLIP) promises rapid micromachining of virtually any material with sub-wavelength resolution. A control of intense laser light modifies the filler particle size distribution in nanocomposite films. This paper demonstrates DLIP of periodic patterns with pitches of 564 nm and 1306 nm in reactive magnetron sputtered hydrogenated amorphous diamond-like carbon nanocomposite thin films with embedded silver nanoparticles (DLC:Ag). Periodic patterns of regularly repeating areas with modified size distributions of silver nanoparticles are obtained by a variation of fluences and number of pulses by second harmonic of Yb:KGW femtosecond laser. Depending on the silver content in nanocomposite films, nanoparticle size distributions are either bimodal (for 14.1 at.% Ag containing films) or unimodal (7.9 at.%) with effective average diameters shifting from 13 nm to 69 nm, depending on the laser processing parameters. The importance of localized surface plasmon absorption and
localized field enhancement at the DLC–Ag interface for lowering the ablation threshold of DLC:Ag nanocomposites to below 6 mJcm$^{-2}$ at 1000 pulses is demonstrated. This is at least 4 times lower than the threshold for pure DLC obtained employing the same DLIP setup.

1. Introduction

The ability to manipulate light by organized nanoscale structures led to the development of the field of nano-optics. Additionally, various nanopatterns imposed in free-electron metal films are attractive due to their plasmonic properties.$^{[1]}$ The interaction between light and nanoparticles possessing localized surface plasmon resonances (LSPR) has been extensively studied for a vast range of applications such as optical polarizers, filters, switches, sensors, surface enhanced Raman spectroscopy (SERS), and so forth.$^{[2,3]}$ Silver is one of the most widely used metals for plasmonic applications.$^{[4]}$ In addition, silver nanoparticles have antibacterial properties and can be utilized for biomedical applications like sunscreens or plasters.$^{[5,6]}$ However, silver is rapidly oxidizing material under ambient conditions.$^{[4]}$ Oxidation can be avoided without losing plasmonic properties by placing silver nanoparticles in a matrix of passivating material.$^{[7,8]}$ For this purpose, amorphous diamond-like carbon (DLC) has been widely applied, because noble metals stay in the metallic phase when introduced into DLC, they do not form nitrides and carbides.$^{[9]}$ Diamond-like carbon describes a broad term referring to several forms of amorphous carbon (hydrogenated (a-C:H) and hydrogen-free (a-C))$^{[10]}$ and can be applied in biosensors, electronics, protective coatings for mechanical and medical components, and so forth.$^{[11]}$ Characteristic disadvantages of DLC (poor thermal stability, high internal stresses) can be overcome by introducing metal nanoparticles to the film.$^{[12]}$ By combining the best properties of matrix and filler (in our case, DLC and Ag nanoparticles, respectively), the resulting nanocomposite films have promising applications in multidisciplinary fields of mechanics, optics and photonics, electronics, and medicine.$^{[9]}$

The optical properties of plasmonic material-based nanocomposites can be tuned by changing the size distribution of the nanoparticles and the refractive index of the surrounding matrix.$^{[7]}$ Such
nanocomposites can be formed by evaporation, sputtering, ion implantation, chemical reduction, and other techniques. There are methods for controlling the filler size distribution during the deposition of the films, but they are valid only to a limited extent and lack spatial control. One of the ways to tailor the size distribution of nanoparticles of already deposited nanocomposite films is to irradiate them with ultrashort laser pulses. Applying close to Gaussian distribution tightly focused laser beams it is possible to reach close to half-wavelength resolution by employing direct laser interference patterning (DLIP), which is a highly reproducible and easily scalable micromachining method.

Despite that laser ablation mechanisms of various DLC films were quite extensively investigated, studies on laser ablation and laser induced effects of metal containing DLC films are still very limited. Depending on the energy densities applied, carbonaceous films are usually ablated, delaminated or graphitized, while the nanoparticles can melt, coalesce or fragment. In order to achieve a high patterning accuracy and to prevent melting, lower laser repetition rates are preferred. Also, shorter pulse durations (i.e., femtosecond pulses) are desirable for improved accuracy, reduction of the heated zone and absence of plasma shielding. One of the most important parameters in laser patterning is the ablation threshold: the ablation occurs solely when the incident laser irradiation energy surpasses the threshold, which, in turn, depends on the combination of laser properties and the chosen material. Moreover, the ablation threshold of nanocomposites is different than that for its separate components. The ablation threshold can be reduced by applying multiple laser pulses at certain repetition rates, which is referred to as incubation effect. When the material is irradiated with fluence levels below the ablation threshold, other types of surface modifications, defined as “gentle ablation”, “melting threshold”, “visible damage threshold”, and so forth, are possible. Similarly, the threshold, which is required to impose the pattern to the thin film by its modification, can be termed “patterning threshold”.

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Among many applications, sub-wavelength pitch periodic structures in DLC:Ag nanocomposite films can be applied for refractive index sensing.[28] The arrangement of nanoparticles in diffraction grating-like periodic structures modifies the effective refractive index and alters the diffraction efficiency of the periodic structure, which is required to be as high as possible for most optical applications, especially for increased sensitivity of plasmonic diffractive optical sensors and resonator structures.[29,30] Tailored nanostructures are also very promising materials for the enhancement of the efficiency of solar cells via light trapping and plasmonic scattering mechanisms.[31,32]

In the present work we demonstrate an application of DLIP for the fabrication of one-dimensional (1D) periodic structures with sub-wavelength features in amorphous hydrogenated diamond-like carbon (a-C:H, further in the text DLC) nanocomposite thin films with embedded silver nanoparticles (DLC:Ag, 7.9-14.1 at.% Ag). We have varied the energy densities (laser fluence $\Phi = 1–145 \text{ mJcm}^{-2}$, number of pulses $N = 1000–125,000$) of Yb:KGW fs-laser second harmonic irradiation in order to determine ablation and patterning thresholds and have analyzed incubation effects together with the resulting modifications of silver nanoparticle effective diameter size distributions. The proposed synergistic patterning mechanism of nanocomposite thin films was supported by DLIP analyses of separate nanocomposite film components, namely, DLC and silver thin films. We demonstrate the importance of localized surface plasmon resonance governed absorption and localized field enhancement at the DLC–Ag interface on the ablation threshold of DLC:Ag nanocomposites.
2. Results and Discussion

2.1. Analysis of the Pristine Thin Films

Prior to the laser ablation experiments, the optical properties and structures of the pristine films were investigated. From X-ray energy dispersion spectroscopy (EDS) it was determined that the silver atomic concentration in reactive magnetron sputtered DLC:Ag samples was 7.9 at.% (sample DLC:Ag-8) and 14.1 at.% (sample DLC:Ag-14). More information about the composition can be found in Table S1 in Supporting Information. Additionally, pure sputtered a-C:H (sample DLC-0) and evaporated silver (sample Ag-100) thin films were prepared. Figure 1 depicts absorbance (a) and Raman scattering (b) spectra of pristine a-C:H having no silver nanoparticles (DLC-0) and DLC:Ag thin films of different Ag content as well as the surface morphology of pristine films obtained using scanning electron (SEM) and helium ion (HIM) microscopes (c). The nanoparticle number density in pristine samples was 920 μm$^{-2}$ (DLC:Ag-8) and 336 μm$^{-2}$ (DLC:Ag-14) as determined from micrographs using image analysis software.
Figure 1. Analysis of pristine a-C:H (DLC-0) and DLC:Ag thin film properties: (a) normalized absorbance of a-C:H and DLC:Ag samples at the visible light wavelength range (blue solid line – DLC-0, red dot-dashed line – DLC:Ag-8, green dashed line – DLC:Ag-14). Vertical dashed line indicates 515 nm wavelength used in DLIP experiments. (b) Raman scattering spectra of samples on quartz substrates with fitted peaks. (c) SEM (DLC-0 – HIM) micrographs of pristine films. Mark size – 300 nm.

The nanocomposite samples DLC:Ag-8 and DLC:Ag-14 show broad absorption peaks (Figure 1a) centered at around 390 nm and 530 nm, respectively, that can be addressed to LSPR. Additionally, DLC:Ag-14 has a shoulder in the absorbance spectrum at around 380 nm. In contrast, the absorbance spectrum of the DLC-0 sample is mostly monotonous, with a decreasing absorbance towards longer wavelengths and transparency starting from 600 nm.

The Raman scattering spectrum (Figure 1b) of the DLC-0 sample is consistent with similar spectra reported in other papers describing amorphous hydrogenated diamond-like carbon films (a-C:H). The peak at 1535 cm\(^{-1}\) in the DLC-0 Raman scattering spectrum and the shoulder
at around 1400 cm\(^{-1}\) are commonly attributed to G peak (bond stretching vibration of all pairs of sp\(^2\) carbon atoms) and D peak (shoulder at lower wavenumbers related to the breathing vibration modes of sp\(^2\) bonded rings). Usually ratio of these two peaks is used to characterize the ratio of sp\(^3\) to sp\(^2\) bonds in DLC.\(^{[35]}\) The increase in D peak intensity and the appearance of additional Raman scattering peaks upon introduction of silver nanoparticles in the a-C:H matrix could be associated with the SERS effect. Š. Meškinis et al.\(^{[33]}\) reported a clearly pronounced SERS effect for nanocomposite DLC:Ag thin films containing 11.3 at.% silver, which is consistent with our findings. The Raman peaks and the absorption spectra of sample DLC-0 are typical for a-C:H films synthesized from C\(_2\)H\(_2\) precursor.\(^{[36]}\) The peak at 932 cm\(^{-1}\) could be attributed to SiC bond and is common for thin films on quartz substrate.\(^{[37,38]}\) 1245 cm\(^{-1}\) shoulder is related to transpolyacetylene (TPA) and its strength increases with increasing hydrogen content in a-C:H film.\(^{[39–41]}\) The peaks above 1700 cm\(^{-1}\) are sidebands associated with precursors used in the deposition process and indicate the existence of carbon chains of different lengths (C-chains).\(^{[42,43]}\)
2.2. Analysis of Laser Imposed Periodic Lines

The complex analysis was performed on DLIP affected DLC:Ag samples, which is summarized in Figure 2: the widths $W$ of laser affected lines and their centers $x_i, x_j$ were determined and the Ag particles were counted as well with their centers $C_i$ falling within the widths $W$.

**Figure 2.** Methodology of nanoparticles size distribution analysis after DLIP processing illustrated for the DLC:Ag-14 sample on a silicon substrate ablated with $\Lambda = 564$ nm pitch interference fringes (a) and two different laser fluence levels of 6 mJcm$^{-2}$ (b) and 11 mJcm$^{-2}$ (c) using 64k pulses. Here: $I$ – laser intensity, $I_{th}$ – ablation or patterning threshold intensity, $x_i, x_j$ – centers of adjacent irradiated lines, $W$ – width of modified line, $C_i(x,y)$ – center of the particle and its coordinates. The SEM micrographs (left side of (b) and (c)) gradually transit into black and white contrast images (right side) used for the particles size analysis. Red contours outline the areas of the nanoparticles.
Typical DLIP processing results of DLC:Ag-8 films on a silicon substrate with their corresponding fast Fourier transformations (FFTs) are depicted in Figure 3. More illustrations of resulting periodic structures in DLC-0, DLC:Ag, and Ag thin films on different substrates of 564 nm and 1306 nm pitches obtained under different laser processing conditions and used in the nanoparticle analysis can be found in the Supporting Information (Figure S1–S10). In the case of DLC:Ag, structures patterned using 1 and 3 mJ cm\(^{-2}\) were excluded from the analysis due to low contrast of lines or because no lines were observed in the micrographs at all, which was confirmed by the FFT analysis. The same is valid for the excluded images of DLC-0 films processed with lower energy densities. DLC:Ag films in Figure 3 show clear periodic patterns in the SEM micrographs. This assumption is backed-up by well-expressed peaks (bright pixels) in the FFTs (Figure 3, bottom). In some HIM micrographs, the pattern of DLC-0 does not demonstrate a well-defined contrast of the line edges, but the pattern is still clearly visible, which is also evident in the FFTs (not shown here). Samples of pure silver were irradiated with the elevated laser fluence as compared with DLC:Ag, but no neat grating throughout the laser illuminated area was achieved. At the highest fluence of 145 mJ cm\(^{-2}\), the film was perforated in the center and the substrate was patterned instead. Some micrographs of patterns in Ag-100 can be found in Supporting Information Figure S10.

![Figure 3](image)

**Figure 3.** SEM micrographs of the DLC:Ag-8 thin film on a silicon substrate, patterned with DLIP of pitch \(\Lambda = 564\) nm, \(\Phi = 17\) mJ cm\(^{-2}\) and different number of pulses: 1k (a); 8k (b); 27k (c); 64k (d); 125k (e). The size of the scale bar is equal to 1 \(\mu\)m. The insets are zoomed in view of laser affected line (here the arrow marks the width \(W\) of this line) with mark size of 200 nm. Images at the bottom show FFTs of corresponding micrographs.

The laser affected line width \(W\) dependences on the number of applied pulses \(N\) for DLC:Ag-8 and DLC:Ag-14 samples for both pitches \(\Lambda\) (564 nm, 1306 nm) and three different laser fluences \(\Phi\).
(6 mJcm\(^{-2}\), 11 mJcm\(^{-2}\), 17 mJcm\(^{-2}\)) are summarized in **Figure 4**. One can see that increasing the number of applied pulses, the laser modified line width tends to increase only to some extent and then reaches saturation, approaching the value close to the pitch.

**Figure 4.** Dependence of the laser affected line width \(W\) on the number of pulses \(N\) in DLC:Ag-8 (blue) and DLC:Ag-14 (red) on silicon (full symbols) and quartz (empty symbols) substrates for \(\Lambda = 564\) nm (a–c) and \(\Lambda = 1306\) nm (d–f) at laser fluences of 6 mJcm\(^{-2}\) (a, d), 11 mJcm\(^{-2}\) (b, e) and 17 mJcm\(^{-2}\) (c, f). Lines are guides to the eyes.

As demonstrated in Figure 4, the patterning threshold could potentially be determined from the relation of the laser irradiated line width and laser fluence. However, this method is troublesome due to uncertainties of the edges between ridge and groove in the periodic patterns. Because the spatial distribution of interference fringe intensity is sinusoidal (see Figure 2a), only those parts corresponding to interference maxima, which reach the sample surface, have an intensity above the threshold. When the laser intensity is increased, a wider area of incident radiation is above the threshold, which results in the increase of width of the irradiated line. In case of in-phase interfering beams, the interference minimum should always stay at zero intensity, thus never reaching the intensity above the patterning threshold and limiting the maximum width of irradiated line.

Considering only the sharpest micrographs, the data set of width \(W\) was too small to make confident conclusions about the patterning threshold of DLC:Ag. Nonetheless, from Figure 4 it is still apparent that the width of the laser irradiated line is increased by either increasing number of pulses...
or laser fluence. Up to irradiation by 27k pulses, the width of the laser affected line increases up to 2 times, while further increasing number of pulses width additionally rises only up to 1.2 times.

Similar results were obtained for nickel foil ablation with the same setup, where only narrow ridges remained at the maximum energy densities applied, and the Gaussian intensity variation within the irradiated spot was stated to be visible as height modulation.\textsuperscript{[44]}

2.3. Laser Ablation Thresholds of DLC:Ag and DLC

The line width analysis of DLC:Ag films presented in Figure 4 already indicates the relation of the laser fluence on the linear dimension of the modified line, but the classical ablation threshold determination approach (see Equation 1 in Materials and Methods section) is suitable only for Gaussian shaped beams and thus it could not be applied for determination of ablation threshold in this case, where the laser intensity distribution was sinusoidal. Nevertheless, the DLIP threshold for DLC:Ag samples could be approximately determined based on an SEM/HIM micrographs analysis obtained under different laser processing conditions (as seen in Figure S2–S9 in Supplementary Information) following the presence of the periodic line contrast in the micrographs and diffraction orders in their corresponding FFTs.

The ablation threshold of pure a-C:H films (DLC-0) was obtained using classical approach from the whole DLIP spot analysis (Figure 5a), because whole irradiated spots can be approximated into a Gaussian shape. The analyzed spots in DLC-0 films were imposed at wider fluence ranges as compared with the DLC:Ag samples. The resulting spot diameter dependencies on applied laser fluence are depicted in Figure 5b, where the threshold value is obtained from the intersection of fitted line with \( x \) (fluence) axis. From the latter results, the clear linear trend of decreasing threshold \( \Phi_{th} \) with increasing number of pulses \( N \) was determined (Figure 5c), which was used for determination of single pulse laser ablation threshold for DLC-0 by extrapolating from the intersection with the \( y \) (fluence threshold) axis.
Figure 5. DLIP threshold determination for the DLC-0 sample. (a) Optical microscope images of different magnification showcasing laser processing results of a-C:H films on quartz substrate after irradiation with moderate ($\Phi = 52 \text{ mJcm}^{-2}, N = 1k$) (i, ii) and high ($\Phi = 145 \text{ mJcm}^{-2}, N = 125k$) (iii, iv) energy densities. The encircled areas were used for the threshold determination. Scale bars are $100 \mu \text{m}$ (i, iii) and $15 \mu \text{m}$ (ii, iv). (b) Spot diameter $D$ dependence on the laser fluence $\Phi$ at different number of pulses (black squares – 1k, red circles – 8k, green up-triangles – 27k, blue down-triangles – 64k, orange diamonds – 125k) for a-C:H films on quartz (top) and silicon (bottom) substrates. (c) Threshold fluence $\Phi_{th}$ dependence on number of laser pulses $N$ (black squares – on quartz substrate, red circles – on silicon substrate). Lines in (b) and (c) are linear fits to the data.

The approximate ablation threshold values for DLC:Ag samples as well as the ones obtained for a-C:H using the classical approach (Figure 5) are summarized in Table 1. Patterning of Ag-100 sample was not well defined, thus it was assumed that the applied laser fluence was not high enough to achieve ablation.
The incubation effect, which is typical for laser irradiation with multiple pulses, effectively lowered the ablation threshold. For a-C:H, where the full spot analysis was feasible, it was obtained that incubation lowered the ablation threshold up to 8 times (comparing single pulse and 125k pulses, Table 1). F. Di Niso et al. state that 25k pulses lowers the ablation threshold up to 4 times.\textsuperscript{[21]} This is consistent with our findings (~5 times at 27k pulses), even though the analyzed materials are different (stainless steel vs. a-C:H). The decreased ablation thresholds are explained by the sample surface modifications and lowering of the reflectivity caused by repetitive laser pulses.\textsuperscript{[22]} The incubation effect was also noticed indirectly for nanocomposites from the linewidth analysis of the ablated DLC:Ag thin films (Figure 4), where the laser processed lines got broader by applying greater number of pulses.

Even though the DLC:Ag ablation threshold could not be determined using the same technique as for a-C:H, it was still possible to determine the laser fluence at which the periodic pattern appears (from FFT images as shown in Figure 3). In such a case, it was determined that adding silver nanoparticles to a-C:H effectively lowers the threshold at least 4 times when 1k pulses are applied and this value can be almost 25 times lower by using 125k pulses compared with pure a-C:H film.

Notably, a lower silver content (7.9 at.\%) lowered the fluence more than a higher content (14.1 at.\%) and this difference can be up to a factor of 2 at 1k pulses. Lowering of the DLIP patterning threshold of DLC:Ag samples and reshaping of silver nanoparticles is likely to be due to the synergistic effects of effective light absorption in silver nanoparticles governed by the LSPR.

\textbf{Table 1. Laser threshold fluence \(\Phi_{\text{th}}\) values for investigated thin films as determined from the spot size analysis (DLC-0) and analysis of FFTs of SEM micrographs (DLC:Ag-8, DLC:Ag-14, Ag-100) compared to the ones available in literature.}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Threshold fluence (\Phi_{\text{th}}) [mJ/cm(^2)] at a certain number of pulses (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>DLC:Ag-8</td>
<td>–</td>
</tr>
<tr>
<td>DLC:Ag-14</td>
<td>–</td>
</tr>
<tr>
<td>DLC-0\textsuperscript{a}</td>
<td>148 / 156</td>
</tr>
<tr>
<td>Ag-100</td>
<td>–</td>
</tr>
</tbody>
</table>

In references:
- a-C:H: 160 (800 nm, 150 fs);\textsuperscript{[16]} 243–251 (800 nm, 120 fs, \(N = 1\))\textsuperscript{[17]}
- Ag: 1500 (800 nm, 100 fs, \(N = 1\));\textsuperscript{[18]} 820 (248 nm, 23 ns, \(N = 1\));\textsuperscript{[47]} 170–1400 (515 nm, 200 fs, \(N = 1\), depending on the numerical aperture)\textsuperscript{[37]}

\textsuperscript{a}Lower values correspond to DLC-0 on silicon, while higher – on quartz substrate. For the rest of the samples same values are valid for both of the substrates. The threshold of a single pulse was possible to determine only for DLC-0.
and field enhancement phenomena taking part at the silver–a-C:H interface under intense light irradiation. A. Stalmashonak et al. obtained similar results and addressed them to the electric field exceeding the breakdown of the surrounding material that results in the formation of a high-density electron plasma in the vicinity of metal particles.[48]

By comparing the Ag ablation threshold values determined by other authors,[45–47] as seen in Table 1, and having in mind the maximum applied laser fluence investigated in our experiments, one can see that it was lower than any of the reported ablation threshold values, which supports the lack of a predominant periodic structure in the Ag-100 sample and delamination of the thin film. The latter could be addressed to the stresses and shockwaves generated by femtosecond laser irradiation, which create disruptions in the interface of film and substrate, and can cause delamination of thin metal films as stated by L. Gallais et al.[49] This effect can already be caused by a single pulse irradiation at higher fluences and thus subsequent pulses do not contribute to the ablation or patterning of silver thin film, but rather of the substrate, which was observed at our experiments.

2.4. Laser Processing Effect on the Nanoparticle Size Distribution

The image analysis software was used to determine the sizes of nanoparticles in DLC:Ag samples. The histograms of effective nanoparticle diameter distributions of pristine and laser processed DLC:Ag-8 and DLC:Ag-14 samples after irradiation at 11 mJcm\(^{-2}\) are showcased in Figure 6a and c, respectively. The bin size for the diameter in the histograms was chosen to be 5 nm. \(P\) represents a percentage of particles from total number of particles in the investigated sample in specific bins. The initial particle distribution of pristine DLC:Ag-14 (in the histograms of Figure 6c it is noted as \(N = 0\), i.e., zero number of pulses) is bimodal with 17 nm and 46 nm central diameters \(x_c\). As seen from Figure 6d, bimodality is maintained only at lower laser fluence (6 mJcm\(^{-2}\)). At moderate fluence (11 mJcm\(^{-2}\)) it is maintained only within low number of applied pulses (1k-8k). From \(N = 64k\) at \(\Phi = 11\) mJcm\(^{-2}\) and at any \(N\) at \(\Phi = 17\) mJcm\(^{-2}\) the distribution becomes unimodal as seen in Figure 6d, where the second peak (empty symbols) disappears. This is valid for both pitches for this article is protected by copyright. All rights reserved
this sample (not shown here). In contrast, the distribution of silver nanoparticles in pristine DLC:Ag-8 thin film is unimodal ($x_c = 24$ nm) and stays unimodal after the laser processing within the investigated energy density ranges (Figure 6a,b). In both samples, the center of distribution $x_c$ shifts to the bigger particles sizes with an increased number of pulses (see Figure 6b,d). The DLC:Ag-8 sample also demonstrates a clear tendency in increasing particle size with increasing laser fluence (Figure 6b). It should be noted that after laser treatment the particle density was reduced up to 7 times.

Figure 6. Dependence of particle sizes in DLC:Ag-8 (a, b) and DLC:Ag-14 (c, d) thin films with $\Lambda = 564$ nm on silicon substrate. (a, c) Silver nanoparticle diameter $d$ distributions after irradiation with $\Phi = 11$ mJcm$^{-2}$ varying $N$. (b, d) Center $x_c$ positions of the lognormal distribution dependencies on $N$ at different $\Phi$ (black – 6 mJcm$^{-2}$, red – 11 mJcm$^{-2}$, blue – 17 mJcm$^{-2}$, lines are guides for the eyes). The positions of $x_c$ are illustrated at the insets of (a) and (c). Green horizontal line represents $x_c$ values of the pristine samples, while the green shaded area represents the error bars. Empty symbols and dashed lines represent a second peak in nanoparticles distribution characteristic to sample DLC:Ag-14.

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When the concentration of nanoparticles in the pristine samples is low and they do not interact (e.g. volume fraction is 0.001), as A. Stalmashonak et al. reported, not only the transformation of particles takes place, but also a region of smaller particles is generated around a main particle after irradiation with femtosecond laser pulses. In our case, the density of the silver nanoparticles is high enough (920 μm⁻² for 7.9 at.% Ag and 336 μm⁻² for 14.1 at.% Ag) for them to interact with each other. The ablation debris is not visible in the micrographs and it could be explained as immediate redistribution between the neighboring particles under laser irradiation. The latter mechanism is also supported by the evolution of the particles diameter distribution histograms and their lognormal fitting (Figure 6b, d): at higher laser fluences the central particle diameter $a_c$ shifts towards higher diameter values, which indicates agglomeration of nanoparticles. Initially, with the lowest number of pulses applied, the size distribution results in smaller particles sizes, compared with the pristine samples (24 nm for DLC:Ag-8 and 17 nm, 46 nm for DLC:Ag-14), which suggests nanoparticle fragmentation at lower energy densities. After laser irradiation with higher number of pulses, several aspects of silver nanoparticles changes are observed: the particle density decreases down to 110 μm⁻² (DLC:Ag-14, $\Phi = 11$ mJcm⁻², $N = 125k$), the diameter $a_c$ of particles increases up to 69 nm (DLC:Ag-14, $\Phi = 17$ mJcm⁻², $N = 64k$), and the diameter size distribution widens (Figure 6a, b). It can be concluded that in the laser irradiated areas some particles are removed, while others merge with near-by particles to form bigger clusters. The manipulation of the nanoparticles (embedding in polymer matrix, control of atomic switches, etc.) was previously reported while studying plasmonic heating. In our case, the applied laser energy density was higher, thus the nanoparticles were not only heated, but also their shape was transformed. The agglomeration can be explained via the Ostwald ripening mechanism, which was also observed in a plasma etching experiment of DLC:Ag films where the matrix was selectively removed.

The bimodal nature of the DLC:Ag-14 sample nanoparticle size distribution can be predicted already from the visible light absorbance spectrum (Figure 1a), where the peak is non-uniform (it has a shoulder at shorter wavelengths). The ability to tailor the particle shape with intense laser
light, aiming for a uniform size distribution, was presented by F. Stietz,\textsuperscript{[54]} where the feasibility was explained by thermal and non-thermal effects under ultra-short laser irradiation. Furthermore, the DLC:Ag-8 absorbance spectrum has a single blue shifted peak, which is in agreement with the unimodal particle distribution having smaller average particle size ($x_c = 24$ nm) compared with DLC:Ag-14 (($x_{c1} + x_{c2})/2 = 31.5$ nm). Lower absorbance at the laser 515 nm line (see Figure 1a) also suggests that DLC-0 should have a higher ablation threshold compared with the investigated DLC:Ag samples. This holds true when comparing multiple pulses ablation threshold values (Table 1). The differences between the extrapolated single pulse a-C:H ablation threshold values for the thin film on silicon (148 mJcm\textsuperscript{-2}) and on quartz substrates (156 mJcm\textsuperscript{-2}) could be addressed to the higher refractive index of silicon compared with fused quartz and the corresponding higher reflectivity as well as differences in absorption at the applied wavelength. The threshold values are slightly lower than reported by other authors,\textsuperscript{[16,17]} however, the difference could be a result of the different laser wavelengths and even lower absorbance at $\lambda = 800$ nm compared with $\lambda = 515$ nm in our experiments.

Here it is also important to address the meaning of different threshold determination methods.

When the laser irradiation is organized with an interference field, the material is removed and, therefore, the periodic pattern is imposed with the laser fluence above ablation threshold only at the vicinity of interference maxima. When the material is not removed, but a clear pattern is still visible in the micrographs, the applied laser fluence might be below the ablation threshold, although still impose the modifications of the surface. In other words, it is not necessary to completely remove layer of the material within the grooves of periodic pattern: it might be enough to slightly modify the surface, which can already be seen under a high-resolution microscope. To distinguish the latter fluence from that resulting in the ablation threshold, we suggest terming it “patterning threshold.” It was proven by our study that slight alterations were made to the surface of the material by formation of a periodic pattern only by changes in the nanoparticles distribution within the irradiated lines without the apparent ablation effect, and confirmed by FFT analysis. This is also...
evident for the a-C:H films as no visible spots were seen under the optical microscope at 11-17 mJcm⁻², but the FFTs of the HIM images already indicate the presence of the periodic pattern even though the latter fluence is below the ablation threshold determined from Equation 1. This confirms the suggested existence of both ablation threshold and patterning threshold intrinsic for DLIP.

3. Conclusions

Direct laser interference patterning was proved to be a very efficient and versatile sub-wavelength line width periodic structures fabrication technology in silver doped hydrogenated amorphous diamond-like carbon nanocomposite thin films. By managing the energy density we were able to control the line widths of patterns in imposed modifications from 150 nm to 420 nm (for 564 nm pitch structures) and from 400 nm to 960 nm (for 1306 nm pitch).

It was demonstrated that the nanoparticle size distributions of DLC:Ag films owning different initial silver content can be tailored during direct laser interference patterning in a controlled way by carefully selecting the ultra-short pulsed laser parameters. The 14.1 at.% Ag containing DLC:Ag film bimodal average effective particles diameter size distribution of 17 nm and 46 nm was changed into unimodal, resulting in an average diameter after irradiation in between 14 nm (11 mJcm⁻² laser fluence, 64,000 pulses) and 69 nm (17 mJcm⁻², 64,000). Moreover, it was demonstrated that the initial unimodal nanoparticle size distribution with average size of 24 nm, characteristic to lower silver content of 7.9 at%, can be tailored from 44 nm (11 mJcm⁻², 125,000) down to ~13 nm (11 mJcm⁻², 8,000).

Patterning of DLC:Ag nanocomposite thin films requires from 4 times (at 1000 pulses) up to 24 times (at 125,000) lower laser fluence than patterning of its components (DLC and Ag) separately. That was addressed to differences in the absorption and local electric field enhancement that in the case of DLC:Ag is governed by the localized surface plasmon resonance.

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Our work illustrates how versatile femtosecond laser irradiation induced modifications can be by choosing specific energy densities: from ablation of periodic patterns to moderately influencing the nanoparticle size distributions above a certain patterning threshold. Note that the latter happens without excessive removal of material.

4. Materials and Methods

*Deposition of Thin Films:* Filler-free a-C:H (DLC-0) and DLC:Ag nanocomposite thin films were deposited employing a custom-made unbalanced reactive magnetron sputtering system in a direct current mode. The principle scheme of the deposition system can be found elsewhere.\(^9\) For the deposition, an acetylene and argon gas mixture was used. A silver target was used for DLC:Ag films, while for a-C:H a carbon target was employed. The distance between the target and the substrate was 8 cm. Base pressure and work pressure were \((7.1 – 8.8) \times 10^{-4} \text{ Pa}\) and 0.72–0.89 Pa, respectively. The substrates were grounded. Appropriate deposition duration was chosen according to the desired film thickness, namely, 60 nm for all of the sample types. Thin films were deposited on silicon and quartz substrates. The specific deposition parameters for different samples are listed in Table 2. Two different DLC:Ag deposition conditions were chosen similar to those reported in,\(^{33}\) where it was addressed that quite different nanoparticle size distributions can be obtained depending on the silver content. Additionally, silver thin films of 60 nm thickness on silicon and quartz substrates (sample Ag-100) were deposited employing e-beam evaporation. The pressure in the chamber was lower than 0.13 Pa and the deposition rate was approximately 1.3 Å/s.
Characterization of Structural and Optical Properties of the Pristine Films: The chemical composition of thin DLC:Ag films was determined by X-ray energy dispersion spectroscopy (EDS) using a Quantax 200 system with XFlash 4030 detector (Bruker) installed in a Quanta 200 FEG (FEI) scanning electron microscope. The atomic concentrations of all detected elements are presented in Supplementary Information Table S1.

Optical transmittance ($T$) and reflectance ($R$) of the pristine a-C:H and DLC:Ag samples were measured using an AvaSpec-2048 (Avantes) spectrometer. For transmittance, the lamp intensity transmitted through a quartz substrate was used as a reference spectrum, and for reflectance it was the lamp intensity reflected from the mirror. The absorbance in the films ($A$) was calculated as $A = 1 - T - R$ and was normalized for each spectrum, not taking into account scattering effects.

Raman spectra of the same films were recorded by an inVia (Renishaw) spectrometer with 532 nm wavelength, 45 mW power excitation laser and 50x, 0.75 NA microscope objective. The background was subtracted from the obtained spectra.

DLIP of the Thin Films: Microfabrication of 1D periodic structures was carried out by a femtosecond laser ablation system using two beam DLIP. A 515 nm (second harmonic) wavelength Yb:KGW laser (Pharos, Light Conversion) with pulse duration of 290 fs and repetition rate of 40 kHz was employed. The laser beam was split into two equal intensity symmetrical beams using a diffractive optical element (DOE) and then overlapped with a 4f lens system to one spot on the sample surface to create the interference pattern. The FemtoLab laser micro-/nano-machining workstation (Altechna R&D), that is, laser and XYZ stages, attenuator, and DOE, were controlled by SCA software (Altechna R&D). The pitch of the pattern was altered by changing the angle of incidence, that is, changing the pitch of the DOE. The general equation, governing the pitch $\Lambda$, is as

\[
\Lambda = \frac{\lambda}{2 \sin \theta}
\]

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follows: \( \Lambda = \frac{\lambda}{2n \sin \theta} \), where \( \lambda \) is the wavelength of the laser, \( n \) is the refractive index of the surrounding medium (in our case air, \( n = 1 \)), \( \theta \) is the incidence angle. More details about the utilized DLIP setup can be found elsewhere. The patterning beam spot size was \( 75 \times 75 \mu m^2 \), and the total patterned area was \( 4 \times 4 \) arrays of beam size resulting in nearly uniformly patterned areas of \( 300 \times 300 \mu m^2 \). A laser fluence of \( 1–17 \text{ mJ/cm}^2 \) was applied for DLC:Ag samples, \( 6–145 \text{ mJ/cm}^2 \) for the Ag sample, and \( 1–145 \text{ mJ/cm}^2 \) for the a-C:H sample. The number of applied pulses for all types of samples was \( 1000–125,000 \). Circular polarization was used in the experiments in order to avoid the phenomenon of laser-induced periodic surface structures.

**Microscopy Analysis of the Laser Ablated Films:** The morphology of the structures was investigated using a scanning electron microscope (SEM) S-4800 (Hitachi) and a helium ion microscope (HIM) ORION NanoFab (Zeiss). SEM was used for investigation of silver films on silicon and quartz substrates and for DLC:Ag films on the silicon substrate. The secondary electron detector was employed with \( 6 \text{ mm} \) working distance, \( 15 \text{ kV} \) and \( 10 \mu A \) accelerating voltage and beam current, respectively. HIM was used for insulating samples, namely, a-C:H (DLC-0) films on silicon and quartz substrates and for DLC:Ag films on quartz substrate. A sample bias (-60 V) and a flood gun (600 eV) for charge neutralization were applied. Working distance was \( 10 \text{ mm} \), scan dwell time was \( 2 \mu s \), beam current was \( 0.260 \text{ pA} \) and an averaging of 32 scans was used. Additionally, patterned a-C:H films were investigated by an optical microscope B-600MET (Optika) with a 20x objective.

**Determination of the Pitch of the Periodic Structures:** SEM micrographs with \( 18 \mu m \) horizontal field of view and HIM images with \( 15 \mu m \) field of view were used to evaluate the pitches \( \Lambda \) of periodic structures: fast Fourier transforms (FFT) of the images were computed using the “ImageJ” software and the pitch was determined from the first maximum in FFT, which was averaged between all images of the same periodicity. The pitches of the obtained structures were \( 564 \pm 14 \text{ nm} \) and \( 1306 \pm 46 \text{ nm} \).
**Determination of Ablation and Patterning Thresholds:** The thresholds for different samples were determined with slightly different approaches based on the laser impact induced optical effects visible under the microscopes. For a-C:H (DLC-0) it was determined from the analysis of the optical microscope images. The whole irradiated beam areas at elevated fluences (6–145 mJcm⁻²) of DLC-0 sample were investigated. At such elevated fluences, circular dark areas were clearly visible in the optical microscope images (as seen in Figure 5a). The diameter \( D \) of each of such areas \((4 \times 4\) for every variation of fluence and number of pulses) was measured and averaged. In case the dark circle diameter overcame the aimed patterning area (due to light diffraction by the pinhole at higher fluence\(^{[22]}\), that is, \( D > 75 \mu m \), only the outer spots of the \(4 \times 4\) arrays were measured due to overlap in inner areas, thus reducing the amount of analyzed areas from 16 to 12. The classical ablation threshold determination approach was used:\(^{[58]}\)

\[
D^2 = 2w^2 \ln(\Phi/\Phi_{th})
\]  

where \( D \) is the diameter of irradiated spot, \( w \) is the laser spot size on the sample surface, and \( \Phi \) is the laser fluence. As can be seen from the equation, plotting the \( D^2 \) dependence on \( \ln(\Phi) \) should yield a linear dependence.

It was not possible to follow the same spot analysis for DLC:Ag samples, because the laser fluence applied was much lower and the squares were affected uniformly, therefore, no dark circles were observed. It was speculated that the diffraction grating line width analysis \((W,\ \text{Figure 2b,c})\) and its dependence on the applied laser fluence could lead to the patterning threshold of DLC:Ag. The lines were drawn in the micrographs on every edge between the ridge and groove and the widths of laser affected lines were estimated. The results were averaged throughout the image. Because of the sinusoidal laser intensity distribution of the interference fringes (Figure 2a), the material was also slightly exposed to the laser radiation within the dark fringes.\(^{[2]}\) Hence in some images, it is not clear where the edge of the affected line is and errors in the measurements might be introduced.

Consequently, some irradiated areas had to be omitted from the width investigation. Additionally,
the FFTs of the SEM micrographs were considered in determining the patterning threshold of DLC:Ag samples. When the FFT of the image indicated diffraction orders, the pattern was assumed to be present and irradiation parameters used were treated to be above the threshold. When there was only one central bright spot in the FFT, the micrographs were excluded from the further analysis, that is, the laser irradiation parameters were assumed to be below the patterning threshold.

Analysis of Nanoparticle Size Distribution: Another set of SEM micrographs (3 μm horizontal field of view) were used for the nanoparticle size distribution analysis. The “ImageJ” software was used once again to process the SEM micrographs and to obtain areas and coordinates of each particle. When the particle was touching the edge of the image, it was not included in the evaluation due to uncertainty of its size. Since images have affected and unaffected zones, further filtering of the results was carried out in order to obtain only laser irradiated areas. For this, only the particles with center coordinates \( C(x, y) \) within the previously measured laser irradiated widths \( W \) were evaluated (see Figure 2b,c). The software returns particles area information, which was recalculated into effective diameters \( d \), assuming the particles to be circular. A lognormal distribution was fitted to the particles diameter distribution histograms, which is most commonly used for such purpose:[59]

\[
y = y_0 + \frac{A}{\sqrt{2\pi} \omega x_c} e^{-\frac{[\ln(x/x_c)]^2}{2\omega^2}} \tag{2}
\]

where \( y_0 \) is the offset, \( A \) is the area, \( \omega \) is the logarithm of standard deviation, and \( x_c \) is the center coordinate.

Supporting Information
Supporting Information is available from Wiley Online Library or from the author.
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Conflict of Interest
The authors declare no conflict of interest.

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The paper demonstrates at least 4 times reduction of amorphous hydrogenated diamond-like carbon laser patterning threshold by incorporation of silver nanoparticles into a thin film. The effect is addressed to localized surface plasmon resonance and localized field enhancement. Feasibility to tailor nanoparticle size distribution with irradiation of laser light is demonstrated.

Direct laser interference patterned nanocomposites

A. Jurkevičiūtė G. Klimaitė T. Tamulevičius *, J. Fiutowski, H.-G. Rubahn, S. Tamulevičius *tomas.tamulevicius@ktu.lt

Tailoring of Silver Nanoparticle Size Distributions in Hydrogenated Amorphous Diamond-like Carbon Nanocomposite Thin Films by Direct Femtosecond Laser Interference Patterning