



Communication

# Hydrophilic Surface Modification of Amorphous Hydrogenated Carbon Nanocomposite Films via Atmospheric Oxygen Plasma Treatment

Algirdas Lazauskas , Mindaugas Andrulevičius , Brigita Abakevičienė, Dalius Jucius , Viktoras Grigaliūnas, Asta Guobienė and Šarūnas Meškiniš

Institute of Materials Science, Kaunas University of Technology, K. Baršausko 59, LT51423 Kaunas, Lithuania

\* Correspondence: algirdas.lazauskas@ktu.edu; Tel.: +370-671-73375

**Abstract:** Herein we investigated hydrophilic surface modification of SiO<sub>x</sub> containing amorphous hydrogenated carbon nanocomposite films (DLC:SiO<sub>x</sub>) via the use of atmospheric oxygen plasma treatment. The modified films exhibited effective hydrophilic properties with complete surface wetting. More detailed water droplet contact angle (CA) measurements revealed that oxygen plasma treated DLC:SiO<sub>x</sub> films maintained good wetting properties with CA of up to 28 ± 1° after 20 days of aging in ambient air at room temperature. This treatment process also increased surface root mean square roughness from 0.27 nm to 1.26 nm. Analysis of the surface chemical states suggested that the hydrophilic behavior of DLC:SiO<sub>x</sub> treated with oxygen plasma is attributed to surface enrichment with C–O–C, SiO<sub>2</sub>, and Si–Si chemical bonds as well as significant removal of hydrophobic Si–CH<sub>x</sub> functional groups. The latter functional groups are prone to restoration and are mainly responsible for the increase in CA with aging. Possible applications of the modified DLC:SiO<sub>x</sub> nanocomposite films could include biocompatible coatings for biomedical applications, antifogging coatings for optical components, and protective coatings to prevent against corrosion and wear.



**Citation:** Lazauskas, A.; Andrulevičius, M.; Abakevičienė, B.; Jucius, D.; Grigaliūnas, V.; Guobienė, A.; Meškiniš, Š. Hydrophilic Surface Modification of Amorphous Hydrogenated Carbon Nanocomposite Films via Atmospheric Oxygen Plasma Treatment. *Nanomaterials* **2023**, *13*, 1108. <https://doi.org/10.3390/nano13061108>

Academic Editors: Meiwen Cao and Antonios Kelarakis

Received: 22 February 2023

Revised: 13 March 2023

Accepted: 18 March 2023

Published: 20 March 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Keywords:** oxygen plasma; hydrophilic; wetting; surface modification; DLC; DLC:SiO<sub>x</sub>

## 1. Introduction

Diamond-like carbon (DLC) films are a class of materials that exhibit unique properties, including high hardness [1], low friction [2,3], and excellent chemical resistance [4]. These properties make DLC films attractive for a wide range of applications, such as protective coatings for medical implants [5–7], wear-resistant coatings for mechanical components [8,9], and anti-reflective coatings for optical devices [10,11].

The wetting properties of DLC films, or the ability of a liquid to spread over the surface and form a uniform and stable contact angle is a very important factor in determining the performance and suitability of DLC films for specific applications. Good wetting properties can enhance the functionality of DLC films in various applications, such as in medical implants, where wetting properties play a crucial role in controlling the interaction between the implant and the surrounding biological fluids [12]. DLC films with good wetting properties can exhibit improved performance in specific applications, such as in optical devices, where a uniform and stable contact angle can help reduce reflections and increase optical transmission. Furthermore, hydrophilic DLC films can be effectively utilized in environments that involve liquids or high humidity [13]. Good wetting properties can improve the adhesion between DLC films and other materials, which is important in applications such as tribological coatings and protective [14,15].

The surface energy of DLC films is an important parameter that determines their wetting and adhesion characteristics [16]. One approach to tailor the surface energy of DLC films is through the use of plasma treatment. This treatment can be easily applied and does not require hazardous chemicals or specialized equipment, making it a cost-effective and scalable method. Plasma treatment involves exposing the DLC film to gas plasma,

which results in the formation/recombination of functional groups on the surface of the film. These functional groups can alter the surface energy of the DLC film and improve its wetting and adhesion properties. For example, oxygen plasma treatment has been reported to be an effective method to increase hydrophilicity as well as hemocompatibility of DLC films [17,18]. The formation of oxygen-related functional groups on the surface of the film after exposure to oxygen plasmas is mainly responsible for the increase in the hydrophilic character and surface energy of DLC [19,20].

Another strategy to improve wetting properties of DLC is through the use of hybrid films. Hybrid films are composed of DLC and other materials, such as metallic or organic compounds, which can affect the surface energy of the film. By carefully selecting the composition of the hybrid film, it is possible to achieve desired surface energy levels for specific applications, such as anti-fog coatings on automobile windshields, and biocoatings on contact lenses [21,22].

In addition to plasma treatments and hybrid films, the surface wetting properties of DLC films can be also tailored through other methods, e.g., chemical (piranha treatments [23]), photochemical (UV light and 30% hydrogen peroxide), ion implantation [24] and laser treatment [25]. These methods can also introduce functional groups onto the surface of the DLC film and modify its wetting characteristics. However, chemical treatment methods can be hazardous due to the highly reactive nature of the chemicals involved, which can pose safety concerns. Moreover, chemical modification methods may result in uncontrolled etching of the DLC film, leading to a reduced film thickness and surface roughness, which can negatively affect the DLC film properties. The photochemical method may not be effective for thicker films, and the process may require longer exposure times to achieve desired surface modification. Moreover, photochemical treatment may cause damage to the DLC film structure, leading to reduced film quality. Ion implantation and laser treatment can be expensive and require specialized equipment, which may not be easily accessible. Furthermore, these treatments may cause localized damage to the film and may not be effective for modifying the entire surface uniformly.

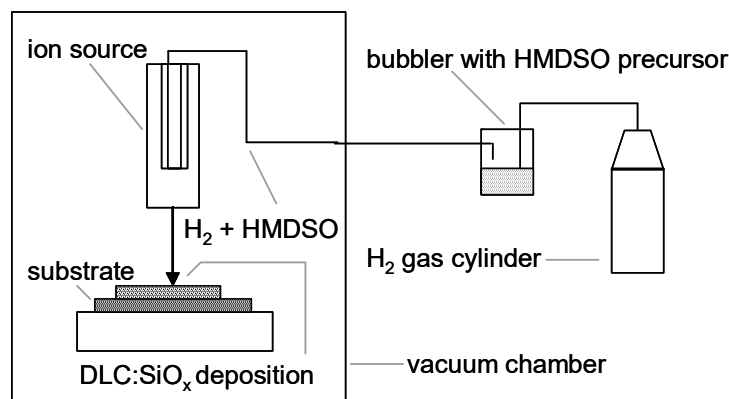
One specific type of DLC film—SiO<sub>x</sub> containing amorphous hydrogenated carbon nanocomposite film (DLC:SiO<sub>x</sub>), which is widely known for its high-hardness (10–20 GPa), low wear rate (10<sup>-5</sup>–10<sup>-8</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>) and friction coefficient (0.02–0.2), as well as low internal stresses (<1 GPa) and high optical transmittance (~80–85%) in the visible spectrum [11,26–28]. However, very little is known about the surface modification of DLC:SiO<sub>x</sub> films with plasma techniques. Herein, we attempt to contribute to this topic by investigating how the wetting properties of DLC:SiO<sub>x</sub> films are affected upon the atmospheric oxygen plasma treatment. We established the possible correlations between the oxygen plasma treatment and the changes it introduces to the surface of the DLC:SiO<sub>x</sub> film via the use of water droplet contact angle (CA) measurements, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). It was found that atmospheric oxygen plasma treatment of the DLC:SiO<sub>x</sub> film modifies its surface to be effectively hydrophilic. The wetting properties of DLC:SiO<sub>x</sub> film deteriorate to some extent with aging in ambient air at room temperature.

## 2. Materials and Methods

A commercial high-grade extra clear float glass Pilkington Microwhite™ (Sheet Glass Co., Tokyo, Japan) was used as a substrate material. Hexamethyldisiloxane (HMDSO) of analytical grade (≥99%, Sigma-Aldrich, Saint Louis, MO, USA) was used as a source of hydrocarbons, silicon, and oxygen for synthesis of DLC:SiO<sub>x</sub> films. Deionized (DI) water with a resistivity higher than 18.2 MΩ/cm at 25 °C was used for CA measurements, and was obtained from a Direct-Q® 3 UV water purification system (Merck KGaA, Darmstadt, Germany).

The Hall-type closed drift ion beam source operating at a constant energy of 800 eV and a current density of 100 μA/cm<sup>2</sup> was used for deposition of DLC:SiO<sub>x</sub> films at room temperature. The base pressure and work pressure in the vacuum chamber were 2 × 10<sup>-4</sup> Pa

and  $2 \times 10^{-2}$  Pa, respectively. Hydrogen gas ( $H_2$ ) was used for transportation of HMDSO vapor into the vacuum chamber. Simplified schematic illustrating experimental setup for DLC:SiO<sub>x</sub> deposition is shown in Scheme 1.



**Scheme 1.** Simplified schematic illustrating experimental setup for DLC:SiO<sub>x</sub> deposition.

Control tests with monocrystalline Si(1 0 0) (UniversityWafer Inc., Boston, MA, USA) substrates were performed in order to determine deposition rate of DLC:SiO<sub>x</sub> for H<sub>2</sub> gas. The thickness of DLC:SiO<sub>x</sub> on Si(1 0 0) was determined using a laser ellipsometer Gaertner L-115 (Gaertner Scientific Corporation, Skokie, IL, USA) equipped with a He–Ne laser (wavelength of 632.8 nm). Film thickness of ~100 nm was chosen for the deposition of DLC:SiO<sub>x</sub> on glass substrates.

The radio frequency capacitive plasma unit Plasma-600T (JSC Kvartz, Kuvasay, Uzbekistan) operating at a frequency of 13.56 MHz and power of 0.3 W/cm<sup>2</sup> was used for surface modification of as-deposited DLC:SiO<sub>x</sub> films. The atmospheric oxygen plasma treatment time was varied in the range of 1–5 min.

CA measurements were performed at room temperature using the sessile drop method. The size of the DI droplets was 5 μL, the wetting angles were recorded after 10 min for all samples. CA were determined using an active contour method based on B-spline snakes (active contours) [29]. The CA is reported as an average of five measurements at different places on the surface of each sample.

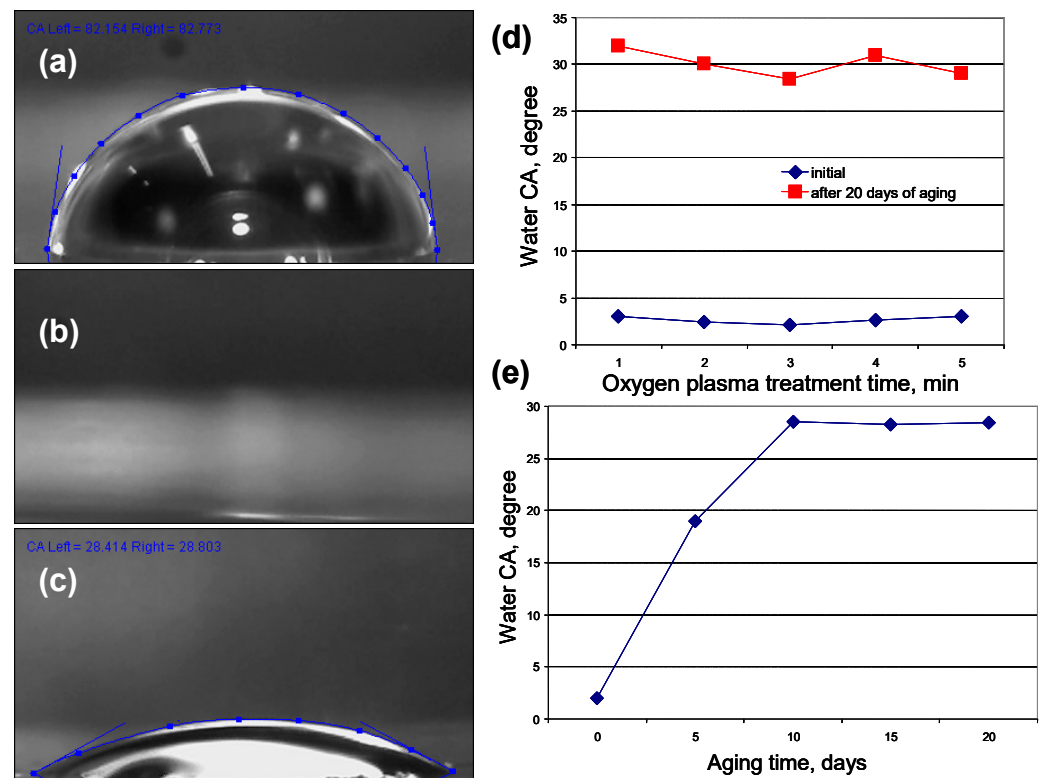
AFM experiments were performed with NanoWizardIII microscope (JPK Instruments, Bruker Nano GmbH, Berlin, Germany) equipped with V-shaped silicon cantilever (spring constant of 3 N/m, tip curvature radius of 10.0 nm and the cone angle of 20°) operating in contact mode at room temperature. Data processing was carried out using a SurfaceXplorer and JPKSPM Data Processing software (Version spm-4.3.13, JPK Instruments, Bruker Nano GmbH).

The XPS measurements were performed employing XSAM800 spectrometer (Kratos Analytical Ltd., Manchester, United Kingdom). The non-monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) was used for XPS spectra acquisition. The base pressure in the analytical chamber was lower than  $8 \times 10^{-8}$  Pa. The energy scale of the system was calibrated according to Au 4f<sub>7/2</sub>, Cu 2p<sub>3/2</sub> and Ag 3d<sub>5/2</sub> peak positions, respectively. The C 1s, O 1s, and Si 2p spectra were acquired at the 20 eV pass energy (0.1 eV energy step), and the analyzer was in the fixed analyzer transmission (FAT) mode. Spectra were fitted using a sum of Lorentzian–Gaussian (ratio of 30:70) functions and symmetrical peak shape; while for graphitic carbon asymmetrical peak shape and 70:30 ratio was used.

### 3. Results and Discussion

Figure 1 shows typical water droplet profile images of DLC:SiO<sub>x</sub> films before and after oxygen plasma treatment for 3 min, as well as the plasma treated DLC:SiO<sub>x</sub> film, which was aged for 20 days in ambient air at room temperature. The as-deposited DLC:SiO<sub>x</sub> film exhibited water CA of  $82 \pm 1^\circ$ , which is very close to the hydrophobic surface. After

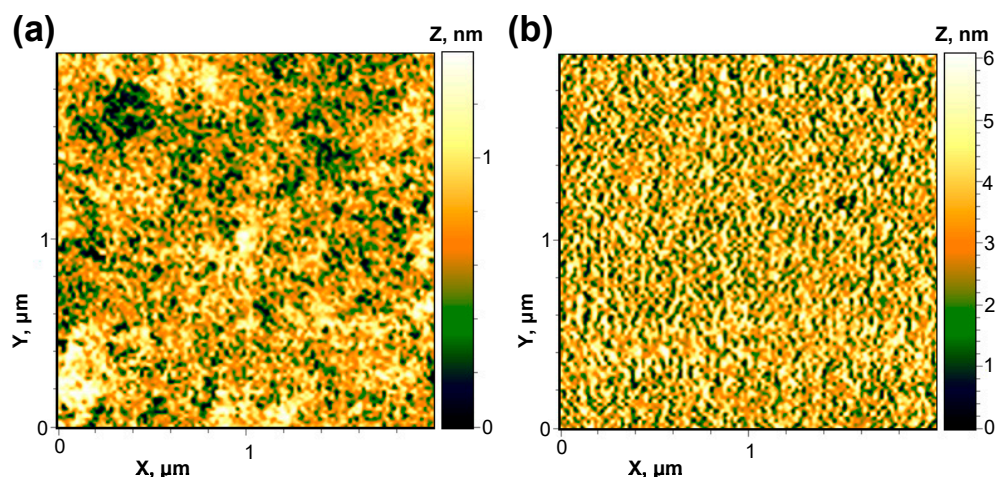
oxygen plasma treatment for 3 min, the surface of the DLC:SiO<sub>x</sub> film was modified to be effectively hydrophilic with complete spreading of water droplet (CA < 2°) on the surface. In [17], DLC films deposited using benzene and diluted silane as the precursor gases were subjected to plasma treatment using various gases such as N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and CF<sub>4</sub>. They found that oxygen plasma treated films exhibited the lowest water CA of 13.4 ± 1.3° as compared to other plasma gases. In contrast, our result is significantly better. Further, we assessed the wetting stability of DLC:SiO<sub>x</sub>. The water CA on the surface of the DLC:SiO<sub>x</sub> film, which was modified using oxygen plasma treatment increased up to 28 ± 1°, still maintaining good hydrophilic properties after 20 days of aging. It was also found that the oxygen plasma treatment time variation (i.e., 1–5 min) of as-deposited DLC:SiO<sub>x</sub> films had little effect on the hydrophilic surface modification as in all cases total surface wetting was observed (Figure 1d), whereas the lowest CA was determined for the 3 min oxygen plasma treated DLC:SiO<sub>x</sub> films (CA 28 ± 1°) after 20 days of aging (Figure 1d). In Figure 1e, CA measurements indicated that during the first 10 days of aging, the oxygen plasma-treated DLC:SiO<sub>x</sub> film rapidly loses its hydrophilic properties to some extent, after which stabilization is reached with CA ~28 ± 1° for the remaining 10 days of aging. S. Narayan et al. investigated oxygen plasma treatment effect on the wetting properties of DLC coatings deposited using plasma enhanced chemical vapor deposition (PECVD) technique [30]. They observed that hydrophilic properties of oxygen plasma treated DLC coatings rapidly deteriorate within 8 days of aging. Afterwards, better stability of CA with aging time was observed. However, CA values of >40° were reported for oxygen plasma treated DLC coatings in all cases after 10 days of aging.



**Figure 1.** Water droplet profile images of DLC:SiO<sub>x</sub> (a) as-deposited, (b) 3 min oxygen plasma treated and (c) oxygen plasma and aged for 20 days; (d) water CA as a function of oxygen plasma treatment time of as-deposited and after aging for 20 days; (e) water CA as a function of aging time.

Figure 2 shows characteristic AFM 2D topographical images of the as-deposited and 3 min oxygen plasma treated DLC:SiO<sub>x</sub> films acquired over 2.0 × 2.0 μm<sup>2</sup> area in air using contact mode. The topography of the as-deposited DLC:SiO<sub>x</sub> surface exhibits a random

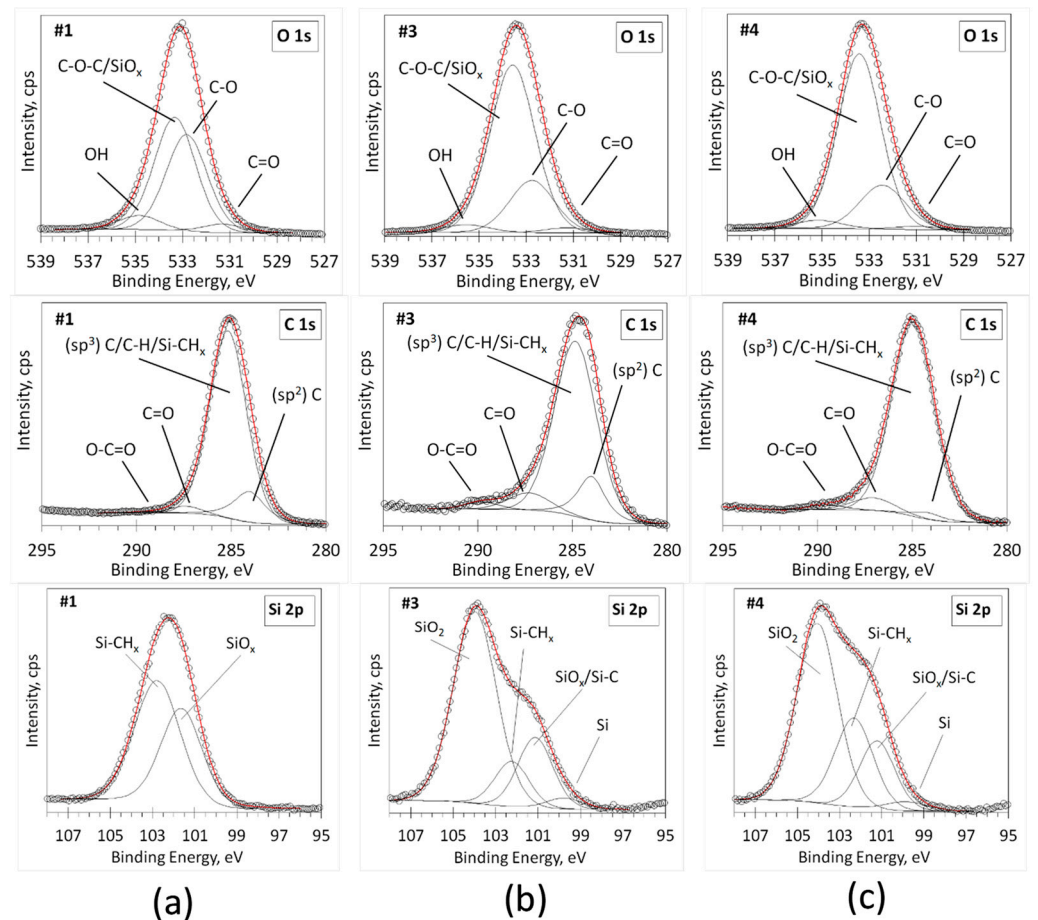
distribution of surface mounds having different angle orientations to each other, without a preferred direction. A mean height of the surface structures ( $Z_{\text{mean}}$ ) was determined to be 0.7 nm. The root mean square roughness ( $R_q$ ) was found to be 0.27 nm. The as-deposited DLC:SiO<sub>x</sub> film surface is dominated by the valleys with skewness ( $R_{sk}$ ) value of  $-0.11$  and has a platykurtic distribution (i.e., relatively few high peaks and low valleys) of surface morphological features with kurtosis ( $R_{ku}$ ) value of 2.7. In contrast, 3 min oxygen plasma treated DLC:SiO<sub>x</sub> film surface exhibited higher  $R_q$  value of 1.26 nm with  $Z_{\text{mean}}$  value of 3.23 nm, and followed similar distribution of surface morphological features with  $R_{sk}$  and  $R_{ku}$  values of  $-0.11$  and 2.46, respectively. In [31,32] surface morphological analysis was performed for as-deposited and oxygen plasma treated DLC films. Their results also indicated an increase in surface roughness after surface modification with oxygen plasma. This increase in surface roughness was attributed to oxygen ion bombardment during the treatment process. In our case, oxygen plasma treated DLC:SiO<sub>x</sub> film maintained very low surface roughness, and therefore it is suggested that this change had negligible effect on the wetting properties.



**Figure 2.** AFM surface topography of (a) as-deposited and (b) 3 min oxygen plasma treated DLC:SiO<sub>x</sub> films.

The effect of oxygen plasma surface hydrophilic modification on the chemical states of DLC:SiO<sub>x</sub> was investigated employing XPS. The deconvoluted high-resolution XPS spectra in the O 1s, C 1s and Si 2p regions of the as-deposited, oxygen plasma treated and 20 days aged DLC:SiO<sub>x</sub> films are shown in Figure 3. The deconvoluted components of DLC:SiO<sub>x</sub> films in the XPS O 1s spectra were assigned to C=O (531.2 eV), C–O (532.6 eV), C–O–C/SiO<sub>x</sub> (533.1 eV) and O–H (534 eV) chemical bonds [33–37]. It can be seen that after oxygen plasma treatment the concentration of hydrophilic C–O–C functional groups on the surface of DLC:SiO<sub>x</sub> increased considerably, remained stable after 20 days of aging. The deconvoluted component originating from C–O bonds decreased after oxygen plasma treatment and also remained stable after 20 days of aging. High-resolution XPS spectra in the C 1s region were deconvoluted into four components, respectively. A high intensity peak at 285 eV represents carbon in sp<sup>3</sup> hybridization, and it overlaps with C–H and Si–CH<sub>x</sub> chemical bonds [38]. A low intensity peak at 284.1 eV was assigned to carbon sp<sup>2</sup> hybridization. The position and asymmetric shape of this component is typical for graphitic carbon [39,40]. Lower intensity peaks at higher binding energies could be assigned to O–C=O and C=O chemical bonds. No considerable changes were observed in C 1s region for oxygen plasma treated DLC:SiO<sub>x</sub> films. The aging of the DLC:SiO<sub>x</sub> films resulted in further oxidation in ambient air, which is indicated by slight increase of C=O component as well as recombination of sp<sup>2</sup> carbon into other functional groups. Two deconvoluted components of as-deposited DLC:SiO<sub>x</sub> film in the XPS Si 2p spectrum were assigned to Si–CH<sub>x</sub> (102.5 eV) and SiO<sub>x</sub> (101.1 eV) chemical bonds [38,41]. Two additional components appeared at 104 eV and 99.8 eV after oxygen plasma treatment of DLC:SiO<sub>x</sub>, assigned

to the SiO<sub>2</sub> and Si-Si chemical bonds, respectively [41]. After oxygen plasma treatment the concentration of hydrophobic Si-CH<sub>x</sub> functional groups on the surface of DLC:SiO<sub>x</sub> decreased significantly, and slightly increased after 20 days of aging, which is in good agreement with CA measurement results. The restoration of Si-CH<sub>x</sub> chemical bonds is mainly responsible for CA increase with aging of DLC:SiO<sub>x</sub> film. The appearance of SiO<sub>2</sub> and Si-Si chemical bonds for oxygen plasma treated DLC:SiO<sub>x</sub> films also significantly contributed to the effective hydrophilic properties of the surface [21]. The concentration of these functional groups on the surface of oxygen plasma treated DLC:SiO<sub>x</sub> film remained relatively stable after 20 days of aging.



**Figure 3.** High-resolution deconvoluted XPS spectra in O 1s, C 1s and Si 2p regions of DLC:SiO<sub>x</sub> (a) as-deposited, (b) 3 min oxygen plasma treated and (c) oxygen plasma treated and aged for 20 days.

Based on the findings of this study, several future directions are of the main importance:

- Investigation of the long-term stability of hydrophilic properties of the oxygen plasma treated DLC:SiO<sub>x</sub> films under various environmental conditions, such as humidity, temperature, and exposure to different chemicals.
- Study of the underlying mechanisms of the restoration of hydrophobic Si-CH<sub>x</sub> functional groups and the ways to prevent or delay this process, enhancing the long-term stability of the hydrophilic properties of the DLC:SiO<sub>x</sub> films.
- Investigation of the effect of the hydrophilic DLC:SiO<sub>x</sub> films on the adhesion, proliferation, and differentiation of various cell types to explore their potential applications in tissue engineering and regenerative medicine.

#### 4. Conclusions

Atmospheric oxygen plasma treatment was used to modify DLC:SiO<sub>x</sub> film wetting properties. The surface of the DLC:SiO<sub>x</sub> film was modified to be effectively hydrophilic with complete spreading of water droplet (CA < 2°) on the surface. The CA increased up to 28 ± 1° after 20 days of aging in ambient air at room temperature, still maintaining good hydrophilic properties. AFM analysis indicated that the root mean square roughness of the film increased from 0.27 nm to 1.26 nm after oxygen plasma treatment. XPS investigation revealed that the highly hydrophilic characteristics of the oxygen plasma treated DLC:SiO<sub>x</sub> is attributed to surface enrichment with C–O–C, SiO<sub>2</sub> and Si–Si chemical bonds as well as significant removal of hydrophobic Si–CH<sub>x</sub> functional groups. During aging process of DLC:SiO<sub>x</sub> film the Si–CH<sub>x</sub> functional groups tend to restore to some extent negatively affecting the wetting properties. The modified DLC:SiO<sub>x</sub> nanocomposite films should be tested in various applications, such as biocompatible coatings for medical purposes, anti-fog coatings for optical components, and protective coatings to prevent corrosion and wear.

**Author Contributions:** Conceptualization, A.L., Š.M. and V.G.; investigation, A.L., Š.M., M.A., B.A., D.J., V.G. and A.G.; writing—original draft preparation, A.L.; writing—review and editing, A.L., M.A., D.J. and Š.M.; visualization, A.L., B.A. and M.A.; project administration, Š.M.; funding acquisition, Š.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research has received funding from European Regional Development Fund (project No. 01.2.2-LMT-K-718-03-0058) under grant agreement with the Research Council of Lithuania (LMTLT).

**Data Availability Statement:** Not applicable.

**Acknowledgments:** A special thanks goes to V. Kopustinskas for technical assistance.

**Conflicts of Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### References

- Ohtake, N.; Hiratsuka, M.; Kanda, K.; Akasaka, H.; Tsujioka, M.; Hirakuri, K.; Hirata, A.; Ohana, T.; Inaba, H.; Kano, M. Properties and classification of diamond-like carbon films. *Materials* **2021**, *14*, 315. [[CrossRef](#)] [[PubMed](#)]
- Liu, Y.; Jiang, Y.; Sun, J.; Wang, L.; Liu, Y.; Chen, L.; Zhang, B.; Qian, L. Durable superlubricity of hydrogenated diamond-like carbon film against different friction pairs depending on their interfacial interaction. *Appl. Surf. Sci.* **2021**, *560*, 150023. [[CrossRef](#)]
- Liu, Y.; Chen, L.; Jiang, B.; Liu, Y.; Zhang, B.; Xiao, C.; Zhang, J.; Qian, L. Origin of low friction in hydrogenated diamond-like carbon films due to graphene nanoscroll formation depending on sliding mode: Unidirection and reciprocation. *Carbon* **2021**, *173*, 696–704. [[CrossRef](#)]
- Nagai, T.; Hiratsuka, M.; Alanazi, A.; Nakamori, H.; Hirakuri, K. Anticorrosion of DLC coating in acid solutions. *Appl. Surf. Sci.* **2021**, *552*, 149373. [[CrossRef](#)]
- Wachesk, C.; Seabra, S.; Dos Santos, T.; Trava-Airoldi, V.; Lobo, A.; Marciano, F. In vivo biocompatibility of diamond-like carbon films containing TiO<sub>2</sub> nanoparticles for biomedical applications. *J. Mater. Sci. Mater. Med.* **2021**, *32*, 117. [[CrossRef](#)]
- Yonezawa, K.; Kawaguchi, M.; Kaneuji, A.; Ichiseki, T.; Iinuma, Y.; Kawamura, K.; Shintani, K.; Oda, S.; Taki, M.; Kawahara, N. Evaluation of antibacterial and cytotoxic properties of a fluorinated diamond-like carbon coating for the development of antibacterial medical implants. *Antibiotics* **2020**, *9*, 495. [[CrossRef](#)] [[PubMed](#)]
- Toyonaga, M.; Hasebe, T.; Maegawa, S.; Matsumoto, T.; Hotta, A.; Suzuki, T. The property of adhesion and biocompatibility of silicon and fluorine doped diamond-like carbon films. *Diamond Relat. Mater.* **2021**, *119*, 108558. [[CrossRef](#)]
- Zhai, W.; Bai, L.; Zhou, R.; Fan, X.; Kang, G.; Liu, Y.; Zhou, K. Recent progress on wear-resistant materials: Designs, properties, and applications. *Adv. Sci.* **2021**, *8*, 2003739. [[CrossRef](#)]
- Yamaki, T.; Osawa, T.; Matsuo, M.; Akasaka, H.; Tanaka, S.; Kikuchi, M.; Hirata, Y.; Ohtake, N.; Yamamoto, H. Wear Resistant DLC Coatings for Soft Metallic Materials. In Proceedings of the International Conference on Leading Edge Manufacturing/Materials and Processing, Online, 3 September 2020; American Society of Mechanical Engineers: New York, NY, USA, 2020. V001T08A015.
- Song, J.-S.; Park, Y.S.; Kim, N.-H. Hydrophobic anti-reflective coating of plasma-enhanced chemical vapor deposited diamond-like carbon thin films with various thicknesses for dye-sensitized solar cells. *Appl. Sci.* **2021**, *11*, 358. [[CrossRef](#)]
- Grenadyorov, A.; Solovyev, A.; Oskomov, K.; Oskirko, V.; Semenov, V. Thermal stability of anti-reflective and protective aC: H: SiO<sub>x</sub> coating for infrared optics. *Appl. Surf. Sci.* **2020**, *510*, 145433. [[CrossRef](#)]
- Love, C.; Cook, R.B.; Harvey, T.; Dearnley, P.; Wood, R. Diamond like carbon coatings for potential application in biological implants—A review. *Tribol. Int.* **2013**, *63*, 141–150. [[CrossRef](#)]

13. Nagashima, S.; Hasebe, T.; Kamijo, A.; Yoshimoto, Y.; Hotta, A.; Morita, H.; Terada, H.; Tanaka, M.; Takahashi, K.; Suzuki, T. Effect of oxygen plasma treatment on non-thrombogenicity of diamond-like carbon films. *Diamond Relat. Mater.* **2010**, *19*, 861–865. [[CrossRef](#)]
14. Anil, M.; Ahmed, S.F.; Yi, J.W.; Moon, M.-W.; Lee, K.-R.; Chan Kim, Y.; Seok, H.K.; Han, S.H. Tribological performance of hydrophilic diamond-like carbon coatings on Ti-6Al-4V in biological environment. *Diamond Relat. Mater.* **2010**, *19*, 300–304. [[CrossRef](#)]
15. Meškiniš, Š.; Kopustinskias, V.; Šlapikas, K.; Tamulevičius, S.; Guobiene, A.; Gudaitis, R.; Grigaliūnas, V. Ion beam synthesis of the diamond like carbon films for nanoimprint lithography applications. *Thin Solid Films* **2006**, *515*, 636–639. [[CrossRef](#)]
16. Rahman, S.M.; Song, J.; Yeo, C.-D. Computational study on surface energy of amorphous DLC with respect to hybridization state of carbon and potential functions. *Diamond Relat. Mater.* **2019**, *95*, 127–134. [[CrossRef](#)]
17. Roy, R.K.; Choi, H.-W.; Park, S.-J.; Lee, K.-R. Surface energy of the plasma treated Si incorporated diamond-like carbon films. *Diamond Relat. Mater.* **2007**, *16*, 1732–1738. [[CrossRef](#)]
18. Marciano, F.; Bonetti, L.; Da-Silva, N.; Corat, E.; Trava-Airoldi, V. Wettability and antibacterial activity of modified diamond-like carbon films. *Appl. Surf. Sci.* **2009**, *255*, 8377–8382. [[CrossRef](#)]
19. López-Santos, C.; Yubero, F.; Cotrino, J.; González-Elipe, A. Lateral and in-depth distribution of functional groups on diamond-like carbon after oxygen plasma treatments. *Diamond Relat. Mater.* **2011**, *20*, 49–56. [[CrossRef](#)]
20. Siow, K.S.; Britcher, L.; Kumar, S.; Griesser, H.J. Plasma methods for the generation of chemically reactive surfaces for biomolecule immobilization and cell colonization—A review. *Plasma Process. Polym.* **2006**, *3*, 392–418. [[CrossRef](#)]
21. Yi, J.W.; Moon, M.-W.; Ahmed, S.F.; Kim, H.; Cha, T.-G.; Kim, H.-Y.; Kim, S.-S.; Lee, K.-R. Long-lasting hydrophilicity on nanostructured Si-incorporated diamond-like carbon films. *Langmuir* **2010**, *26*, 17203–17209. [[CrossRef](#)]
22. Sun, L.; Guo, P.; Li, X.; Wang, A. Comparative study on structure and wetting properties of diamond-like carbon films by W and Cu doping. *Diamond Relat. Mater.* **2017**, *73*, 278–284. [[CrossRef](#)]
23. Wang, J.; Zhang, K.; Wang, F.; Zheng, W. Improving frictional properties of DLC films by surface energy manipulation. *RSC Adv.* **2018**, *8*, 11388–11394. [[CrossRef](#)] [[PubMed](#)]
24. Ma, G.; Gong, S.; Lin, G.; Zhang, L.; Sun, G. A study of structure and properties of Ti-doped DLC film by reactive magnetron sputtering with ion implantation. *Appl. Surf. Sci.* **2012**, *258*, 3045–3050. [[CrossRef](#)]
25. Chen, L.; Minakawa, A.; Mizutani, M.; Kuriyagawa, T. Study of laser-induced periodic surface structures on different coatings exhibit super hydrophilicity and reduce friction. *Precis. Eng.* **2022**, *78*, 215–232. [[CrossRef](#)]
26. Jedrzejczak, A.; Kolodziejczyk, L.; Szymanski, W.; Piwowski, I.; Cichomski, M.; Kisielewska, A.; Dudek, M.; Batory, D. Friction and wear of aC:H:SiO<sub>x</sub> coatings in combination with AISI 316L and ZrO<sub>2</sub> counterbodies. *Tribol. Int.* **2017**, *112*, 155–162. [[CrossRef](#)]
27. Koshigan, K.; Mangolini, F.; McClimon, J.; Vacher, B.; Bec, S.; Carpick, R.; Fontaine, J. Understanding the hydrogen and oxygen gas pressure dependence of the tribological properties of silicon oxide-doped hydrogenated amorphous carbon coatings. *Carbon* **2015**, *93*, 851–860. [[CrossRef](#)]
28. Batory, D.; Jedrzejczak, A.; Szymanski, W.; Niedzielski, P.; Fijalkowski, M.; Louda, P.; Kotela, I.; Hromadka, M.; Musil, J. Mechanical characterization of aC:H:SiO<sub>x</sub> coatings synthesized using radio-frequency plasma-assisted chemical vapor deposition method. *Thin Solid Films* **2015**, *590*, 299–305. [[CrossRef](#)]
29. Stalder, A.F.; Kulik, G.; Sage, D.; Barbieri, L.; Hoffmann, P. A snake-based approach to accurate determination of both contact points and contact angles. *Colloids Surf. A Physicochem. Eng. Asp.* **2006**, *286*, 92–103. [[CrossRef](#)]
30. Bachmann, S.; Schulze, M.; Morasch, J.; Hesse, S.; Hussein, L.; Krell, L.; Schnagl, J.; Stark, R.W.; Narayan, S. Aging of oxygen and hydrogen plasma discharge treated aC:H and ta-C coatings. *Appl. Surf. Sci.* **2016**, *371*, 613–623. [[CrossRef](#)]
31. Yun, D.Y.; Choi, W.S.; Park, Y.S.; Hong, B. Effect of H<sub>2</sub> and O<sub>2</sub> plasma etching treatment on the surface of diamond-like carbon thin film. *Appl. Surf. Sci.* **2008**, *254*, 7925–7928. [[CrossRef](#)]
32. Marciano, F.; Marcuzzo, J.; Bonetti, L.; Corat, E.; Trava-Airoldi, V. Use of near atmospheric pressure and low pressure techniques to modification DLC film surface. *Surf. Coat. Technol.* **2009**, *204*, 64–68. [[CrossRef](#)]
33. Sun, P.; Wang, Y.; Liu, H.; Wang, K.; Wu, D.; Xu, Z.; Zhu, H. Structure evolution of graphene oxide during thermally driven phase transformation: Is the oxygen content really preserved? *PLoS ONE* **2014**, *9*, e111908. [[CrossRef](#)]
34. Bokare, A.; Nordlund, D.; Melendrez, C.; Robinson, R.; Keles, O.; Wolcott, A.; Erogbogbo, F. Surface functionality and formation mechanisms of carbon and graphene quantum dots. *Diamond Relat. Mater.* **2020**, *110*, 108101. [[CrossRef](#)]
35. Kerber, S.; Bruckner, J.; Wozniak, K.; Seal, S.; Hardcastle, S.; Barr, T. The nature of hydrogen in X-ray photoelectron spectroscopy: General patterns from hydroxides to hydrogen bonding. *J. Vac. Sci. Technol. A Vac. Surf. Film.* **1996**, *14*, 1314–1320. [[CrossRef](#)]
36. Shen, Z.; Xia, Y.; Zhao, C.; Ding, Y.; Fan, P.; Li, J. Mechanical Property Evolution Model of Polyimide Film by Far Ultraviolet Irradiation. *J. Phys. Conf. Ser.* **2020**, *1637*, 012040. [[CrossRef](#)]
37. Milošev, I.; Jovanović, Ž.; Bajat, J.; Jančić-Heinemann, R.; Mišković-Stanković, V. Surface analysis and electrochemical behavior of aluminum pretreated by vinyltriethoxysilane films in mild NaCl solution. *J. Electrochem. Soc.* **2012**, *159*, C303. [[CrossRef](#)]
38. Hegemann, D.; Brunner, H.; Oehr, C. Plasma treatment of polymers to generate stable, hydrophobic surfaces. *Plasmas Polym.* **2001**, *6*, 221–235. [[CrossRef](#)]
39. Kaare, K.T.; Yu, E.; Volperts, A.; Dobeles, G.; Zhurinsk, A.; Dyck, A.; Niaura, G.; Tamasauskaitė-Tamasiunaite, L.; Norkus, E.; Andrulevičius, M. Highly active wood-derived nitrogen-doped carbon catalyst for the oxygen reduction reaction. *ACS Omega* **2020**, *5*, 23578–23587. [[CrossRef](#)]



40. Kaare, K.; Yu, E.; Käambre, T.; Volperts, A.; Dobele, G.; Zhurinsh, A.; Niaura, G.; TamasauskaiteTamasiunaite, L.; Norkus, E.; Kruusenbergs, I. Biomass-derived graphene-like catalyst material for oxygen reduction reaction. *ChemNanoMat* **2021**, *7*, 307–313. [[CrossRef](#)]
41. NIST X-ray Photoelectron Spectroscopy Database. *NIST Standard Reference Database Number 20*; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2000; p. 20899.

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.