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Fabrication of Transparent Very Thin SiO_x Doped Diamond-Like Carbon Films on a Glass Substrate

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Abstract: A novel direct current (DC) magnetron sputtering system via radio frequency (RF) bias with hexamethyldisiloxane (HMDSO) plasma polymerization was developed for the deposition of SiO_x-doped diamond-like carbon (DLC) films on a glass substrate. As the RF bias increased, the ratio of intensity of D peak and G peak (I(D)/I(G)) decreased and the G peak shifted to a low position, leading to high hardness and a large portion of sp^3 bonds. Additionally, weak sp^2 graphite bonds were broken and sp^3 diamond bonds formed because the RF bias attracted hydrogen ion bombarding the DLC films. Increasing DC power was helpful to improve the hardness of the DLC films because the proportion of sp^3 bonds and the I(D)/I(G) ration was increased. HMDSO was introduced into this process to form SiO_x:DLC films with enhanced optical performance. The average transmittance in the visible region of these very thin SiO_x:DLC films with a thickness of 37.5 nm was 80.3% and the hardness of the SiO_x:DLC films was increased to 7.4 GPa, which was 23.3% higher than that of B270 substrates.

Keywords: SiO_x:DLC; hexamethyldisiloxane (HMDSO); RF bias; hardness; plasma polymerization

1. Introduction

Diamond-like carbon (DLC) films are various forms of amorphous carbon materials with some of the unique properties of natural diamond [1,2]. The DLC films are composite materials that consist of carbon atoms with sp^2 bonds (graphite-like) and sp^3 bonds (diamond-like). The properties of DLC films are determined by the compositional concentrations of sp^2 bonds, sp^3 bonds, and hydrogen atoms. In 1971, Aisenberg and Chabot became the first to produce amorphous carbon films with many of the properties of diamond, using ion-beam deposition [3]. DLC films are already well-known for their superior properties, such as high hardness, high wear resistance, low friction coefficient, chemical inertness, thermal conductivity, and others [4–7]. Hence, DLC films have had various applications, such as in car engine parts, electromechanical devices, magnetic storage disks, articulations, and bio-lubricants [2,8–12]. Unlike diamond films, which are prepared in a high temperature process [13,14], DLC films can be fabricated at low temperature [15–18]. However, DLC films have some disadvantages, such as a high internal compressive stress, poor adhesion, and low transmittance [19,20]. DLC films have been prepared using various deposition methods such as plasma-enhanced chemical vapor deposition [21–23] and physical vapor deposition [24,25]. The doping of DLC films to widen their range of application has been extensively investigated. Zhao et al. prepared Ti-doped hydrogenated DLC films on polished stainless steel substrates and Si wafers in a radio frequency (RF) plasma-enhanced chemical vapor deposition (PECVD) and unbalanced magnetron sputtering system with an ultra-low friction coefficient of ~0.008 [26]. Zou et al. deposited Cr:DLC nanocomposite coatings on Si and WC–Co cemented carbide substrates in a middle frequency magnetron sputtering and ion plating system, and reported that a 9.7 at.% Cr content reduces the stress of the coatings to 0.49 GPa [27].

Sharma et al. reported a new technique called grid-based PECVD for depositing DLC films on conducting and insulating substrates and discussed theirs corrosion resistance [28]. Paul et al. prepared DLC films on SnO_2-coated glass substrates by electrodeposition and found them to be extremely hydrophobic [29]. Ding et al. reported on the optical and electrical properties of DLC films that were deposited by the pulsed laser ablation of a graphite target on quartz substrate. The thickness of their DLC films was approximately 200 nm [30]. These studies reported on the deposition of DLC films on Si, quartz, and SnO_2-coated glass substrates, but unfortunately not glass substrates. The transmittance and thickness of the DLC films were all less than 63% and more than 100 nm, respectively. However, the literature works that studied DLC films neither discussed transmittance nor high transmittance.

Damasceno et al. fabricated SiO_x:DLC–SiO_x films on crystalline silicon, glass, and polycarbonate substrates in the cathode of a conventional RF parallel plate glow discharge reactor system, and indicated that these films exhibited decreasing residual stress [31]. Paul et al. synthesized DLC films (~2 μm thick) on glass substrates with various sp^2/sp^3 ratios by sputtering a vitreous carbon target in Ar + H_2 plasma, and they found that the films were hydrophobic [32]. Ahmed et al. deposited silver-doped DLC films by RF reactive sputtering on glass and silicon substrates. An Ag concentration of 12.5 at.% yielded an optical band gap of 1.95 eV and reduced the transmittance [33]. These authors subsequently reported on the optical properties of fluorine-doped DLC thin films that were synthesized by PECVD on glass and silicon substrates at visible and near-infrared wavelengths [34]. Even though these studies involved DLC films on glass, their thickness always exceeded 170 nm, and sometimes even exceeded 2.9 μm. Additionally, neither transmittance of the DLC films nor high transparency was discussed. In these studies, the highest transmittance was less than 80%.

In this study, transparent very thin SiO_x:DLC films were deposited on a glass substrate using direct current (DC) magnetron sputtering system via RF bias by hexamethyldisiloxane (HMDSO) plasma polymerization. The transmittance in the visible region was improved by increasing the HMDSO flow rate, and the deposition thickness was controlled from 9.8 to 87.2 nm.

2. Experimental Section

2.1. Deposition of Transparent Very Thin Films

The DC magnetron sputtering system with RF bias and plasma polymerization was used to deposit SiO_x:DLC films on B270 glass substrates. The B270 substrates were obtained by I-MEI Materials Co., Ltd., (New Taipei, Taiwan) and successively cleaned in acetone, isopropanol, and deionized (DI) water for 10 min in each substance by ultra-sonication, and dried using nitrogen gas. Figure 1 schematically depicts the deposition system, which involved a carbon target (99.99% purity and 3 inch in diameter) and a substrate holder that was connected to an RF power source with a frequency of 13.56 MHz. The sputtering chamber was pumped down to 3×10^{-5} torr using a diffusion pump prior to the deposition. The working gas was methane (CH_4), the organic silicon monomer was HMDSO, and the working pressure was 3×10^{-3} torr. In this process, HMDSO was ionized by plasma polymerization to supply SiO_x dopant.

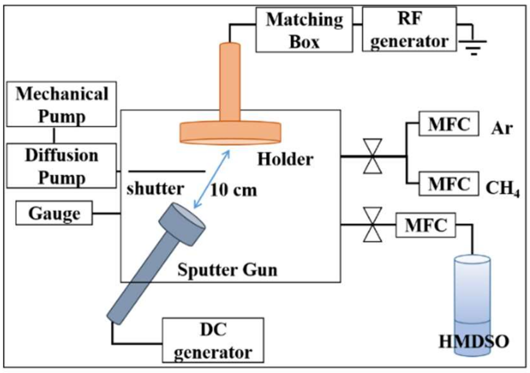


Figure 1. Schematic diagram of the apparatus used for deposition of SiO_x: diamond-like carbon (DLC) films. Radio frequency (RF), hexamethyldisiloxane (HMDSO), mass flow controller (MFC).

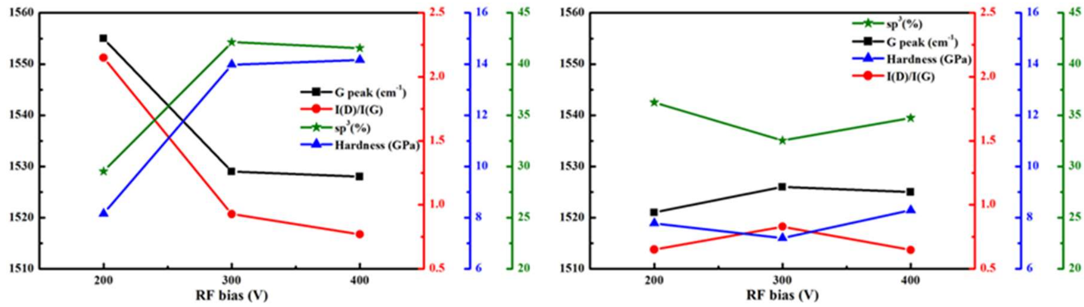
2.2. Measurements

The thickness of transparent very thin SiO_x:DLC films was measured using an alpha-step profile meter (Dektak 6M, Veeco, Plainview, NY, USA). The hardness was obtained using a nano-indenter (MTS Nano-Indenter, Keysight Technologies, Santa Rosa, CA, USA) worked in a continuous stiffness measurement mode and the maximum load was 10 mN. The proportion of sp^3 bonds and the relative atomic contents of C, Si, and O were obtained using X-ray photoelectron spectroscopy (XPS) (VG Sigma Probe, VG-Scientific Ltd., East Grinsted, UK) with a microfocus monochromator Al anode X-ray device. The ratio of intensity of D peak and G peak (I(D)/I(G)) was obtained using a Raman spectrometer (RAMaker, ProTrus Tech Co. Ltd., Tainan, Taiwan) with a 532 nm laser. The optical transmittance of SiO_x:DLC films was measured using a Hitachi U4100 spectrometer in the wavelength range from 400 to 700 nm.

3. Results and Discussion

3.1. The Optimized DLC Films

According to the literature, the properties of DLC films were characterized by bias voltage of deposition systems [35–37]. Figure 2a,b shows the properties of DLC thin films deposited using CH_4 plasma with various RF biases from 200 to 400 V with and without 50 W DC power, respectively. As depicted in Figure 2a, the G peak shifted to a low wavenumber and of I(D)/I(G) ratio decreased as the RF bias increased. Both the D peak (1350 cm^{-1}) and the G peak (1580 cm^{-1}) originated from the sp^2 bonding in the amorphous carbon films. The intensity ratio of the corresponding two bands, I(D)/I(G), was closely related to the graphite that was formed during the growth of the film. In DLC films, a small I(D)/I(G) ratio corresponds to a high proportion of sp^3 [38]. The proportion of sp^3 bonds and hardness increased with the increasing RF bias. Hydrogen ions that were attracted by RF bias bombard the DLC films, weak sp^2 graphite bonds were then broken and sp^3 diamond bonds were formed [39]. As the RF bias increased, the I(D)/I(G) ratio decreased and the G peak shifted to a low position resulting in a great hardness and a larger proportion of sp^3. From Figure 2b, the position of the G peak, hardness, proportion of sp^3 bonds and I(D)/I(G) ratio did not obviously vary with the RF bias since the energy of the CH_4 plasma achieved only using RF bias without DC power was not enough to increase the proportion of sp^3 bonds when the DLC films were deposited. From Figure 2, the optimal RF bias for depositing the DLC films was 400 V with 50 W DC power. The DLC films were deposited in a DC power range of 25–100 W with an RF bias of 400 V. Figure 3 displays the G peak, the I(D)/I(G) ratio and the hardness of DLC films. The G peak and the I(D)/I(G) ratio of the DLC films increased with the DC power, because the DC power as an additional source provided extra energy for hydrogen ions bombardment. The highest hardness and thickness of the DLC films, obtained by deposition using a DC power of 50 W, were 10.1 GPa and 155 nm, respectively. These results showed that the optimal parameters of the deposition of the DLC films were an RF bias of 400 V and a DC power of 50 W.



(**a**) (**b**)

Figure 2. The analysis of DLC properties in the RF bias range of 200–400 V (**a**) with, and (**b**) without DC power of 50 W with CH_4 flow rate of 15 sccm. (CH_4 = 15 sccm, thickness: (a) 470 nm and (b) 110 nm).

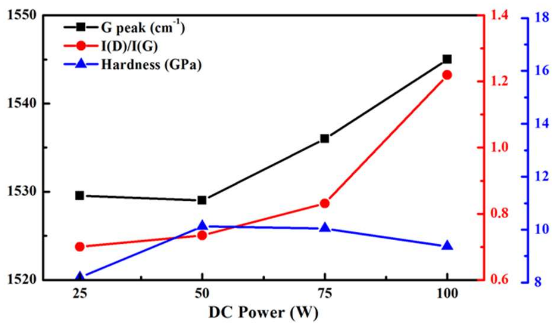


Figure 3. The analysis of DLC properties in the DC power range of 25–100 W with RF bias of 400 V. (CH_4 = 15 sccm, Thickness = 150 ± 10 nm).

Carbon source of DLC films deposited in this system were provided from CH_4 plasma. Under the above conditions of an RF bias of 400 V and a DC power of 50 W, DLC films were fabricated using various CH_4 flow rates as shown in Figure 4. The wavenumber of the G peak was between 1522 and 1528 cm^{-1} at a CH_4 flow range of 10 to 20 sccm. The $I(D)/I(G)$ ratio and the hardness showed that the structures and the mechanical properties of the DLC films did not significantly change. The highest transmittance of the DLC films in the visible region was 66.2%, which was achieved at a CH_4 flow rate of 12.5 sccm, which was therefore used in the rest of this study. The hardness and the thickness of the DLC films were 8.6 GPa and 133 nm, respectively.

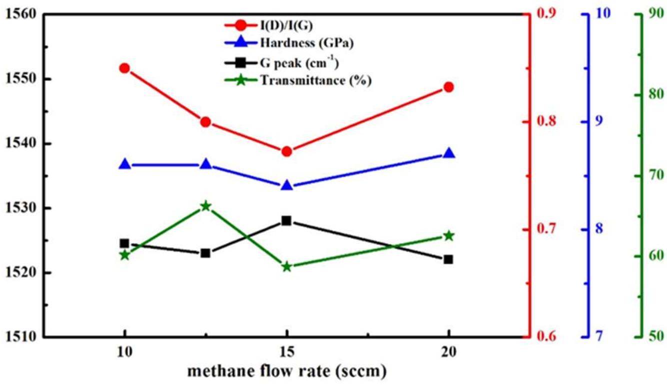


Figure 4. The analysis of DLC properties and transmittance at the different CH_4 flow rates with RF bias of 400 V and DC power of 50 W. (thickness = 135 ± 10 nm).

3.2. The Transparent Very Thin SiO_x:DLC Films

In the above study, the transmittance of DLC films in the visible region was poor, even when their thickness was approximately 130 nm. Hence, the DLC films were doped with SiO_x by HMDSO plasma polymerization to improve their transmittance at an RF bias of 400 V, a DC power of 50 W, and a CH_4 flow rate of 12.5 sccm. The thickness of the transparent SiO_x:DLC films was controlled in the range of 65 ± 5 nm. Figure 5 displays the transmittance spectra of the thin films in the visible region with an HMDSO flow rate of 0–1.2 sccm and Figure 6 presents the DLC properties. The hardness decreased and the transmittance increased as the HMDSO flow rate increased. Similar results were also reported by Batory et al. [40]. Figure 7 presents the XPS relative atomic contents of C, Si, and O. The elemental C content of the SiO_x:DLC films at an HMDSO flow rate of 0 sccm was 95.85%. The elemental C content decreased and the elemental Si and O contents increased with the HMDSO flow rate from 0 to 1.2 sccm. As the HMDSO flow rate increased, more SiO_x was doped into the DLC films, improving transmittance and reducing hardness. The transmittance was improved to 86.8% at an HMDSO flow rate of 1.2 sccm but the hardness was only 7 GPa. An HMDSO flow rate of 0.9 sccm was chosen in further experiments because the achieved transmittance and hardness were then both better than those of non-doped DLC films. The hardness of a B270 substrate was 6 GPa. The hardness of SiO_x:DLC films achieved at an HMDSO flow rate of 0.9 sccm was increased to 8.6 GPa, which was 43.3% higher than that of a B270 substrate. The average transmittance of the SiO_x:DLC films in the visible region was 78.6%.

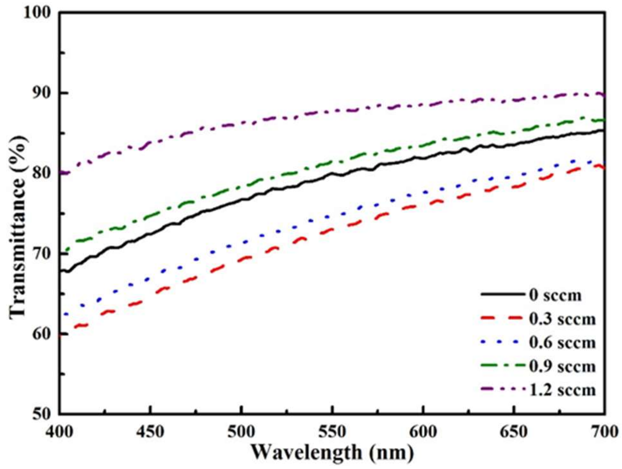


Figure 5. The transmittance spectra of SiO_x:DLC films with the different HMDSO flow rates. (RF bias = 400 V, DC power = 50 W, CH_4 = 12.5 sccm, thickness = 65 ± 5 nm).

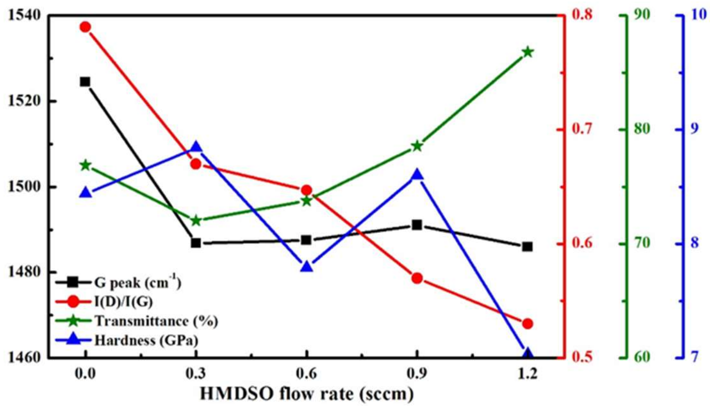


Figure 6. The analysis of DLC properties and transmittance at the different HMDSO flow rates. (RF bias = 400 V, DC power = 50 W, CH_4 = 12.5 sccm, thickness = 65 ± 5 nm).

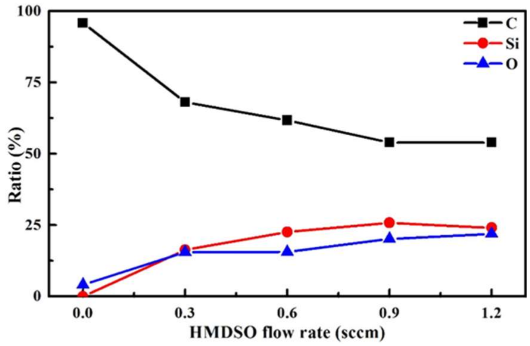


Figure 7. The X-ray photoelectron spectroscopy (XPS) relative atomic content of C, Si, and O at the different HMDSO flow rates. (RF bias = 400 V, DC power = 50 W, CH_4 = 12.5 sccm, thickness = 65 ± 5 nm).

The thickness of the SiO_x:DLC films was controlled from 9.8 to 87.2 nm. Figures 8 and 9 display the properties and transmittance spectra of the SiO_x:DLC films of various thicknesses, respectively. The transmittance decreased as the thickness of SiO_x:DLC films increased. Figure 8 reveals that the wavenumber of the G peak was between 1490 and 1498 cm^{-1}, and the I(D)/I(G) ratio was between 0.5% and 0.6%. The structure of the SiO_x:DLC film was independent of thickness. The hardness decreased and the transmittance increased as the thickness decreased. When the thickness was only 37.5 nm, the average transmittance was 80.3% and the hardness was 7.4 GPa, which was 23.3% higher than that of B270 substrate. When the thickness of the SiO_x:DLC films on the B270 substrate was 64 nm, the hardness was 8.6 GPa, which was 43.3% higher than that of B270 substrate, and the transmittance in the visible region was 78.6%.

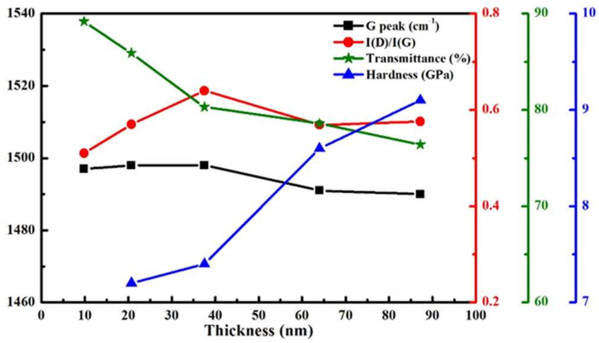


Figure 8. The analysis of DLC properties and transmittance in the different thickness of SiO_x:DLC films. (RF bias = 400 V, DC power = 50 W, CH_4 = 12.5 sccm, HMDSO = 0.9 sccm).

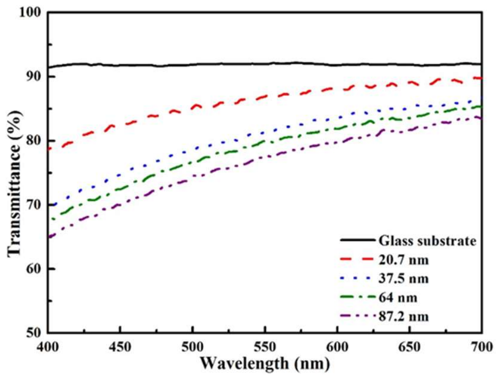


Figure 9. The transmittance spectra of SiO_x:DLC films with different thickness. (RF bias = 400 V, DC power = 50 W, CH_4 = 12.5 sccm, HMDSO = 0.9 sccm).

4. Conclusions

Transparent very thin SiO_x:DLC films were deposited on a glass substrate using a novel DC magnetron sputtering system via RF bias with HMDSO plasma polymerization. Increasing the DC power increased the proportion of sp^3 bonds and the I(D)/I(G) ratio, improving the hardness of the thin films. The highest hardness and thickness of the DLC films were 14.2 GPa and 470 nm; these were achieved at an RF bias of 400 V, a DC power of 50 W, and a CH_4 flow rate of 15 sccm. Doping with SiO_x increased the transmittance of the DLC films. The optimal parameters of SiO_x:DLC films were an RF bias of 400 V, a DC power of 50 W, a CH_4 flow rate of 12.5 sccm, and an HMDSO flow rate of 0.9 sccm. The transmittance in the visible region and the hardness of SiO_x:DLC films with a thickness of 37.5 nm on a B270 substrate in were 80.3% and 7.4 GPa, respectively. Reducing the thickness of the SiO_x:DLC films increased the transmittance of the DLC films by 14.1% from 66.2% to 80.3%, although it reduced the hardness of the thin films by 1.2 GPa from 8.6 to 7.4 GPa.

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Conflicts of Interest: The authors declare that they have no conflict of interest.

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