Electrical Properties of Multilayer (DLC-TiC) Films Produced by Pulsed Laser Deposition

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Graphical abstract
Highlights

- Multilayer (ML (DLC-TiC)) films were deposited on Si and Glass substrates using PLD technique.
- The substrate temperature was varied in the range 20-450°C to control film properties.
- Raising substrate temperature helps to create Nano-graphitic structure, decrease sp³/sp² ratio and increase the smoothness of the films.
- The electrical properties (conductivity) of the ML (DLC-TiC) films enhanced with increasing the substrate temperature.

Abstract

In this work, pulsed laser deposition was used to produce a multilayer (ML (DLC-TiC)) thin film. The ML (DLC-TiC) films were deposited on Si (100) and glass substrates at various substrate temperatures in the range of 20–450°C. Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy were utilized to characterize the prepared films. Raman analysis revealed that as the substrate temperature increased, the G-peak position shifted to a higher wavenumber and the full width at half maximum of the G and D bands decreased. XPS analysis indicated a decrease in sp³/sp² ratio and an increase in Ti-C bond intensity when the substrate temperature was increased. Additionally, the surface roughness of ML (DLC-TiC) films is affected by the type and temperature of the substrate. The electrical measurement results indicated that the electrical resistivity of the ML (DLC-TiC) film deposited on Si and glass substrates showed the same behavior—the resistivity decreased when substrate temperature increased. Furthermore, the ML (DLC-TiC) films deposited on silicon showed lower electrical resistivity, dropping from 8.39E-4 Ω-cm to 5.00E-4 Ω-cm, and the films on the glass substrate displayed a drop in electrical resistivity from 1.8E-2 Ω-cm to 1.2E-3 Ω-cm. These enhanced electrical properties indicate that the ML (DLC-TiC) films have widespread potential as transducer for biosensors in biological research; electrochemical electrodes, because these films can be chemically modified; biocompatible coatings for medical tools; and more.

1) Introduction

The ability to form many different allotropes, such as diamond, graphite, graphene, carbon nanotubes, and amorphous carbon, makes carbon one of the most useful elements for commercial
applications. Diamond (100% sp\(^3\) bond) has excellent mechanical properties, whereas graphite (100% sp\(^3\) bond in their networks) has excellent electrical properties\cite{1}. Amorphous carbon (a-C), which is a metastable form of carbon, has a wide range of forms, including graphite-like carbon, diamond-like carbon (DLC), and polymeric-like carbon. These forms vary based on factors such as hydrogen percentage, sp\(^2\)/sp\(^3\) ratio, deposition process, and defects\cite{2-4}. These factors determine the nature and behavior of an a-C. Various techniques have been used to synthesize DLC films, including ion beam-assisted deposition\cite{5}, filtered cathodic vacuum arc (FCVA) \cite{6,7}, and pulsed laser deposition (PLD)\cite{8}. These techniques are able to synthesize a variety of types of a-C films, depending on precursors or incorporation with other elements to enhance some of their characteristics\cite{9,10}. DLC films have a wide range of electrical conductivity, from semimetal to high insulator, which is controlled by deposition parameters,\cite{11,12} element doping,\cite{13-15} and heat treatment\cite{16}. For instance, bombarding a DLC film with high-energy ions or electrons leads to a decrease in its resistivity to ca. 1m\(\Omega\). cm and increase in adhesion to the substrate\cite{17}. Additionally, DLC films can be doped with different elements such as boron, nitrogen, and metals to control their electrical properties \cite{9,13-15,18}.

Recently, DLC films incorporated with transition metals (Ti, Cr, V, etc.) have attracted considerable attention due to their extraordinary microstructure. The transition metals are chosen based on their ability to create a strong metallic bond with carbon, which produces carbide \cite{19}. Many different methods can be used to incorporate metallic elements with a-C films\cite{20}. For example, researchers have used PLD to dope tetrahedral amorphous carbon (ta-C) with tantalum and nickel at room temperature. The pure ta-C film has high sp\(^3\) sites, similar to pure DLC films. It was noted that, in specific conditions, the resistivity of the films decreases sharply with a low percentage of metal doping\cite{21}. FCVA has also been used to prepare DLC films with a small amount of Ti (1 at. %) implanted from a MeVVA ion source. The DLC-Ti film showed a decrease in electrical resistivity from 38E\(^{-3}\) \(\Omega\)-cm to 6E\(^{-3}\) \(\Omega\)-cm when the annealing temperature increased from 200°C to 600°C \cite{22}.

The PLD is a sophisticated, versatile technique for producing various types of hybrid thin films. In the following research, multilayer (ML (DLC-TiC)) thin films were deposited via PLD on different substrates (silicon (Si) and glass) at various substrate temperatures. The effect of substrate temperature and substrate type on the atomic structure, morphology and electrical
properties of ML (DLC-TiC) films were studied. A schematic diagram of PLD system is shown in Figure 1.

2) Experimental Methods

2-1) Fabrication of Multilayer (DLC-Ti) films
ML (DLC-TiC) films were deposited on two types of substrates, Si (100) and glass. The substrates were each cut into 1 cm × 1 cm pieces and cleaned in a sonication bath with acetone and methanol for ten minutes. The pieces were then rinsed with deionized water repeatedly and dried by compressed nitrogen. The clean substrates were mounted on a rotating substrate holder using silver paste adhesive. The targets, highly ordered pyrolytic graphite (HOPG) (purity 99.99%, 2.0” in diameter, and 1/8” thick) and titanium (purity 99.9%, 2.0” in diameter, and 1/8” thick), were then mounted on a carousel capable of rastering and rotating simultaneously. The distance between the sample and the targets was set to 8 cm. A pulsed excimer laser (KrF) with a wavelength of 248 nm, 20 ns pulse duration, and 10Hz repetition rate was fired on the targets at an angle of 45° through a quartz window and a focusing lens. The substrate was rotated at 5 rpm during deposition to ensure film uniformity. The growth chamber was evacuated to a base pressure of 10⁻⁶ mbar by a turbo pump. All samples were deposited under the same laser energy density, ~1.8 J/cm² per pulse, pulse size 5mm², and various substrate deposition temperatures, ranging from 20–450°C. The HOPG and titanium targets were ablated sequentially in order to fabricate the ML (DLC-TiC) films, with deposition rates of around 0.07 and 0.04 Å/pulse, respectively. The total number of layers was 31 (DLC: 16 layers; Ti: 15 layers), with carbon (DLC) being the last two layers. The thickness of the DLC and TiC layers was ~7 Å and 4.5 Å, respectively. The film thickness was kept constant for all prepared samples (17±2 nm). A schematic representation of the ML (DLC-TiC) films on Si and glass substrates is shown in Figure 2.

2-2) Characterization of ML (DLC-TiC) films
A number of techniques were used to analyze the prepared samples. First, the fabricated ML (DLC-TiC) films were analyzed using Raman spectroscopy (Horiba Jobin Yvon HR 800 UV) (Ar-Kr laser source, \( \lambda_{exc} = 514.5 \) nm, \( E_{exc} = 2.41 \) eV, power 10 mW, as the excitation source). Raman spectroscopy is a sensitive, effective, and mostly non-destructive technique that can be utilized for a wide range of chemical analyses, including identification of small changes in the orientation of C-C bonds in various types of carbon materials. Microscope resolution was 1.6 μm, spectral
scanning area $2 \times 2 \, \mu m^2$, and resolution $1 \, cm^{-1}$. The Raman signal was measured in the range of 1000–3000 $cm^{-1}$. The position of D and G bands and the ratio ($I_D/I_G$) of their corresponding intensities were estimated for all Raman spectra by two Gaussian curve fittings. Atomic Force Microscopy (Bruker Dimension Icron AFM) by bruker was used to study the morphology of the ML (DLC-TiC) films. A sharp silicon tip connected to a soft cantilever moving in x, y, and z directions scanned the surface area ($5 \times 5 \, \mu m^2$) of the samples. Slow scanning frequency (0.5 Hz) was applied to produce clear images. NanoScope Analysis software (Ver. 1.5) was used to analyze and optimize the image quality, removing artifacts and distortions (noise) from the images.

We employed the Thermo Scientific K-Alpha x-ray photoelectron spectroscopy (XPS) system to study the chemical bonds and elemental ratios on the surface of the films. Thermo Scientific Avantage Software was used to perform smart background subtraction and peak fitting and find the elemental ratio. Survey spectra (0–1300 eV) were used to identify the elements on the surface and estimate the element percentage from the normalized area under curves.

The Van der Pauw method was used to measure the electrical resistivity of the films at room temperature, using the ECOPIA (HMS 5000) system. PLD technique also was used to deposit small metal electrodes (Au/Ti) on 4 corners of the ML (DLC-TiC) thin films to perform electrical measurements. The current was set to 1 mA after the confirmation of Ohmic contact of electrodes, to avoid any Schottky effect. The IV curve was obtained by scanning the current automatically from -1 mA to 1 mA and by measuring the corresponding voltage. The data was collected on a computer.

3) Results and Discussion

3-1) Raman spectra analysis

The most important peaks for carbon in the Raman spectra are the G and D bands, which appear in the first-order Raman spectrum. A G-band around 1581 $cm^{-1}$ indicates that the sp$^2$ hybridization is dominant in the carbon network. This is due to the doubly degenerate zone center $E_{2g}$ mode[23]. A D-band around 1350 $cm^{-1}$ indicates the disordered density of carbon atoms at the plane edges[24-26].

Figure 3 shows the Raman spectra of the ML (DLC-TiC) thin films deposited onto Si and glass substrates at various deposition temperatures. Asymmetrical broad peaks appeared in the 1000–2000 $cm^{-1}$ range for all the ML (DLC-TiC) films. The Raman spectra for the films deposited in a temperature range of 20–450°C showed almost the same behavior regardless of substrate type.
At low temperatures, less than 200°C, the films showed a broad G-band around 1550 cm\(^{-1}\) and weak D-band. Increasing deposition temperature above 200°C caused a small shoulder—a D-band—around 1350 cm\(^{-1}\). The appearance of this band, caused by the breakdown of the momentum conversation principle, is evidence of a small graphite crystallite structure. After the deposition temperature was increased, the G and D bands separated and became clearer, confirming that the ML (DLC-TiC) film transformed from an amorphous structure to a more ordered nano-graphitic structure. Further, G-band positions shifted to a higher wavelength, and the full width at half maximum of G bands (FWHM\(_G\)) decreased with respect to deposition temperature. The G band and D band are related to sp\(^2\) carbon configuration. The sp\(^2\) configuration was able to be analyzed due to the high cross section under the visible laser (514 nm, 10mW) used to achieve the Raman spectra; this analysis would not have been possible for sp\(^3\) configuration, which is invisible in this wavelength. This confirms that the prepared samples contain an abundance of sp\(^2\) networks.

The Raman spectra were deconvoluted to analyze overlapping peaks. Gaussian function was carried out to decompose the Raman spectra of the ML (DLC-TiC) thin films into two main peaks (G and D peaks). The G and D peak positions, FWHM of the G and D peaks, and the \(I_D/I_G\) are revealed from Raman curve fitting. Figure 4 shows Raman spectra with the curve fitting of the two kinds of films, ML (DLC-TiC)/Si and ML (DLC-TiC)/glass, with various deposition temperatures. All curves showed two main peaks around 1350 and 1580 cm\(^{-1}\). Figure 5 a–f shows the G-peak positions, the FWHM\(_G\), and the \(I_D/I_G\) as a function of deposition temperature for the two kinds of films. FWHM\(_G\) is related to the disorder in the carbon-carbon bond[23, 24]. It is clear from Figure 5 a and d that the \(I_D/I_G\) ratio increased with increasing deposition temperature for both substrates. Additionally, This ratio is proportional to the graphitic grain size in carbon film[27, 28]. Since the deposition temperature is considered to be a crucial factor in increasing the graphitic structures in amorphous carbon film. Figure 5 b and e shows the FWHM\(_G\) of the films as a function of deposition temperature. The increased distortion in the angle and length of the C-C bond led to a rise in FWHM\(_G\). Therefore, as a result of the low deposition temperature, the FWHM\(_G\) was high, causing disorder in the ML (DLC-TiC) films. Thus, the higher deposition temperature produced a more ordered structure by decreasing the FWHM\(_G\). In Figure 5 c and f, it can be seen that there was no significant change in G-peak position for the films deposited in the low temperature range of 100°C, but there was an obvious increase in the G-peak position when deposition temperature increased to around 200°C. The shifting G-peak position from a low wavenumber to a higher
wavenumber is evidence of the increase in the size and number of graphitic structures (sp² carbons networks). These results are consistent with those found by Ferrari et al. Ferrari [24].

3-2) Surface morphology of ML (DLC-TiC) films

The thickness of the ML (DLC-TiC) films deposited on Si and glass substrates was determined using AFM. The average thickness of the prepared films was around 17±2 nm. Figure 6 a–f shows the morphology and roughness of ML (DLC-TiC) films deposited at different temperatures. An analysis of the topography of the films revealed that the surface roughness gradually decreased and became smoother with increasing substrate temperature. The root mean square roughness of films deposited on the Si substrate varied slightly, between 0.525 nm, 0.21 nm, and 0.17 nm, compared with films on the glass substrate, which varied between 4.07 nm, 4.0 nm, and 2.97 nm, under deposition temperatures of 20, 200, and 400°C, respectively. This behavior confirms that a low substrate temperature is not conducive to developing a smoother structure and that a higher temperature produces denser and smoother ML (DLC-TiC) films.

Based upon these and previous results, a nano-smoothing mechanism of ML (DLC-TiC) films can likely be developed by increasing substrate temperature, because that increases the diffusion rate of carbon and titanium species [29]. The carbon and titanium atoms start growth properly and generate more even structures as the substrate temperature rises. Furthermore, the morphology of the substrate determines the smoothing mechanism of prepared films [30].

3-3) X-ray photoelectron spectroscopy analysis

The XPS survey-scan of ML (DLC-TiC) films deposited on Si and glass substrates at various substrate temperatures revealed that the film surface was composed mainly of carbon, titanium, and oxygen. The elemental concentration of all the prepared films is shown in Table 1. The oxygen concentration in the range below 10% is probably due to the sample’s exposure to the atmosphere and/or from the deposition chamber. Figure 7 shows the XPS C1s core level of ML (DLC-TiC) films deposited at various temperatures. It has been reported that a C1s peak around 284.4 eV corresponds to the graphitic structure (100% sp²) and that for the diamond structure (100% sp³), the binding energy is around 285.0 eV[31]. Figure 7 clearly shows that the binding energy for all the ML (DLC-TiC) films ranged between these two values. It seems that, for both substrates, the C1s binding energy shifted lower when the substrate temperature increased. This behavior indicates that the sp² configuration rather than the sp³ configuration increased in the films.
Figure 8 a–f shows the C1s XPS spectra of the ML (DLC-TiC) films deposited on the two substrates at various temperatures. All the asymmetric peaks of carbon (C1s) were fitted using Gaussian-Lorentzian distribution mixture (G/L ratio 20%). The presence of broad peaks between 284.3–285.3 eV proves that the prepared films are DLC films. This peak exists in both sp² and sp³-hybridized carbon. The curve fitting process was applied to find attribution of each carbon configuration. The FWHM values of sp² and sp³ configurations were determined to be the same as those of pure diamond (FWHMsp³: 1.4 eV) and pure graphite (FWHMsp²: 1.3 eV) [32, 33]. Another parameter that is kept constant during the fitting process is the energy separation between sp² and sp³ bonding. To achieve the best and more flexible fitting, the peaks high of sp², sp³ configurations and sp² position were allowed to be varying [34].

The deconvoluted C1s spectra of the ML (DLC-TiC) films deposited on the two substrates exhibited seven peaks in the range of ~282–289 eV. In figure (8 a-f), all peaks in the (286–289 eV) range (C3) are attributed to C-O, C=O and O-C=O bonds due to film contamination from exposure to the atmosphere. As is shown in Figure 5 a and d, the presence of a small peak at 281.86 eV (C1) in the films deposited at low temperatures is attributed to the Ti-C bond, and the peak at 282.8 ± 0.1 eV (C2) is attributed to a Ti sub-carbide (TiC*) formed from the Ti ions incorporated in the films. The low temperature reactivity of Ti and C atoms is possible if the formation enthalpy of carburization is negative as in our case [35]. The sp² and sp³ carbon configurations are located at 284.39±0.1 eV and 285.28±0.1 eV, respectively. The sp³/sp² ratio of the ML (DLC-TiC)/Si and ML (DLC-TiC)/glass films was estimated to be around 0.51 and 0.46, respectively, based on calculating the relative ratio for C-C sp² peak area and C-C sp³ peak area. As shown in Figure 8 b and e, increasing the substrate temperature to 200°C caused the sp² and sp³ configuration to be located at 284.38 eV and 285.28 eV, respectively. The sp³/sp² ratio of ML (DLC-TiC)/Si and ML (DLC-Ti)/glass films was estimated to be 0.33 and 0.32, respectively. The small peaks at 281.8± 0.1 eV and 282.8 ± 0.1 are attributed to Ti-C and Ti sub-carbide, respectively.

As is shown in Figure 8 c and f, further increase in substrate temperature led to the Ti ions bonding to surrounded carbon atoms, creating a carbidic bond at 282.18 eV (C1) and sub-carbide at 282.90 eV (C2) in both substrates [38, 39]. It seems that the carbidic bonding intensity becomes more prominent in ML (DLC-TiC) films when the substrate temperature rises, because the carbon atoms that react with Ti ions are increased, leading to the production of more carbide [35]. The peaks at 284.32±0.1 and 285.22±0.1 eV correspond to sp² and sp³ carbon bonding. The sp³/sp² ratio...
ratio of ML (DLC-TiC)/Si and ML (DLC-TiC)/glass films was 0.23 and 0.26, respectively. An increase in substrate temperature led to reduced sp³ intensity compared to the sp² intensity in the films. In other words, with increasing substrate temperature, the ML (DLC-TiC) film gained more graphitic structures. This can be seen clearly in Figure 9 a and b. With increasing substrate temperature the sp³/sp² ratio drops slightly at low temperature until it reaches some kind of saturation at high temperature around 350 °C confirming increasing graphitic structures with increasing substrate temperature. This behavior was also confirmed by Raman analysis, as described in the previous section.

The XPS spectra of Ti2p of ML (DLC-TiC)/Si and ML (DLC-TiC)/glass films deposited at various substrate temperatures are shown in Figure 10 a–f. All Ti2p spectra were deconvoluted into four main peaks using Gaussian function. The metallic titanium peak of Ti2p₃/₂, 453.8 eV, does not appear in any figure. This proves that all pure titanium particles bonded with other species in the carbon film. For both ML (DLC-TiC)/Si and ML (DLC-TiC)/glass films deposited at low temperatures, the peaks at 455.5±0.2 eV (FWHM: 2.22 eV) and 461.7±0.2 eV (FWHM: 2.67 eV) can be identified as the Ti2p₃/₂ and Ti2p₁/₂ peaks of titanium carbide, respectively. It has been reported that the binding energy Ti2p₃/₂ of Ti-C is located in the range of around 454.6–455.5 eV [40]. The peaks shifted to higher binding energies, 457.63±0.3 eV (FWHM: 4.12 eV) and 463.96±0.3 eV (FWHM: 3.12 eV), indicating the presence of titanium oxide; these peaks correspond to the Ti2p₃/₂ and Ti2p₃/₂, respectively [41]. The presence of oxide is usually due to the combining of titanium with oxygen molecules inside the deposition chamber and/or from exposure to the atmosphere [38]; titanium particles readily bond with oxygen molecules and form different kinds of oxides [42]. Figure 10 c–f shows an increase in Ti-C peak intensity, relative to the Ti-sub oxide, with increasing substrate temperature. The titanium carbide peaks became sharper and narrower (FWHM: 2.09 eV, 2.90 eV), with the binding energies 454.39± 0.5 eV and 460.28± 0.5 eV corresponding to Tip₃/₂ and Tip₁/₂, respectively. On the other hand, the peak positions of titanium oxide located at 457.05±0.2 eV (FWHM: 2.9 eV) and 462.74±0.3 eV (FWHM: 3.10 eV) corresponds to Tip₃/₂ and Tip₁/₂, respectively.

The chemical composition of the ML (DLC-TiC) thin films was further investigated by depth profile analysis, using XPS with Ar ion sputtering at 3 kV on a 2 mm × 2 mm area. The depth profile was achieved on the ML (DLC-TiC)/Si thin film surface by obtaining XPS data after every 15 seconds of etching with an etching rate of ~0.4 nm/15 seconds, towards the silicone
substrate, to analyze the interface of film layers. As seen in Figure 11, the contribution of carbon C1s on the uppermost layer was \(~86\%\pm2\%\); on the lower layers, the concentration of carbon in the DLC layer decreased to \(~78\%\pm1\%\). However, the oxygen concentration did not rise in the deeper layers, staying in the range of \(7\%\pm1\%\); this implies that the oxygen absorption occurred in the layers during the deposition process. The contribution of Ti2p is less than 5% in the uppermost layer because the uppermost layer was made from two carbon layers to prevent oxidation of titanium. Further increase in etching depth showed that the concentration of Ti2p increased, fluctuating between 11%-14% higher than the top layer.

After deconvolution, the C1s core level was analyzed in each depth profile. Figure 12-a shows the atomic percentages of chemical components as a function of etching depth. It can be seen that in the C1s fitting curve, the major contributions (~50% and 21%, respectively) came from carbon in sp\(^2\) and sp\(^3\) configurations in the DLC layer, with a small amount (~10%) resulting from carbon atom bonds with oxygen. On the other hand, the Ti contribution in the carbon peak was around 19% and appeared in two phases, Ti-C and Ti-C\(^*\) (distorted Ti-C). The first phase came from Ti atom bonds with carbon and produced carbide in the interfaces between carbon layers, while the other phase resulted from the incorporated carbon ions in Ti-C interstices [43]. Also, the curve shows that the contribution of these components was almost constant with increasing etching depth.

Figure 12-b presents the relationship between the atomic percentages of titanium components and the etching depth for the Ti2p profile. After fitting peaks at each depth, the titanium carbide contribution in the interface layer was ~65% of the total concentration of titanium and appeared in two phases, titanium carbide (Ti-C) and distorted carbide (Ti-C\(^*\)), which has a higher binding energy than Ti-C, as shown in previous XPS surface analysis. These two phases mostly occurred in the interface between DLC layers. The other contribution, around 35%, came from titanium oxidation during the deposition process [44]. The absent Ti-Ti bond confirms that the Ti atoms in the interfacing layers completely combined with the C and O atoms.

3-4) Electrical properties of ML (DLC-Ti) films

Before starting the resistivity measurements, it was important to be sure that the contact between the electrodes and the samples was Ohmic. To do so, at two electrodes on the sample, the
current and the voltage across were measured to find the I-V curve, as shown in Figure 13 a and b. The I-V curves showed linear characteristics (Ohmic contact) for both ML (DLC-TiC)/Si and ML (DLC-TiC)/glass films. All our measurements for electrical resistivity were carried out at current to avoid any probability of the Schottky effect.

Figure 14 a and b shows the electrical resistivity (ρ) of the ML (DLC-TiC) films deposited on Si and glass at various temperatures. The prepared films showed initially a gradual decrease in electrical resistivity at low substrate temperatures. This behavior might be attributed to the formation of metallic sub carbide or may be related to the Ti induced graphitization due to the incorporation of Ti ions into the carbon film during the deposition process [35]. With increasing substrate temperature over 200°C, the resistivity decreased sharply, eventually reaching 5.0E-4 Ω-cm and 1.27E-3 Ω-cm at 350°C for the Si and glass substrates, respectively [45]. As noted by our Raman and XPS analysis, this is due to the films’ starting to convert from a fully amorphous to Nano-crystalline structure above 200°C. Thus, the sp² phase of the carbon film becomes more dominant than the sp³. In other words, the electrical properties of a carbon film depend strongly on the number and size of sp² clusters in the film. Increasing the number of sp² sites leads to an increase in the localized hopping states [13, 18]. In addition, Ti-C nano-crystals between DLC layers also contribute to decreasing electrical resistivity. As known from XPS analysis, the Ti-C bond is metallic and its’ presence in ML (DLC-TiC) films enhances electrical conductivity. Furthermore, with increasing substrate temperature above 350°C, the resistivity gets saturated. This trend is consistent with XPS (Figure 9 ) and Raman (Figure 4) results, where the sp³/sp² ratio and ID/IG ratio, respectively, exhibit dependence on the deposition temperature and saturating above 350 °C. This is happening mainly due to the formation of graphitic structure and Ti-C nanocrystals in the interface is completed and hence above 350 °C, the electrical resistivity remains almost constant.

Conclusion

Pulsed laser deposition was used to fabricate ML (DLC-TiC) films on Si and glass substrates at various substrate temperatures. The results indicate that the type and temperature of
a substrate strongly effect film microstructure. Atomic force microscopy showed that the substrate temperature and type effected ML (DLC-TiC) film morphology. Increasing substrate temperature produced a smoother film, and the Si substrate exhibited a more even film than glass. Raman spectroscopy and XPS characterization revealed that at low temperatures, the energetic Ti ion and carbon atoms interacted together, producing small carbide peaks and high sp\textsuperscript{3} contribution. The graphitic structures (sp\textsuperscript{2}) became more dominant than sp\textsuperscript{3} carbon hybridization and carbide bond (Ti-C) intensity increased when the substrate temperature was raised over 200°C. These results suggest that a substrate temperature above 200°C is sufficient to enhance the structure of ML (DLC-TiC) films. Increasing sp\textsuperscript{2} configuration and Ti-C peak intensity in ML (DLC-TiC) films led to improved electrical properties of the prepared film by decreasing the electrical resistivity from high values to 5.0E-4 Ω-cm and 1.27E-3 Ω-cm for Si and glass substrates, respectively. These ML (DLC-TiC) films have tremendous potential for a wide range of applications, such as biomolecule detection in biological research and biocompatible coatings in medical applications.

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References

Figure 1) Schematic of pulsed laser deposition

Figure 2) schematic of ML (DLC-TiC) thin films
Figure 3) Raman spectra of ML (a-C-TiC) thin film deposited at various substrate temperatures on a) an Si substrate and b) a glass substrate.
Figure 4) Deconvoluted Raman spectra of ML (DLC-TiC) film deposited on an Si substrate (a, b, c) and a glass substrate (d, e, f) at various substrate temperatures.
Figure 5) Effect of deposition temperature on G-peak position, FWHM$_G$, and $I_D/I_G$ of ML (DLC-TiC) films deposited on silicon substrates (a, b, c) and on glass substrates (d, e, f).
Figure 6) 3D AFM images (5 µm x 5 µm) of ML (DLC-TiC) films deposited on Si substrates (a, b, c) and glass substrates (d, e, f) at various substrate temperatures.
Figure 7) C1s core level peaks of HOPG target and ML (DLC-TiC) films deposited at various temperatures on a) Si substrates and b) glass substrates.
Figure 8) Deconvolution of C1s core-level of ML (DLC-TiC) films deposited on Si (a, b, c) and Glass (d, e, f) at various substrate temperature.

Figure (9) sp3/sp2 ratio as function of substrate temperature for ML (DLC-TiC) thin film deposited on a) Si and b) glass substrates.
Figure 10) Deconvolution of Ti2p of ML (DLC-TiC) films deposited on Si (a, b, c) and Glass (d, e, f) at various substrate temperatures.

Figure11) XPS depth profile of ML (DLC-TiC)/Si thin film deposit at 20 °C.
Figure 12) Atomic percentage of components for ML (DLC-TiC)/Si thin film as a function of etching depth calculated from fitting a) C1s peaks. b) Tip2 peaks.

Figure 13) I-V curves of ML (DLC-TiC) films deposited on a) Si and b) glass substrates.
Resistivity (ohm-cm) vs. Deposition Temp. (°C)
Figure 14) Effect of substrate temperature on electrical resistivity of ML (DLC-TiC) thin films deposited on
a) Si substrate b) glass substrate.
Table 1) surface chemical composition as conducted by XPS for ML (DLC-TiC) film on Si and Glass substrates.

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<td>88.45</td>
<td>7.52</td>
</tr>
</tbody>
</table>