Enhancement of adhesion strength and corrosion resistance of nitrogen or platinum/ruthenium/nitrogen doped diamond-like carbon thin films by platinum/ruthenium underlayer

N.W. Khun, E. Liu*

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ABSTRACT

A platinum/ruthenium (PtRu) underlayer was grown on highly conductive p-Si (100) substrates, on which nitrogen doped diamond-like carbon (N-DLC) thin films without or with incorporation of Pt and Ru (PtRuN-DLC) were deposited, both via a DC magnetron sputtering system. The effect of PtRu underlayer on the bonding structure, surface morphology and adhesion strength of the N-DLC and PtRuN-DLC films was investigated using X-ray photoelectron spectroscopy (XPS) and micro-Raman spectroscopy, atomic force microscopy (AFM) and micro-scratch testing, respectively. The effect of the PtRu underlayer on the corrosion performance of these films in a 0.1 M HCl solution was diagnosed using electrochemical impedance spectroscopy (EIS). Although the incorporation of Pt and Ru into the N-DLC films promoted sp² sites in the films via metal-induced graphitization, the PtRu underlayer along with the incorporation of Pt and Ru in the N-DLC films could enhance the charge transfer resistance of the films, indicating the increased corrosion resistance of the films.

1. Introduction

Diamond like carbon (DLC) thin films have been developed for a wide range of mechanical, tribological, optical, electrical and biomedical applications because of their unique properties such as high hardness and wear resistance, low friction coefficient, chemical inertness and good biological compatibility [1,2].

Hanging mercury drop electrodes (HMDE), noble metal electrodes and glassy carbon and graphite electrodes have been widely used for electroanalysis, but the poisoning of Hg used in HMDE electrodes to the environment, and surface oxidation and reduction of the metal and carbon electrodes limit their use for electrochemical applications. Boron doped diamond (BDD) film electrodes have been successfully introduced for stripping voltammetric analysis of Pb, Mn, Cd, Cu and Ag, but fabrication of these films demands a high substrate temperature [3–7].

DLC films can be produced at room temperature and achieve similar properties to those of diamond films, so they have been explored as electrode materials for heavy metal tracing [3–5,8,9]. However, high electrical resistivity and residual stress of DLC films have confined their electrochemical applications. The electrical conductivity of DLC films is very important for electrochemical analysis because it can abruptly affect the sensitivity of the film electrodes. A high residual stress in a DLC film apparently reduces the adhesion strength of the film. In a corrosion environment, a lower adhesion strength of a DLC film allows undermining of the film by attacking the interfacial bonds between film and substrate with electrochemically active species permeated through the porosities in the film.

It was reported that the introduction of nitrogen into DLC films could lower the electrical resistivity and at the same time promote the adhesion strength of the films because of the increased sp² sites in the films [3,9]. However, the incorporation of N could degrade the corrosion performance of DLC films via (i) a decrease in density of the films by promoting sp² bonds and (ii) an increase in galvanically induced corrosion current due to the increase in the electrical conductivity of the films [10–12]. A lowered corrosion resistance of DLC films can negatively affect the durability, repeatability and sensitivity of the films when they are used as electrodes for electrochemical purposes.

Some efforts have been made to improve the adhesion strength of DLC films by doping metals such as Ti, V, Ni, Cu, Al, etc. but the introduced metals can serve as active sites on the film surface, resulting in a rapid dissolution of the films in corrosive media due to the potential differences between metal sites and C matrix [13,14]. Nevertheless, addition of noble metals such as Pt and Ru into DLC films may improve the corrosion resistance of the films since they may be electrochemically more stable than DLC films. In addition, it is well
known that Pt and Ru possess outstanding catalytic properties. Therefore, it can be expected that doping of Pt and Ru into N-DLC films would improve not only the corrosion resistance but also the sensitivity of the films for electrochemical analysis. It was reported [15] that a metal underlayer between DLC film and substrate could improve the adhesion and ohmic contact between the film and the substrate, consequently improving the reliability and sensitivity of the film.

In this study, nitrogen doped DLC films (N-DLC) without or with Pt and Ru doping (PtRuN-DLC) were deposited on highly conductive p-Si substrates without or with a PtRu underlayer to investigate the influences of Pt and Ru doping and PtRu underlayer on the structure, adhesion strength and corrosion resistance of these films. It is expected that the PtRu underlayer may be able to lower the dissolution of the substrates by preventing direct access of electrolytes to the substrates and at the same time its higher electrochemical stability than the Si substrates may also reduce galvanically induced corrosion current between films and substrates, though it has seldom been reported.

2. Experimental details

Before introducing p-Si (100) substrates (0.0035–0.001 ft cm) into the film deposition chamber, they were cleaned with ethanol in an ultrasonic cleaning bath for 20 min followed by distilled water. Prior to film deposition, the Si substrates were etched with an Ar+ plasma at a substrate bias of −250 V in the vacuum chamber under a pressure of 10 mTorr for 20 min. In this study, nitrogen doped diamond-like carbon (N-DLC) thin films were deposited on Si substrates without or with incorporation of Pt and Ru (N-DLC or PtRuN-DLC) were deposited on the Si substrates without or with PtRu underlayer (PtRu/N-DLC or PtRu/PtRuN-DLC) via DC magnetron sputtering. For the PtRu/N-DLC and PtRu/PtRuN-DLC films, the PtRu underlayers were first deposited on the pre-cleaned Si substrates for 5 min by sputtering a Pt50Ru50 target (99.95%) of 4 in in diameter with a DC power of 25 W under the deposition pressure of 3 mTorr and substrate bias of −10 V at room temperature. Then, the N-DLC films were deposited on the Si substrates without and with the PtRu underlayer by sputtering a graphite target (99.999% C) of 4 in in diameter with a DC power of 850 W and fixed nitrogen and argon gas flow rates of 15 and 50 sccm, respectively. Similarly, the PtRuN-DLC films were deposited on the Si substrates without and with the PtRu underlayer by co-sputtering the same graphite (850 W) and Pt50Ru50 (40 W) targets with the same N2 and Ar flow rates. The substrate bias, substrate rotation speed and deposition time used for all the DLC films were −90 V, 20 rpm and 30 min, respectively.

X-ray photoelectron spectroscopy (XPS) (Kratos-Axis Ultra) was employed to characterize the chemical composition and bonding structure of the samples. A pass energy of 40 eV was used in all the measurements. The X-ray source used was a monochromatic Al Kα line (hν = 1486.71 eV) powered with 10 mA and 15 kV. The C 1s, N 1s, Ru 3d, N 1s, Pt 4f and Ru 3p spectra were fitted with Gaussian line shapes along with separating the contribution of backgrounds with Shirley’s method.

The bonding structure of the DLC films was also characterized using a confocal micro-Raman spectroscopy (Renishaw RM1000) having a He-Ne laser (632 nm) over the range of 800–2000 cm⁻¹. The Raman instrument had a spectral resolution of 1 cm⁻¹ and a spatial resolution of 1 µm. Average values of the Raman parameters such as positions, full-widths-at-half-maximum (FWHM) and intensity ratios (I(D)/I(G)) of D and G peaks were taken from five random measurements on each sample.

Scanning electron microscopy (SEM, JEOL-JSM-5600LV), transmission electron microscopy (TEM, JEOL-JEM-3000) and atomic force microscopy (AFM, Digital Instruments, S-3000) were used to study the morphological characteristics of the films. For surface roughness (Ra) measurement with AFM, five measurements were randomly conducted on each sample and an average value was taken.

The adhesion strength of the films was measured with a micro-scratch tester (Shimadzu SST-101) having a diamond stylus of 15 µm in radius that was dragged down the films under a progressive loading condition at room temperature. The oscillation amplitude, oscillation frequency, scratch rate and down speed for all the tests were set as 50 µm, 30 Hz, 10 µm/s, and 2 µm/s, respectively. Five measurements were conducted on each sample and an average value of critical load was taken.

All electrochemical (EC) measurements of the DLC coated samples were carried out in a 0.1 M HCl solution using an Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Eco Chemie, Netherlands) with a three-electrode cell at room temperature after immersion in the solution for 1 h at the free corrosion potential. Before the EC measurements, a gold layer was coated on the backsides of the DLC coated samples to obtain a good electrical connection during the EC tests. The tested area on the films was a circle of 1 cm in diameter. A saturated standard calomel reference electrode (SCE) in a saturated KCl solution (244 mV vs. SHE at 25 °C) and a platinum mesh counter electrode were used. Bode and Nyquist plots of the samples were acquired at the open circuit potential in the frequency range of 10⁵ to 10⁻³ Hz with an AC excitation signal of 10 mV.

3. Results and discussion

Fig. 1 shows a TEM micrograph of the PtRuN-DLC film, which clearly shows that Pt and Ru exist as nano-aggregates embedded in the N-DLC matrix probably due to their larger atomic radii compared to that of carbon. In addition, similar electronegativity values among Pt, Ru and C are one of the reasons for the undissolved PtRu aggregates in the carbon matrix [16–18]. The sizes of the nano-aggregates are about 2–5 nm.

The atomic ratios of N/(C+N), N/(C+Ru+Pt+N), Pt/(C+Ru+Pt+N) and Ru/(C+Ru+Pt+N) are determined from the integrated areas of the XPS C 1s, N 1s, Pt 4f and Ru 3d spectra and presented in Table 1. It is found that the N/(C+N) ratio of the N-DLC film is about 0.21 but the PtRu/N-DLC film has a higher nitrogen fraction of about 0.27 though the two N-DLC films were deposited under the fixed N2 flow rate of 15 sccm. The results point out that the PtRu underlayer probably favors the incorporation of N in the PtRu/N-DLC film through graphitization of amorphous carbon structure because N atoms preferentially exist in the sp² configuration [19]. A similar effect of the PtRu underlayer on the N content of the PtRuN-DLC film is also expected.

Fig. 1. TEM micrograph of the PtRuN-DLC film.
DLC films is also observed, i.e., the N/(C + Ru + Pt + N) ratios for the PtRuN-DLC and PtRu/PtRuN-DLC films are about 0.18 and 0.2, respectively. However, the Pt and Ru contents in the both PtRuN-DLC and PtRu/PtRuN-DLC films are not affected by the PtRu underlayer with their Pt/(C + Ru + Pt + N) and Ru/(C + Ru + Pt + N) ratios of about 0.03 and 0.05, respectively. It is found that the Ru contents are consistently higher than the Pt contents for the PtRuN-DLC films, which may be attributed to a core-shell structure of the PtRu aggregates, which is in agreement with the finding by Babu et al. [20], in which the inner core is enriched with Pt and the outer shell is enriched with Ru. In the core-shell structure, one element that is enriched in the core always exhibits a stronger preference for the selection of homometallic bonding than the other element existing in the shell [16,20,21]. Liu et al. [21] have reported that the Pt atoms exhibit a preference of forming homometallic bonding and thus there are more neighboring atoms around the cores of Pt aggregates.

Furthermore, the chemical concentrations of the N-DLC and PtRuN-DLC films are analyzed with XPS depth profiling after sputtering for 5 min at a pressure of about 3.5 × 10⁻⁸ Torr. It is found that the N/(C + N) ratio in the N-DLC films and N/(C + Ru + Pt + N) ratio in the PtRuN-DLC films decrease to about 10% and 5%, respectively. However, it is found that the Pt/(C + Ru + Pt + N) and Ru/(C + Ru + Pt + N) ratios in the PtRuN-DLC films increase to about 21% and 29%, respectively, implying that the Ru contents are still higher than those of Pt in the bulk of the films. The decreased N contents in the bulks of the films than those on the film surfaces after 5 min sputtering are due to the existence of the adsorbed nitrogen atoms on the film surfaces.

Each C 1s spectrum of the N-DLC (Fig. 2a) and PtRuN-DLC (Fig. 2b) films is mainly composed of four components located at around 285, 284.1, 286, and 287.3 eV corresponding to C=C sp², C=C sp², C=O (adsorbed surface oxygen), and C-N bonds, respectively. However, it is observed that the C 1s spectrum of the PtRuN-DLC film overlaps with Ru 3d₅/₂ and partially overlaps with Ru 3d₃/₂, so additional spin-orbit doublets of Ru at about 280.5 eV and Ru – O at about 281.7 eV are found in Fig. 2b [22,23]. The existence of the Ru – O component at the higher binding energy than the Ru⁰ is due to extra coulombic interactions between photon-emitted electrons and ion cores.

It is found that the C=C sp²/C=C sp² ratios, which are estimated from their relevant peak areas, of the PtRuN-DLC films (about 1.42 for the PtRuN-DLC film and 2.19 for the PtRu/PtRuN-DLC film) are higher than those of the N-DLC films (about 0.75 for the N-DLC film and 1.27 for the PtRuN-DLC films) as shown in Table 1. All the DLC films used in this study were deposited under the same process parameters except the sputtering power applied to the Pt⁵₀Ru⁵₀ target during the depositions of the PtRuN-DLC films. It can be deduced that the introduction of Pt and Ru mainly contributes to the increased C=C sp²/

<table>
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<tr>
<th>Sample</th>
<th>N/(C + N)</th>
<th>N/(C + Ru + Pt + N)</th>
<th>Pt/(C + Ru + Pt + N)</th>
<th>Ru/(C + Ru + Pt + N)</th>
<th>Csp²/Csp³</th>
<th>Nsp²/Nsp³</th>
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<tr>
<td>N-DLC</td>
<td>0.21</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.75</td>
<td>1.3</td>
</tr>
<tr>
<td>PtRuN-DLC</td>
<td>0.27</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.27</td>
<td>1.52</td>
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<tr>
<td>PtRu/PtRuN-DLC</td>
<td>0.18</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>1.42</td>
<td>2.21</td>
</tr>
<tr>
<td>PtRu/PtRuN-DLC</td>
<td>0.2</td>
<td>0.03</td>
<td>0.05</td>
<td>2.19</td>
<td>3.08</td>
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Fig. 2. Fitted XPS C 1s and C 1s + Ru 3d spectra of (a) N-DLC and (b) PtRuN-DLC films, respectively, and fitted N 1s spectra of (c) N-DLC and (d) PtRuN-DLC films.
C–C sp$^3$ ratios of the PtRuN-DLC films. It was reported that metal phases could promote graphitization of amorphous carbon around them because the metal phases could act as catalysts [16,24–27]. A sputtering process can provide a sufficient energy to locally heat amorphous carbon on metal surface according to a thermal spike mode [1,16,24]. Moreover, amorphous carbon in contact with metal phases can graphitize at relatively low temperature [16,24,26,27]. Therefore, it can be deduced that the increase of sp$^2$ bonds in the amorphous carbon matrices is induced by metal-induced graphitization, which is also consistent with the literature [28–30]. At the same time, the effect of the DC sputtering power applied to the Pt$\text{Ru}$ target used during depositions of the PtRuN-DLC films should also be taken into account because it may be one of the reasons promoting the metal-induced graphitization via producing the energetic metal species.

Furthermore, the higher C–C sp$^3$/C–C sp$^2$ ratios of the N-DLC (about 0.75 to 1.27) and PtRuN-DLC (about 1.42 to 2.19) films with the introduction of the PtRu underlayers as seen in Table 1 are probably due to interfaces between the DLC films and PtRu underlayers, which favor the metal-induced graphitization of the DLC films.

The N 1s spectra of the N-DLC and PtRuN-DLC films (Fig. 2c and d) are composed of three components, i.e., N–sp$^2$ at about 398.5 eV, N–sp$^3$ at about 400.2 eV and broad N–O component at about 401.4 eV [31]. A similar trend of the N–sp$^3$/N–sp$^2$ ratios of the N-DLC (about 1.3 to 1.52) and PtRuN-DLC (about 2.21 to 3.08) films to that of the respective C–sp$^3$/C–sp$^2$ ratios with the addition of the PtRu underlayer and the introduction of Pt and Ru in the N-DLC films is observed.

The Raman spectra of the N-DLC and PtRuN-DLC films fitted with Gaussian functions for both G and D peaks shown in Fig. 3, from which the Raman parameters are deduced and summarized in Table 1. It is found that both the G and the D peak positions shift to higher wave numbers, i.e., 1535 to 1544 cm$^{-1}$ for the G peak and 1360 to 1370 cm$^{-1}$ for the D peak with the insertion of the PtRu underlayer due to the metal-induced graphitization of the N-DLC films. The metal-induced graphitization may reduce some bond-angle disorder.
and lateral cracks developed during scratching, reveals a high cohesive strength of the film and implies that the kinetic energy of the sputtered C species is sufficient to form the rigid amorphous carbon networks with a high enough sp³ fraction even with the incorporation of N in the film.

The PtRu underlayer deposited on the Si substrate appears to strengthen the adhesion of the N-DLC film, which is confirmed by a higher critical load of about 373 mN (Table 3). It is well known that a high residual stress is associated with a high fraction of sp³ bonds in a DLC film, which abruptly affects the adhesion of the film to its substrate [25,36]. A certain amount of sp³ bonds formed in a DLC film can relax certain strain developed in the film [34,37,38]. Therefore, certain graphitization of the PtRu/N-DLC double-layer configuration improves the adhesion strength of the N-DLC film. Besides, Khun et al. proposed [9] that C=N bonds attributed to N incorporation could decrease the residual stress in DLC films because a C-N bond has a shorter bond length of about 1.29 Å compared to either C–C (1.54 Å) or C=O (1.42 Å). The presence of a less stiff PtRu underlayer between stiffer N-DLC film and Si substrate can also lessen the internal stress of the film, which indirectly enhances the adhesion strength of the film [39]. The scratched PtRu/N-DLC film surface shows larger fragments (Fig. 5b) compared to those seen from the fractured N-DLC film (Fig. 5a). The reduced brittleness of the PtRu/N-DLC film may lower the density of possible neighboring cracks formed in the film under indentation and allow a rapid propagation of the cracks so that the platelets are removed as larger fragments.

It is found that the incorporation of Pt and Ru into the N-DLC film apparently further promotes the adhesion strength of the film so the critical load of the PtRu-N-DLC film is even higher (about 393 mN) than those of the N-DLC films as shown in Table 3 due to a higher degree of metal-induced-graphitization. The PtRu aggregates existing in the DLC film also degrade the sp³-bonded cross-liking structure, leading to a lower residual stress in the film. In addition, the PtRu aggregates could lower the crack density by blocking the crack propagation inside the film, which allows the removal of the scratched materials as platelets as shown in Fig. 5c. The observed spallations in some scratched areas reveal that the incorporation of Pt and Ru into the N-DLC film improves the adhesion strength of the film so that the detachment of the film at the critical load comes from the bulk region of the Si substrate instead of the interface between the film and the substrate.

The PtRu/PtRu-N-DLC double-layer configuration shows the highest critical load of about 417 mN among all the DLC samples used in this study. As discussed above, metal-induced graphitization induced by both the incorporation of Pt and Ru in the N-DLC film and the addition of the PtRu underlayer mainly contributes to the high adhesion strength of the film. A clear scratch path can be seen at the critical load as shown in Fig. 5d, where the less stiff PtRu underlayer plays a cushioning role to relax the normal load applied by the stylus by forming a so-called ‘sink-in’ deformation [40], leading to breaking of the film at the edges of the traction that is perpendicular to the scratch path when the surrounding film cannot sink with the underlying layer (inset in Fig. 5d). Consequently, the occurrence of the undistorted film delamination from the underlying layer at the edges of the traction is attributed to the breaking of the film and the compliance of the underlayer. The observed spallation at the edges of the traction indicates that the adhesion strength of the DLC film is stronger than the cohesive strength of the underlying substrate bulk regions so the breaking takes place in the substrate bulk regions.

It is found that the introduction of Pt and Ru into the N-DLC films increases the thickness of the films, which is confirmed by the higher thickness (about 250 nm) of the PtRu-N-DLC films than those (about 160 nm) of the N-DLC films. Robertson [1] reported that the residual stress in DLC films came along increased film thickness. However, the increased critical loads of the PtRu-N-DLC films with increased film thickness compared to those of the N-DLC films indicate that the

![Fig. 4. AFM images showing surface morphologies of (a) N-DLC and (b) PtRu-N-DLC films.](image-url)

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<th>Sample</th>
<th>( R_s ) (nm)</th>
<th>Critical load (mN)</th>
</tr>
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<tbody>
<tr>
<td>N-DLC</td>
<td>0.81 (±0.05)</td>
<td>359 (±7)</td>
</tr>
<tr>
<td>PtRu/N-DLC</td>
<td>1.06 (±0.1)</td>
<td>373 (±3)</td>
</tr>
<tr>
<td>PtRu-N-DLC</td>
<td>1.18 (±0.1)</td>
<td>393 (±9)</td>
</tr>
<tr>
<td>PtRu/PtRu-N-DLC</td>
<td>1.83 (±0.8)</td>
<td>417 (±4)</td>
</tr>
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influence of the film thickness on the adhesion strength of the films in terms of residual stress is not significant. On the other hand, a thicker film may need a higher load for the indenter to break through the film [41]. Therefore, it may be supposed that the higher thicknesses of the PtRuN-DLC films are one of the reasons giving rise to their higher critical loads than those of the N-DLC films.

Fig. 6a proposes an equivalent electrical circuit to simulate the frequency responses of the N-DLC and PtRuN-DLC coated samples in an electrolytic solution for EIS measurements. In the circuit, $R_1$ is the bulk resistance of the solution, $R_2$ represents the charge transfer resistance, $R_3$ is the bulk resistance of the film, and $Q_2$ and $Q_3$ are the constant-phase-elements (CPE) to replace the double-layer capacitance at the film/solution interface and the capacitance of the film, respectively. The results deduced from the Nyquist plots shown in Fig. 6b are summarized in Table 4 in which $R_2$ is directly related to the structural characteristics such as porosities and sp$^2$ and sp$^3$ contents in the DLC films and $n_2$ describes the deviation of an actual electrochemical process occurring at the film/solution interface ($Z_{CPE}=[Q/(jo)^n]^{-1}$) from an ideal one with $n=1$ where a CPE resembles a capacitor ($Z_C=[jo]^{-1}$). A non-uniform electron transport on a 2D film surface produces inhomogeneous electrochemical reaction rates on the surface. Thus, a high surface roughness can result in uneven electron transfers over the surface and consequently degrades the capacitive behavior of the electrical double layer at the film/surface interface. However, it may not be the case for the DLC films because of their atomically smooth surfaces. Several factors such as aggregation of N, non-uniform composition, non-uniform electron transport and non-uniform electrochemical reaction rate are proposed to mainly contribute to the CPE behavior of the film/solution interface.

Novotny et al. [42] reported that DLC films even with a high quality could almost always contain certain porosities. The pores in a DLC film can grow in an electrolytic solution with immersion time to allow the ions to permeate into the substrate, causing an ionic conduction in the bulk of the film. The high $R_2$ value (Table 4) of the N-DLC film reveals that is responsible for a high corrosion resistance of the film by preventing a prompt dissolution of the film. A high bulk resistance ($R_3$) of the N-DLC film can also be related to the high sp$^3$ content in the film. A high sp$^3$ content in a DLC film reduces its bulk electrical conductivity by increasing the distances between the nearest sp$^2$-hybridized sites since the electrical conductance of a DLC film is associated with a charge carrier hopping between sp$^2$-hybridized states [30,43]. In addition, a cross-linking structure resulted from a high sp$^3$ content is a possible reason lessening the porosity density in the film which reduces the ionic conduction in the bulk of the film.

A PtRu underlayer deposited on the Si substrate enhances the charge transfer resistance of the N-DLC films as depicted by the higher $R_2$ value of the PtRu/N-DLC film than that of the N-DLC film (Table 4). It is known that an anodic current induced by dissolution of the underlying Si substrate occurs when the electrolyte permeates into the film.
The introduction of Pt and Ru into the N-DLC films increases their $R_2$ and $R_3$ values since the PtRu aggregates probably reduce the anodic dissolution of the film and isolate the conduction paths. It was reported [30,43] that isolated metal aggregates were electrically inactive in DLC film bulk and thus noble metals were not effective dopants in DLC films, meaning that they did not obviously increase free charge carriers. For the PtRu/N-DLC film, its lower $n_2$ value (0.932) than that of the N-DLC film indicates a greater deviation from an ideal process, but its higher $n_3$ value (0.872) reveals its improved capacitive behavior. Zeng et al. [44] reported that DLC films had a significantly smaller capacitance than that of Pt. Therefore, it can be expected that the Pt and Ru doping enhances the capacitance behavior of the film. The decreased $n_2$ value results from the catalytic properties of the PtRu aggregates, which facilitates the charge transfer at the film/solution interface.

A higher $R_3$ (34 MΩ) of the PtRu/PtRuN-DLC film than that of the PtRuN-DLC film is consistent with the effect of the PtRu underlayer on the $R_3$ value of the PtRu/N-DLC film. It is shown in Table 4 that the $R_3$ value of the PtRu/PtRuN-DLC film is higher than that of the PtRuN-DLC film though the $R_2$ value of the PtRu/N-DLC film is significantly lower than that of the N-DLC film. It can be deduced that the PtRu aggregates in the bulk of the film probably block the ionic conducting paths, which contribute to the higher bulk resistance of the PtRu/PtRuN-DLC film, in addition to the increased bulk electrical resistivity of the film with Pt and Ru incorporations as mentioned above. In addition, the increased thickness of the PtRuN-DLC films compared to the N-DLC films should be taken into account because the higher film thickness can reduce the ionic conduction by lessening the formation of the possible pores and permeation of the electrolyte. The higher $R_2$ and $R_3$ values of the PtRuN-DLC films than those of the N-DLC films (Table 4) imply that the PtRu aggregates appear to have an overwhelming influence on the corrosion resistance of the films upon the metal-induced graphitization. The $R_3$ values for all the experiments fluctuate between 84.6 and 90 Ω.

Apart from the effects of the PtRu underlayer and the incorporation of Pt and Ru into the N-DLC films on the corrosion resistance of the films, the adhesion strength of the films can influence their corrosion resistance as well. A poor adhesion strength allows an easy attack to weak interfacial bonds by electrochemically active species in the electrolyte permeated into the film/substrate interfaces through the porosities, which undermines the DLC films. The further permeation of the electrolyte inside the undermining areas accesses larger areas of the substrates and thus results in the dissolution of the substrates, which contributes to the overall corrosion of the DLC films. Thus, compared to the N-DLC films, the higher adhesion strengths (Table 3) of the PtRuN-DLC films can be related to their improved corrosion resistance (Table 4).

### 4. Conclusions

The effects of PtRu underlayer and incorporation of Pt and Ru into the N-DLC films on the structure, adhesion strength and corrosion resistance of the films deposited on the p-Si substrates using DC magnetron sputtering deposition were investigated in detail. The introduction of the PtRu underlayer and the incorporation of Pt and Ru into the N-DLC films promoted the sp$^2$ sites via metal-induced
graphitization, increased the surface roughness, and enhanced the adhesion strength and corrosion resistance of the films. The enhancement of the corrosion resistance was confirmed by the increased charge transfer resistances of the DLC films. The observed constant phase element behavior of all the samples indicated that the aggregation of N and PtRu in the DLC films induced non-uniform currents and consequently non-uniform electrochemical reaction rates.

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