Nitrogen-Induced Degradation of Corrosion Resistance of Platinum/Ruthenium/Nitrogen-Doped Diamond-like Carbon Thin Films

N. W. Khun and E. Liu

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

An influence of nitrogen incorporation on the chemical composition, bonding structure, surface morphology and activity, adhesion strength, and corrosion resistance of platinum/ruthenium/nitrogen-doped diamond-like carbon (PtRuN-DLC) films deposited on conductive p-Si(100) substrates using dc magnetron sputtering deposition was investigated using X-ray photoelectron spectroscopy, micro-Raman spectroscopy, atomic force microscopy, sessile liquid drop method, microscratch test, potentiodynamic polarization test, and electrochemical impedance spectroscopy in terms of nitrogen flow rate. The sp² sites in the PtRuN-DLC films increased with increased nitrogen flow rate, which was confirmed by increased C sp²/C sp³, N sp²/N sp³, and I_D/I_G ratios. The experimental results indicated that the decreased corrosion resistance of the PtRuN-DLC films in a 0.1 M NaCl solution with increased nitrogen flow rate was due to the changes in the chemical composition, bonding structure, porosity level, surface morphology and activity, and adhesion strength of the films associated with nitrogen incorporation. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3428724] All rights reserved.

Diamond-like carbon (DLC) thin films have attracted considerable attention due to their high hardness, low friction coefficient, chemical inertness, and good biocompatibility. Presently, nitrogen-doped diamond-like carbon (N-DLC) films are of interest as electrodes for electrochemical (EC) analysis of trace heavy metals. At the same time, the introduction of N into DLC films improves the adhesion of the films to their substrates, which prevents the delamination of the films in corrosive media. However, the incorporation of N into DLC films lowers the corrosion resistance of the films, which is attributed to (i) a decrease in the density of the films by promoting sp³ bonds and (ii) an increase in galvanically induced corrosion current due to increased electrical conductivity of the films. The degraded corrosion resistance of the films abruptly affects the EC performance of the films, such as sensitivity, repeatability, long-term response stability, and robustness. Therefore, it becomes a tough challenge to improve the corrosion resistance of N-DLC films. Because noble metals such as platinum and ruthenium are high corrosion-resistant materials and have excellent catalytic properties, it may be expected that the introduction of platinum and ruthenium into N-DLC films can improve the EC properties of the films such as corrosion resistance and sensitivity to trace heavy metals.

The physical properties of N-DLC films can be characterized by a balance between sp³ and sp² bonds, which can be controlled by film deposition methods and parameters. Though N-DLC films prepared by sputtering deposition with various deposition parameters have been studied, novel platinum/ruthenium/nitrogen-doped diamond-like carbon (PtRuN-DLC) films fabricated with dc magnetron sputtering deposition have not been widely reported yet. N² flow rate introduced into a deposition chamber as a reactive gas is an important deposition process parameter in magnetron sputtering process and influences the chemical composition of the films, which in turn significantly affects the structure of the films.

This study aims to investigate the effect of nitrogen content on the structure and corrosion resistance of PtRuN-DLC films deposited on conductive p-Si substrates using dc magnetron sputtering deposition by diagnosing the chemical composition, bonding structure, surface morphology and activity, and adhesion strength of the films in terms of N² flow rate.

Experimental

PtRuN-DLC thin films were deposited on conductive p-Si(100) (0.02–0.005 Ω cm) substrates using dc magnetron sputtering deposition by varying the nitrogen flow rate from 5 to 30 sccm. Before the film depositions, the substrates were cleaned with plasma etching at a substrate bias of −250 V for 20 min to remove oxide layers and other contaminants on the substrate surfaces. All the film depositions were carried out by cosputtering graphite (99.999% C) and PtRu (99.95%) targets of 4 in. in diameter at a deposition pressure of about 3 mTorr and a fixed argon flow rate of 50 sccm for 60 min. DC powers on the C and PtRu targets were fixed at 650 and 20 W, respectively. During the film depositions, the substrates were biased at −80 V and rotated at 30 rpm. Though all the depositions were conducted at room temperature, the substrate temperature reached about 50°C.

The chemical composition and bonding structure of the PtRuN-DLC films were investigated using an X-ray photoelectron spectroscopy (XPS, Kratos-Axis Ultra) with a pass energy of 40 eV for detailed scans of C 1s + Ru 3d, N 1s, and Pt 4f. The X-ray source used was a monochromatic Al Kα line (hv = 1486.71 eV) with a power source of 10 mA × 15 kV. These detail spectra were deconvoluted into several components with a Gaussian line shape and a contribution of Shirley’s background.

The bonding structure of the PtRuN-DLC films was also characterized using a confocal micro-Raman spectroscopy (Renishaw RM1000) having a He–Ne laser with a 632 nm line over the range of 800–2000 cm⁻¹. Five measurements per sample were randomly carried out to take average values for all Raman parameters.

The surface morphology of the PtRuN-DLC films was studied using an atomic force microscope (AFM, Digital Instruments, S-3000) with a tapping mode Si₃N₄ cantilever at a scan size of 1 × 1 μm and with a scanning electron microscope (JEOL-JSM-5600LV). An average of surface roughness values was determined from five measurements per sample.

The water contact angles of the PtRuN-DLC films were measured with a sessile liquid drop method (FTA 200). Five measurements on each sample were conducted to take an average value of water contact angles.

The adhesion strength of the PtRuN-DLC films was evaluated using a microscratch tester (Shimadzu SST-101) having a diamond stylus of 15 μm radius, which was dragged down the films under progressive loading conditions at room temperature. The scan amplitude and frequency, scratch rate, and downspeed were set as 50 μm, 30 Hz, 10 μm/s, and 2 μm/s, respectively. Five measurements on each sample were carried out and an average of the critical load values was taken.

The corrosion resistance of the PtRuN-DLC films in a 0.1 M NaCl solution was measured with potentiodynamic polarization tests using a potentiostat/galvanostat (EG&G 263A) at a scan rate of 0.8 mV/s and electrochemical impedance spectroscopy (EIS) using an Autolab Type II potentiostat/galvanostat with GPES 4.9 software.

E-mail: MEJLiu@ntu.edu.sg
(Eco Chemie, The Netherlands) at room temperature. A standard three-electrode flat cell, in which a standard saturated calomel reference electrode (SCE) (244 mV vs standard hydrogen electrode at 25°C) and a platinum mesh counter electrode were employed, was used for all the EC measurements. The volume of the solution used was 250 mL. An exposure area of the sample to the solution was a circle of 1 cm diameter. For all the EC measurements, the PtRuN-DLC thin-film coated samples were cut into 2 cm by 2 cm square pieces and a gold layer was deposited on the back sides of the cut samples to make a good electrical connection during the tests. Potentiodynamic polarization curves of the PtRuN-DLC films measured in the 0.1 M NaCl solution were analyzed using a Tafel technique to obtain corrosion parameters such as corrosion potential ($E_{corr}$) and current ($I_{corr}$). Thereafter, polarization resistance ($R_p$) was calculated from anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes and corrosion current ($I_{corr}$) according to the following formula

$$R_p = (\beta_a \times \beta_c)/2.3I_{corr}(\beta_a + \beta_c)$$

where $R_p$ is in k$\Omega$ cm$^2$; $\beta_a$ and $\beta_c$ are in terms of $V/I$, and $I_{corr}$ is in $\mu$A cm$^{-2}$. In the EIS measurements, Bode and Nyquist plots of the samples were acquired in the 0.1 M NaCl solution at the open-circuit potential in the frequency range of $10^4$–$10^{-3}$ Hz with an ac excitation signal of 10 mV after immersion in the solution for 60 min.

**Results and Discussion**

Figure 1 shows the chemical composition of the PtRuN-DLC films as a function of $N_2$ flow rate. N atomic percentage increases from about 16.2 to 23.5 atom % with increased $N_2$ flow rate from 5 to 30 sccm, which results from an increase in the amount of ionized Ar+ species, leading to the decreased Pt and Ru contents in the PtRuN-DLC films. Another possible reason for the decreased Pt and Ru contents is the chemical inertness with N. That the Ru content is higher than that of Pt for all the $N_2$ flow rates is probably due to a core–shell structure of PtRu aggregates.14,15

Figure 2a shows the fitted XPS C 1s + Ru 3d spectrum of the PtRuN-DLC film deposited with 5 sccm $N_2$, in which the C 1s band entirely covers Ru 3d$_{x2}$ and partially overlaps with Ru 3d$_{y2}$, which is deconvoluted into several components; C sp$^2$ at about 285 eV, C sp$^3$ at about 284.1 eV, C–O at about 286.4 eV, C–N at about 287.8 eV and spin-orbit doublets of Ru$^0$ and Ru–O at about 280.4 and 281.6 eV, respectively.

Figure 2b shows the XPS N 1s spectrum of the PtRuN-DLC film deposited with 5 sccm $N_2$, which is deconvoluted into three components: N sp$^2$ at about 398.8 eV, N sp$^3$ at about 400.5 eV, and N–O at about 401.5 eV.14

The inset in Fig. 2a shows the C sp$^2$/C sp$^3$ and N sp$^2$/N sp$^3$ ratios, which are estimated from the ratios between the C sp$^2$ and C sp$^3$ component areas (Fig. 2a) and between the N sp$^2$ and N sp$^3$ component areas (Fig. 2b), respectively, of the PtRuN-DLC films as a function of $N_2$ flow rate. Increasing $N_2$ flow rate from 5 to 30 sccm apparently increases the C sp$^2$/C sp$^3$ ratio from about 0.83 to 2.18 and the N sp$^2$/N sp$^3$ ratio from about 0.98 to 2.76, implying that the increased N content in the PtRuN-DLC films enhances the formation of sp$^2$ sites in the films because nitrogen encourages the formation of new sp$^2$ sites in the films.14,15 Therefore, the increased sp$^2$ sites in the PtRuN-DLC films consequently result in the relaxation of the C sp$^2$–bonded configuration to the C sp$^3$ bonded one via decreased density of the films.18,19 At the same time, the bonding configuration of N atoms incorporated in the films changes from N sp$^3$ to N sp$^2$, which is attributed to the increased N content due to the preferential $\pi$ bonding of nitrogen and the preferentially increased number of the N atoms in the sp$^3$ bonded configuration via the decreased density of the films.14,15 It is reported17,18 that the introduction of metals into an amorphous carbon matrix enhances sp$^2$ sites through metal-induced graphitization. However, the increased C sp$^2$/C sp$^3$ and N sp$^2$/N sp$^3$ ratios cannot be related to the decreased Pt and Ru contents in the PtRuN-DLC films, indicating the significant influence of nitrogen doping on the bonding structure of the PtRuN-DLC films.

As shown in Fig. 3, the intensities of the Raman spectra of the PtRuN-DLC films with respect to $N_2$ flow rate become significantly stronger with increased $N_2$ flow rate from 5 to 30 sccm because the
Raman spectrum of a DLC film is mainly dominated by sp\(^2\) sites, indicating an increase in the sp\(^2\) sites in the films.\(^{16}\) All the Raman spectra of the PtRuN-DLC films are fitted into G and D peaks using Gaussian functions with a linear background, as shown in Fig. 3. The upward shifts of the positions of the G and D peaks from about 1531 to 1552 cm\(^{-1}\) and from about 1367 to 1387 cm\(^{-1}\), respectively, show an increase in sp\(^2\) sites and a decrease in bond disorder with increased N\(_2\) flow rate.\(^{3,25}\) A decrease in full width at half-maximum (fwhm) of the G peaks from about 184 to 166 cm\(^{-1}\) also reveals the decrease in the level of bond disorder. However, the fwhm of the D peaks increases from about 361 to 375 cm\(^{-1}\) with increased N\(_2\) flow rate, implying an increase in ring disorder because nitrogen can adopt several bonding configurations such as pyridine and pyrrole.\(^{15,16,21}\) Though the increased nitrogen content in the PtRuN-DLC films promotes the ring disorder, a slight increase in the intensity ratio (I\(_D\)/I\(_G\)) between the D and G peaks from about 1.5 to 1.9 points out a small increase in clustering of the rings.\(^3\)

Figure 4a shows the potentiodynamic polarization curves of the PtRuN-DLC films measured in the 0.1 M NaCl solution with respect to N\(_2\) flow rate. The corrosion results such as corrosion potential (E\(_{corr}\)) and polarization resistance (R\(_p\)) obtained from the polarization curves shown in Fig. 4a are summarized in Fig. 4b. Increasing N\(_2\) flow rate from 5 to 30 sccm lowers the E\(_{corr}\) and R\(_p\) values of the PtRuN-DLC films from about 197 to 69 mV vs. SCE and from about 183 to 23 kΩ cm\(^2\), respectively, revealing that the corrosion resistance of the PtRuN-DLC films falls with increased N\(_2\) flow rate. Because noble metals such as Pt and Ru are electrochemically nobler than C, the introduction of the noble metals enhances the corrosion resistance of DLC films as reported.\(^9\) Therefore, the decreased Pt and Ru contents in the PtRuN-DLC films with increased N\(_2\) flow rate facilitate the formation of the porosities, which is one of the factors lowering the corrosion resistance of the films.

The corrosion resistance of the PtRuN-DLC films is closely related to the compositional and structural changes of the films with N\(_2\) flow rate. Because noble metals such as Pt and Ru are electrochemically nobler than C, the introduction of the noble metals enhances the corrosion resistance of the PtRuN-DLC films. However, the increased N content in the PtRuN-DLC films promotes the ring disorder, a slight increase in sp\(^2\) sites with increased N\(_2\) flow rate.\(^4,26\) Therefore, the increased electrical conductivity of the PtRuN-DLC films accelerates the galvanically induced corrosion by facilitating the kinetics of electron transport through the films.

DLC films almost always contain certain porosities that allow the electrolyte to permeate into the interfaces between the films and substrates and then the electrochemically active species in the permeated electrolyte attack the interfaces.\(^7\) Therefore, the resulting dissolution of the Si substrates contributes to the overall corrosion of the films. The increased sp\(^2\) sites in the PtRuN-DLC films with increased N\(_2\) flow rate facilitate the formation of the porosities, which is one of the factors lowering the corrosion resistance of the films.

Figure 5 shows the surface morphology of the corroded PtRuN-DLC film deposited with 30 sccm N\(_2\) obtained after the applied potential is driven to a positive value of 2 V, which contains many pits on the film surface, indicating the occurrence of pitting corrosion in the NaCl solution. The PtRuN-DLC film deposited with the highest nitrogen flow rate of 30 sccm may have the highest porosity level. Combined with the degraded cross-linking structure with nitrogen incorporation, the porosities grow with driving the applied potential to more positive values and, finally, the growing porosities connect with adjacent porosities to form the pits. The nitrogen ag-
Aggregation accelerates the localized pitting corrosion via locally increased sp² sites. Some localized solid products can be seen inside the pits, as shown in the inset of Fig. 5. The corrosion reaction of the pits during the development of the localized pits accumulates the solid products inside them. The accumulated solid products prevent further access of the electrolyte inside the pits, lessening the corrosion, so the pits without the solid products have more severe corrosion than the ones with the products, as shown in Fig. 5. A moderate corrosion is found in a circular region around the developed pits, indicating a transition region between the pitting and general corrosion. The pits are only observed on the PtRuN-DLC film deposited with 30 sccm N₂, indicating that a high nitrogen incorporation in the PtRuN-DLC films encourages the pitting corrosion in the NaCl solution.

Figure 6 shows the Nyquist and Bode plots of the PtRuN-DLC films deposited with different N₂ flow rates measured after immersion in the 0.1 M NaCl solution for 60 min. From the Nyquist plots shown in Fig. 6a, a complete semicircle is observed only from the film deposited with 30 sccm N₂ while the incomplete semicircles, whose diameters become increased with decreased N₂ flow rate, are observed from the film deposited with lower N₂ flow rates revealing that the protective behavior of the PtRuN-DLC films decreases with increased N₂ flow rate. This result is consistent with the potentiodynamic polarization result reported above.

Figure 6b shows the Bode plots of the PtRuN-DLC films deposited with different N₂ flow rates, in which the phase angle (θ) and impedance are functions of frequency of the ac voltage applied. In the phase spectra, both the low and high frequency peaks are obvious for the films deposited with N₂ flow rates above 5 sccm N₂ and the high frequency peaks at around 1.5 × 10⁵ Hz become significant with increased N₂ flow rate, which indicates the development of the porosities in the films with increased nitrogen incorporation. The increased porosity density in the PtRuN-DLC films with nitrogen incorporation allows a larger amount of electrolytic solution to permeate into the bulks of the films, which supports the statement that the increased nitrogen incorporation in the DLC films facilitates the formation of the porosities.

Furthermore, the influence of the surface roughness of the PtRuN-DLC films on the corrosion resistance of the films should be investigated because a high surface roughness induces a larger exposed area to the electrolyte and may increase the EC reactions of the films with the electrochemically active species in the electrolyte. Figure 7 shows the surface morphologies of the PtRuN-DLC films deposited with different N₂ flow rates, in which the films deposited with 5 and 30 sccm N₂ have smaller and larger asperities on the surfaces, respectively. The larger asperities on the PtRuN-DLC film surface (30 sccm N₂) are due to the increased sp² sites and N aggregation, which is also confirmed by the apparently increased Rₛ values of the PtRuN-DLC films with increased N₂ flow rate, as shown in Fig. 8a. Therefore, the higher surface roughness of the PtRuN-DLC films with increased N incorporation can be correlated with the lowered corrosion resistance of the films.

The corrosion behavior of the PtRuN-DLC films can also be related to the surface activity of the films. A high surface activity of the films enhances the reactions of the films with the electrochemically active species in the electrolyte. Figure 8b shows that the water contact angles of the PtRuN-DLC films decrease from 69.4° to 59.2° with increased N₂ flow rate from 5 to 30 sccm. Because a small contact angle corresponds to a higher surface energy, the decreased water contact angle with increased N₂ flow rate points out that the increased N content in the PtRuN-DLC films promotes the surface energy of the films attributed to an increase in polar nitrogen–carbon bonds that enhance the surface polarity, giving attraction force to H₂O molecules. In addition, the decreased Pt and Ru concentrations in the PtRuN-DLC films with increased N₂ flow rate point out that the increased N content in the PtRuN-DLC films promotes the surface energy of the films attributed to an increase in polar nitrogen–carbon bonds that enhance the surface polarity, giving attraction force to H₂O molecules. The poor adhesion strength of DLC films induced by a high residual stress in the films can cause undermining and delaminating of the films in corrosive medium. Therefore, the adhesion strength of the PtRuN-DLC films is investigated in terms of critical load that is
taken from an abrupt change in tangential force and the resulting critical loads of the films are presented in Fig. 8c with respect to N₂ flow rate. In Fig. 8c, increasing N₂ flow rate from 5 to 30 sccm increases the critical loads of the PtRuN-DLC films from ~295 to 394 mN, which indicates the improved adhesion strength of the films with nitrogen incorporation due to the increased sp² sites and C–N bonds.⁹,²² The incorporation of Pt and Ru into the N-DLC films can improve the adhesion strength of the films through the relaxation of the residual stresses in the films due to several factors such as metal-induced graphitization of amorphous carbon matrix, formation of metal–carbon nanocomposite, aggregation of metal inclusions in the films, and different stiffnesses between the films and metal aggregates.⁹,²⁸–³⁰ Therefore, the introduction of Pt and Ru can effectively reduce the residual stress of the PtRuN-DLC films, but no correlation between the increased critical loads of the films and the decreased noble metal contents in the films indicates that the structural change induced by N incorporation is a main causative factor affecting the adhesion strength of the films. The increased adhesion of the PtRuN-DLC films to their substrates with increased N₂ flow rate partly improves the corrosion performance of the films by preventing the undermining and delamination of the films.

In the insets of Fig. 8c, the observed brittle fracture only at the end of the scratch on the PtRuN-DLC film deposited with 30 sccm N₂ reveals a high cohesive strength of the film probably due to a significant cross-linking structure existing in the amorphous carbon matrix. It can be alternatively supposed that the PtRuN-DLC films used in this study still have high resistance to the prompt dissolution in the corrosive NaCl solution due to their high cohesive strengths though the increased N content in the films lowers the corrosion resistance of the films to certain extent.

Conclusions

The effect of nitrogen incorporation on the chemical composition, bonding structure, surface morphology, surface energy, adhesion strength, and corrosion resistance of the PtRuN-DLC films deposited on the p-Si substrates using dc magnetron sputtering deposition was discussed in terms of N₂ flow rate. Increased N₂ flow rate led to higher N contents but lower Pt and Ru fractions in the PtRuN-DLC films. The sp² sites in the films increased with increased N₂ flow rate, which was confirmed by higher C sp²/C sp³, N sp²/N sp³, and I₀/I₂ ratios. From the potentiodynamic polarization and EIS tests, the corrosion resistance of the PtRuN-DLC films in the 0.1 M NaCl solution was lowered with higher N₂ flow rates. The experimental results pointed out that the causative factors for lowering the corrosion resistance of the PtRuN-DLC films were the changes in the chemical composition, bonding structure, porosity level, surface roughness and activity, and adhesion strength of the films associated with nitrogen doping.

Acknowledgments

This work was supported by the research grant (EWI-0601-IRIS-035-00) from the Environment and Water Industry Development Council (EWI), Singapore. N.W.K. is grateful for the Ph.D. scholarship from Nanyang Technological University (NTU), Singapore.

References


Figure 7. AFM images showing surface morphologies of PtRuN-DLC films deposited with (a) 5 and (b) 30 sccm N₂.

Figure 8. (a) R₀ values, (b) water contact angles, and (c) critical loads of PtRuN-DLC films as a function of N₂ flow rate. The insets in (b) show water drops formed on PtRuN-DLC films deposited with 5 sccm N₂ (bottom left) and 30 sccm N₂ (top right) respectively. The insets in (c) show scratch trace and surface morphology of scratched PtRuN-DLC film deposited with 30 sccm N₂.