



Electronic Bond Structure of Carbon Nitride Thin Film Deposited by HiPIMS and dc Magnetron Plasma

Abhijit Majumdar^{a,c,*}, Sadhan Chandra Das^{a,b}, Vitaslav Stranak^a and Rainer Hippler^a

^aInstitute of Physics, University of Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany

^bUGC-DAE Consortium for Scientific Research, Indore 452017, MP, India

^cDepartment of Physics, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-3, West Bengal, India

Abstract: We report the difference in electronic bond structure and surface chemical property of amorphous carbon nitride (a-CN_x) film as a function of N/C which has been deposited by high power impulse magnetron sputtering (HiPIMS) and DC magnetron (dc-MS) plasma. The spectroscopic analyses suggest that the presence of oxide layer is the major cause for the surface charging in the core level peak. The core electron peaks (C1s, N1s and O1s) in x-ray photoelectron spectroscopy (XPS) show higher surface charging in HiPIMS compare to the film deposited by dc-MS plasma. The core peaks are moved gradually toward its virgin position as the etching duration is increased from 1 min to 80 mins. The films deposited by HiPIMS retain a higher N/C ratio following ion etching as compared to those deposited by DC magnetron sputtering suggesting denser films with a higher degree of cross-linking.

Received on 15-10-2014

Accepted on 09-02-2015

Published on 24-04-2015

Keywords: Carbon nitride, HiPIMS, dc-MS, a-CN_x disintegration by Ar-sputter clean, Surface charging, X-ray photoelectron spectroscopy.

1. INTRODUCTION

Amorphous carbon nitride (a-CN_x) films are expected to be applicable widely as, for example, super hard coating material with low friction coefficient [1, 2], low band gap protective material on hard disks and read heads [3, 4], photoluminescence layers [5], carbon nitride nano-tubes [6, 7], biosensor [8] and anti-biomaterials [9, 10], ultra low dielectric constant material [11] or variable band gap properties [12]. Hypothetical prediction regarding the mechanical properties of β-C₃N₄ solid to those of diamond [13] has attracted a great interest towards carbon-nitrogen materials. Until now there is no conclusive evidence about the possibility of synthesizing such super hard crystalline solids. Major significant obstacles to the synthesis of crystalline β-C₃N₄ are 1) the incorporation of the nitrogen in the carbon layer to reach a N/C ratio of ≈1.33 and 2) the existence of N-H and C-H_x bonds which are formed in most of the deposition systems. The graphitic carbon nitride polymers also possess a stacked two-dimensional structure, which could be regarded as N-substituted graphite in a

regular manner as mentioned by Zhang *et al.* [14]. Most of the published research work on a-CN_x or a-HCN_x is based on dc and rf magnetron sputtering [15, 16], pulsed laser deposition [17], ion beam deposition [18], PECVD [19], cathodic arc deposition [20], DBD [9-12, 21-24], etc. Schmidt *et al.* reported the influence of inert gases on the sputter process of carbon-nitride (CN_x) thin films by HiPIMS. They reported that the deposition of CN_x species is higher in case of 14% N₂ in Ar inert gas medium compare to Ne or Kr. Furthermore, it is mentioned that the CN⁺ flux rises constantly with the N₂ content [25, 26]. Liao *et al.* studied the influence of atomic mixing on profiling of metal-semiconductor interfaces which depicts the penetration of one Ar ion into a sample during the sputtering process [27].

The main advantage of HiPIMS coatings include a denser coating morphology and higher hardness compared to conventional PVD coatings [28, 29, 30]. In plasma discharge volume, mostly atoms of buffer gas (Ar) are ionized, resulting in ion flux of about 0.1 - 1.0 mA/cm² towards the substrate which is hard to exceed in dc-MS. Further increase of discharge current leads to overheating of the magnets, melting of the target or the occurrence of arc when the target is covered by electrically insulating layer [30]. The ions in

*Department of Physics, IEST, Shibpur, Howrah-3, W.B., India;
Tel: +913326684561; Fax: +913326682916;
E-mail: majuabhijit@gmail.com

HiPIMS are more energetic than conventional dc-MS. HiPIMS exhibits higher energy C⁺ ions compare to dc-MS discharge. Another factor is that the electron density measured in HiPIMS systems usually exceeds 10^{18} m^{-3} [30, 31], which is about two-three orders of magnitude higher than in conventional dc-MS [2]. HiPIMS discharges produce ultra-high dense plasma (plasma density is higher by two - three orders of magnitude than in dc magnetron discharges) with large fraction of carbon (graphite target) ionized species. Hence, the C/N ion flux towards the substrate is large and leads to growth of smooth and dense films with higher adhesion. The plasma density during HiPIMS pulse is typically large, due to high applied power density, but their mean values, averaged over the whole period, are similar to those of with dc discharges [32-35]. The surface chemical property and chemical bonding states of a-CN_x films are frequently analyzed by XPS. The chemical bonding states have been analyzed based on the peak fitting of C1s and N1s spectra [1-3, 13, 14, 21, 24], and there have been several differing arguments regarding the fitting of these spectra. However, the interpretation of these data varies widely in the literature, since the different bonding configuration is mostly close in energy to each other. Moreover, the surface contamination, surface chemical bonding, surface charging due to nitrogen incorporation of those film is a big concern.

In this paper we discuss the bond structure and chemical transformations of amorphous carbon nitride film (deposited by HiPIMS and dc-MS) as a function of etching time (1 to 80 minutes).

2. EXPERIMENT

2.1. a-CN_x Films Prepared by dc-MS and HiPIMS

a-CN_x films were deposited in DC/HiPIMS magnetron sputtering system under different partial pressures (in this case at 5 Pa) of Ar/N₂ buffer gas mixture, that was attached to a high vacuum chamber (base pressure $\sim 1 \times 10^{-6}$ mbar). The carbon target of diameter 50 mm with thickness 6 mm is connected to the magnetron sputtering gun (magnetron SW50 by Gencoa Ltd.). Thin films prepared by two different sputtering methods (i) conventional dc magnetron sputtering (dc-MS) [34] and (ii) High Power Impulse Magnetron Sputtering (HiPIMS) are compared in this paper. The discharge was always operated with a constant (average) current 0.3 A; the magnetron was powered by a supply, Pinnacle 3000 (Advanced Energy) [35, 36]. The HiPIMS discharge was operated in a pulse regime with low repetition frequency of 100 Hz and the pulse width 100 μs . In this way the peak discharge current in HiPIMS configuration reached up to 35 A while averaged current 0.3 A was held always. Hence, we can expect that some fraction of sputtered C atoms is ionized due to high peak discharge current [35]. The HiPIMS discharge was ignited using home-build electronic power switch combined with dc supply, Pinnacle 3000; the system is described elsewhere e.g. [37, 49]. The a-CN_x film is

deposited on p-type Si (100) substrate and the duration of the deposition is 1 h for all the deposition.

2.2. Ar Etching

The deposited films were transported to another chamber (ex situ) and the films were etched by argon ion (99.999% pure) with inbuilt etching gun (instruments-SPECS, model PU-IQE 12/38). The executing pressure during etching is about 2×10^{-6} mbar. The etching was performed at 2000V, emission current is ~ 5 mA and ion current of 10 μA . The sample has been etched at different time duration (1 min to 80 min time span).

2.3. Film Characterization

The deposited films have been characterized by XPS. XPS measurements of a-CN_x films were performed on a multi-technique 100 mm hemispherical electron analyser (VSW), using Al K α radiation (photon energy 1486.6 eV) as the excitation source and the binding energy (BE) of Au (Au 4f_{7/2}: 84.00 eV) as the reference. The XPS spectra were collected in a constant analyser energy mode, at a chamber pressure of 10^{-9} mbar and pass energy of 23.5 eV at 0.125 eV/step [21, 24, 50]. A clear image of the possible chemical bonds between nitrogen and carbon can be deduced from the peak fitting of the individual C-1s, N-1s and O-1s lines into Lorentzian-Gaussian-shaped lines. The general strategy of the data evaluation was identical to those for standard spectroscopic techniques. The C1s, N1s peaks are broadened and also became asymmetric as the film is sputtered. The observed surface charging is caused by an anomalous surface charge distribution of the a-CN_x film. Si (2p) with a Binding Energy (BE) = 99.3 eV was taken as a reference. The calibration details about this surface charging are discussed in our previous work [21, 24]. We used a-CN_x film (both HiPIMS and dc-MS), deposited on a Si substrate, of which a small part of the deposited film had been removed in order to get access to the Si surface. The binding energy of C1s is 284.5, for N1s is 398.1 eV and for O1s is 531.1 eV taken as reference, and with respect to this value we have calculated the surface charging of C1s, N1s and O1s peak which have been obtained from experimental results [24, 50]. The results shown below were corrected by subtracting the experimentally observed shift for all the analyses.

3. RESULTS

3.1. XPS of a-CN_x Film

Figure 1 shows the survey scan (200 eV to 600 eV) of XPS spectra of a-CN_x film. It shows the C1s, N1s and O1s core level XPS spectra with different etching duration (from 1 minute to 80 minutes) for the films deposited by HiPIMS and dc-MS. There is drastic increase of carbon in the case of dc-MS film compare to HiPIMS at longer etching duration. There are no shake up satellite peaks in the core level spectra and the peaks are asymmetric with medium FWHM (full width at half maximum) as shown in Figures 2, 3 and 4. A common

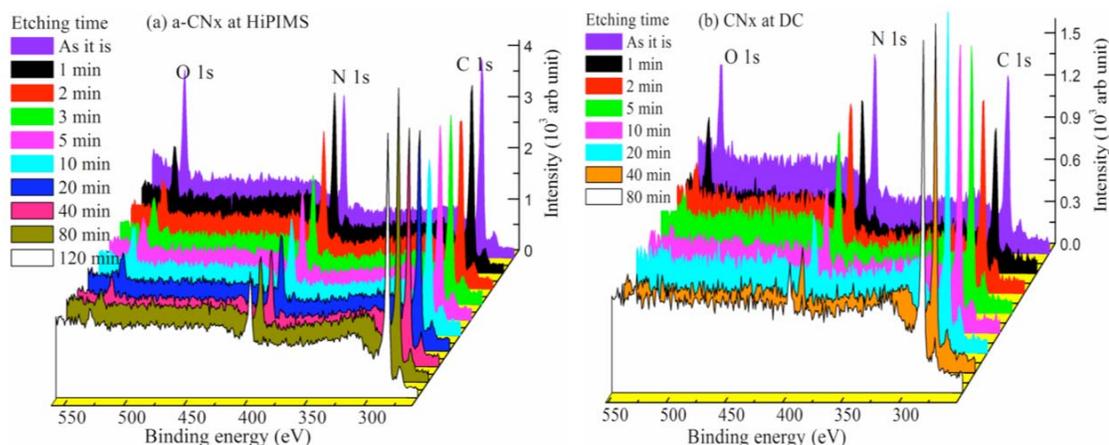


Figure 1: (Color online) Survey scan (200 eV to 600 eV) of XPS spectra of a-CN_x films deposited by (a) HiPIMS and (b) dc-MS. XPS spectra of a-CN_x are plotted as a function of sputtering duration. The film was etched by Ar gas up to 80 mins.

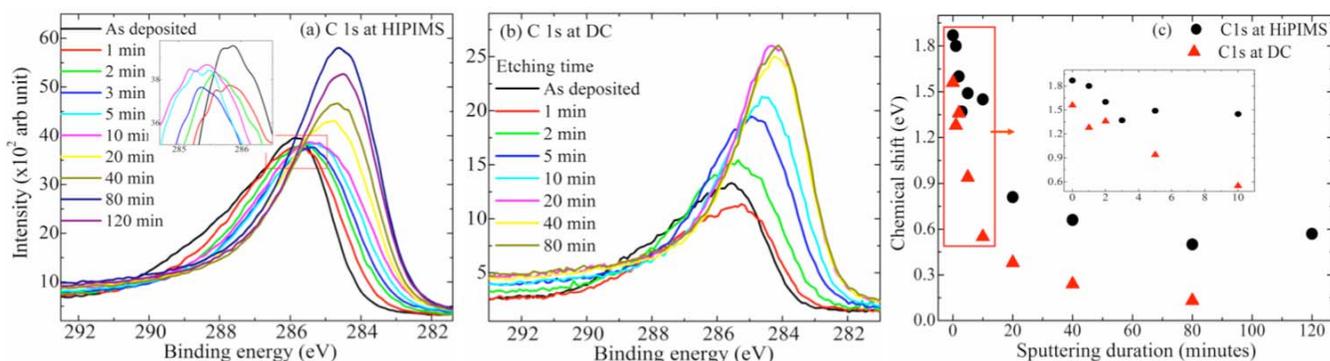


Figure 2: (Color online) XPS spectra of C1s peak of the a-CN_x film deposited by (a) HiPIMS, (b) dcMS. The C1s spectra plotted with respect to the duration of sputtering time. And (c) shows the surface charging of the corresponding C1s spectra as a function of sputtering time duration.

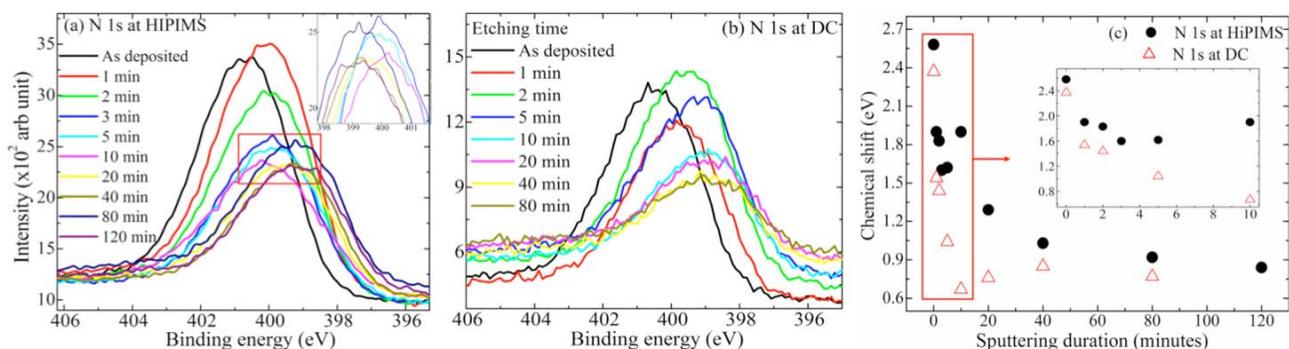


Figure 3: (Color online) XPS spectra of N1s peak of the a-CN_x film deposited by (a) HiPIMS, (b) dcMS. The N1s spectra plotted with respect to the duration of sputtering time. And (c) shows the surface charging of the corresponding N1s spectra as a function of sputtering time duration.

feature is observed in both HiPIMS and dc-MS assisted deposited film that the oxygen and nitrogen is decreased as the etching duration is prolonged. The oxygen layer is persisting (11%) in HiPIMS even at 120 min of etching whereas it is almost removed (only 2 %) at 80 min in the case of dc-MS film (Figure 5).

The C1s core peak is shifted gradually with longer duration of etching as shown in Figure 2a, b. It shows the XPS spectra of

the HiPIMS and dc-MS films, sputtered at 1 to 120 min and 1 to 80 min, respectively. The film deposited by HiPIMS shows higher values of surface charging (in binding energy) compare to the dc-MS film as shown in Figure 2c. The red (color) marked area (zoom insight) shows the etching duration is 1 min to 10 mins. Up to 10 minutes of etching, the dc-MS film shows a drastic change in surface charging from 1.56 eV to 0.55 eV whereas it is 1.87 eV to 1.45 eV in the case of HiPIMS film. As the etching duration is prolonged

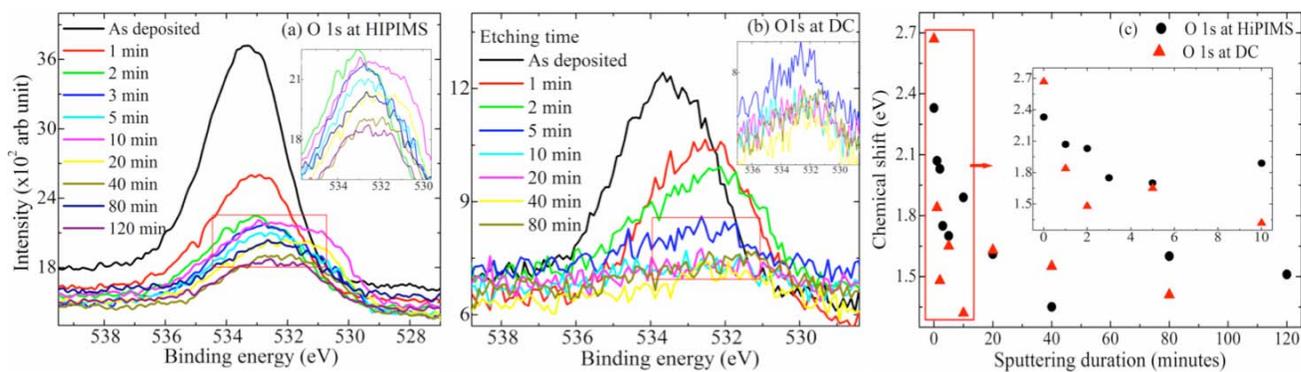


Figure 4: (Color online) XPS spectra of O1s peak of the a-CN_x film deposited by (a) HiPIMS, (b) dcMS. The C1s spectra plotted with respect to the duration of sputtering time. And (c) shows the surface charging of the corresponding O1s spectra as a function of sputtering time duration.

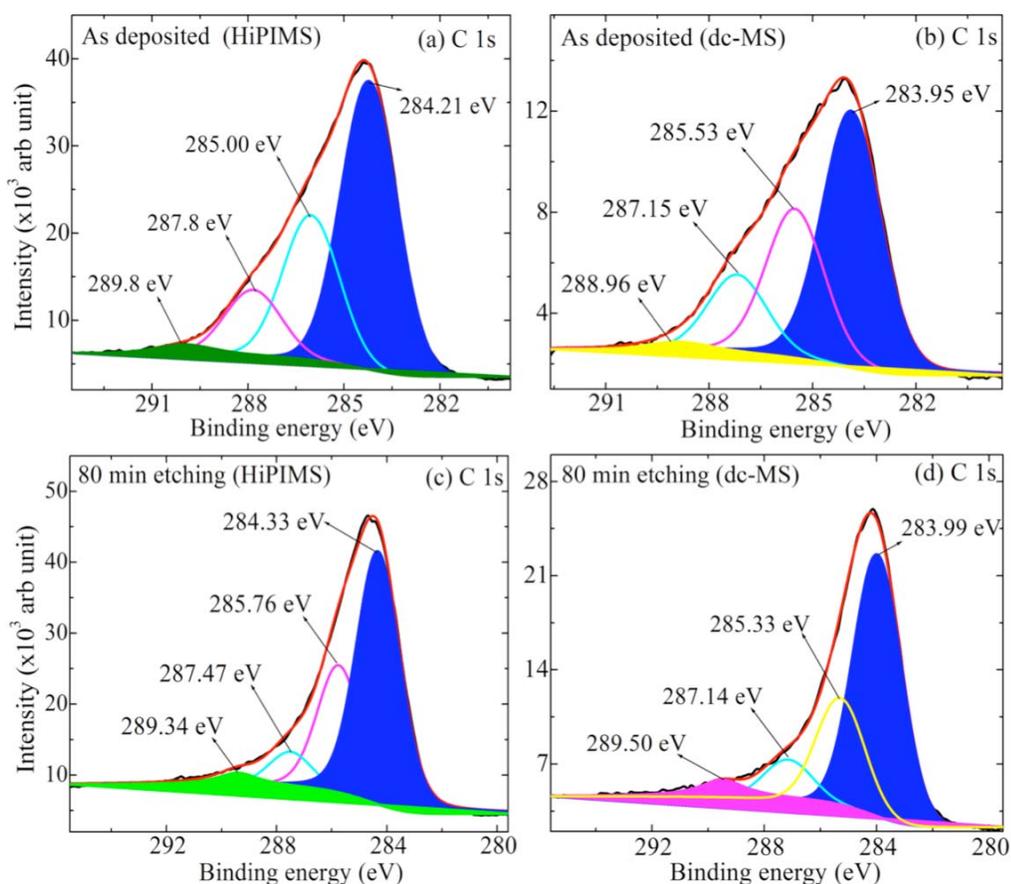


Figure 5: (Color online) XPS spectra of C1s, where (a), (b) As it is and (c), (d) 80 min sputtered a-CN_x film deposited by HiPIMS and dc-MS, respectively. The un-etched film is referred as “As deposited”. The data are presented after inelastic background subtraction and using Lorentzian-Gaussian fits. The intensity scales for the C spectra are not the same. The reference binding energy of C1s at 284.00 eV and the core level components are representing the peak position of the fitted area.

from 10 to 80 minutes, the surface charging drop down from 1.45 eV to 0.50 eV and 0.55 eV to 0.13 eV in HiPIMS and dc-MS films, respectively.

Figure 3a, b show the shift of N1s core spectra of the films deposited by HiPIMS and dc-MS with prolonged Ar etching time (1 min to 80 min). The film deposited by HiPIMS shows higher values of surface charging compare to the dc-MS as

shown in Figure 3c. The red (color) marked area (zoom insight) shows the etching duration of 1 min to 10 mins. Up to 10 minutes of Ar ion etching, the dc-MS film shows a drastic change in surface charging from 2.37 eV to 0.67 eV whereas it is 2.58 eV to 1.91 eV in the case of HiPIMS film. At 20 to 80 minutes of etching, the surface charging is almost constant in the case of dc-MS film whereas it is shifted from 1.29 eV to 0.92 eV for HiPIMS film. It is noticeable that at 10 mins to 20

mins of etching the binding energy of HiPIMS film shifted from 1.92 to 1.29 eV and on the other hand it is 0.67 eV to 0.76 eV for dc-MS film.

Figure 4a, b shows the shift of O1s core spectra with prolonged etching time as similar to the C1s and N1s spectra. The red (color) marked area (zoom insight) shows that up to 10 minutes of etching, dc-MS film shows a drastic fall in surface charging from 2.65 to 1.32 eV, whereas it is 2.3 to 1.7 eV for HiPIMS (Figure 4c). At longer etching duration (20 to 80 min) the dc-MS film shows a gradual decrease in surface charging. On the other hand HiPIMS film shows a random behavior as it is decrease from 1.61 eV (20 min) to 1.35 eV at 40 min and at 80 min it is increased to 1.6 eV; finally it is decreased to 1.51 eV at 120 min of etching.

In Figure 5a and b, C1s spectra of virgin a-CN_x film deposited by HiPIMS and dc-MS exhibit four core level components in the range 283.95 to 284.21 eV, 285.00 to 285.53 eV, 287.15 to 287.8 eV and 288.96 to 289.8 eV which are assigned to C-C, C=N, C≡N and C-O bonds, respectively [21, 24, 49-61]. Similarly, C1s spectra of the 80 mins sputtered a-CN_x film show four core level components in the range at 283.99 to 284.33 eV, 285.33 to 285.76 eV, 287.14 to 287.47 eV and 289.34 to 289.50 eV which are assigned to C-C, C=N, C≡N

and C-O bonds. After 80 mins of Ar ion etching the fitted XPS spectra of C1s peak shows four core level components.

Figure 6a, b and c, d show the peak fitted XPS spectra of N1s, un-sputtered and 80 min sputtered a-CN_x film. Here, Figure (a, c) and (b, d) are the N1s spectra of a-CN_x deposited by HiPIMS and dc-MS, respectively. The N1s spectrum of as it is film, (Figure 6), exhibits two core level components of core level spectra in the range (for HiPIMS and dc-MS) 398.17 to 398.47 eV and 399.74 to 400.1 eV are assigned to N-C, and N-O bond, respectively [21, 24, 50, 51]. On the other hand 80 mins sputtered (c), (d) films exhibit three core level components in the range 398.66 to 398.75 eV, 400.40 to 400.61 eV and 403.50 to 404.02 eV are assigned as N≡C-, N=C- and N-O, respectively. We assign the peak at lower binding energy (397.88 to 398.5 eV) to nitrogen bonded to sp³ carbon and the peak at higher binding energy (398.6 to 399.80 eV) to nitrogen bonded to sp carbon [21, 24, 50-62]. The virgin “(a) and (b)” are plotted after the surface charging correction. On the other hand 80 min sputtered film is plotted without any shift correction.

Figure 7a, b and c, d show the peak fitted XPS spectra of O1s, un-sputtered and 80 min sputtered a-CN_x film, whereas (a, c) and (b, d) are the O1s spectra of a-CN_x deposited by

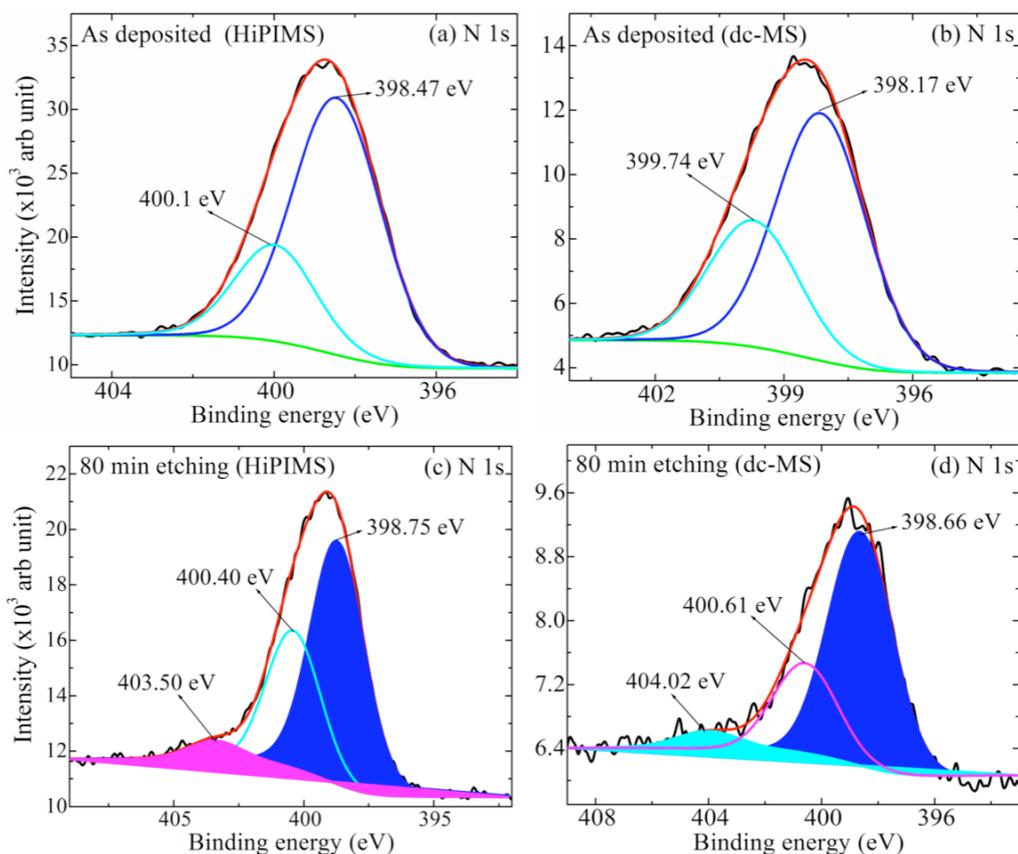


Figure 6: (Color online) XPS spectra of N1s, where (a), (b) As it is and (c), (d) 80 min sputtered a-CN_x film deposited by HiPIMS and dc-MS, respectively. The un-sputtered film is referred as “As deposited”. The data are presented after inelastic background subtraction and using Lorentzian-Gaussian fits. The intensity scales for the N spectra are not the same. The reference binding energy of N1s at 398.03 eV and the core level components are representing the peak position of the fitted area.

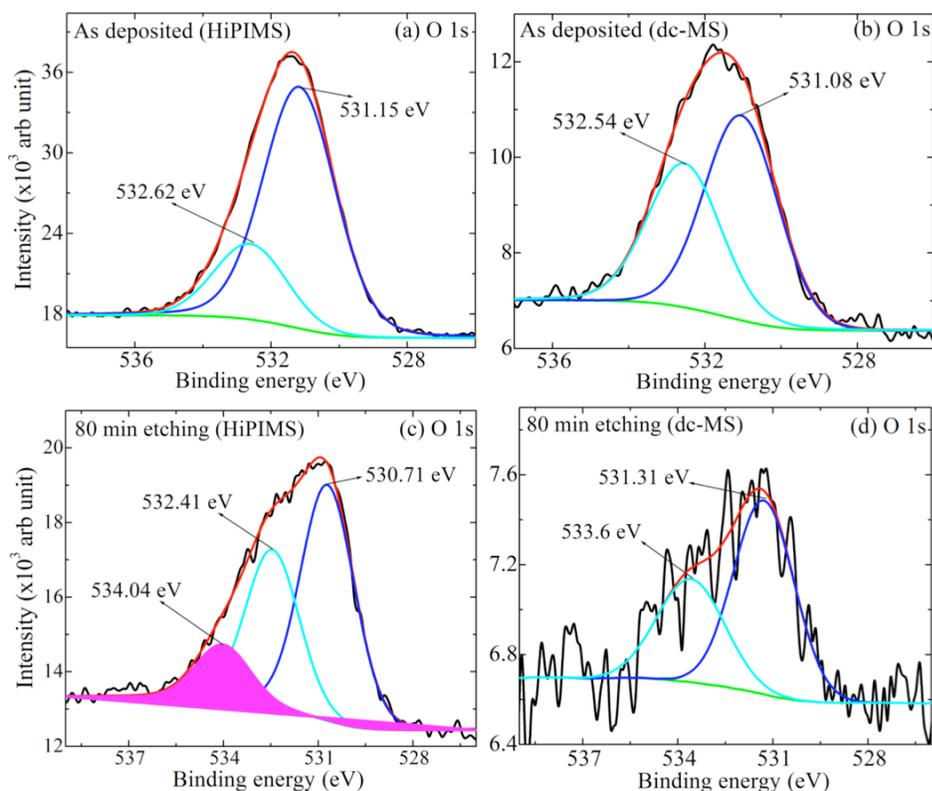


Figure 7: (Color online) XPS spectra of O1s, where (a), (b) As it is and (c), (d) 80 min sputtered a-CN_x film deposited by HiPIMS and dc-MS, respectively. The un-sputtered film is referred as “As deposited”. The data are presented after inelastic background subtraction and using Lorentzian-Gaussian fits. The intensity scales for the O spectra are not the same. The reference binding energy of O1s at 531.05 eV and the core level components are representing the peak position of the fitted area.

HiPIMS and dc-MS, respectively. O1s spectra in Figures 7a, b show two core level components in the range 531.08 to 531.15 eV and 532.54 to 532.62 eV assigned to adventitious (extrinsic or accidental) oxygen and surface oxygen and C-O bonds, respectively [50, 61]. Figure 7c shows three core level components in O1s spectrum, that are 530.71 eV, 532.41 eV and 534.04 eV, are assigned as N-O, C-O and C=O, respectively. Figure 7d shows two core level components in O1s spectrum at 531.31 eV, 533.6 eV are assigned as N-O and C-O, respectively. The oxygen peaks give evidence on undesired absorptions or reactions of oxygen or moisture on the top of the film and formation of a surface layer of oxygen containing species. Even at 80 mins of etching there is 6% oxygen is present in HiPIMS film due to the presence of C=O bond in the film layer (Figures 4 and 9).

Figure 8a shows the FWHM of C1s, N1s and O1s of a-CN_x film. Figure 8b, c depict the total amount of element (at%) of C, N and O of a-CN_x as function of etching duration in HiPIMS and dc-MS, respectively.

4. DISCUSSION

Figure 5, shows the comparative study of core level spectra of C1s of un-sputtered and sputtered a-CN_x film deposited by HiPIMS and dc-MS. One common feature for HiPIMS and dc-

MS as well as the virgin and sputtered film is that they exhibit four core level components in the peak fitted spectrum. The core level components of carbon (blue colour filled area) at the binding energy range 284.00–284.55 eV is identified as originating from adventitious (extrinsic or accidental) carbon. Similarly, the C1s peak binding energy range at 288.5–289.8 eV is identified as originating from CO type bonds which are depending on the type of bonding such as ketones/aldehydes (–CO/–CHO) and carbonates (–CO₃). There is no shake up satellites peak in Figures 2-4 and 5-7, so CO type bond can only originate from C-O and C=O bond structure. Figure 5 shows that there are two C1s peaks (2nd and 3rd) in the range of 284.90 to 286.0 eV and 286.50–to 287.90 eV which are assigned as substitutional sp² N in graphite like structures (C=N) and volatile phase like iso-nitrile (–C≡N), respectively [21, 24, 50-62].

Figure 8 shows the FWHM of core level peaks of virgin and 80 mins sputtered film deposited by HiPIMS and dc-MS. Noticeable interesting features are observed in C1s spectra: a) un-sputtered dc-MS films show higher FWHM (4.17 eV) compare to the same of HiPIMS film (3.65 eV). b) FWHM decreases at 80 mins of Ar ion sputtering of the film surface. The four C1s spectrums in Figure 5 shows a steep rise at lower binding energy and it decreases abruptly (or sudden drop) towards 286 eV region with a broaden tail. At 80 mins of sputtering the FWHM is decreased from 3.65 eV to 3 eV in

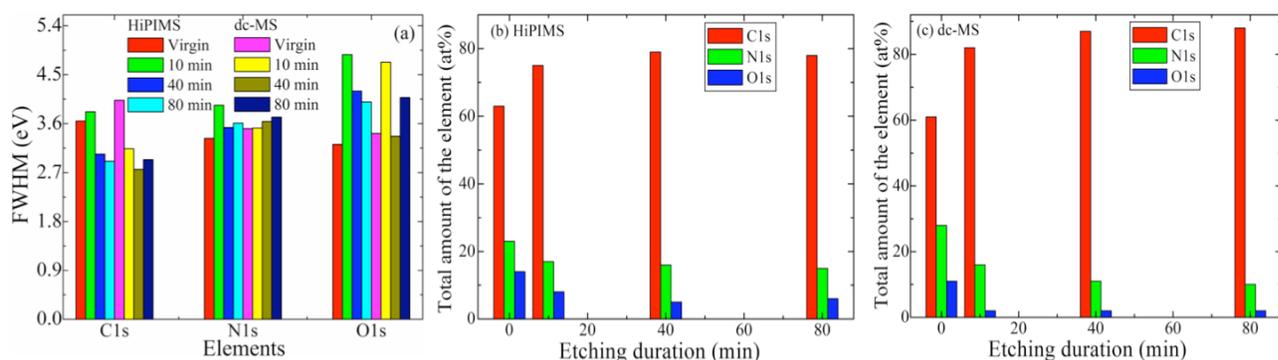


Figure 8: (Color online) (a) FWHM of C1s, N1s and O1s, and (b), (c) Relative intensity of C1s, N1s and O1s as a function of Ar-ion etching duration.

HiPIMS film whereas it is decreased from 4.17 eV to 2.7 eV in dc-MS film. It is interesting to observe that at 10 to 20 mins of sputtering the surface charging of HiPIMS film is about 0.7 eV whereas it is 0.09 eV for dc-MS film. An anomalous change is observed at 5 mins to 10 mins of sputtering in the case of HiPIMS film whereas it shows the binding energy shift increase from 1.62 eV to 1.90 eV. c) A shift of 1.5 ± 0.7 eV was noted which is considered as system calibration for virgin (as it is) films. As deposited films “(a) and (b)” are plotted with the surface charging correction. On the other hand 80 mins sputtered film is plotted without any shift correction. In HiPIMS film the 2nd core level component of C1s at 285.00 eV appears at 285.76 eV after 80 mins of Ar ion etching treatment whereas in dc-MS film, the 2nd core level component of C1s peak remains in the same. It is observed in Figure 2-4, that the core level spectra moved to its virgin position due to etching. The higher surface charging is due to the presence of absorb oxygen layer at the top surface. The oxygen layer is removed gradually by the longer etching process and the core level peak is moved towards its virgin position. The reason behind the surface charging is explained in more details in our previous work [24]. d) The relative intensity of carbon in un-sputtered and sputtered HiPIMS films are about 63 % and 78 % respectively, whereas the ratios are 61 % and 88 % in dc-MS film (Figure 8b, c). e) The relative intensity of C-C, C-O bond is increased and C≡N is decreased in both HiPIMS and dc-MS film at 80 mins etching,

respectively. On the other hand, the relative intensity of C=N is increased in HiPIMS whereas it is decreased in dc-MS film (Figure 9).

Figure 6, shows the comparative study of un-sputtered and sputtered spectra of N1s of a-CN_x film deposited by HiPIMS and dc-MS. One common feature for HiPIMS and dc-MS film is that they show two core level components in virgin and three core level components in 80 mins sputtered film. Some noticeable features are observed in N1s spectra: a) un-sputtered HiPIMS and dc-MS films show almost similar FWHM which are 3.3 eV and 3.5 eV, respectively. b) FWHM at 80 mins of etching and it is 3.61 eV and 3.72 eV for HiPIMS and dc-MS film, respectively (Figure 9). Moreover, FWHM of N1s is increased by ± 0.15 eV at 80 mins sputtered in both categories of films. Here we can notice that the peak FWHM of dc-MS film is relatively larger than HiPIMS in both sputtered and virgin films. The same phenomenon has been observed in the case of virgin C1s spectrum of a-CN_x film. c) One additional core level components is appeared in N1s spectrum in sputtered film (both in HiPIMS and dc-MS). The 2nd and 3rd core level components are in the range 400.40 eV to 400.61 eV and 403.50 to 404.02 eV are assigned as N=C and N-O. The 1st core components (in the range of 398.66 to 398.75 eV) covered by blue color is assigned as N-C. Virgin film is plotted with shift correction (1.5 ± 0.4 eV) and the sputtered one is without shift correction. The 1st core level

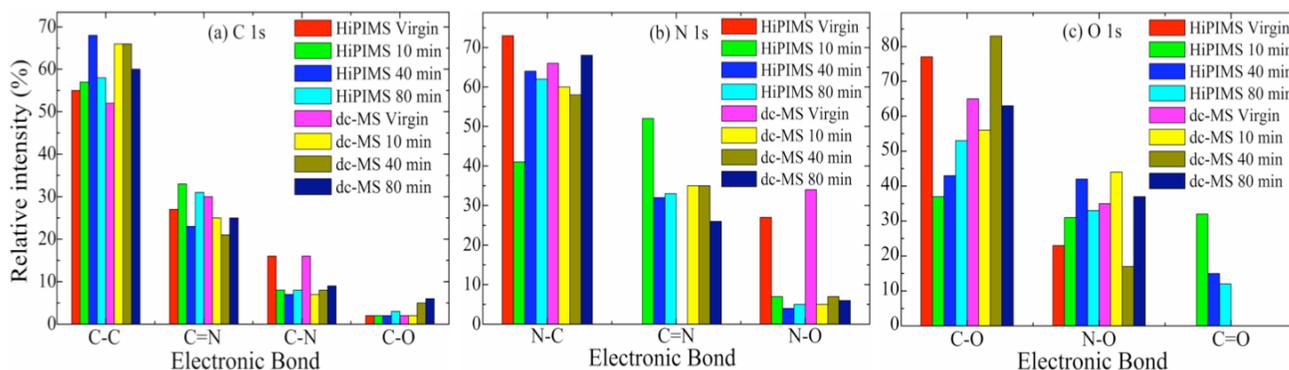


Figure 9: (Color online) Relative intensity of electronics bond in XPS spectra of (a) C1s, (b) N1s and (c) O1s as a function of Ar-ion etching duration. The un-etched film is referred as “Virgin”.

components of N1s spectra in sputtered film show ± 0.35 eV shift compare to the same of virgin film. d) In sputtered film the relative intensity of N=C bond is higher in HiPIMS (33%) compare to the same of dc-MS (26%). Relative intensity of N-C bond decreases from 72% to 62%, after etching treatment in HiPIMS whereas in dc-MS it is almost invariant. At 80 mins of etching the relative intensity of N-O bond decreases drastically from 27% to 5% and 34% to 6% in HiPIMS and dc-MS, respectively. e) The relative intensity of nitrogen in un-sputtered and sputtered HiPIMS films are about 23% and 15% respectively, whereas they are 28% and 10% in the case of dc-MS film (Figure 8b, c).

Figure 7a, b and c, d show the comparative study of un-sputtered and sputtered O1s spectra of a-CN_x film deposited by HiPIMS and dc-MS, respectively. Here some noticeable features are observed in O1s spectra; a) it shows two core level components in un-sputtered film for both HiPIMS and dc-MS film. b) Interestingly at 80 mins sputtered HiPIMS film shows three core level components whereas there are two components in the case of dc-MS. Sputtered HiPIMS and dc-MS films show almost similar FWHM which are 4.01 eV and 4.08 eV, respectively. At 80 mins of etching the FWHM is decreased from 3.65 to 2.91 eV in HiPIMS film whereas it is decreased from 4.03 eV to 2.94 eV in dc-MS film (Figure 9). The peak FWHM of dc-MS film is relatively larger than HiPIMS in both sputtered and virgin film. The same phenomenon has been observed in the case of virgin C1s spectrum of a-CN_x film. c) O1s shows two core level components in virgin a-CN_x film deposited by both the methods. These two core level components are assigned as N-O and C-O. In Figure 7c, one additional core components is appeared at 534.04 eV in O1s spectrum is assigned as C=O bond (80 mins sputtered HiPIMS). Two core components in O1s spectra is observed at 80 mins sputtered film assigned as N-O and C-O bond in dc-MS film.

d) Oxygen decrease from 11% to 2% after 80 mins etching treatment of dc-MS film whereas it is decreased from 14% to 6% in the case of HiPIMS film. The sputtered (at 80 mins) HiPIMS film shows higher residue of oxygen (6%) compare to dc-MS film and it is in the form of double bond (C=O at 534.04 eV). Figure 9 shows the relative intensity of C-C, C=N, C-N/C≡N, C-O, N-O and C=O bond obtain from peak fitted C1s, N1s and O1s spectra. The C and N bonds are mostly sp² and sp³ type but oxygen dominated by conjugated double bond in HiPIMS film at C1s spectra. The spectra of N1s and O1s show two core level components in virgin a-CN_x film deposited by both methods. These two core components are assigned as N-C and N-O in N1s spectra and N-O and C-O, respectively. At 80 mins of etching the films deposited dc-MS and HiPIMS exhibits almost similar trend.

Oxygen formed single (C-O) and conjugated double (C=O) bond in HiPIMS film whereas it is only C-O bond in dc-MS film. C-O and C=O bonds strength are 358 kJ/mol and 799 kJ/mol, respectively. We know that the higher bonding strength offers the lower stability due to more "s" character is

involved in sp hybridization (where stability vary as sp³>sp²>sp). The hybrids are defined by the p to s ratio of the contributing orbital. For example, an sp³ hybrid has ¼ (25%) of s and ¾ (75%) of p. This fraction is called an s (or p) character of the orbital. Thus, an sp³ hybrid has 25% s character. Covalent bond (sp² bond) is more stable bond than triple bond (sp). The relative intensity of C-O, N-O bond is increased in HiPIMS at 80 mins etching.

The pulse operation provides new and additional parameters to control the deposition process that optimize the elemental composition in the deposited film. For these reasons HiPIMS is an attractive alternative which should be implemented in industrial coating processes. However, HiPIMS have still some disadvantages, such as lower deposition rate and higher cost of pulse power supplies. The carbon concentration of the up-sputtered film is almost same for both dc-MS and HiPIMS. The number of core level components obtained by peak fitting of C1s, N1s and O1s spectra of HiPIMS and dc-MS film shows more or less similar trend except some changes in 80 min sputtered film. On the other hand, the carbon concentration is higher in dc-MS compare to HiPIMS film at 80 mins of etching (Figure 8b, c). Moreover, it is observed that the absorption of oxygen on the surface layer of the film is higher in HiPIMS compare to dc-MS film. There is 6% of oxygen in HiPIMS film whereas it is 2% in dc-MS film even the film is sputtered at 80 mins. It is interesting that the nitrogen concentration is lower at the top surface but it is higher in deeper layer of the HiPIMS films compare to the same of dc-MS film.

5. CONCLUSION

The spectroscopic analyses suggest that the presence of oxide layer is the major cause for the surface charging in the core peaks in a-CN_x film deposited by HiPIMS and dc-MS. At longer duration of etching, the core electron peaks (C1s, N1s and O1s) in XPS show higher binding energy shift in HiPIMS compare to the film deposited by dc-MS plasma. The core peaks moved gradually toward its virgin position as the etching duration is prolonged from 1 min to 80 mins. The carbon concentration of the un-sputtered film is higher in dc-MS compare to HiPIMS film at 80 mins of etching. Nitrogen incorporation in a-CN_x is higher in HiPIMS etching compare to dc-MS. The relative intensity of C increased in both whereas N decreases faster (deep into the layer) in dc-MS film compare to HiPIMS at longer duration of etching. At 80 mins of sputtering there is 6% of oxygen in HiPIMS film due to majority of sp² bonding (C=O) whereas it is only 2% in dc-MS. XPS spectra of un-sputtered dc-MS films show higher FWHM compare to the same of HiPIMS.

ACKNOWLEDGEMENTS

The work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich SFB/TRR24. The author would like to thank to Mr. Steffen

Drache, Institute for Physik, University of Greifswald, Germany, for the technical help during the experiment.

The authors like to thank Mr. Steffen Drache (Greifswald) for his assistance during the experiment.

REFERENCE

- [1] Li D, Chung YW, Wong MS, Sproul WD. *J Appl Phys* 1993; 74: 219. <http://dx.doi.org/10.1063/1.355304>
- [2] Yao H, Ching WY. *Phys Rev B* 1994; 50: 11231. <http://dx.doi.org/10.1103/PhysRevB.50.11231>
- [3] Mansour A, Ugolini D. *Phys Rev B* 1993; 47: 10201. <http://dx.doi.org/10.1103/PhysRevB.47.10201>
- [4] Robertson J. *Thin Solid Films* 2001; 383: 81. [http://dx.doi.org/10.1016/S0040-6090\(00\)01786-7](http://dx.doi.org/10.1016/S0040-6090(00)01786-7)
- [5] Zambov LM, Popov C, Abedinov N, Plass MF, Kulisch W, Gotszalk T. *T Adv Mater* 2000; 12: 656. [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(200005\)12:9<656::AID-ADMA656>3.0.CO;2-S](http://dx.doi.org/10.1002/(SICI)1521-4095(200005)12:9<656::AID-ADMA656>3.0.CO;2-S)
- [6] Wang J, Miller DR, Gillan G. *Chem Commun* 2002; 19: 2258. <http://dx.doi.org/10.1039/b207041c>
- [7] Plass MF, Popov C, Ivanov B, Mandl S, Jelinek M, Zambov LM. *Appl Phys A* 2001; 72: 21. <http://dx.doi.org/10.1007/s003390000687>
- [8] Lee SP. *Sensors* 2008; 8: 1508. <http://dx.doi.org/10.3390/s8031508>
- [9] Majumdar A, Schröder K, Hippler R. *J Appl Phys* 2008; 104: 074702. <http://dx.doi.org/10.1063/1.2990054>
- [10] Majumdar A, Ummanni R, Schröder K, Walther R, Hippler R. *J Appl Phys* 2009; 106: 034702. <http://dx.doi.org/10.1063/1.3190558>
- [11] Majumdar A, Das SC, Shripathi T, Hippler R. *Chem Phys Lett* 2012; 524: 62-67. <http://dx.doi.org/10.1016/j.cplett.2011.12.054>
- [12] Majumdar A, Bogdanowicz R, Mukherjee S, Hippler R. *Thin Solid Films* 2013; 527: 151. <http://dx.doi.org/10.1016/j.tsf.2012.11.020>
- [13] Liu AY, Cohen ML. *Science* 1989; 245: 841. <http://dx.doi.org/10.1126/science.245.4920.841>
- [14] Zhang Y, Mori T, Ye J. *Sci Adv Mater* 2012; 4: 282. <http://dx.doi.org/10.1166/sam.2012.1283>
- [15] Yu KM, Cohen ML, Haller EE, Hansen WL, Liu AY, Wu IC. *Phys Rev B* 1994; 49: 5034. <http://dx.doi.org/10.1103/PhysRevB.49.5034>
- [16] Li Y, Zhang ZB, Xie SS, Yang GZ. *Chem Phys Lett* 1995; 247: 253. [http://dx.doi.org/10.1016/0009-2614\(95\)01209-7](http://dx.doi.org/10.1016/0009-2614(95)01209-7)
- [17] Riedo E, Comin F, Chevrier J, Bonnot AM. *J Appl Phys* 2000; 88: 4365. <http://dx.doi.org/10.1063/1.1309041>
- [18] Ogata K, Chubaci JFD, Fujimoto F. *J Appl Phys* 1994; 76: 3791. <http://dx.doi.org/10.1063/1.358497>
- [19] Freire FL, Franceschini DF. *Thin Solid Films* 1997; 293: 236. [http://dx.doi.org/10.1016/S0040-6090\(96\)08979-1](http://dx.doi.org/10.1016/S0040-6090(96)08979-1)
- [20] McCulloch DG, Merchant AR. *Thin Solid Films* 1996; 290: 99. [http://dx.doi.org/10.1016/S0040-6090\(96\)09069-4](http://dx.doi.org/10.1016/S0040-6090(96)09069-4)
- [21] Majumdar A, Schäfer J, Mishra P, Ghose D, Meichsner J, Hippler R. *Surf Coat Technol* 2007; 201: 6437. <http://dx.doi.org/10.1016/j.surfcoat.2006.12.011>
- [22] Majumdar A, Scholz G, Hippler R. *Surf Coat Technol* 2009; 203: 2013. <http://dx.doi.org/10.1016/j.surfcoat.2009.01.038>
- [23] Majumdar A, Hippler R. *Rev Sci Instrum* 2007; 78: 75103. <http://dx.doi.org/10.1063/1.2751408>
- [24] Majumdar A, Das G, Basvani KR, Heinicke J, Hippler R. *J Phys Chem B* 2009; 113: 15734. <http://dx.doi.org/10.1021/jp906654m>
- [25] Schmidt S, Czigan Z, Greczynski G, Jensen J, Hultman L. *J Vac Sci Technol A* 2013; 31: 011503. <http://dx.doi.org/10.1116/1.4769725>
- [26] Schmidt S., Czigan Z, Greczynski G, Jensen J, Hultman L. *J Appl Phys* 2012; 112: 013305. <http://dx.doi.org/10.1063/1.4733692>
- [27] Liao ZL, Tsaur BY, Mayer JW. *J Vac Sci Technol* 1979; 18: 121. <http://dx.doi.org/10.1116/1.569883>
- [28] Hippler R, Kersten H, Schmidt M, Schoenbach KH, Eds. *Low Temperature Plasmas*, Wiley-VCH: Wein-Heim 2008; Vol. 2.
- [29] Ellmer K. In: *Low Temperature Plasmas*. Hippler R, Kersten H, Schmidt M, Schoenbach KH, Eds. Wiley-VCH: Weinheim 2009; Vol. 2: p. 675.
- [30] Chapman B. *Glow Discharge Processes*, Wiley and Sons 1981.
- [31] Bradley JW, Welzel T. *J Phys D: Appl Phys* 2009; 42: 093001.
- [32] Helmersson U, Lattemann M, Bohlmark J, Ehasarian AP, Gudmundsson JT. *Thin Solid Films* 2006; 513: 1. <http://dx.doi.org/10.1016/j.tsf.2006.03.033>
- [33] Gudmundsson JT, Alami J, Helmersson U. *Appl Phys Lett* 2001; 78: 3427. <http://dx.doi.org/10.1063/1.1376150>
- [34] Ellmer K. *Magnetron Discharges for Thin Film Deposition*; in: *Low temperature plasma physics*, Eds. Hippler R, Pfau S, Schmidt M, Schoenbach KH, Wiley-Vch 2008; 329.
- [35] Gudmundsson JT, Brenning N, Lundin D, Helmersson U. *J Vac Sci Technol* 2012; A30(3): 030801. <http://dx.doi.org/10.1116/1.3691832>
- [36] Sarakinos K, Alami J, Konstantinidis S. *Surf Coat Technol* 2010; 204: 1661. <http://dx.doi.org/10.1016/j.surfcoat.2009.11.013>
- [37] Stranak V, Quaaas M, Wulf H, Hubicka Z, Wrehde S, Tichy M, Hippler R. *J Phys D: Appl Phys* 2008; 41: 055202.
- [38] Stranak V, Cada M, Hubicka Z, Tichy M, Hippler R. *J Appl Phys* 2010; 108: 043305. <http://dx.doi.org/10.1063/1.3467001>
- [39] Stranak V, Drache S, Cada M, Hubicka Z, Tichy M, Hippler R. *Contrib Plasma Phys* 2011; 51(2-3): 237. <http://dx.doi.org/10.1002/ctpp.201000065>
- [40] Stranak V, Wulf H, Bogdanowicz R, Drache S, Hubicka Z, Cada M, Tichy M, Hippler R. *Eur Phys J D: Appl Phys* 2011; 64: 427.
- [41] Stranak V, Wulf H, Rebl H, Zietz C, Arndt K, Bogdanowicz R, Nebe B, Bader R, Podbielski A, Hubicka Z, Hippler R. *Mat Sci Eng C* 2011; 31: 1512. <http://dx.doi.org/10.1016/j.msec.2011.06.009>
- [42] Hoene A, Patrzyk M, Walschus U, Stranak V, Hippler R, Testrich H, Meichsner J, Juergen, Finke B, Rebl H, Nebe B, Zietz C, Bader R, Rainer, Podbielski A, Schlosser M. *J Mater Sci - Mater Med* 2013; 24: 761. <http://dx.doi.org/10.1007/s10856-012-4839-4>
- [43] Konstantinidis S, Ricard A, Ganciu M, *et al.* *J Appl Phys* 2004; 95: 2900. <http://dx.doi.org/10.1063/1.1646452>
- [44] Kouznetsov V, Macak K, Schneider JM, Helmersson U, Petrov I. *Surf Coat Technol* 2006; 122: 293.
- [45] Gudmundsson JT, Alami J, Helmersson U. *Appl Phys Lett* 2001; 78: 3427. <http://dx.doi.org/10.1063/1.1376150>
- [46] Helmersson U, Lattemann M, Bohlmark J, Ehasarian AP, Gudmundsson JT. *Thin Solid Films* 2006; 513: 1. <http://dx.doi.org/10.1016/j.tsf.2006.03.033>
- [47] Vethuska A, Ehasarian AP. *J Phys D: Appl Phys* 2008; 41: 015204.
- [48] Alami J, Sarakinos K, Uslu F, Klever C, Dukwen J, Wuttig M. *J Phys D: Appl Phys* 2009; 42: 115204.
- [49] Ehasarian AP, Munz WD, Hultman L, Helmersson U, Petrov I. *Surf Coat Technol* 2003; 267: 163.
- [50] Majumdar A, Das SC, Shripathi T, Heinicke J, Hippler R. *Surf Sci* 2013; 609: 53. <http://dx.doi.org/10.1016/j.susc.2012.11.003>
- [51] Moulder JF, *et al.* *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, Minnesota 1992.
- [52] Ronning C, Feldermann H, Merk R, Hofsass H, Reinke P, Thiele JU. *Phys Rev B* 1998; 58: 2207. <http://dx.doi.org/10.1103/PhysRevB.58.2207>
- [53] Zheng WT, Yu WX, Li HB, Wang YM, Cao PJ, Jin ZS, Broitman E, Sundgren JE. *Diamond Relat Mater* 2000; 9: 1790. [http://dx.doi.org/10.1016/S0925-9635\(00\)00314-9](http://dx.doi.org/10.1016/S0925-9635(00)00314-9)

- [54] Rodil SE, Ferrari AC, Robertson J, Milne WI. J Appl Phys 2001; 89: 5425.
<http://dx.doi.org/10.1063/1.1365076>
- [55] Ohta R, Lee KH, Saito N, Inoue Y, Sugimura H, Takai O. Thin Solid Films 2003; 434: 296.
[http://dx.doi.org/10.1016/S0040-6090\(03\)00457-7](http://dx.doi.org/10.1016/S0040-6090(03)00457-7)
- [56] Souto S, Pickholz M, dos Santos MC, Alvarez F, Phys Rev B 1998; 57: 2536.
<http://dx.doi.org/10.1103/PhysRevB.57.2536>
- [57] Boyd KJ, Marton D, Todorov SS, et al. J Vac Sci Technol 1995; A13: 2110.
<http://dx.doi.org/10.1116/1.579528>
- [58] Bhattacharyya S, Cardinaud C, Turban G. J Appl Phys 1998; 83: 4491.
<http://dx.doi.org/10.1063/1.367211>
- [59] Bhattacharyya S, Hong J, Turban G. J Appl Phys 1998; 83: 3917.
<http://dx.doi.org/10.1063/1.367312>
- [60] Lindberg BJ, Hamrin K, Johansson G, Gelius U, Fahlman A, Nordling C, Siegbahn K. Physica Scripta 1970; 1: 286.
<http://dx.doi.org/10.1088/0031-8949/1/5-6/020>
- [61] Rodil SE, Muhl S. Diamond Relat Mater 2004; 13: 1521-1531.
<http://dx.doi.org/10.1016/j.diamond.2003.11.008>
- [62] Hamrin K, Johansson G, Fahlman A, Nordling C, Siegbahn K, Lindberg BJ. Chem Phys Lett 1968; 1: 557.
[http://dx.doi.org/10.1016/0009-2614\(68\)80020-X](http://dx.doi.org/10.1016/0009-2614(68)80020-X)