Optimizing rf Power for Preferential C≡N Bond Formation in a-CN_x Thin Films Prepared by rf-PECVD Technique

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Abstract. Effects of rf power on the chemical bonding in carbon nitride films deposited using radio-frequency (rf) plasma enhanced chemical vapor deposition in pure methane and nitrogen gas mixtures were investigated. The rf power was varied from 60 to 100 W. The deposition rate of the films increased constantly with increasing rf power up to 80 W, before saturating with further increase in rf power. Fourier transform infra-red spectroscopy (FTIR) studies showed a systematic change in the spectra and revealed three main peaks namely the G-peak, D-peak and C≡N triple bond. This work showed that rf power has significant effects on the chemical bonding of the a-CN_x films and the optimum rf power for the high C≡N absorption intensity is 80 W.

1. Introduction
Research on carbon nitride (CN_x) thin films has intensified with the prediction by Liu and Cohen that the properties of crystalline carbon nitride (β-C_3N_4) might be similar or superior to diamond [1]. However, in many cases a-CN_x thin films deposited are mostly obtained in amorphous phase. Nevertheless even these films shows many attracting properties such as extreme hardness, chemical inertness, low friction coefficient, and variable optical band gap [2]. One of the main reason why carbon nitride tends to forms in amorphous phase is because of the presence of hydrogen commonly found in these carbon nitride films. These hydrogen atoms can easily break C≡N and C=N bonds in the film to form C-H and N-H bonds [3]. However, if hydrogen defects were formed intentionally and bonded weakly, a-CN_x thin films can be a good candidate as a humidity sensor [3]. To achieve good a-CN_x thin films for humidity sensor, the films must have high C≡N and C=N bonds content.

There are various techniques capable of producing a-CN_x. These includes rf magnetron sputtering, [4], hollow cathode discharge [5], electron cyclotron resonance microwave plasma chemical vapor deposition [6], graphite hollow cathode system [7] and radio frequency plasma enhanced chemical vapor deposition (rf-PECVD). Among these rf-PECVD is favoured since this technique has the advantage of uniform large area deposition, easy handling, low pinhole density, good adhesion and good step coverage [8]. Furthermore the film characteristic could be tuned simply by controlling the deposition parameters such as rf power, gas flow rate ratios, and substrate temperature. In this owrk we are employing rf-PECVD to
obtain a-CN$_x$ thin films. The main focus is to investigate the effect of rf power on the chemical bonding of a-CN$_x$ thin films and to determine the optimum rf power for highest C=N and C≡N bonds.

2. Experimental details

a-CN$_x$ thin films were deposited by rf-PECVD using a mixture of pure (99.999 %) methane, CH$_4$ and nitrogen, N$_2$ gas. The type of substrates used in this study was p-type (111) silicon chemically cleaned using acetone and deionized water in ultrasonic baths prior to deposition. The substrate was heated at 100 °C during deposition. Prior to the film deposition, the substrates were treated to hydrogen plasma for 10 min with the H$_2$ flow rate and rf power fixed at 50 sccm and 50 W respectively. This was done to remove impurities on the substrate surface and improve the adhesion of CN layers onto the substrate [9]. The distance between the rf powered top electrode and substrate holder was kept constant at 1 cm while pressure and deposition duration was 0.8 mbar and 90 min. A set of film was prepared at rf power of 60, 70, 80, 90 and 100 W. The films thickness was determined using a surface profilometer. Chemical bonding were characterized using Perkin-Elmer System 2000 FTIR Spectrometer and Horiba Jobin Yvon 800 UV Micro Raman Spectrometer at wavenumber range 1300 – 2500 cm$^{-1}$ and 100 – 3000 cm$^{-1}$, respectively.

3. Results and discussions

3.1. Deposition rate of a-CN$_x$ thin films

The thickness of the films and corresponding deposition rate for the samples were calculated and presented in Table 1. The deposition rate increased with the increase in rf power up to 80 W and begins to saturate and even decrease slightly with further increase in rf power, as shown in Figure 1. The initial increase in deposition rate may be due to the corresponding increase in dissociation of reactive gases [9]. The deposition of these radicals formed from this dissociation influences the etching and H atom passivation of the radical sites on the deposition surface. The increase in rf power also increase the concentration of reactive H atoms reaching the deposition surface creating significant increase in the number of nucleation sites [10]. Apparently, the growth of the film through the subplantation of the impinging radicals and neutral species, surpasses the etching of the film resulting in the increase in the deposition rate.

When the rf power exceeds 80 W, CH$_4$, main precursor gas is completed dissociation resulting in the saturated of available radicals and consequently the deposition rate [8]. Normally the radicals formed would react with unreacted molecules in secondary reactions in the plasma. With the complete dissociation of the CH$_4$ gas in the primary reaction at rf power above 80 W, this suppresses the secondary reaction and thus decrease the radicals in the plasma which otherwise will contribute to the growth of the film. The complete dissociation if the precursor cas also significantly decrease the main species CH$_3$ which largely contributes to the expecsion of the film. This could be explaining the saturation in deposition rate at rf power above 80 W. Furthermore, due to the decrease in subplantation of these radicals, particularly of CH$_3$, the etching effects on the film surface becomes significant and this explains the slight decrease in deposition rate above this rf power.
Deposition rate of a-CN$_x$ at different rf power (Line is drawn as guide to the eye)

| rf power, P (W) | Thickness, t (nm) | Deposition rate (nm/min) |
|-----------------|-------------------|--------------------------|
| 60              | 1685              | 18.72                    |
| 70              | 1769              | 19.66                    |
| 80              | 1853              | 20.51                    |
| 90              | 1821              | 20.23                    |
| 100             | 1795              | 19.94                    |

3.2 FTIR analysis of a-CN$_x$, thin films

The FTIR spectra of the a-CN$_x$ thin films deposited as a function of rf power is shown in Figure 2. The broad FTIR transmission band ranging from 1300-1800 cm$^{-1}$ is due to the presence of sp$^2$ and sp$^3$ carbon [11]. The transmission peaks in this range represents the Raman activated peaks and corresponds to the disorder D-band and graphite (G-band). The D band arises from the breathing modes of sp$^3$ atoms in rings and its intensity is strictly correlated with the presence of the six fold aromatic ring while the G band is associated with the bond stretching of all pairs of sp$^2$ atoms in both rings and chains [12]. The weak intensity of the D-band at 1350-1450 cm$^{-1}$ in all these films was associated to the presence of sp$^2$ C-N bonds in the film [10] and clearly indicated content of C-N bonds are low. The broad G-band at 1500-1800 cm$^{-1}$ was associated to the presence of C-C and sp$^2$ graphitic domain. These bands are discussed further in the Raman analysis of these thin films.
The transmission band lying between 2100 and 2200 cm\(^{-1}\) suggests the presence of nitrile (-C≡N), isonitrile (-N≡C) and carbodiimide (-N=C=N-) groups [13]. The peak centers at ~2150 cm\(^{-1}\) which corresponds to the preferential formation of C≡N triple bond. These bonds are network terminators groups. The intensity of this bands increase as the increase in rf power up to 80 W, becoming prominent at rf power of 70 and 80 W. With further increase in rf power their intensities decreases significantly and almost vanishes at rf power of 100 W. This indicate that very few C≡N bonds, if any, were formed in this film. It is possible that the strong etching effects on the film surface at rf power above 80W as discussed earlier effectively breaks the C≡N bond in the CN\(_x\) films [13]. These results also suggest that the formation of the C≡N bond in the CN\(_x\) films can be controlled by varying the applied rf power.

![Figure 2. Variation of FTIR spectra as function rf power](image)

3.3 Raman analysis of a-CN\(_x\) thin films

In a typical a-CN\(_x\) films, two broad partly-overlapping bands, centered at approximately 1360 and 1580 cm\(^{-1}\) lies in the broad band region between 1300 and 1700 cm\(^{-1}\) of the Raman spectra. The Raman spectra can be deconvoluted using Gaussian and Lorentz fitting [15] in order to calculate the D and G bands. Similar to FTIR the D band centered at 1360 cm\(^{-1}\) is due to the presence of disorder and variation in the size of graphitic domains, while the G-band centered at 1580 cm\(^{-1}\) is due to carbon-carbon vibration in the aromatic rings. The deconvolution is shown in the example in Figure 3. The G-band is associated to C≡N bond originated from the replacement of N atoms at carbon sites in C=C sp\(^2\) bond [14]. There is an increase in intensity of the G-band and thus the corresponding C≡N bond with the increase in rf power up to 80 W. With further increase in rf power above 80 W, the intensity of G band begins to decrease as shown in Table 2 which could be the result of the hydrogen etching as discussed earlier.
Table 2. The variation of intensity D band ($I_D$) and intensity G band ($I_G$)

| rf power (W) | $I_D$ (a.u.) | $I_G$ (a.u.) |
|--------------|--------------|--------------|
| 60           | 130.42317    | 273.06389    |
| 70           | 161.02497    | 341.67020    |
| 80           | 276.23464    | 617.15321    |
| 90           | 148.43525    | 308.60477    |
| 100          | 67.59846     | 155.26008    |

Figure 3. Raman spectra deconvoluted Gaussian and Lorentz fitting

4. Conclusion

a-CN$_x$ films were successfully deposited using a home-built rf-PECVD from the discharge of CH$_4$ and N$_2$ gas mixture. The variation of chemical bonding of these a-CN$_x$ films as a function of rf power was studied. The deposition rate of the films was influenced by the applied rf power which was associated to the competing effects of dissociation process and surface etching. FTIR spectrum reveals three main peaks at ~1360, ~1570, and ~2150 cm$^{-1}$ corresponding to the D-peak, G-peak and C≡N triple bond, respectively. There are little changes in the position of the peak when the rf power was changed. The results suggest that variation in rf power give effect to the structural properties of the a-CN$_x$ thin films owing to the change in the content of C≡N and C≡N bonds in these films. Hence, this will determine the potential of a-CN$_x$ films as a humidity sensor. The optimum rf power that gave high C≡N content is 80 W based on FTIR analysis. In the near future, test will be carried out to confirm if the a-CN$_x$ thin films prepared at 80 W could be used as humidity sensor.
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References

[1] A.Y. Liu, M.L. Cohen. 1989. Prediction of new low-compressibility materials. Science 245: 841.

[2] Y. Aoi, K. Ono, E. Kamijo. Journal of Applied Physics. 86, 2318 (1999)

[3] Ji Gong Lee, Sung Pil Lee. Sensors and Actuators B. 108, 450-454 (2005)

[4] I. Banerjee, Neelam Kumari, Ashis K. Singh, Mukesh Kumar, Pinaki Laha, A.B. Panda, A. K. Pabi, P. K. Barhai, S. K. Mahapatra. Thin Solid Films. 518, 7240-7244 (2010)

[5] M. Balaceanu, E. Grigore, F.. Truica-Marasescu, D. Pantelica, F. Negoita, G. Pavelescu, F. Ionescu. Nuclear Instruments and Methods in Physics Research B 161-163, 1002-1006 (2000)

[6] Wai-Chung Chan, Man-Keung Fung, Kai-Ho Lai, Igor Bello, Shuit-Tong Lee, Chun-Sing Lee. Journal of Non-Crystalline Solids. 254, 180-185 (1999).

[7] Stephen Muhl, Adriana Gaona-Couto, Juan Manuel Mendez, Sandra Rodil, Gonzalo Gonzalez, Alexander Merkulov, Rene Asomoza. Thin Solid Films. 308-309, 228-232 (1997).

[8] Maisara Othman, Richard Ritikos, Noor Hamizah Khanis, Nur Maisarah Abdul Rashid, Saadah Abdul Rahman, Siti Meriam Ab Gani, Muhamad Rasat Muhamad. Thin Solid Films. 519, 4981-4986 (2011).

[9] L. Valentini, J. M. Kenny, Y. Gerbig, A. Savan, H. Haefke, L. Lozzi, S. Santucci. Thin Solid Films. 398-399, 124 (2001).

[10] C. Y. Hsu, F. C. N. Hong. Diamond and Related Materials. 8, 1315 (1999).

[11] A. Crunteanu, M. Charbonnier, M. Romand, F. Vasiliiu, D. Panelica, F. Negoita, R. Alexandrescu. Surf. Coat. Technol., 125, 301 (2000).

[12] A. C. Ferrari, S. E. Rodil, J. Robertson. Physical Review B. 67, 155306 (2003).

[13] A. C. Ferrari, S. E. Rodil, J. Robertson. Physical Review B. 61, 14095 (2000).

[14] Sang Hoon Kim, Cheol Min Choi, Kil Mok Lee, Yoon-Bong Hahn. Synthetic Metals. 160, 2442-2446 (2010).

[15] Myung, S. H., Park, S. Y., Hong, B., Han, G. J. dan Shaginyan, R. L. Thin Solid Films. 506 87-91 (2006)