



# Influence of RF power on the electrical and mechanical properties of nano-structured carbon nitride thin films deposited by RF magnetron sputtering

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## ABSTRACT

Nano structured carbon nitride thin films were deposited at different RF powers in the range of 50 W to 225 W and constant gas ratio of (argon: nitrogen) Ar:N<sub>2</sub> by RF magnetron sputtering. The atomic percentage of Nitrogen: Carbon (N/C) content and impedance of the films increased from 14.36% to 22.31% and  $9 \times 10^{-1} \Omega$  to  $7 \times 10^5 \Omega$  respectively with increase in RF power. The hardness of the deposited films increased from 3.12 GPa to 13.12 GPa. The increase in sp<sup>3</sup> hybridized C–N sites and decrease of grain size with increase in RF power is responsible for such variation of observed mechanical and electrical properties.

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## 1. Introduction

Carbon nitride films have emerged to be a promising material due to its optical, electrical and tribological properties with high biocompatibility that can lead to useful for engineering and biomedical applications [1,2]. Cuomo et al. [3] were reported about this material in 1979. Since then no considerable work has been noted until a theoretical study on calculation of a hypothetical crystalline  $\beta$ -C<sub>3</sub>N<sub>4</sub> phase with short bond length ( $\sim 1.47 \text{ \AA}$ ) and low bond ionicity ( $\sim 7\%$ ) resulting in high bulk modulus and hardness of the compound similar or even superior to diamond by Liu and Cohen [4–7]. Literature reveals that the unusual combination of these physical properties of carbon nitride is due to the hybridization between nitrogen and carbon existing in the material [8]. The percentage of nitrogen incorporation in the material can even change the electrical response from conductive to highly resistive [9]. High resistive carbon nitride films have gained importance in the thrust areas of very large scale integrated circuits (VLSI) and ultra-scale integrated circuit (ULSI) [10]. The wide variation in electrical response of carbon nitride is attributed to its microstructure. It consists of sp<sup>2</sup>, sp<sup>3</sup> and sp<sup>1</sup> of different atomic percentage of C and N combinations resulting in resistivity values varying from those of graphite to diamond and organic polymers. Sputtering method is by-far considered to be the most effective for synthesis of carbon nitride films among different deposition methods like hot filament chemical vapour deposition (CVD), ion beam deposition, laser ablation, etc. [11–16].

Although a large number of studies have been made, proper correlation between the bonding structure of nitrogen and carbon with its mechanical and electrical properties has not yet been fully explored. Looking into the applications of high resistant, hard and flexible carbon nitride films, the present paper reports on the optimization of RF power to control the frequency dependent impedance as well as hardness of carbon nitride films. The paper gives emphasis on the correlation of nitrogen content, chemical bonding and microstructure of the films with mechanical and electrical properties.

## 2. Experimental details

The carbon nitride films were deposited using radio frequency (RF: 13.56 MHz) magnetron sputtering on crystalline silicon [100] wafer. High purity (99.99%) pyrolytic graphite target (3 in. diameter) was used as target. The substrates (10 mm × 10 mm) were chemically cleaned in ultrasonic bath and dried at room temperature prior to deposition. The distance between the target and the substrate was kept at 45 mm. The chamber was evacuated to  $10^{-6}$  mbar by diffusion pump before deposition. The working pressure was maintained at  $5 \times 10^{-2}$  mbar during deposition by keeping the Ar:N<sub>2</sub> gas flow rate at 1:1 (3 sccm each) through MFC and deposition time 3 h. In this way, a number of CN films were deposited at different plasma power varying from 50 W to 225 W by keeping constant gas ratio and deposition time. The carbon vapour produced through sputtering is allowed to react with reactive nitrogen vapour. The carbon nitride vapour formed gets deposited atom by atom on the substrate through heterogeneous nucleation. The film growth process is driven by the solid–vapour transformation through the heat released to the substrate [17]. The whole process may be considered to be physical

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vaporization followed by chemical reaction, nucleation growth and finally deposition on the substrate.

The elemental analysis of the deposited films was carried out by Electron diffraction spectroscopy (EDS) using Jeol, Japan, Model No. JSM-6390 LV. The C and N bonding was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy. The grain size and surface morphology was done by Atomic Force Microscope (AFM). Film thickness was measured by ellipsometer. The hardness of the carbon nitride thin film was analyzed by nano indentation technique, whereas, the frequency dependent impedance of the film was studied using Impedance Analyser. Impedance the samples were measured by Impedance Analyzer. For the Impedance measurement, CN was deposited on the aluminium wafer of size 10 mm × 10 mm × 0.5 mm. The top layer (CN) of the sample was connected to one terminal of the impedance analyzer and other terminal to the bottom (Al). Silver paste was used for the proper contact of aluminium and carbon nitride (CN) to the connectors of the impedance analyzer (MODEL HIOKI 3532-50 LCR meter). In this way, Impedance of the all samples was measured with frequency variations in the range 1 KHz to 1 MHz.

### 3. Results and discussions

Thicknesses of the deposited samples were measured by the ellipsometer. It was found that the thicknesses of the deposited films were 75.86 nm, 86.44 nm, 147.09 nm and 152.03 nm, 161.65 nm, 170.63 nm obtained from the RF power of 50, 100, 150, 175, 200 and 225 W respectively. It shows that the thickness of the sample was increasing with increase in RF power. The increase in RF power increases the sputtering rate of the carbon and reaction between C and N atoms which enhanced the film thickness.

#### 3.1. Elemental and structural analysis

The atomic concentrations of N and C atoms in the deposited films have been obtained from the EDX spectra. The variations of N/C atomic concentration ratio of the deposited samples with RF power are shown in Fig. 1. It was observed that the N/C ratio increased from 14.36% to 22.3% with increase of RF power from 50 W to 225 W. Although increase in RF power causes sputtering of more carbon atoms, the deposited films showed increase in nitrogen content. This might be explained by the mechanism of physical vaporization (sputtering of carbon atoms) followed by chemical reactions (reaction between carbon and nitrogen). Since, nitrogen is diatomic gas having

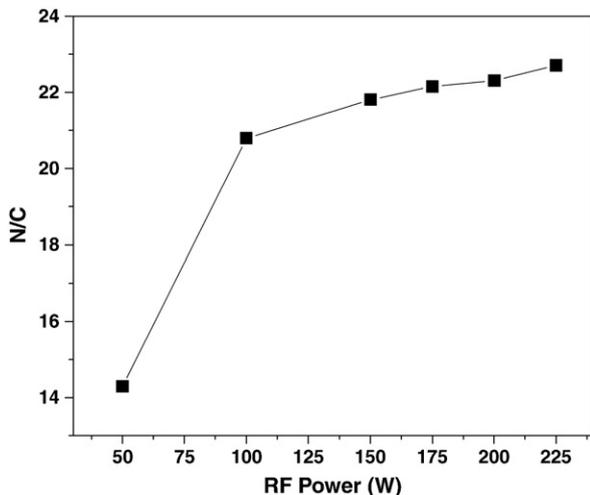


Fig. 1. Variation of N/C ratio in atomic percentage in the samples deposited at different RF power.

higher ionization potential; the chemical reaction predominates at higher RF power showing more nitrogen content in the films [18,19].

The effect of RF power on the chemical bonding between nitrogen and carbon in the deposited films was investigated by IR absorption studies. The deposited films were found to be IR active which is the direct evidence of nitrogen incorporation in the films since nitrogen free amorphous carbon is IR inactive [20]. The IR activity arises due to the nitrogen sitting at the substitution sites of the carbon matrix [21]. Nitrogen breaks the symmetry of the aromatic groups of carbon chain and produce bond dipoles in the materials [22]. This causes charge redistribution and bond polarization in the lattice [22]. The IR spectrum of the deposited samples with various RF power in the range of 600–2400  $\text{cm}^{-1}$  is shown in Fig. 2. It shows, the absorption peaks between 600  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$ , 1100  $\text{cm}^{-1}$  and 1800  $\text{cm}^{-1}$ , 2200  $\text{cm}^{-1}$  and 2235  $\text{cm}^{-1}$ , at 1560  $\text{cm}^{-1}$  and 1680  $\text{cm}^{-1}$  for all the deposited samples. The absorption peak between 600  $\text{cm}^{-1}$  and 1000  $\text{cm}^{-1}$  as observed in the spectrum, represents the out of plane bending mode for graphite-like  $\text{sp}^2$  domains. Little changes in the peak of the deposited samples at 150 W and 175 W, whereas, for 200 W and 225 W noticeable changes were observed. These IR active peaks get generated due to nitrogen incorporation into the bonding network in amorphous films [23]. The broad absorption peak at 1000  $\text{cm}^{-1}$  to 1800  $\text{cm}^{-1}$  is due to the presence of [24]  $\text{sp}^2$  and  $\text{sp}^3$  carbon. The absorption band at 1280–1450  $\text{cm}^{-1}$  with the peak positioned at  $\sim 1370 \text{ cm}^{-1}$  represents C–N bond [9,24–27]. The strong peak at 1680  $\text{cm}^{-1}$  corresponds to C–C and  $\text{sp}^2$  graphitic domain, while the peak around 1560  $\text{cm}^{-1}$  corresponds to C–N. The IR peaks at  $\sim 1370 \text{ cm}^{-1}$  and 1560  $\text{cm}^{-1}$  of amorphous CN originates from the large dynamic charge of delocalized  $\pi$  bonding of  $\text{sp}^2$  bonded networks [28]. The higher the  $\text{sp}^2$  fraction (conjugated systems), stronger the  $\pi$ -electrons delocalization [28,29]. The IR activity of the deposited films arises due to the effect of  $\text{sp}^2$  nitrogen atoms replacing the carbon atoms in graphitic rings [28,29]. Fig. 2 shows the existence of less intense peaks corresponding to C–N, C–N and C–C bonds in samples deposited at 150 W and 175 W, whereas, these peaks become more dominant for samples deposited at 200 and 225 W. The very weak absorption peak at approximately 2218  $\text{cm}^{-1}$  is attributed to the stretching vibration of the  $\text{C}\equiv\text{N}$  (the nitrile groups) [24–27]. The  $\text{C}\equiv\text{N}$  indicates content of  $\text{sp}^1$  carbon in the film. This type of bonding produces bond-terminating sites inducing lack of connectiveness, resulting in less densely packed structure in the films [24–27].

Fig. 3 illustrates the variation of integrated absorption intensity ratio of C–N to C–N ( $I_{\text{C-N}}/I_{\text{C-N}}$ ) for the present films. It is observed that the intensity ratio increases with increase in RF power. It can be related to the reaction mechanism in the vicinity of the substrate which is driven by solid–vapour phase transformation undergoing

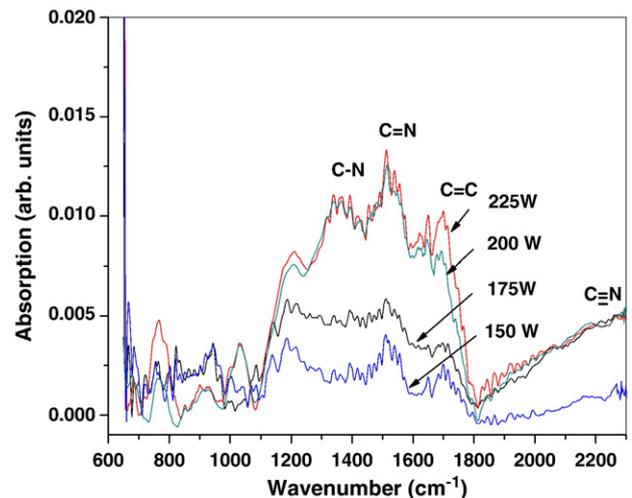


Fig. 2. FTIR spectra of the carbon nitride films deposited at different RF power.

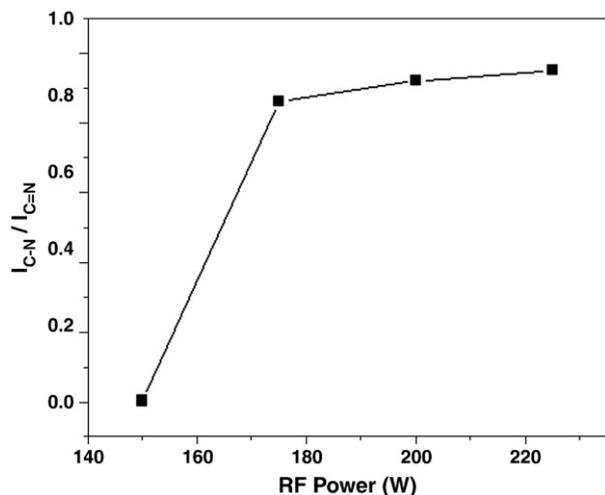


Fig. 3. Variations absorption intensities ratio for C–N and C≡N absorption peaks with RF power.

heterogeneous nucleation. This affects both the nitrogen incorporation in the films and consequently their microstructure.

The chemical bonding analysis observed in the deposited films was further supported by Raman spectroscopic studies. Fig. 4 shows, the typical Raman spectra of the films deposited at different RF powers. In the figure, Raman peaks were observed at  $\sim 1550 \text{ cm}^{-1}$  and  $\sim 1350 \text{ cm}^{-1}$  corresponding to G band of crystalline graphite and D band associated with disorder-allowed zone-edge modes of graphite. It was observed that on increasing RF power the intensity and widths of the Raman G and D peaks also increases.

The Raman active D band appears due to bond angle disorder in the  $\text{sp}^2$  graphite-like micro domains or lack of correlation between adjacent graphite-like planes. The G peak behavior is characteristic of a transition to more graphitic films [26]. The incorporation of nitrogen breaks the long-range order of the graphitic structure.

The grain size and surface morphology of carbon nitride thin films deposited on silicon substrates were studied by atomic force microscopy (AFM, NT-MDT Moscow, Russia, Model No. Solver P47-PRO). Fig. 5(a) and (b) shows the typical AFM images of the deposited CN films at lowest and highest operating powers respectively. The grain size was found to decrease from 180 nm, 124 nm, 65 nm to 45 nm with

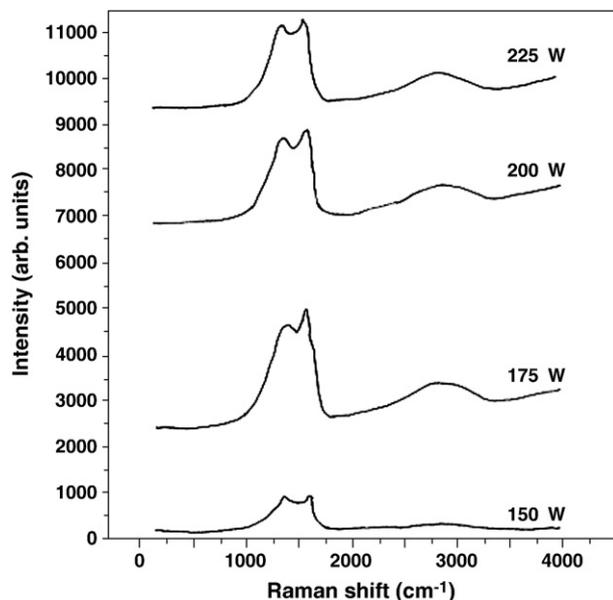


Fig. 4. Raman spectra for the samples deposited at 150 W, 175 W, 200 W and 225 W.

increase in RF power. The uniformity of the thin film was found to increase with RF power. The increase of RF power results in a decrease of surface roughness. The surface roughness (rms) of bare silicon substrate was found to be 594.68 nm. The maximum surface roughness, corresponding to minimum power was found to be 70.35 nm while the minimum surface roughness corresponding to maximum operating power was 1.60 nm. Comparing AFM of the deposited films, the area under the grain boundary is maximum for sample deposited at 225 W and minimum for sample deposited at 50 W. This increase in the area under the grain boundary with increase in RF power causes the sample more insulating.

From the results of FTIR and Raman spectroscopy, it was found that the amount of N atoms bonded to  $\text{sp}^3$  C atoms (C–N) increases rapidly with RF power while the content of C≡N bond and the content of disordered  $\text{sp}^2$  C atoms and N atoms bonded to  $\text{sp}^2$  C (CN) atoms increases slowly. The intensity ratio of C–N to CN increases with RF power as shown in Fig. 3. The increase of N/C ratio results in the decrease in surface roughness which is generally attributed to the formation of a three-dimensional network (C–N) with a long-range order.

### 3.2. Mechanical and electrical properties

The hardness of the as deposited films was carried out by nano-indenter. Variation of hardness with RF power is shown in Fig. 6. The plot shows increase of hardness with increasing RF power. The maximum hardness of the film was found to be 13.12 GPa for 225 W RF power and minimum to be 3.12 GPa at 150 W of RF power. The increase in hardness is due to the increase in N/C content in the film, chemical bonding between carbon and nitrogen and surface roughness [30]. The  $\text{sp}^3$  hybridized C–N has tetrahedral 3-D geometry, which has stable and compact structure. In the present case, since increase in RF power shows an increase in the amount of C–N sites (Fig. 3) and surface smoothness hence hardness increases.

Nitrogen has five electrons in its outer shell ( $1s^2, 2s^2, 2p^3$ ) and so is able to bond in sp,  $\text{sp}^2$  and  $\text{sp}^3$  hybridizations with carbon ( $1s^2, 2s^2, 2p^2$ ) [31]. Nitrogen also has lone-pairs (where one bond is doubly filled by two electrons) which induce polarization effect in carbon nitride. The bondings produced are C–N, CN and C≡N which are linear, trigonal and tetrahedral having one dimension, two dimension and three dimension structure respectively. The C–N is  $\text{sp}^3$  hybridized having linear geometry which is more compact and stable than other two (C≡N, CN). The increase in  $\text{sp}^3$  hybridized species increases the hardness of the materials [32].

From the results of FTIR and Raman spectroscopy, it was found that the amount of N atoms bonded to  $\text{sp}^3$  C atoms (C–N) increase rapidly with RF power while the N atoms bonded to sp C atoms (C≡N) and the content of disordered C atoms bonded to  $\text{sp}^2$  (CN) atoms increases slowly. The intensity ratio of C–N/CN increases with RF power as shown in Fig. 4.

It was expected because during chemical reaction in the plasma chamber, with increase in RF power more nitrogen atoms get ionized and hence more C–N is produced [18,19]. The increase in N atoms trigger  $\text{sp}^3$  hybridizations, this in turn increase the hardness of the films.

The electrical response of the deposited carbon nitride films were studied using Impedance Analyzer (Nova Control 80B). Variation of impedance of the deposited samples with frequencies ranging from 0 to  $10^6$  Hz is shown in Fig. 7. The graph shows the maxima of the impedance value vary from  $9 \times 10^{-1} \Omega$  to  $7 \times 10^5 \Omega$  for deposited samples at different RF powers in the range of 50 W to 200 W. This was an interesting result showing the film property changing from conductor to insulator with increase in RF power. The high % of C–C bonding sites in the film at lower RF powers is responsible for high conducting nature [33], whereas, increase in C–N structure due to

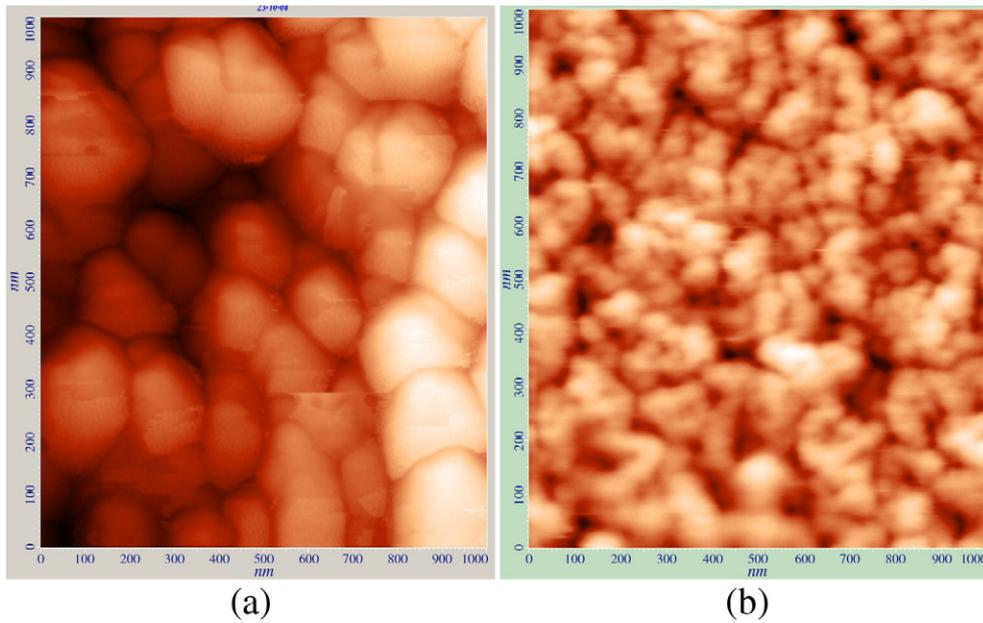


Fig. 5. Typical AFM image showing the grains in the deposited film at (a).50 W and (b).150 W.

nitrogen incorporation in the films for higher RF power is responsible for enhancement of impedance in the film.

The electrical response of the deposited films is due to two fold effects; (a) effect of grain size and compactness of the particles i.e. structural morphology in the films and (b) effect of charge carriers due to nitrogen incorporation in the films. The AFM images showed decrease in grain size with increase in RF power under the same area of grain boundary. This contributes towards increase in impedance of the films deposited at higher RF power. This governs the structural effect on the impedances of the films. Nitrogen incorporation in the films also affects the electrical properties due to generation of charge carriers. In a-carbon films, C C is non polar and bond dipole moment of the conjugated system cannot be changed. However, in nitrogen incorporated a-carbon films, two effects results in generation of dipole moment. In CN films, nitrogen sits in the aromatic rings forming pyridine structure. Due to considerable difference of electro negativity C (2.5) and N (3.1), nitrogen attracts the  $\pi$ -electron to create an electronic dipole. On the other hand, the conjugation effect of the aromatic hexagon also induces the conjugated e-flow towards nitrogen [28,29]. These together lead to degree of dipole change and

permanent dipole moments results. The sudden jump in the impedance from the sample obtained at 150 W to 200 W might be due to high space charge (electronic) polarization compare to 150 W. It is speculated that this impedance variation may be due to more grain boundary and C–N bond of the sample obtained from 200 W.

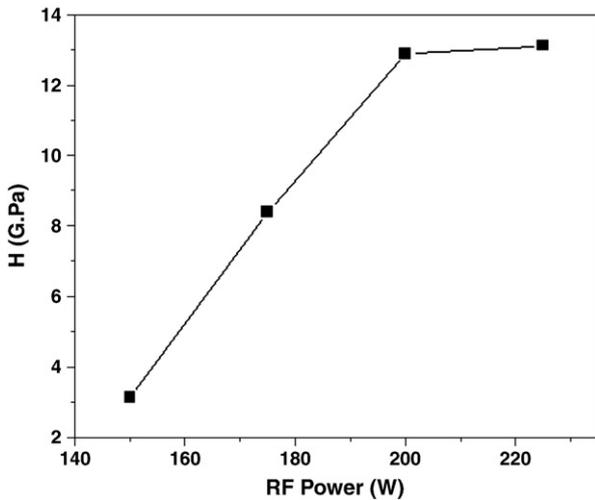


Fig. 6. Variation of hardness for the films deposited at different RF power.

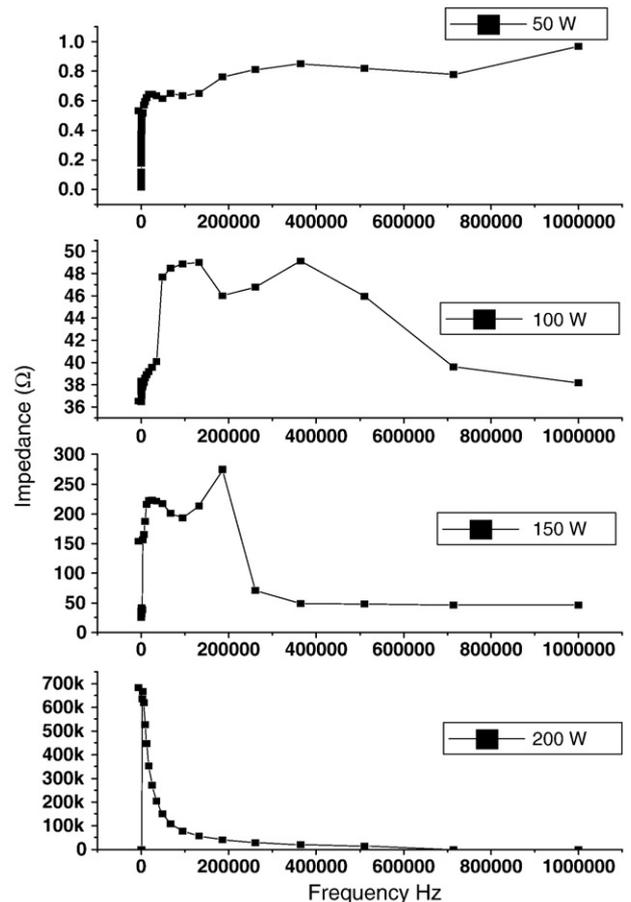


Fig. 7. Variation of impedance with frequency for the samples deposited at different RF power.

#### 4. Conclusions

Amorphous carbon nitride films of varied mechanical and electrical properties ranging from conducting to even insulating were deposited using RF magnetron sputtering. The RF power could be optimized to maintain the nitrogen content of the films. It has been found that the effect of nitrogen incorporation in the deposited films plays an important role in modification of its tribological and electrical properties. The nitrogen incorporation triggers the  $sp^3$  hybridized C–N sites breaking the C–C bonds of graphite. The increase in RF power also causes decrease in grain size and surface roughness which also contributes towards the mechanical and electrical properties of the films.

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