

# Nanoindentation study on nitrogenated tetrahedral amorphous carbon thin films with ultra low load

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This paper reports the improved nanomechanical properties of as grown and nitrogen incorporated tetrahedral amorphous carbon (ta-C, ta-C: N) films deposited by S-bend filtered cathodic vacuum arc (FCVA) technique using nanoindentation. The effect of varying amount of nitrogen incorporation on the nanomechanical properties of ta-C films deposited at a high substrate bias of -300 V at ultra low load of 1.4 mN has been studied. It has been found that the nitrogenation has improved the mechanical properties of ta-C films. The hardness  $H$  of 27.8 GPa with improvement of ~30 % and plastic index parameter (ratio of  $H$  to elastic modulus  $E$ ) ( $H/E$ ) of 0.091 with improvement of ~ 25 % has been obtained for ta-C: N films deposited at a nitrogen partial pressure of  $1.9 \times 10^{-2}$  Pa. Improved  $H$  and  $H/E$  of ta-C: N films may be due to the better ionization and incorporation of nitrogen in a carbon matrix at the high negative substrate bias used in the deposition of FCVA technique.

**Keywords:** Thin films, Arc discharges, Nanoindentation, Nanomechanical properties, FCVA

## 1 Introduction

Amorphous carbon films such as diamond like carbon (DLC) and tetrahedral amorphous carbon (ta-C) have been center of attention in the research group as well as in the industry due to their remarkable electronic, optical and nanomechanical properties<sup>1-6</sup>. The ta-C films with a high content of  $sp^3$  bonding are being studied with increasing interest for use in diverse areas which include electronics, optoelectronics, vacuum microelectronics, micro electromechanical systems, sensors and in tribological applications, especially as protective coatings for hard disc drives<sup>4,5,7-11</sup>. These ta-C films<sup>4, 12-14</sup> have been grown using a wide variety of processes including filtered cathodic vacuum arc (FCVA) direct and pulsed source, pulsed laser ablation, and sputtering processes. Among the methods for the preparation of ta-C films, the FCVA technique is useful for industrial applications because it provides highly ionized plasma of energetic carbon ions, from which dense films of amorphous carbon can be grown at reasonable high deposition rates<sup>15</sup>. The cathodic

vacuum arc is a relatively low voltage and high current discharge, in which the macroscopic fragments of the cathode material are also present. Electromagnetic deflections of the plasma through  $L$  bend ( $90^\circ$ ) using a curved solenoid have first been used by Aksenov *et al*<sup>16</sup> to remove the macro particles from the carbon plasma. Such a macro particle filter, on the other hand, has the limited transport efficiency. The pulsed mode of the plasma also allows better filtering of the macro particles because the ions tend to be entrained in the plasma beam during the pulse but fall out of the plasma when the beam stops<sup>17-23</sup>. The plasma stability using a magnetic field mechanism in the FCVA system has been discussed by Zhang and Komvopoulos<sup>24</sup>. All the processes mentioned above are highly energetic processes and the control of ion energy leads to variation in the material properties. Thus, very subtle variations in the process parameters lead to variations in the material properties. However, the systematic and detailed study of ta-C films deposited by the FCVA process has been reported using an  $S$  bend magnetic filter at higher energies<sup>25-32</sup>. The properties of the films investigated in many cases are found to be system dependent<sup>1</sup>. The characteristic of ta-C films is found

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to be an average of structurally ordered diamond, graphite and hydrocarbon polymers, consistent with the  $sp^3$ ,  $sp^2$  and  $sp^1$  hybridization (bonding configuration) of carbon atoms, respectively. Hard coatings hold the key to the improved performance of many types of product. However, the achievement of these improvements requires the selection of appropriate deposition parameters. The large range of materials properties is mainly due to the ability of carbon to form different types of inter-atomic bonds, to take different sites and to adopt different structures. Neuville and Matthews<sup>14</sup> reported a perspective on the optimization of hard carbon and related coatings for engineering applications relating to the intrinsic material properties and practical aspects to provide a framework for the development, selection and use of coatings in practical situations.

Nanomechanical studies are essential in order to develop fundamental understanding of the device physics at nano or micro level in these materials. For the evaluation of nanomechanical properties of thin films nanoindentation has emerged as an important method at applied load. The technique is based on the continuous reading of applied force and resulting depth of penetration of an indenter in the film throughout the whole loading and unloading process, when applied force is well controlled<sup>33</sup>. In this method displacement control is also possible. This technique allows calculation of the traditional values of hardness without the need to measure the residual size of an indentation produced by an applied force. Lemoine *et al*<sup>34</sup> reported intrinsic mechanical properties of ultra thin amorphous carbon layers as hard film on soft substrate. Tan<sup>35</sup> has reported composite hardness and Young's modulus from the nanoindentation study of 2-3 nm thin films/substrate system of amorphous hydrogenated carbon (a-C: H) and amorphous nitrogenated carbon (a-C: N) films deposited by ion beam deposition and sputtering, respectively. Abbas *et al*<sup>36</sup> reported the properties of the ta-C films deposited on Si without any substrate bias by an off plane double bend FCVA system with the variation of arc current.

One of the challenges in developing carbon based hard coating is the inherent residual stress, which limits the adhesion of these films on various substrates. Although many studies have been reported in the literature about the improvement of mechanical properties of ta-C thin films by nitrogen incorporation, but no detailed report of

nanomechanical properties measured at the ultra low indentation load of ta-C and ta-C: N thin film is available till date. In this work, an attempt has been made to reduce the residual stress of ta-C films by nitrogenation using FCVA process at a high negative substrate bias of -300 V. The effect of nitrogen partial pressure on the nanomechanical properties such as hardness, elastic modulus etc have been studied in detail.

## 2 Experimental Details

The deposition of amorphous carbon films has been carried out using an indigenously built double bend (S bend) FCVA system<sup>27</sup> and a well controlled process on cleaned, highly doped  $<100> n^{++}$  silicon wafer kept below 40 °C. Before the deposition of ta-C and ta-C: N films, the surface of the silicon substrate was cleaned. The silicon substrate was first treated in ultrasonic vibrator for 5 min. It was then rinsed in deionized water at room temperature for 2 min and then rinsed at 95 °C. It was then treated with deionized water at room temperature in ultrasonic vibrator for 2 min. It was then treated with isopropyl alcohol (IPA) at room temperature for 5 min. It was then treated with tri chloroethylene first at room temperature for 5 min and then treated at 50 °C for 2 min. It was again treated twice with IPA for 2 min. It was then rinsed with deionized water at room temperature and then rinsed at 95 °C and lastly it was dried with dry nitrogen gas. Typically a vacuum better than  $10^{-4}$  Pa was achieved in the system. The arc was initiated using a mechanical striker (a retractable graphite rod of purity ~99.999% and diameter of 7 mm) and a direct current (dc) arc supply. The cathode target has been made of ~99.999% pure graphite of 50 mm dia. The deposition has been carried out at an applied arc voltage of 25 V and an arc current of ~75 A. Other details about the FCVA system and deposition conditions have been described earlier<sup>25-32</sup>. For a carbon cathode, the emitted material is primarily  $C^{++}$  ions with kinetic energy broadly peaked at ~ 20-25 eV. The sum of the bias voltage and the incident ion energy of the carbon ions constitute the incident ion energy. A substrate bias of -300 V was applied to the substrate for studying nanomechanical properties in a conscious effort to enhance the ion energy, understand and utilize the higher pseudo thermo dynamical conditions during the film growth leading to efficiently doped material with a higher  $sp^3$  content growth. All other studies of ta-C: N films have already been reported at this bias<sup>25-32</sup>. The partial

pressure of high purity nitrogen gas has been varied from  $5.0 \times 10^{-3}$  to  $1.0 \times 10^{-1}$  Pa to deposit ta-C: N films. During the deposition of ta-C: N films, the negative dc substrate bias has been kept constant at -300 V and the arc current and the magnetic field in the S bend duct have also been kept constant. The residual stress  $\sigma$  in a film was evaluated using curvature method. The Raman spectra was performed using 514 nm excitation laser using 5 mW incident power at  $\sim 50$   $\text{cm}^{-1}$  at room temperature by a Renishaw spectrophotometer (micro-Raman model in Via reflex). The nanomechanical properties and load-displacement curve of the films have been measured using IBIS nanoindentation (Fisher-Cripps Laboratories Pvt Ltd, Australia) having triangular pyramid diamond Berkovich indenter with a normal angle of  $65.3^\circ$  and tip radius of  $\sim 100$  nm. The thicknesses of the samples were  $50 \pm 1$  nm measured by Talystep (Taylor and Hobson).

### 3 Results and Discussion

#### 3.1 Raman study

The Raman spectra together with the deconvoluted spectra of the ta-C film deposited at  $1.2 \times 10^{-3}$  Pa ( $N_p=0$ ) and the ta-C: N films deposited at nitrogen partial pressures of  $5.0 \times 10^{-3}$ ,  $1.9 \times 10^{-2}$  and  $1.0 \times 10^{-1}$  Pa in the wave number range from 1100 to 1900  $\text{cm}^{-1}$  are shown in Fig. 1(a-d). It is evident from the figure that all the spectra showed a peak at around 1550-1580  $\text{cm}^{-1}$  with a shoulder at about 1440-1445  $\text{cm}^{-1}$ . The film deposited without nitrogenation ( $1.2 \times 10^{-3}$  Pa,  $N_p=0$ , ta-C) showed *G* peak at 1566.8

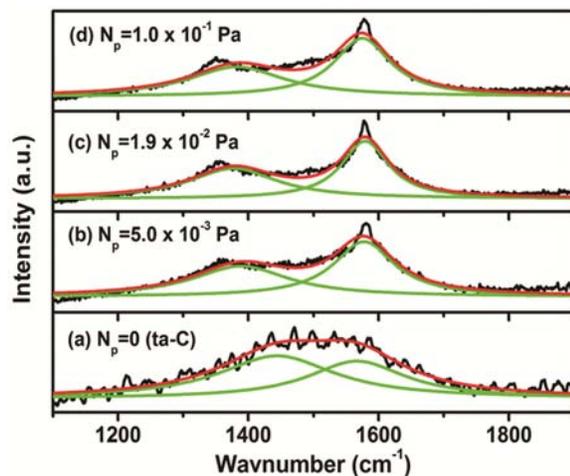


Fig. 1 — Raman spectra and deconvoluted spectra in the wave number range 1100-1900  $\text{cm}^{-1}$  of (a) ta-C film,  $N_p=0$  and (b) ta-C: N films deposited at different nitrogen partial pressures

$\text{cm}^{-1}$  and *D* peak at 1444  $\text{cm}^{-1}$ . On nitrogenation of the ta-C films, *G* peak shifted towards the higher wavenumber and *D* peak shifted towards the lower wave number in the ta-C: N films deposited up to a nitrogen partial pressure of  $1.9 \times 10^{-2}$  Pa and beyond this partial pressure there is a reversal in the trend. It is interesting to note that a shift in the Raman *G* peak from 1566.8 to 1578.8  $\text{cm}^{-1}$  indicates the generation of residual stress in the film caused by the lack of atomic arrangement. Neuville<sup>37</sup> reported that in harder ta-C films containing no clusters, a *G* peak cannot be observed at 1550  $\text{cm}^{-1}$  which corresponds to the overlapping of  $Csp^3$ - $Csp^2$  and  $Csp^2$ - $Csp^2$  isolated and dangling bonds.

#### 3.2 Nanoindentation study

Nanoindentation<sup>38-40</sup> is an indentation test used to study the mechanical properties of thin films in which the length scale of the penetration is measured in nanometers rather than microns as used in the conventional Vickers micro hardness test. In the conventional tests, the area of contact is calculated from the direct measurements of the dimension of the residual impression left in the specimen surface upon the removal of the load. In the nanoindentation tests, the size of the residual impression is of the order of nanometer and difficult to measure directly using conventional methods. Thus, the area of contact is estimated by measuring the depth of penetration of the indenter into the specimen. This together with the known geometry of the indenter provides an indirect measurement of contact area at full load.

Figure 2(A) shows the typical sketch of load *P*-displacement  $h_f$  curve. The important physical quantities from the load versus depth of penetration plot are the peak load  $P_{max}$ , maximum penetration depth  $h_{max}$ , final penetration depth  $h_f$  and the contact stiffness *S*. The ratio of hardness *H* to elastic modulus *E* ( $H/E$ ) is a plastic index parameter<sup>39</sup> to explain elastic-plastic and wear resistance properties of thin film due to the combined effect. Particularly high (low) values of  $H^3/E^2$  are correlated to a highly elastic (plastic) behavior. For some cases this behavior is also confirmed by load-displacement (compression decompression cycle) curves. Figure 2(B) shows the load-displacement curves obtained by the nanoindentation of ta-C: N films at a fixed negative substrate bias of -300 V at different nitrogen partial pressures of zero (ta-C),  $5.0 \times 10^{-3}$  Pa,  $1.9 \times 10^{-2}$  Pa and  $1.0 \times 10^{-1}$  Pa at a maximum load of 1.4 mN. The shape of the load-displacement curves revealed that the

deformation is elastic-plastic in nature. The residual stresses  $\sigma$  present in all the ta-C: N films were found to be compressive in nature<sup>27</sup>. The values of  $\sigma$  in ta-C: N films were found to be 0.18, 0.10, 0.04 and 0.02 GPa with the nitrogen partial pressures of zero (ta-C),  $5.0 \times 10^{-3}$ ,  $1.9 \times 10^{-2}$  and  $1.0 \times 10^{-1}$  Pa, respectively<sup>27</sup>. Nitrogen incorporation in the ta-C films reduced the stress continuously with the increase of nitrogen partial pressure. One can clearly see that the unloading curve meets the loading curve in the ta-C: N films which indicates that the nitrogen incorporation improves the  $E$  value of ta-C film. Moreover, the penetration depth of the nanoindenter decreases with the increase of nitrogen partial

pressure and it suggests that the nitrogen incorporation improves the  $H$  value of ta-C film.

The variations of  $H$  and  $E$  of the ta-C: N films as a function of nitrogen partial pressure are shown in Figs 3(a) and 3(b), respectively. The value of  $H$  was calculated by the ratio of applied pressure to the projected area of the film. The maximum depth of penetration for a particular load, together with the slope of the unloading curve measured at the tangent to the data point at maximum load, leads to a measure of both hardness and elastic modulus of the specimen material. The hardness  $H$  is determined from a measure of the depth of the penetration  $h$  such that the projected area of the contact is:

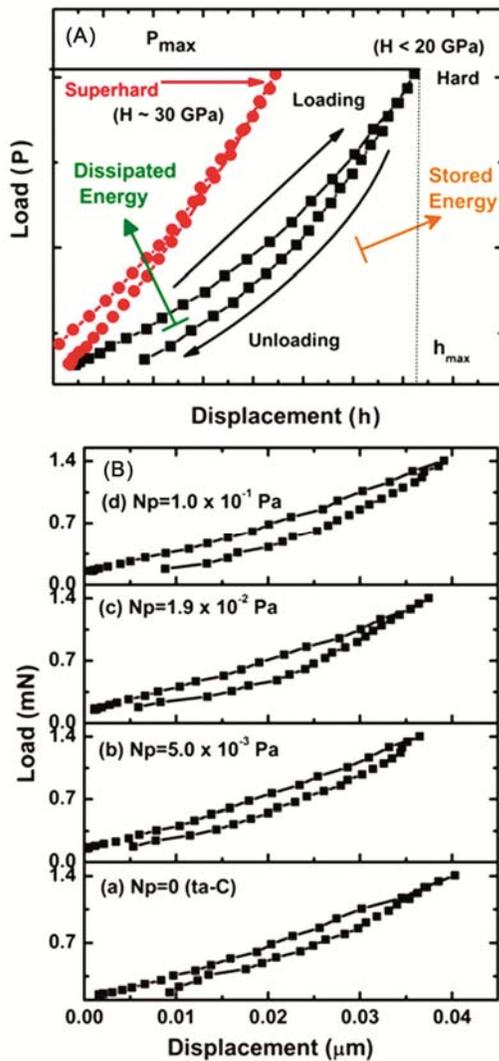


Fig. 2 — (A) Typical load  $P$  vs displacement  $h$  curve, (B) load vs displacement curves of the ta-C: N films deposited at a fixed substrate bias of -300 V at different nitrogen partial pressures  $N_p$  at a maximum load of 1.4 mN.

$$A = 3\sqrt{3} h^2 \tan^2 \theta \quad \dots (1)$$

where  $\theta = 65.27^\circ$ . Thus:

$$A = 24.5 h^2 \quad \dots (2)$$

The expression for  $H$  is defined as<sup>38</sup>:

$$H = \frac{P}{24.5 h^2} \quad \dots (3)$$

The value of elastic modulus  $E$  of both the sample and indenter is given by<sup>38</sup>:

$$E = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad \dots (4)$$

where  $\beta$  is a constant with a value of 1.034 for Berkovich indenter and  $S$  is the contact stiffness. The value of  $E$  increases continuously with the increase of nitrogen partial pressure, whereas the value of  $H$  increases up to  $1.9 \times 10^{-2}$  Pa nitrogen partial pressure

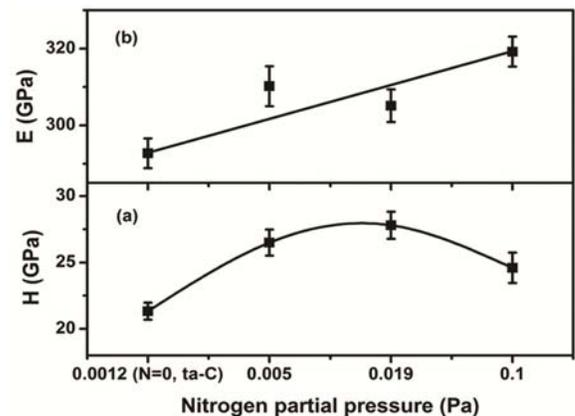


Fig. 3 — Variations of (a)  $H$  and (b)  $E$  at a fixed 1.4 mN load of the ta-C: N films vs nitrogen partial pressure.

and decreases beyond this pressure. The highest value of  $H$  of 27.8 GPa was obtained for the ta-C: N film deposited at the nitrogen partial pressure of  $1.9 \times 10^{-2}$  Pa whereas the highest value of  $E$  of 319.2 GPa was obtained for the ta-C: N film deposited at the nitrogen partial pressure of  $1.0 \times 10^{-1}$  Pa. The values of  $H$  and  $E$  of the ta-C: N film was correlated with the  $sp^3$  content<sup>2</sup>. Another plausible explanation for the improved  $H$  and  $E$  of ta-C: N film is that the high substrate bias (-300 V) increases the ionization of the nitrogen gas resulting into the efficient incorporation of nitrogen in the carbon network which in turn promotes the carbon nitride of formation<sup>26</sup> and stabilization of  $sp^3$  network which improves the quality of hard carbon coatings.

Figures 4(a) and 4(b) show the variations of the  $H/E$  and  $H^3/E^2$  ratio of the ta-C: N film as a function of nitrogen partial pressure. The values of  $H/E$  and  $H^3/E^2$  for the ta-C film are found to be 0.073 and 0.114 GPa, respectively. Nitrogen incorporation in the ta-C films up to  $1.9 \times 10^{-2}$  Pa partial pressure increases the value of  $H/E$  and  $H^3/E^2$  ratio and beyond that both the  $H/E$  and  $H^3/E^2$  ratio decrease. The value of  $H/E$  varies between 0 (plastic behavior) and 0.1 (elastic behavior) for carbon coatings<sup>38</sup>. The increase of  $H/E$  and  $H^3/E^2$  ratio with the increase of nitrogen partial pressure indicates that the nitrogenation promotes the wear resistance of the ta-C coating. Nitrogen incorporation in the ta-C film up to  $1.9 \times 10^{-2}$  Pa nitrogen partial pressure increases the value of  $H/E$  from 0.073 to 0.091. This may be due to the higher energy or the higher substrate bias which could lead to the enhanced ionization of the introduced gas leading to the efficient incorporation of nitrogen in

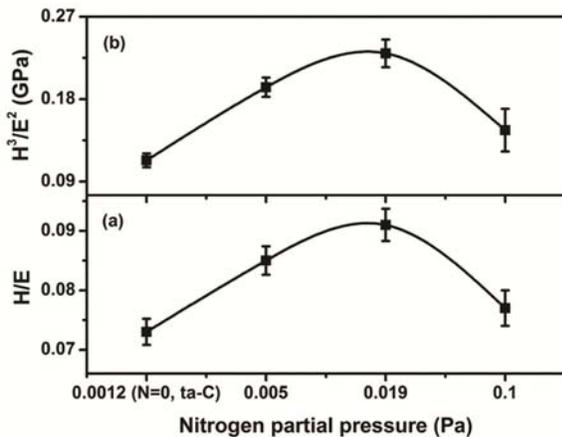


Fig. 4 — Variations of (a)  $H/E$  and (b)  $H^3/E^2$  at a fixed 1.4 mN load of the ta-C: N films vs nitrogen partial pressure.

the carbon network. For the protective coating over the magnetic hard disc or good wear resistant coating over that,  $H/E$  ratio must be very high. This is the reason why less hard films having a high  $H/E$  ratio are widely accepted for this kind of applications. The high  $H/E$  ratio is used to describe the deformation mechanism of the material. High value of  $H/E$  means that these films are highly resistant to plastic deformation<sup>38</sup>. It may be mentioned that the value of  $H/E$  (0.073 to 0.091) reported here are close to the  $H/E$  (0.10-0.12) of the ta-C and ta-C: N films reported in the literature by other worker<sup>38</sup>. It is also pointed out that the low values of  $H$  are not necessarily a disadvantage for a protective coating and the parameter of importance for a good wear resistance coating is  $H^3/E^2(H/E)$  linked to the plasticity index. Many beneficial properties such as the hardness correlate with the fraction of C-C  $sp^3$  bonding<sup>2</sup>. This is because all the mechanical properties increase linearly with the increase of  $sp^3$  content.  $H/E$  ratio is not playing a significant role in the nanomechanical properties of polycrystalline diamond due to the poor plasticity<sup>37</sup>.

Load-displacement curve has been used to estimate the percentage of elastic recovery ( $\% ER$ ) using the relation<sup>38,39</sup> given by:

$$\% ER = \left[ \left( \frac{h_{max} - h_{res}}{h_{max}} \right) \right] \times 100 \quad \dots (5)$$

where  $h_{max}$  and  $h_{res}$  are the displacement at the maximum load and residual displacement after the removal of the load, respectively. To explore elastic-plastic properties of the film in terms of energy, the plastic deformation energy  $U_r$  has also been estimated by the loading-unloading curve in the load displacement given by the relation<sup>38</sup>:

$$U_r = \left( \frac{1}{3} \sqrt{\frac{1}{\pi \tan^2 \alpha}} \right) \frac{1}{\sqrt{H}} P^{3/2} \quad \dots (6)$$

where  $\pi$ ,  $\alpha$ ,  $P$ ,  $H$  are the constant 3.14, angle of  $65.3^\circ$  between the tip axis and the faces of triangular pyramid for Berkovich indenter, load and hardness, respectively. Thus, the higher is the value of  $H$  lower is the value of  $U_r$ .

The elastic recovery ( $\% ER$ ) behavior of the ta-C: N film as a function of nitrogen partial pressure is shown in Fig. 5(a). The value of  $\% ER$  for the ta-C film is found to be 73.25%. It is evident from the

figure that the nitrogen incorporation in the ta-C film up to  $1.9 \times 10^{-2}$  Pa partial pressure improves the %ER from 73 to 85.5 %, which again confirms the hard behavior of the ta-C: N films but beyond  $1.9 \times 10^{-2}$  Pa nitrogen partial pressure the value of %ER decreases. Figure 5(b) shows the plastic deformation energy  $U_r$  as a function of nitrogen partial pressure. The value of  $U_r$  for the ta-C film is found to be  $4.8 \times 10^{-11}$  J and the nitrogen incorporation in the ta-C film up to  $1.9 \times 10^{-2}$  Pa partial pressure reduced the value of  $U_r$  and beyond this pressure the value of  $U_r$  increases. The value of  $U_r$  follows an inverse relationship with the elastic recovery, elastic modulus and hardness. This suggests that the less energy is dissipated for the plastic deformation with the increase of nitrogen partial pressure which is in agreement with the elastic recovery data. The penetration depth at 1.4 mN load in the ta-C: N films were found to be in the range between 36 and 40 nm. The nanohardness of silicon substrate<sup>41</sup> is found as 12.1 GPa and elastic modulus 160 GPa.

The effect of substrate on the mechanical properties of thin films has also been studied in the literature<sup>42,43</sup>. Two different cases of the soft films on the hard substrates and the hard films on the soft substrates have been considered. It has been realized that the hard films on the soft substrates exhibited decrease in the hardness with the increase in the penetration depth, whereas the soft films deposited on the hard substrates exhibited an increase in the hardness with the increase in the penetration depth. The  $H$  value of the ta-C: N films in the present study are found to be larger than the  $H$  value of silicon substrate which belongs to the former case discussed. The value of the  $H$  reported in the present study might

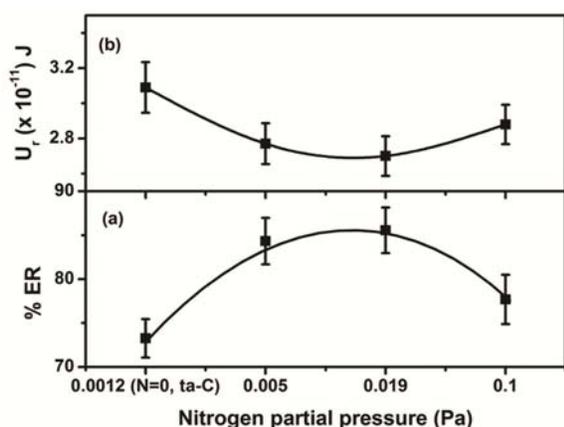


Fig. 5 — Variations of (a) %ER and (b)  $U_r$  at a fixed 1.4 mN load of the ta-C: N films vs nitrogen partial pressure.

be a lower value whereas the actual value of  $H$  may be larger than the reported value<sup>42, 43</sup>. Ma *et al*<sup>44</sup> reported that the values of composite hardness obtained at different indentation depths are not having a constant value and the entire nanoindentation process can be separated into three main stages. At stage 1, the local plasticity in the film is observed (indentation size effect) and at the second stage, the local plasticity of substrate appears (interaction of the indentation size and substrate effects). Finally, at the third stage the plasticity of the substrate dominates the indentation deformation (substrate effect). It may be mentioned that the value of  $H/E$  reported here are very close to the  $H/E$  (0.10-0.12) of ta-C, ta-C: N and other amorphous carbon based films reported in the literature by other worker<sup>45, 46</sup>.

Figure 6 shows the variation of  $H$  at 1.4 mN load of the ta-C: N films versus % of  $sp^3$  content evaluated from the x-ray induced Auger electron spectroscopy (XAES) study reported earlier<sup>26</sup>. It is revealed from the XAES studies<sup>26</sup> made on these ta-C: N films that with the increase of nitrogen partial pressure the  $sp^3$  content increases and it follows a relation of the form  $H = \text{constant} \times (\% \text{ of the } sp^3 \text{ content})$ . Hardness initially increases in the ta-C: N films deposited up to  $1.9 \times 10^{-2}$  Pa nitrogen partial pressure and beyond  $1.9 \times 10^{-2}$  Pa nitrogen partial pressure the hardness values start decreasing. Similar relation has been observed between the values of hardness and % of the  $sp^3$  content for ta-C: N films in the literature<sup>45</sup> and the value of the slope 0.159 GPa obtained in the present study is found to be less than the value of the slope

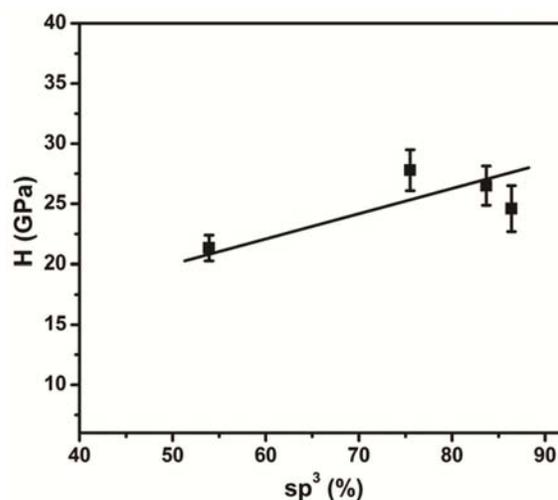


Fig. 6 — Variation of the hardness  $H$  at 1.4 mN load of the ta-C: N films vs % the  $sp^3$  content evaluated.

(0.31-2.42 GPa) reported in the literature<sup>2,45,47</sup>. It is known that the elasticity  $E$  and plasticity have no relation. It is pointed out that low  $H$  value is not necessarily a disadvantage for a protective coating. Moreover, the parameter of importance for a good wear resistance is the ratio of plastic resistance parameter  $H^3/E^2$  which is linked to the plasticity index ( $H/E$ ). The term  $H^3/E^2$  combines the  $H$  and  $E$  values of a material and set the amount of elasticity exhibited by the film. In particular high/low values of  $H^3/E^2$  implies a highly elastic (plastic) behavior of the film. Amorphous carbon materials are thus found to show a variety of behaviors so that the  $E/H = 10$  rule is restricted<sup>48</sup>. The estimated value of the plastic resistance parameter ( $H^3/E^2$ ) of the ta-C films deposited by the  $S$  bend FCVA at -300 V substrate bias is found to be 0.114. Nitrogen incorporation in the ta-C films increases the values of  $H^3/E^2$  to 0.146 – 0.230. The values of  $H^3/E^2$  evaluated in the present study are found to be less than the values of  $H^3/E^2 = 0.694$ - 0.894 for the ta-C films of thickness 70-76 nm deposited by the  $S$  bend FCVA system by Ferrari *et al*<sup>48</sup>.

Neuville and Matthews<sup>14</sup> have provided a coherent perspective on the many factors which are important for the optimization and appropriate use of hard carbon coatings while also challenging in certain preconditions. They stated that it is believed that the presence of  $sp^3$  sites is the only criterion for diamond-like properties which is the source of much confusion. Many soft polymers contain high  $sp^3$  concentrations, but are not considered as diamond-like. In pure diamond which is hard all carbon atoms reside in  $sp^3$  sites and their sites are interlinked by strong covalent bonds whereas in polymers, most of the chains of covalent bonds are terminated by hydrogen atoms. Neuville<sup>8</sup> while studying the extension of fundamentals on  $sp^3$  growth mechanism and stress optimization in hard carbon coating engineering and antiwear material criteria, discussed issues related to deposition rate, substrate shape and size, adhesion and stress. He suggested the ways to optimize the process parameters to enhance the  $sp^3$  orbitals and at the same time to reduce the stress and friction coefficient. He has also studied a correlation between electronic orbital activation and selective properties and growth of carbon nanotubes and related materials<sup>8</sup>. Many different categories of DLC films have been reported in the literature. It is apparent that the  $sp^3$  concentration alone is not a sufficient criterion by which to determine property differences among different amorphous

carbon types which may have a similar concentration of  $sp^3$  sites. In practice the mechanical and physical properties are the factors which define and differentiate DLC films. Charitidis<sup>45</sup> while studying the nanomechanical and nontribological properties of carbon based thin films stated that the hardness and elastic modulus of a-C films depend upon their local bonding and mean coordination of the network. The elastic recovery of carbon related thin films was related to its density and hybridization.

#### 4 Conclusions

It has been demonstrated in the present study that nitrogen incorporation improved the nanomechanical properties of the ta-C films. The highest hardness value of ~27.8 GPa and plastic index parameter ( $H/E$ ) of 0.091 are obtained in the ta-C: N films deposited at a nitrogen partial pressure of  $1.9 \times 10^{-2}$  Pa. This may be due to the higher ion energy or the higher substrate bias which could lead to enhanced ionization of the introduced gases, leading to efficient incorporation of nitrogen in the carbon network. Thus, the study shows the possibility of using higher energy (higher negative substrate bias) as an interesting route to ta-C or associated mixed phase nanocarbons grown using the cathodic arc process as useful material for hard coatings.

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