Effect of ambient gaseous environment on the properties of amorphous carbon thin films

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1. Introduction

Apart from the silicon, germanium and groups II–VI compound based semiconductors, carbon based materials have been extensively investigated because of their presence in various allotropic forms such as diamond, graphite and non-crystalline (amorphous) and tunability of band gap from graphite to diamond. Along with these allotropes, various other allotropic forms of carbon are also present such as buckyball, nanotubes, nanofibers, fullerene, nanobuds and nanodiamond [1–12]. Besides, commonly known allotropes, some intermediate forms of carbon are also found such as diamond like carbon (DLC), tetrahedral amorphous carbon (ta-C), nitrogenated and hydrogenated ta-C (ta-C: N, ta-C: H) and various amorphous carbon matrix doped with nanostructures. These materials have excellent electronic, tribological and chemical properties. It has been suggested by many researchers that if it is possible to form diamond into sheet form and then it becomes easier to protect the products from tearing and wearing. In this direction, an enormous research has been carried out for the development of diamond like hard coating [13–20]. For the growth of hard coating, various methods have been developed such as sputtering, plasma enhanced chemical vapor deposition (PECVD), pulsed laser deposition (PLD), ion beam and more exhaustive vacuum arc process [21–30]. Filtered cathodic vacuum arc (FCVA) is one of the most promising techniques, which offers the opportunity to the researchers to decide the ion energy and environmental conditions during the growth of the films. The films deposited by this technique have excellent physical, chemical and electrical properties and are useful for electronic (field emission display) and tribological applications [21,31–36]. The properties of the amorphous carbon films are governed by the type of chemical bonding (hybridization) of carbon atoms. Carbon atoms have graphite like (sp2 hybridization) and diamond like (sp3 hybridization) hybridizations, with a negligible amount of sp1 type of hybridization. The sp2 hybridization is governed by the weak π–π bonding and it decides the electrical and optical properties of the films. On the other hand, sp3 hybridization occurs due to strong σ–π bonding of carbon atoms and offers the mechanical properties to the films. The type of the bonding (hybridization) between carbon atoms depends upon the ion energy and the surrounding gaseous environment during the growth of the films [31,35,37].
Here, we report the results based on amorphous carbon (a-C) thin films deposited by filtered cathodic jet carbon arc (FCJCA) technique under different gaseous environment. The deposited films were characterized for the surface morphological, mechanical, electrical and chemical bonding of carbon atoms with dopant gaseous atoms to observe the effect of ambient gas environment on the properties of the a-C films.

2. Experimental details

2.1. Sample preparation

The a-C films used in the present study have been deposited by the FCJCA technique under four different gaseous environments (without introducing external gas (NG), introducing helium, nitrogen and hydrogen gases) at ∼100 V substrate bias. The well cleaned 7059 glass and polished silicon wafer were used for the deposition of these films at room temperature. The substrates were kept at a distance of ∼32 cm away from the graphite cathode (purity of 99.999%) of dia. ∼50 mm used as a source of carbon plasma. Another graphite electrode (∼7 mm dia.) of same purity was used as a mechanical striker (anode) to initiate the arc by a direct current (D.C) arc supply. A magnetic field of ∼350 G was achieved inside the duct by a D.C. power supply. Before each deposition the chamber was evacuated down to a low pressure of ∼3 × 10⁻⁶ mbar. One set of films have been deposited at the base pressure (1.2 × 10⁻⁵ mbar) while for the deposition of another set of films highly pure nitrogen, helium and hydrogen gases were introduced through the cathode having a 1 mm cavity. A partial pressure of 8.6 × 10⁻³ mbar was maintained during deposition of these sets of the films. The injection of gases creates a high pressure of few mbar at the vicinity of the cathode and a comparatively low pressure regime towards the substrate. This allows the expansion of a carbon plasma plume away from the cathode towards the substrate and the films of carbon and their composites were deposited.

2.2. Sample characterization

The thickness measurements of these films have been performed by Talystep (Rank Taylor and Hobson) thickness profiler. For the thickness measurement, a step has been made on the substrate during the deposition of the films by covering some portion of the substrate with aluminium foil. When we move the stylus on this step, this will provide us the film thickness data. The film thicknesses of deposited films are found to be in the range of 300–500 nm. The surface morphology of the films was evaluated by scanning electron microscope (SEM) (Leo Electron Microscope – model no. 7060) in the secondary emission mode. The atomic force microscope (AFM) (Nanoscope Veeco – V) was used for the evaluation of surface topography; particle size and root mean roughness. X-ray photoelectron spectroscopic (XPS) measurements were performed by Perkin-Elmer (model no. 1257) X-ray spectrophotometer operating at a base pressure of ∼6 × 10⁻¹⁰ mbar. From the dual anode X-ray source, MgKα (1253.6 eV) line was used for the present analysis. The XPS general survey scan were acquired using a 100 eV pass energy at a step of 1.0 eV and XPS C1s core level spectra were acquired at 0.05 eV step with a pass energy of 60 eV. A grounded metal clamp was used for the charge compensation generated on the surface of the sample during measurement. Raman spectroscopic measurements have been performed on the deposited films by Renishaw InVia Reflex micro Raman spectrometer. Air cooled argon laser of wavelength ∼514.5 nm was used as a source. It provides a spectral resolution better than 1 cm⁻¹ and a spatial resolution of about 1 μm. The nanoindentation measurements have been performed for hardness (H), the elastic modulus (E), plastic index parameter (H/E) and 5% elastic recovery (%) on the deposited samples using IBIS nanoindenter (Fisher-Cripps Laboratories Pvt. Ltd., Australia). The hardness and elastic modulus have been evaluated from the loading and unloading curve taken at 5 mN load. The indentation has been made at 20 places on the sample with different force and load (force) versus displacement curve has been drawn which provided the hardness and elastic modulus data. Keithley 610 C Solid State Electrode was used for the electrical conductivity measurement on co-planar samples.

3. Results and discussion

3.1. Morphological studies

The SEM and AFM studies have been carried out for morphological investigations on the a-C films deposited under different gaseous environments. Fig. 1(a–d) elucidates the 3D view of SEM micrograph of the a-C films deposited without gas (NG), under helium, nitrogen and hydrogen gas environment, respectively. It is evident from the figure that large numbers of small grains are present on the film surfaces with some agglomerations. The grains present on the films surfaces have no regular pattern which exhibited the amorphous nature of the samples. SEM studies revealed that the films deposited without gas has a small numbers of grains or their agglomerations whereas the grain density increases on the introduction of gases such as helium, nitrogen and hydrogen. The increase in grain density could be due to higher degree of ionization of the introduced gas. The higher degree of ionization causes the production of large number of carbon ion from the cathode surface and their subsequent deposition along with the gaseous ion (hydrogen and nitrogen) and the film density increases. A closer examination of SEM micrographs revealed that the film deposited under helium environment (Fig. 1b) have larger agglomeration on the film surface whereas the film deposited in the presence of hydrogen gas (Fig. 1d) is smoother than other films. Fig. 2(a–d) exhibits the surface line profile (which has been taken at three places on the film surface) for surface roughness of the deposited a-C films under without gas, helium, nitrogen and hydrogen gas environment, respectively. The surface line profile also confirms that the films deposited without gas and hydrogen gas environment are smoother than the films deposited under helium and nitrogen environments. The film deposited under hydrogen gas environment has the lowest value of the surface roughness whereas the film deposited under helium environment has the highest roughness value. Fig. 3(a–c) shows the 3D view of AFM micrographs of the a-C films deposited under helium, nitrogen and hydrogen gas environment, respectively. It can be seen clearly from the figure that the film surface is constituted by large number of grains of different shapes and sizes. It is reflected from the figure that the film deposited under hydrogen gas environment has large number of small grains as compared to films deposited under helium and nitrogen environment. The film deposited under nitrogen environment have spherical shaped grains on the film surface whereas the films deposited under helium and hydrogen gas environment has random shaped grains distributed throughout the surface. The closer examination of the AFM micrographs shows the corroboration of the film surface to the surface morphology evaluated by SEM micrographs. The grain size and the root mean roughness of the deposited samples of the a-C films are also evaluated by AFM study. The values of grain size for the film deposited under helium, nitrogen and hydrogen gas environment are found to be 202 nm, 90.28 nm and 38.19 nm whereas the roots mean roughness values are 18.3 nm, 9.67 nm and 0.367 nm, respectively. It is found that the particle size and root mean roughness value decrease, when we go from helium to nitrogen and then to hydrogen gas environment. Thus, the results obtained from the SEM studies are well matched with the results evaluated from the AFM studies. The results obtained from the surface morphological studies on the deposited film are found to be dependent on the energy of incoming ions to the substrate, plasma density, ionization energy and atomic mass of the ambient gas used for the growth of carbon films. Under a balanced condition of these parameters, the films have excellent surface morphology. Since the ionization energy of the helium (∼24.59 eV) is higher than the ionization energy of the nitrogen (∼14.534 eV) and hydrogen ion (∼13.6 eV) hence these gases have different ionization rates and ion energy. When we introduced these gases through the cathode, the ionization of these gases takes place near the cathode (cathode spot). These highly energetic gaseous ions strike onto the surface of the substrate along with carbon ion, with the different ion energy. At the substrate surface, the carbon ions combined with the present gaseous ions to form the composites onto the substrate surface through chemical bondings and govern the surface morphology and other properties. When we go from helium to nitrogen and then to hydrogen, the ionization rate and the ion energy of these gases increase as a result the plasma density increases. With increase of the plasma density (ion energy) the films surfaces becomes more and more dense and smooth. Because of the highest ion energy of the hydrogen,
the highly energetic ions strike on the film surface which results in highly smooth films as compared to other gases (Figs. 1–3). The highly dense films with low roughness value (films deposited under hydrogen environment) have a large number of applications for the coating on the movable parts of a machine to avoid the wear and tear of the parts. This type of coating can also be applicable for biocompatible parts such as heart valve etc. Thus, by choosing the gaseous environment, gas content and ion energy, these coatings can be used for various applications.

3.2. XPS and Raman measurements

The XPS measurements have been performed on the deposited a-C films for the evaluation of various bonding states of carbon and introduced gaseous atoms and their chemical compositions etc. To avoid the surface modification and bonding states on the film surface, the XPS measurements have been carried out without argon ion cleaning. Fig. 4 shows the general survey scan of the a-C films deposited under different gaseous environment. It is evident from the figure that the films deposited without gas, under hydrogen and helium gas environments have only two components at ~284 and ~532 eV which are attributed to carbon and oxygen, respectively, whereas for the films deposited under nitrogen gas environment, it has one more reflection observed at ~399 eV. The peak obtained at ~399 eV confirms the presence of nitrogen incorporation in the films. The observed binding energy peak positions for carbon, oxygen and nitrogen are well matched with the reported value in the literature [38]. The oxygen component observed in all the films may come from the exposure of the films with the laboratory atmosphere. Fig. 5 shows the C1s spectra of the a-C films deposited under different gaseous environments. It is reflected from the figure that the C1s peaks have an asymmetry towards higher binding energy and also some shifting of peaks position of the C1s peaks with different gaseous environment are observed. The asymmetry of the C1s peaks indicates the presence of different bonding states of carbon atoms in the films [39] whereas the change in the peaks position value indicates the changes in chemical bonding of the carbon atom with the gaseous environment. The binding energy peaks position of graphite (sp²-hybridized) and polycrystalline diamond film (sp³ hybridized) are found to be at 284.5 eV [38] and
285.3 eV [40], respectively, whereas for sp²-hybridized C–N bond and for sp³-hybridized C–N bond are found to be at 286.1 eV and 287.7 eV [41], respectively, in the C1s spectra of the a-C films. For the evaluation of different bonding states, the C1s peaks and N1s peaks are deconvoluted into different components. The C1s peaks of the a-C films deposited under without gas, helium and hydrogen gas conditions are deconvoluted into three component of Gaussian peaks after subtraction of the background from the spectra by Shirley mode whereas the C1s peak of the a-C films deposited under nitrogen gas environment is deconvoluted into five components. During the deconvolution of C1s peaks, all the parameters such as peak position, full width at half maxima (FWHM) and the % area under different components are left free to adjust for the uniformity and repeatability of the process. For the accuracy of the method used, it is tried to calculate the peaks positions, FWHM and area covered under the curve up to an accuracy of 0.005 eV, 0.01 eV and 0.0001, respectively, with a tolerance values of 0.00001. All the processes are repeated three times to check the repeatability of the method used for the deconvolution.

Fig. 6 illustrates the fittings of deconvoluted XPS spectra of C1s peak of the a-C film deposited under various gaseous environments. The peaks located at 284.3 ± 0.3, 285.4 ± 0.2, 287.9 ± 0.4 eV were assigned to C–C sp² hybridized carbon in graphite like carbon–carbon structure, C–C sp³ hybridized carbon atoms in diamond like carbon–carbon structure and C≡O bonding between carbon and oxygen, respectively, for the a-C films deposited without gas, under helium and hydrogen gas environment. While the films deposited under nitrogen gas environment have two more components located at ~285.7 and 286.8 eV and were attributed as C≡N sp² hybridized carbon in graphite-like carbon–nitrogen bonds, sp³ hybridized carbon in C–N in –C–N bond like structures, respectively. The peaks positions observed for the sp³ hybridized (C–C at 284.3 ± 0.2 eV) and sp² hybridized (C≡N at 284.3 ± 0.3 eV) carbon are well matched with the peak value reported in the literature [20,42–49] and peaks observed for the sp³ hybridized (C–N at 285.7 eV) and sp² hybridized (C≡N at 286.3 eV) carbon–nitrogen are consistent with the peaks reported in the literature [39,49–55]. The small shifting observed in the binding energy peaks position could be due to the generation of some charge on the films surfaces during the XPS measurement. However, a metal clamp was used for the charge compensation but it may be possible that all the charges were not neutralized.

Fig. 7 shows the deconvoluted spectra of the N1s peak of the a-C film deposited under nitrogen gas environment. The N1s peak of the a-C films has been deconvoluted into three components. The peaks were located at ~398.7, 400.3 and 401.9 eV binding energies and were attributed to N–C (sp³ bonded), N–C (sp² bonded) and bonding of state nitrogen with oxygen (N≡O). The sp³ hybridized N–C
bonds have lower binding energy as compared to sp²-hybridized C=N bonds in deconvoluted N1s spectra because when nitrogen is incorporated into a-C film, it has priority to form N–C (sp³-hybridization) bonding instead of N=C (sp² hybridization) bonding. This means that sp³ C–N bonds not only have lower binding energy as compared to sp² bonded C=N bonds but also have simple σ bond rather than more complicated double bonds (σ bond and π bonds). The observed peaks positions in N1s spectra are consistent with the peaks reported in the literature [48–55]. The values of binding energy of peaks position of the deconvoluted spectra of C1s and

Fig. 3. AFM micrographs of the a-C films deposited under (a) helium, (b) nitrogen and (c) hydrogen gas environments.

Fig. 4. XPS general survey scans of the a-C film deposited under different gaseous environments.

Fig. 5. Variation of C1s peak position versus binding energy of the a-C films deposited under different gaseous environments.
Fig. 6. Deconvoluted XPS spectra of C1s peaks of the a-C films deposited under different gaseous environments.

Fig. 7. Deconvoluted XPS spectra of N1s peaks of the a-C film deposited under nitrogen gas environment.

Fig. 8. Raman spectra of the a-C films deposited under different gaseous environments.

N1s peaks with different bonding configuration, their FWHM values and the % area covered under the curves obtained by fitting of the a-C films deposited under different environments have been summarized in Table 1.

The value of sp3 and sp2 content present in the a-C films were evaluated from the deconvoluted spectra of C1s peaks of the a-C films deposited under different environments. The values of sp2 and sp3 for the a-C films deposited without gas, under helium and hydrogen gas environments are evaluated from the ratio of the corresponding peak area of the peaks located at peak position of 284.3 ± 0.3 and 285.4 ± 0.2 to the total area of C1s peaks, respectively. But for the film deposited under nitrogen gas environment, the total sp3 content is the sum of sp3 content in C–C bonds (peak at ∼284.8 eV) and sp3 content in C–N bonds (peak at ∼286.8 eV). Similarly the sp2 content is the sum of sp2 content in C=C bonds (peak at ∼284.2 eV) and sp2 content in C≡N bonds (peak at ∼285.7 eV).

Fig. 8 elucidates the Raman spectra taken in the wavenumber range from 1000 to 2000 cm⁻¹ on the a-C films deposited under without gas, nitrogen and helium gas environments. It is reflected from the figure that the Raman spectra of the deposited films have a pronounced shoulder (band observed around ∼1360 cm⁻¹) towards the lower wavenumber side of the spectra with a main peak (band observed around ∼1570 cm⁻¹). The shoulder becomes more pronounced, when we move from without gas to nitrogen and then to helium gas environment, indicating graphitization of the films with the change in the environment. The Raman spectra at any wavelength generally depends on: (1) the clustering of sp2 phase, (2) bond length and bond angle disorder and (3) presence of sp2 ring or chains and the sp3/sp2 ratio. The band observed at ∼1570 cm⁻¹ corresponds to the symmetric E2g C=C stretching mode in graphite like materials whereas the band located at ∼1360 cm⁻¹ was attributed to bond angle disorder in graphite like microdomains affected by sp3 bonds and were assigned as G-band and D-band, respectively. The broad band at ∼1570 cm⁻¹ indicating coating with significant fraction of sp3 bonded carbon. The band positions are well matched with the positions observed by various research groups [20,45,56,57]. It has been observed that when, we go form helium to without gas spectra, the band located at ∼1360 cm⁻¹ becomes weaker and weaker whereas the band located at ∼1570 cm⁻¹ becomes more pronounced. The film deposited under helium environment has sharp reflection of this band (D-band) whereas for the film deposited without gas, this band almost disappears. Since, the sp3 bonded carbon coatings are optically transparent and the visible-Raman spectroscopy is 50–230 times more sensitive to sp2 bond than sp3 bond because visible photons (2.2 eV) preferentially excite the π states [30,45]. Thus, the sp2 bonds are easily detectable by Raman spectroscopy and sp3 bonding can be indirectly assessed. For the evaluation of quantitative results, the Raman spectra were deconvoluted into two Gaussian peaks associated with their microstructures and the G band at ∼1570 cm⁻¹ due to disordered graphite and D band at ∼1360 cm⁻¹ due to small domain size graphite regions were separated. For the estimation of the amount of sp3 and sp2 contents
present in the films, the intensity ratio of the peaks corresponding to D-band to G-band \((I_D/I_G)\) has been taken and it was found to be \(\sim 1.5\). The intensity ratios \((I_D/I_G)\) are found to decrease from helium (1.33) to nitrogen (1.28) and to without gas (0.77) and it has been demonstrated in the literature \([20,45,56–59]\) that decrease of \((I_D/I_G)\) ratio corresponds to increase of \(sp^3\) content. Thus, the film deposited under helium environment has the lowest value of \(sp^3\) content whereas the film deposited without gas has the highest value of \(sp^3\) content. Gou et al. \([56]\) also suggested that higher is the \((I_D/I_G)\) ratio, higher is the size of the \(sp^2\) carbon cluster and larger is the roughness value. Similar, results were observed by us in the present studies. The roughness values evaluated from the SEM and AFM measurements are found to vary with the \((I_D/I_G)\) ratio. Thus, the results, obtained in the present study are well matched with the results observed by Gou et al. \([56]\). It has been further observed that the peak position of the G-band shifted towards the lower wavenumber side from the film deposited under helium (1579.2 cm\(^{-1}\)), to nitrogen (1559.2 cm\(^{-1}\)) and to without gas (1552.5 cm\(^{-1}\)) environments and the FWHM value of G-band increases from helium (116.5 cm\(^{-1}\)), to nitrogen (118.3 cm\(^{-1}\)) and to without gas (270.8 cm\(^{-1}\)) environments. Champi et al. \([57]\) and Jiang et al. \([20]\) suggested that shifting to G-band peak position towards the lower wavenumber side and increase of FWHM value of G-band favor the formation of the \(sp^3\) bonded carbon. Thus, the results obtained from the shifting of G-band peak position and FWHM value of G-bands further confirm the result obtained from the intensity ratio of D-band and G-band. The Raman spectroscopic studies illustrate that the \(sp^3\) content present in the deposited films increases from helium to nitrogen and to without gas environment. Thus, the results obtained from the XPS studies and Raman spectroscopic investigations are well corroborated. However, Raman measurements are more useful for the qualitative informations about the deposited samples whereas XPS measurements provided more pronounced quantitative results.

### 3.3. Effect of gaseous environment on the properties of the a-C films

#### 3.3.1. Effect on the \(sp^3\) and \(sp^2\) contents

The \(sp^3\) and \(sp^2\) contents evaluated in the a-C films are found to be dependent on gaseous environment, which may lead to form new bonding states between carbon–carbon, carbon–nitrogen and carbon–hydrogen atoms. Fig. 9 shows the variation of the \(sp^3\) and \(sp^2\) contents with the gaseous environment. It is evident from the figure that the value of \(sp^3\) content in the a-C film increases, when we move from helium to nitrogen to without gas and to hydrogen gas environments whereas \(sp^2\) contents show a reverse order. This may be because of the formation of diamond-like structure, when we move from helium to hydrogen.

There are two main sources of the formation of new chemical bonding in the carbon films: (1) the energy of the incoming ions towards the substrate and (2) the gaseous environmental condition in which the films were deposited. The a-C films deposited without any external gas with high \(sp^3\) content are generally called tetrahedral amorphous carbon films. Generally, undoped and hydrogenated a-C films are of p-type whereas the nitrogen incorporation makes them n-type. These films are formed by highly energetic carbon ions. Various research groups investigated the effect of noble gas (helium or argon) environment on the properties of the a-C films. They suggested that when some inert gases such as helium, argon or neon are introduced in the carbon environment, the plasma density is enhanced as a result of which highly dense carbon films are formed with the enhanced mechanical properties. But after a certain amount of inert gas, plasma becomes more inert like and the films deposited under this condition becomes graphitic and with the increase of inert gas content, the graphitic character of the films become more and more intense. The \(sp^2\) content in the a-C films increases whereas the \(sp^3\) content decreases because of the high ionization rate of the noble gases as compared to carbon ions. This effect could be due to the increase of

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>C≡C</th>
<th>C–C</th>
<th>C≡O</th>
<th>C≡N</th>
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<td>22.27</td>
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<tr>
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**Fig. 9.** Variation of \(sp^3\) and \(sp^2\) contents with the change of gas environments.
inert gas content beyond a critical concentration; the ion bombardment type of effect takes place on the films surface which causes the sputtering or bond breaking process (dangling bond formation) at the film surface. This results in increasing sp² phase and making the films more graphitic [1,54,55,60]. A similar type effect may take place in the present study with the introduction of the helium gas. As it has been observed that with the introduction of the helium gas in the carbon environment the sp² content in the film increases by transforming the sp³ sites into sp² sites and the film becomes graphitic as compared to the film deposited without using gas.

The value of sp³ content is also found to decrease with the incorporation of nitrogen in the a-C films. The nitrogen incorporation in the a-C films plays a vital role in deciding the properties of the film with the formation of new type of bondings between carbon and nitrogen atoms. The nitrogen incorporation may result in transformation of sp³-bonded carbon to sp²-bonded carbon which changes the electronic properties of the films. The higher is the nitrogen content incorporated in the film, the higher will be the sp² content which leads to the more graphitic character of the film deposited [61,62]. The sp³ and the sp² contents in the nitrogen incorporated a-C films are found to be dependent strongly on the ion energy and the bonding between carbon and nitrogen atoms. The value of sp³ and sp² content of the a-C films deposited under nitrogen gas environment lies between the films deposited without gas and the film deposited under helium gas environment.

The value of sp³ content is found to increase with the introduction of the hydrogen gas in the carbon plasma. It is well known phenomena observed by various research groups [13,16–18] that with the increase of the hydrogen content, the sp³ content increases. The type of hybridization depends upon the carbon-hydrogen bonds and at a very high value of hydrogen content (~67%) long polymer-like chains are formed with the high sp³ content. The ion energy and the bonding of carbon–hydrogen are the main source of sp³ content in the a-C film deposited under hydrogen gas environment. Because of the lesser value of ionization energy of hydrogen gas, there is a high degree of ionization together with a highly dense film formation. Thus, the high degree of ionization (very high value of ion energy) of the hydrogen gas and carbon ions are the cause of the higher value of sp³ content in a-C films deposited under hydrogen gas environment.

3.3.2. Effect on the conductivity and mechanical properties

Fig. 10 shows the variation of dark conductivity (σ_D) with the inverse of temperature for a-C films deposited under different gaseous environments. As it can be seen from the figure that the variation of σ_D is a thermally activated process that follows a relation \( \sigma_D = \sigma_o \exp(-\Delta E/kT) \); where \( \sigma_o \) is the conductivity pre exponential factor, \( \Delta E \) is the activation energy, \( k \) is the Boltzman's constant and \( T \) is the temperature in Kelvin. The conductivity of the films increases with the increase of temperature which shows the semiconducting behavior of the films.

It is revealed from the figure that the value of \( \sigma_D \) decreases, when we move from the films deposited under helium to nitrogen to without gas and to hydrogen gas environments. The decrease of the conductivity of the a-C films from helium to hydrogen could be due to the increase of sp³ content and decrease of sp² (graphite-like) content. The variation of the conductivity has the same trend as that of the sp² content with the change of gaseous environments. The sp² content mainly governs the electronic properties to the a-C films by tailoring the optical band gap whereas the sp³ content leads to mechanical properties. The sp² hybridized sites form the π states through weak π bonds and these weak π bonds introduce the π valence and π⁺ conduction states in between σ and σ⁺ states of sp³ sites. These π and π⁺ states form the band edges and control the band gap and conductivity of the deposited films. The greater

is the hydrogen content higher is the optical gap energy and the lower is the sp² value which leads to the lowest conductivity [60].

When nitrogen gas is introduced into the carbon plasma, the p-type character of the a-C films changes into n-type and at a sufficient high value of the nitrogen content the conductivity of the films increases. As, with the introduction of nitrogen gas, the Fermi level moves from middle to towards the conduction band and the conduction take place from some Fermi level sites to the conduction band as a result of which the conductivity of the films increases with the doping of nitrogen in the a-C films. The a-C films deposited under helium environment has the highest conductivity value because of highest sp² content (graphite-like structure) accompanied with the lowest sp³ content value [63–65].

Fig. 11(a–c) demonstrates the mechanical parameters such as hardness (H), elastic modulus (E), plastic index parameter (H/E) and elastic recovery factor evaluated from the nanoindenter studies performed on the deposited samples. Since, the film thicknesses for the films deposited under helium (497 nm), nitrogen (460 nm), without gas (325 nm) and hydrogen (385 nm) are very small. Therefore, in order to avoid the substrate effect in the mechanical parameters (hardness data), nanoindentation measurements have been performed at lesser value of load (5 mN). Fig. 11(a) shows the load (force) versus displacement curve used for the estimation of mechanical parameters of the deposited films. There is no pop in (cracking of film) observed at this load in the deposited film. Fig. 11(b) illustrates the dependence of hardness and elastic modulus of the deposited films on the ambient gas environment. The values of hardness and elastic modulus of the deposited films are found to increase, when we move form helium to nitrogen to without gas and to hydrogen gas environment. The film deposited under hydrogen environment has the highest value of hardness (~21 GPa) and elastic modulus (~237 GPa) whereas the film deposited under helium environment has the lowest value of hardness (~15 GPa) and elastic modulus (~195 GPa). This indicates that the film deposited under hydrogen environment is more diamond like. The hardness and the elastic modulus of the deposited films have the same trend as that of sp³ content because of the formation of the new bonding states under different gaseous environment. Fig. 11(c) shows the variation of plastic index parameter (H/E) and the elastic recovery (ER) factor of the deposited films with ambient gas environment. Plastic index parameter is an important parameter to differentiate between the elastic and the elastic–plastic behavior. For protective coating on magnetic hard
disk or wear resistant coatings, the value of $H/E$ must be very high. It is illustrated from the figure that film deposited under hydrogen environment exhibited maximum $H/E$ (0.088), which slightly decreases for the film deposited without gas (0.086). However, for the film deposited under nitrogen and helium environment the value of $H/E$ reduces considerably and were found to be 0.080 and 0.077, respectively. Thus, the films deposited under hydrogen and without gas are more useful for protective coatings as compared to films deposited under nitrogen and helium environment. Another important parameter used for the evaluation of quality of the films is the elastic recovery factor. Higher is the elastic recovery factor value higher will be the hardness value of the films and more useful the coatings will be for the tribological applications. The elastic recovery of deposited films can be evaluated by the expression

$$\% \text{ ER} = \left( \frac{d_{\text{max}} - d_{\text{res}}}{d_{\text{max}}} \right) \times 100$$

where, $d_{\text{max}}$ and $d_{\text{res}}$ are the displacement at the maximum load and residual displacement after load removal, respectively. It has been observed from the figure (Fig. 11c) that the elastic recovery factor of the deposited films depend on the gas environments and varies from 58 to 74.6%. The value of elastic recovery of the films deposited under without gas, hydrogen, nitrogen and helium gaseous environments are found to be 74.5, 69.3, 59.4 and 58%, respectively. This indicates that the elastic recovery factor has a considerable high value and has a good agreement with the hardness data. However, it has been observed that the elastic recovery factor has the highest value for the film deposited without gas ($\sim$74.6%) whereas the film deposited under hydrogen environment has the highest value of hardness ($\sim$21 GPa). However, the difference was not much ($\sim$5%). It may be due to occurring of some deformation in the structure of the films deposited without gas as compared to film deposited under hydrogen environment by the application of the load. The mechanical properties of the films have a similar trend as that of $sp^3$ content and are found to depend on the ion energy and the gas environment used for the growth of the films. Thus, the ion energy and the gas environment decide the properties of a-C films. The nanoindentation studies have been performed by various research groups for the evaluation of the mechanical properties on the deposited a-C films [59,60,66–68]. On the basis of these properties these films can be for different applications. The films having high $sp^3$ content and high hardness value are used for the tribological application such as coating on lazer blades and hard disk etc. Also the high $sp^3$ content undoped (without gas) and nitrogen and hydrogen incorporated a-C films have very good application for the field emission displays. The nitrogen incorporated and the films deposited under helium environment have high conductivity value and can be used for the electrical application. Thus, by deciding the environmental condition and enhanced $sp^3$ and $sp^2$ contents, the a-C films are useful for various applications.

Fig. 11. Variation of the mechanical parameters of the deposited films under different environments. (a) Load versus displacement curve, (b) variation of hardness and elastic modulus with gas environment, (c) variation of plastic index parameter and % elastic recovery with gas environment.
4. Conclusions

The effect of gaseous environments on the properties of the a-C films deposited by FCJCA technique has been investigated. The surface morphology and the amorphous nature of the films were examined by SEM and AFM studies which show that the grain size and the root mean roughness values decrease when we go from helium to nitrogen and to hydrogen gas environment. The X-ray photoelectron spectroscopic studies have been performed for the investigation of the bonding states of carbon atoms with the gaseous atoms in the a-C films. The Raman measurements have been carried out on the deposited a-C films. It has been observed that sp³ content present in the films increases from the film deposited under helium to nitrogen and to without gas environment. The results obtained from the XPS measurement. The sp² contents, electrical conductivity and hardness values of a-C films deposited under different gaseous environments are found to increase with the change of gas environment from helium to nitrogen to without gas and to hydrogen. Film deposited under helium gas environment has the lowest value of hardness (15 GPa) and sp³ content (37 at.%) whereas the film deposited under hydrogen gas environment has the highest value of hardness (21 GPa) and sp³ content (54.7 at.%). The sp² content show a reversal in the trend with gas environment.

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References