Deposition of hydrogenated amorphous carbon films with enhanced sp³-C bonding on nanocrystalline palladium interlayer

M. Roy a, Kunal Mali b, Niraj Joshi c, D.S. Misra d, S.K. Kulshreshtha a,⁎

a Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400085, India
b Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai-400085, India
c Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Centre, Mumbai-400085, India
d Department of Physics, Indian Institute of Technology Bombay, Mumbai-400076, India

Abstract

The present study deals with the deposition of hydrogenated amorphous carbon (a-C:H) films on Si (100) substrates with and without an interlayer of nanocrystalline palladium (nc-Pd) on them, by high-voltage electro-dissociation of N,N-dimethyl formamide (DMF). Significant improvement in the sp³ carbon content has been observed for a-C:H films grown on nc-Pd interlayer as revealed by Fourier transformed infrared (FTIR), Raman, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopic techniques. It is inferred that H2 activation on palladium sites leads to the stabilization of sp³-C bonding, thereby improving the quality of the deposits grown on them.

Keywords: a-C:H; Nanocrystalline palladium; Interlayer; Electro-deposition; Raman; XPS

1. Introduction

Since the beginning of the last decade, thin films of amorphous carbon have attracted considerable interest [1–8] due to their properties akin to diamond that make them quite promising for the coating technology. These amorphous carbon films encompass a broad class of carbon materials comprising of different combinations of diamond, graphite and polymeric bonding in an intimately mixed amorphous structure and hence describe a wide range of material properties. Depending on their structure they can have a maximum of 90% of the carbon atoms in sp³ hybridized tetrahedral bonding configuration, similar to that in diamond [3–6], on which the diamond-like properties in these materials such as hardness, electrical resistivity, transparency in the IR region, etc. depend [1–3,9–11]. However it is not easy to grow amorphous carbon films with very high fraction of carbon atoms in sp³ hybridized tetrahedral bonding configuration. Of late high-voltage electro-dissociation of common organic solvents [12–16] has provided with a simple and inexpensive technique for depositing hard amorphous carbon films at around room temperature, practically on any conducting substrate. But the quality (i.e. excellent material properties, exhibited by the films with high sp³-C content) of the deposits still remains a major concern. So, it will be of tremendous practical significance if one can improve upon the content of sp³-C in these electro-deposited films. It is known from the existing literature [13] that the hydrogen evolved during electro-dissociation of the protic solvents, upon activation, can participate in the process of bond breaking and bond making, thereby modifying the carbon linkages within the films. It is also known that palladium films can adsorb and activate H2 even at room temperature (RT) [17] and the process of activation commences through its surface adsorption, especially at the grain boundaries [18]. Maximum efficiency is therefore expected when the grain size of palladium is in the nanometer scale. Hence the natural question arises if nanocrystalline palladium-induced in-situ activation of evolved H2 could improve the sp³-C content of the electro-deposited amorphous carbon films. To find an answer to this question, we deposited amorphous carbon films on both bare and nanocrystalline palladium coated silicon substrates by high-voltage electro-dissociation of N,N-dimethyl formamide (DMF). To discriminate the effect due to variation in current density, all samples
were deposited under a constant current density of \( \sim 20 \text{ mA/cm}^2 \) and were characterized ex-situ using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy. The results of our investigations on the positive effects of \( \text{nc-Pd} \) interlayer in enhancing the \( \text{sp}^3 \)-C content of electro-deposited amorphous carbon films are reported in this communication.

2. Experimental

Thin films of nanocrystalline palladium were deposited on boron-doped (p-type) silicon (100) single crystal wafers (electrical resistivity \( \sim 1 \, \Omega \text{ cm} \)) obtained from Wacker Chemitronic using “inert gas condensation” technique [19]. In this technique the size of the grains is controlled by varying the pressure of the inert gas e.g. argon in the present case. Prior to deposition the substrates were thoroughly cleaned with dilute HF solution to remove the native oxide layer. A 0.8 mg palladium (99.99%) wire was completely evaporated by heating it on a tungsten filament, while the substrate kept at a distance of 10 cm from the filament was maintained at liquid N\(_2\) temperature. Deposition was done at a base pressure of \( 10^{-6} \text{ Torr} \). Film thickness, estimated using a quartz crystal thickness monitor is typically \( \sim 100 \text{ nm} \). The films have been characterized ex-situ using XRD and AFM.

The setup used for the deposition of amorphous carbon films is described elsewhere [14]. Analytically pure \( N,N\)-dimethyl formamide (DMF) was used as the electrolyte. Bare as well as \( \text{nc-Pd} \) coated Si wafers were used as negative electrodes, while a graphite plate served as the positive electrode. The distance between the two electrodes was set to \( \sim 5 \text{ mm} \). A high-voltage power supply unit was operated in current-limited mode to provide constant current density during the entire deposition process. An optimized current density of \( \sim 20 \text{ mA/cm}^2 \) was used for depositing the samples. The bath was maintained at around room temperature by constant water circulation. Films were deposited for \( \sim 5 \text{ h} \) and were characterized ex-situ using different techniques.

AFM micrographs were recorded at room temperature and under atmospheric pressure using a scanning probe microscope (SM-P47, NT-MDT, Russia) in contact mode with rectangular silicon nitride tips (tip radius \( \sim 10 \text{ nm} \)). SEM micrographs were recorded in a VEGA MV 2300T/40 scanning electron microscope (Oxford make). X-ray diffraction patterns were recorded in a Philips X-ray diffractometer PW 1710 using Cu K\( \alpha \) line (1.54060 Å) from an X-ray generator operated at \( \sim 30 \text{ kV} \) and 20 mA. FTIR measurements were done in transmission mode using a Jasco FT/IR-610 instrument with a resolution of 2 cm\(^{-1}\). Air reference was used for correcting the background. Micro-Raman measurements were done using a LABRAM-HR spectrometer (Jobin-Yvon make) in a backscattering geometry. The 514.5 nm line of a 10 mW Ar\(^+\) laser was focused onto the sample using a 100× microscope (Olympus make) objective that corresponds to a spot of less than 1 mm in diameter for excitation and a Peltier cooled charge coupled device (CCD) was used for multi-channel detection. Spectra were recorded at different spots on the samples to ensure for
their homogeneity. Room temperature steady-state photoluminescence measurements were carried out with a Hitachi F4010 spectrometer using a xenon arc lamp for excitation. XPS spectra were recorded using Mg Kα radiation and constant pass energy of 13 eV. Nanohardness measurements were done at different spots on the carbon films using ultra-nanohardness tester (CSM instruments make). A maximum load of 15 mN was applied using Berkovich indenter, the loading and unloading rates being 30 mN/min. Data acquisition was done at the rate of 10 Hz. Mean value hardness was obtained by averaging the data acquired from indents made at different spots on the films and thus reported. Film surface profiles were obtained using a profile meter.

3. Results and discussion

Fig. 1 shows the AFM topography along with 3D contour map and roughness profile (inserts) of a typical palladium deposit. The crystallites which grow via 3D nucleation and growth mechanism are nearly hexagonal in shape and their size is typically less than 20 nm. However at places, bigger clusters of ~100 nm in size are formed due to agglomeration of more than 5–6 grains. Average surface roughness (Ra) and root mean square (RMS) roughness of the film are estimated to be ~21 nm and ~26 nm respectively. Room temperature (RT) electrical resistivity (ρ) of the nc-Pd film is typically ~8.2 mΩ cm.

Upon high-voltage dissociation of DMF, brownish black coatings are obtained on both bare silicon substrate and the palladium layer. The coatings are subjected to “scotch tape” test wherein an adhesive containing tape (scotch tape) is first made to stick to the film surface and then pulled out by applying a force. A coating is said to be adherent if it does not fail under the said operation. Both the coatings under study are found to adhere well on to their respective substrates. Fig. 2 shows the load vs. indentation graph of a typical sample. Nanohardness of the film was estimated by tangent method to be 10,335 MPa (10.3 GPa). Mean hardness was found to vary between 9 and 11 GPa for different samples. The values are in very good agreement with that reported for DLC films by S. Gupta et al. [15] and at the same time almost an order of magnitude higher than that reported for polymeric stuffs [20]. So, it may be concluded in comparison with the existing literature that hardness of the amorphous carbon films deposited by this technique are at par with any DLC films deposited by electro-chemical means. Fig. 3
shows the scanning electron micrograph (SEM) of a typical amorphous carbon film grown on nc-Pd interlayer along with its roughness profile tagged as inserts. Grains are irregular shaped without any well-defined structure and the grain size is typically more than 100 nm. From the roughness profile [insert (a)], Ra and RMS values have been estimated for the film to be ∼80 nm and 100 nm respectively. Detailed deposition mechanism of amorphous carbon films formed by high-voltage electro-dissociation of organic solvents is described elsewhere [21].

The WDS spectrum was recorded from a spot size of 1 μm. X-ray beam energy was varied to reduce contribution from the silicon substrate well below the background level. The bulk atomic concentration of carbon and oxygen in the film [i.e. C/O] has been estimated from WDS spectrum to be approximately in the ratio of 2:1. Fig. 4 shows the XRD patterns of a typical palladium deposit and amorphous carbon film grown on top of it. The bare palladium film exhibits only a broad peak at ∼2θ = 40° corresponding to diffraction from its (111) planes. From FWHM [(Δ2θ)/2 = 0.01 rad] of the peak, grain size has been estimated using the Scherrer formula to be ∼15 nm. The carbon film exhibits only a broad hump at ∼2θ = 20° confirming its amorphous nature. Fig. 5 shows the FTIR spectra [absorption coefficient (ε) vs. wave number] of two representative deposits grown on bare Si and nc-Pd interlayer recorded over the entire range. Peak intensities (absorbance) are normalized to their respective film thickness for absolute comparison between the absorption coefficients of the two films. The deposits are found to absorb rather weakly (ε ∼ 10^3/cm) implying both the films to be fairly transparent in the IR region. Since the spectra were recorded in transmission mode, slightly higher absorption coefficient is observed for the later sample possibly due to the presence of embedded metallic/metal oxide interlayer. Both spectra exhibit a sharp peak at ∼1100 cm⁻¹, a double hump at ∼1450 and 1650 cm⁻¹ and a host of features in the spectral range 2800–3000 cm⁻¹, respectively assigned to C–O–C, C–C and C–H stretching vibration. The presence of C–H stretching bands in the IR spectra of the samples indicates the films to be hydrogenated in nature. The bands are slightly more intense for the sample grown on nc-Pd interlayer indicating greater extent of hydrogenation in them. Besides, a broad peak also appears at ∼3400 cm⁻¹ due to O–H stretching mode. This shows that the samples are oxy-hydrogenated as well. In order to obtain quantitative information about the nature of carbon–hydrogen bonding in the samples, the spectra in the wave number region 2750–3050 cm⁻¹ are deconvoluted using multi-Gaussian line-shape, after carefully subtracting the background by using a suitable polynomial fit. Fig. 6 shows part of the spectra along with their deconvoluted features. The spectra in this region are superpositions of carbon–hydrogen vibrations in different sp^m CH_n species where m, n= 1, 2, 3. The spectrum of amorphous carbon film grown on bare silicon substrate (Si/a-C:H) exhibits six distinct features while that grown on nanocrystalline palladium interlayer (Si/nc-Pd/a-C:H) exhibits five. The peaks have been assigned to different sp^m CH_n vibrational modes following reports published in the literature [21]. The deconvoluted peak positions, % stretch area under each curve and the
assigned vibrational modes are shown in Table 1. The \( \chi^2 \) and \( R^2 \) values shown in the leftmost column indicates goodness of the fits. The peak at \( \sim 2820 \text{ cm}^{-1} \) in the former spectrum has been assigned to vibration of the C–H bond attached to the nitrogen atom in >N–CH\(_3\) group and is indicative of the presence of nitrogen in the film that might have originated as a result of the decomposition of N,N-dimethyl formamide, the solvent. It may be noted that the peak almost vanishes in the spectrum of Si/nc-Pd/α-C:H signifying its lower nitrogen content. Since each individual sp\(^n\)CH\(_n\) vibrational mode can be associated with a characteristic IR absorption peak, researchers [23] tried to estimate sp\(^3\)/sp\(^2\) of hydrogen-bonded carbon (CH\(_n\)) in hydrogenated amorphous carbon (α-C:H) films by integrating the % stretch area under each IR band, assuming uniform absorption cross-section for all vibrating groups. Following their recipe, the ratio is found to be \( \sim 15.4 \) for Si/α-C:H and \( \sim 21.2 \) for Si/nc-Pd/α-C:H. From sp\(^3\)/sp\(^2\), a parameter \( R_{\text{CH}_n} \) defined by \( R_{\text{CH}_n} = [\text{sp}^3/\text{sp}^2 + \text{sp}^3/\text{sp}^2] \) that represents sp\(^3\) fraction of the hydrogen-bonded carbon atoms has been estimated. However, accuracy of this method is often seriously limited by the resolution of these C–H bands and ambiguity in assigning them to correct vibrational modes. Moreover, the assumption that all the CH\(_n\) bands are of uniform absorption cross-section may not hold good if the local surroundings significantly affect the bond strength as indicated by several researchers [24,25]. MacNamara et al. [25] proposed to multiply the integrated intensity of an IR band with a constant \( A_n \) representative of its characteristic oscillator strength in order to find out precise concentration of a particular oscillating species. These proportional constants differ from material to material. Unfortunately there is no report on \( A_n \) values for hydrogenated amorphous carbon films. Titus et al. [26] reported a set of proportionality constants \( (A_n) \) for diamond films. Since absorption strength of diamond is different from that of α-C:H, estimation of its oscillator concentration using these reported \( A_n \) values would certainly involve the risk of incorporating errors in absolute terms. But qualitatively the trend exhibited by these proportionality constants for different vibrational modes may not be very much different for these two related materials and hence have been adopted in the present article for calculating modified sp\(^3\)/sp\(^2\) of hydrogen-bonded carbon (CH\(_n\)) in the two samples. The proportionality constants \( (A_n) \), sp\(^3\)/sp\(^2\) (CH\(_n\)) and \( R_{\text{CH}_n} \) parameters (both modified and unmodified) for the two samples are also appended in Table 1. It may be noted that the modified values are not very much different from the uncorrected numbers and show the same trend as regards to both the samples. Moreover \( R_{\text{CH}_n} \) parameter for both the samples is found to be rather low indicating that hydrogen is predominantly bonded to sp\(^3\) hybridized carbon atoms. The \( R_{\text{CH}_n} \) parameter is slightly lower for Si/nc-Pd/α-C:H suggesting of an increase (\( \sim 2–3\% \)) in the sp\(^3\)-C–H bonding in the sample. Fig. 7 shows the µ-Raman spectra of Si/α-C:H and Si/nc-Pd/α-C:H recorded in two distinct spectral ranges 1000–2000 cm\(^{-1}\) and 2700–3000 cm\(^{-1}\). Both spectra exhibit peaks at \( \sim 1330 \text{ cm}^{-1} \) and \( \sim 1440 \text{ cm}^{-1} \) and a broad feature at \( \sim 2900 \text{ cm}^{-1} \). The peaks at \( \sim 1330 \) and 1440 cm\(^{-1}\) are respectively assigned to disorder-allowed zone edge mode (D-band) and optically allowed E\(_{2g}\) zone centre mode (G-band) of crystalline graphite, while the multi-featured broad band at \( \sim 2900 \text{ cm}^{-1} \) is attributed to their 2nd order counter parts [27]. It is known from the literature [28] that the structure and properties of amorphous carbon films depend primarily on the fraction of the sp\(^3\)-bonded carbon sites and their hydrogen content. Raman spectroscopy is a versatile and non-destructive technique that has been extensively used for qualitative estimation of sp\(^3\)/sp\(^2\)-C content in amorphous carbon films. Since

![Fig. 7. Micro-Raman spectra of the samples grown on bare Si and nc-Pd interlayer.](image-url)
visible laser light (typically like that used in the present experiments) can resonantly excite electrons only in the low lying $\pi$ states and not the higher lying $\sigma$ states, [28], Raman cross-section for sp$^2$ sites is very much higher (50–230 times) in the visible range than that for the sp$^3$ sites [29]. So, visible Raman spectroscopy can only probe the configuration of sp$^2$ sites in sp$^2$-bonded clusters. Nevertheless, it can used to indirectly estimate the sp$^3$-C fraction in cases where sp$^2$ clustering is affected by the sp$^3$ fraction, such as in a-C:H films. The simplest approach is to fit the visible Raman spectra of a-C:H films with either two Lorentzian line-shapes or two Gaussian line-shapes and from the intensity ratio $I_D/I_G$, it is possible to obtain a qualitative idea about the extent of sp$^2$ and sp$^3$ carbon bonding in the samples. Raman spectra (in the range 1000–2000 cm$^{-1}$) of both samples are separately fitted with two Lorentzian and two Gaussian line-shapes after carefully subtracting the background using a suitable polynomial fit. It is evident from the residual plots (not shown) that either of the two Lorentzian and two Gaussian line-shapes could adequately reproduce the data for both the samples and use of more elaborate line-shape functions were not required. Fig. 8 shows the spectra along with their deconvoluted features and the fitted parameters are given in Table 2. It is observed that the relative peak intensity given by $I(D)/I(G)$ decreases significantly for Si/nc-Pd/a-C:H as compared to that of Si/a-C:H. Since the G-peak is associated with the relative motion of sp$^2$-C pairs irrespective of its configuration (cluster or open chain) it is not significantly affected by the introduction of defects in the form of sp$^3$-C sites. But the intensity of the D-band relative to that of the G-band i.e. $I(D)/I(G)$ decreases as the D-band strength is found to be proportional to the number of ordered six-fold rings in the cluster [29]. Tuinstra and Koenig (TK) relation of inverse dependence of $I(D)/I(G)$ on $L_a$ as applicable to disordered graphite no longer holds good and a modified equation in the form of $I(D)/I(G) \propto L_a^2$ has been proposed by Ferrari and Robertson [29]. Therefore, it is clear that an increase in sp$^3$ carbon fraction in a-C:H films not only decreases the number of sp$^2$-C clusters but also their size that allows to estimate sp$^2$-C/sp$^3$-C in them indirectly from $I(D)/I(G)$. Dependence of $I(D)/I(G)$ on sp$^3$-C fraction of a-C:H films has been verified experimentally by Tay et al. [30]. However the information about the ordered aromatic rings lies in the intensity maximum of the D-band and not in its width which again depends on the disorder. So, with the introduction of sp$^3$-C sites in a-C:H, D-peak height decreases while its width increases and the two parameters are expected contribute in opposite sense to

![Raman spectra](image)

**Fig. 8.** Raman spectra of the samples grown on bare Si and nc-Pd interlayer fitted with multi-Gaussian and multi-Lorentzian line-shapes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Line-shape</th>
<th>D-band</th>
<th>G-band</th>
<th>$I(D)/I(G)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line-shape</td>
<td>Position</td>
<td>Width</td>
<td>Position</td>
<td>Width</td>
</tr>
<tr>
<td>Si/a-C:H</td>
<td>Gaussian</td>
<td>1331±1</td>
<td>269±2</td>
<td>1440±1</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>1319±1</td>
<td>298±5</td>
<td>1440±1</td>
<td>43±2</td>
</tr>
<tr>
<td>Si/nc-Pd/a-C:H</td>
<td>Gaussian</td>
<td>1334±1</td>
<td>253±2</td>
<td>1446±1</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>1316±1</td>
<td>259±3</td>
<td>1446±1</td>
<td>51±1</td>
</tr>
</tbody>
</table>
the peak area making it less sensitive to the change compared to peak height. So, it is more logical to use peak height ratio for \( \frac{I(D)}{I(G)} \). In the present article, \( \frac{I(D)}{I(G)} \) has been calculated both from peak height and peak area and tabulated (Table 2). Needless to say, both exhibit the same trend as regards to the samples under study. Hence, it may be qualitatively concluded from the above discussion that Si/nc-Pd/a-C:H films contain higher sp\(^3\)-C fraction as compared to Si/a-C:H. Fig. 9 shows the room temperature photoluminescence (PL) spectra of the samples in the range 690—720 nm recorded with excitation at 462 nm radiation. Photo-excitation in a-C:H creates electron-hole pairs around band (mobility) edges, where they lose energy by thermalisation and fall into the tail states. Thermalisation allows spatial separation of the carriers. Luminescence then takes place by tunneling recombination across the gap. But carriers which instead reach a non-radiative recombination centre either by hopping or tunneling will recombine giving out phonons and heat and will not contribute to PL. Both the spectra exhibit intense peak assigned to the bound excitonic transitions. The PL peak appears at a higher energy (lower wavelength) and is also more intense for Si/nc-Pd/a-C:H. It has been previously reported that the energy for excitonic emission in a-C:H samples increases almost linearly with the optical band (Tauc) gap and hence with sp\(^3\)-C fraction in the samples [31 and references thereof]. Therefore the blue shift of the PL peak in case of Si/nc-Pd/a-C:H, is indicative of a greater number of sp\(^3\)-C sites in them. Moreover quantum efficiency of PL emission (\( \eta \)) depends on the extent of non-radiative recombination of the electron-hole pairs and hence on defect concentration (\( N_d \)) within the tunneling capture radius (\( R_c \)) of that particular non-radiative centre according to the equation [31]

\[
\eta = \eta_0 \exp \left( -\frac{4\pi}{3} \frac{R_c^3}{1-Z} N_d \right), \tag{ii}
\]

where \( Z \) represents the sp\(^2\)-C fraction in the sample. The physical significance of this equation is that in a narrow gap sp\(^3\)-C rich sample, carriers can easily tunnel out of the excited cluster via other clusters to a non-radiative recombination centre where it can recombine by non-radiative mode thereby decreasing the PL efficiency, which is not that easy in case of higher band gap sp\(^3\)-C rich samples. The large difference of local band gaps of the sp\(^3\) and sp\(^2\) sites creates band edge fluctuations with the sp\(^3\) sites actually acting as the tunnel barriers between the \( \pi \) states of the sp\(^2\) clusters, thereby localizing the carriers within the same cluster, forcing them into radiative recombination. So, greater the sp\(^3\)-C fraction in the sample more is the quantum efficiency of PL. This explains the enhanced intensity of the band to band PL emission in Si/nc-Pd/a-C:H.

In order to obtain quantitative affirmation to our speculation regarding the sp\(^3\)- and sp\(^2\)-bonded carbon atoms in the samples, X-ray photoelectron spectra were recorded in a slow scan. Fig. 10 shows the survey spectrum of a typical deposit on silicon and nc-Pd interlayer. Apart from the C1s signal, an intense peak appears at \( \sim 531 \) eV along with a weak feature at \( \sim 24 \) eV respectively assigned to the binding energies of O1s and O2s photoelectrons. Oxygen in the samples is believed to have resulted primarily from the oxidation and/hydroxylation of highly reactive carbon surface during the deposition process and is commonly observed in the XPS spectra of a-C:H films. However there can be contamination from the atmosphere and also from the solution as well. Besides the residual gas in the XPS chamber (if any; operational pressure \( \sim 10^{-9} \) Torr) might have also contributed to the intense O1s peak in the survey spectrum of our samples. Guo et al. [16] reportedly observed similar intense O1s peak in the XPS survey spectrum of amorphous carbon films grown on Si by electro-deposition of DMF. From the height ratio of the C1s and O1s peaks in the survey spectrum, a rough estimate can be made about the relative atomic concentration of carbon and oxygen at/near the film surface, after making due corrections for their respective atomic sensitivity factors taken to be 0.2 for C1s and 0.63 for O1s. The C/O comes out to be \( \sim 1.24 \). The value is lower than that estimated by WDS implying higher oxygen contamination at the film surface as compared to the bulk. Fig. 11 shows the O1s spectra of Si/a-C:H and Si/nc-Pd/a-C:H along with their deconvoluted features obtained by fitting the spectra with line-shapes having different Gaussian:Lorentzian ratios, after

**Fig. 9.** Room temperature photoluminescence spectra of the samples grown on bare Si and nc-Pd interlayer.

**Fig. 10.** Survey XPS spectrum of Si/a-C:H and Si/nc-Pd/a-C:H.
approximating the background contribution with a Shirley-type baseline. All the parameters viz. peak position, FWHM and the area under the curves were taken for optimization as fixing any one of them would have made the quality of the fit even worse. Small $\chi^2$ values (1.2 and 1.7 respectively) denote that the deconvoluted features nicely represent the raw data. Fitting was carried out with "XPS peak 4.1" software freely available in the web and the optimized values of the fitted parameters are tagged as an insert in the figure. The O1s spectrum upon deconvolution exhibits three distinct peaks at $\sim$531, 530 and 529 eV. The peak at $\sim$530 eV is attributed to O=C type of bonding [32] in the films and that $\sim$531 eV is due to oxygen attached to (COO$^-$) moieties [33]. The third peak at $\sim$529 eV is possibly due to oxygen attached to the hydroxyl group. It may be noted that for Si/nc-Pd/a-C:H, the peak at $\sim$531 eV increases in intensity at the cost of the peak at $\sim$530 eV. The observation is further supported by C1s spectra of Si/nc-Pd/a-C:H (to be discussed subsequently) where an additional peak appears at $\sim$293 eV. Fig. 12 shows the set of main core level C1s spectra of both Si/a-C:H and Si/nc-Pd/a-C:H along with their deconvoluted features obtained by curve-fitting following same recipe as described for the O1s spectrum. $\chi^2$ value of 1.4 implies that reasonably good fit to the data has been achieved and the optimized values of the fitted parameters are inserted in the figure. The C1s spectrum of Si/a-C:H exhibits three distinct features at $\sim$284, 285 and 289 eV respectively assigned to sp$^2$-C, sp$^3$-C and carbon associated with the ester or carboxylic groups formed upon oxidation of highly reactive surface species [34,35], while an additional peak appears at $\sim$293 eV in case of Si/nc-Pd/a-C:H. Clearly, there is a blue shift in the peak position of the C1s spectrum of Si/nc-Pd/a-C:H with respect to that of Si/a-C:H. Ratio of the peak areas under the first two component curves provides a direct estimate of the sp$^2$-/sp$^3$-C–C carbon fraction in the films. It is clear from the deconvoluted features that sp$^2$/sp$^3$-C–C is much higher for Si/a-C:H ($\sim$0.4) as compared to that for Si/nc-Pd/a-C:H ($\sim$0.2). In case of the former sample, sp$^2$-C comprises of $\sim$30% of C–C linkages, while in case of the later sample it is only $\sim$16% indicating an undoubted decrease ($\sim$14%) in sp$^2$–C bonding in the deposits formed on nanocrystalline interlayer. It is well known from the literature that an increase in the sp$^3$-C–C content in a-C:H films increases its hardness or elastic constant, thereby improving its diamond-like nature. Therefore it can be argued that Si/nc-Pd/a-C:H is of better quality as compared to Si/a-C:H. However there is simultaneous increase in the ester fraction as well. Nevertheless XPS provides information only about the surface layers (depth resolution is only 3 nm) and does not reflect the bulk property of the films that can substantially differ from that of the surface layers. It is proposed that some of the sp$^2$ carbon sites at the film surface get converted into hydrogenated sp$^3$ sites due to catalytic action of nc-Pd interlayer leading to structural reconstruction thereby stabilizing the precursors against the hostile and reactive deposition environment and finally they get incorporated into the C–C network via usual hydrogen abstraction and hydrocarbon insertion mechanism described elsewhere [36].
4. Conclusions

It has been demonstrated from a series of experiments that the films deposited by high-voltage electro-dissociation of DMF on \( nc-Pd \) interlayers are of superior quality in terms of sp\(^3\)-C content compared to those deposited on bare Si. The effect of current density on the quality of the deposits was discriminated by using a high-voltage power supply in current-limited mode. The observation has been independently confirmed from XPS, PL, Raman and FTIR analysis. sp\(^2\)/sp\(^3\) has been estimated from CH\(_n\) bands in FTIR spectra, which shows there is an increase in sp\(^3\) CH by 2–3% for Si/\( nc-Pd/a\)-C:H. But the increase is much more (~14%) for sp\(^2\)-C/sp\(^3\)-C as estimated from C\(_1s\) peak in the XPS spectra of the samples. This is out of proportion increase in sp\(^3\)-C–C linkages in Si/\( nc-Pd/a\)-C:H undoubtedly proves that its diamond-like properties has got improved significantly. \( H_2 \) activation at the surface of \( nc-Pd \) layer is believed to be responsible for the improved sp\(^3\) carbon content in those films.

Acknowledgement

The authors are thankful to Mr. Atindra Mohan Banerjee of Chemistry Division, BARC for recording FTIR spectra, Ms. Nidhi Mithal of TP & PE Division, B.A.R.C. for recording the XPS spectra, Mr. K. P. Muthu of the same division for recording the SEM micrographs, Dr. R. Kishore of Material Science Division, BARC for nanohardness measurements, Mr. Bhakare and Mr. Khobragade of CD & M, BARC for thickness and surface profiling. The authors also thank Dr. S. K. Gupta of TP & PE Division, BARC and Dr. T. Mukherjee, Director Chemistry group, B.A.R.C. for their keen interest in the work.

Appendix A

Enhancement in sp\(^3\)-C–C fraction was also observed in amorphous carbon films deposited on other transition metal interlayers such as silver, nickel, etc.

References