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Characterization of a Diamond-Like Carbon Film Produced from an Electrosynthesized Pre-Ceramic Polymer

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ABSTRACT: In this study, we aimed to prepare diamond-like carbon film from the electrosynthesized poly(hydridocarbyne) polymer and to investigate its surface, compositional and structural properties. The polymer was coated on Si substrate and then heated from room temperature to 1050 ^{o}C under argon atmosphere. More detailed characterizations than the previous studies revealed some new results. Surface morphology was examined by scanning electron microscopy. X-ray photoelectron spectroscopy analysis revealed that the film consisted of mainly carbon, with lesser percentages of oxygen, ferrum and silicium. From deconvolution of C 1s peak, sp^3/sp^2 ratio was found 0.55. Raman spectroscopy showed two broad bands at approximately 1347 cm^{-1} and 1597 cm^{-1}, related to the D and G band of DLC, respectively. Furthermore, several peaks which were matched with the Fe_3O_4 and the Fe_2SiO_4 phase appeared in the Raman spectrum. Although these peaks were observed in the previous studies, they were not matched with any bound or structure. By means of analyses it was concluded that electrosynthesized polymer includes iron oxide due to the erosion of steel electrodes and this phase is also included in the DLC films produced from this polymer. Additionally, Fe_2SiO_4 is seen due to the reaction between iron oxide included in the polymer solution and Si substrate at the interface between the Si substrate and DLC film.

Keywords: *Pre-ceramic polymers, Diamond-like carbon, Raman spectroscopy*

1. Introduction

Due to their excellent chemical, physical and mechanical properties diamond and diamond-like carbon (DLC) films are attractive for many applications (Sun et al., 1997; Zhang et al., 2007; Zhang et al., 2008; Donnet and Erdemir 2008; Meskinis et al., 2010; Zeng et al., 2014). These materials are used in different kind of application including, tribology, optics and electronics (Yan et al., 2004; Yan et al., 2005; Wan et al., 2010; Nery et al., 2010; Tao et al., 2011; Chaus et al., 2014). Diamond and DLC films have been synthesized with various methods, including; combustion flame, chemical vapor deposition, physical vapor deposition and the use of polymeric precursors (Wan et al., 2010; Rusop et al., 2006; Zhang et al., 2008; Honglertkongsakul et al., 2010; Li et al., 2013).

Polymeric precursors, named poly(carbynes), can be converted to diamond/diamond-like carbon upon heating. Different types of poly(carbynes) such as, poly(phenylcarbyne) (I), poly(methylcarbyne), 75:25 poly(phenyl-co-methylcarbyne), and 99:1 poly(phenyl-co-hydridocarbyne) and poly(hydridocarbyne) were synthesized in the past two decades. These materials offer to take advantage of large area coatings as they are soluble in the organic coatings. However, these polymers could be synthesized via sonochemistry and Grignard

reagents (Visscher et al., 1994; Bianconi et al., 2004; Nur et al., 2011; Nur et al., 2008). Recently, Nur et al. proposed that poly(carbynes) can be obtained by electrochemical polymerization (Nur et al., 2011; Nur et al., 2008, Nur et al., 2009). They could obtain poly(hydridocarbyne) (Phc) by electrochemical polymerization of chloroform and hexachloroethane, and they converted Phc to diamond/diamond-like carbon by pyrolysis. Thus far, diamond or DLC films have not been attained from this polymer, and as a coating film, its properties have not been explored yet. Moreover, there is lack of knowledge on detailed structural, morphological, and compositional properties of diamond/diamond-like carbon material obtained from this electrochemically routed polymer.

This study was conducted to produce diamond-like carbon film from poly(hydridocarbyne) and to investigate detailed morphological, structural and compositional properties of this film. Poly(hydridocarbyne) was obtained from electrochemical polymerization of chloroform, as it was more common and cheaper than hexacloroethane.

2. Materials and Methods

2.1 Materials

Chloroform ($CHCl_3$), acetonitrile (AN), and tetrabutylammonium tetrafluoroborate (TBAFB) were purchased from Merck and used as received. Tetrahydrofuran (THF) was bought from Merck and purified over sodium metal. Lithium aluminum hydride ($LiAlH_4$) was purchased from Sigma Aldrich and used as received. 430 stainless steel electrodes were used as an anode and cathode.

2.2. Preparation of the sample

Poly(hydridocarbyne) was synthesized by electropolymerization of chloroform. A detailed description of the synthesizing method can be found elsewhere (Nur et al., 2008). After the polymer was dissolved in THF, we observed that some amounts of materials were precipitated. This insoluble material was presumed to be a high molecular weight polymer by Nur et al. (2008). This precipitated part which also included some amount of soluble material was separated. The soluble and the precipitated material were coated onto Si substrate (p-Si, 100) via spin coating from THF solution and coded as S1 and S2 films, respectively. These films were pyrolyzed from room temperature to 1050 ^oC. Pyrolysis conditions were carried out under argon atmosphere and 10 °C/min ramp rate. Surface of the films were characterized by a FEI FEG Quanta 450 model SEM.

2.3. Raman and XPS Studies

Raman spectra were recorded by a Renishaw 1000 type Raman spectrometer with an argon ion laser (514 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo K-Alpha Monochromated high performance XPS spectrometer. The vacuum of the chamber was 2×10^{-9} Torr. The spectra were recorded between 0-1100 eV. Detailed survey was also carried for each element.

3. Results and Discussion

In our previous work FTIR and NMR characterization of Phc polymer were made and it was observed that the results confirmed the $(CH)_n$ structure (Başman et al., 2012).

3. 1. Surface analysis

SEM micrographs of the S1 film are shown in Fig. 1a and 1b. The rough and continuous film consists of micron sized particles. It is thought that these micro-particles arise due to aggregation of the polymer converting upon heating. The sub-micron shiny particles are also seen on the surface of the film. These particles marked with a circle in Fig. 1b are different from the main phase. The SEM images of the S2 film are shown in Fig. 2a and 2b. As can be seen from Fig. 2, 10 micron and smaller-sized particles appear on the surface of the sample. These particles seem different from micro-particles which were formed due to the aggregation of polymer. Energy dispersive X-ray (EDX) elemental mapping was employed to define chemical compositions of particles appeared on S1 and S2 films. Figs 3 and 4 show Fe and O mapping of S1 and S2 films, respectively. From the figures the chemical compositions were defined as Fe-O compounds. To define these particles and global composition of the films further analyses were required. Therefore, XPS and Raman analyses were also performed.

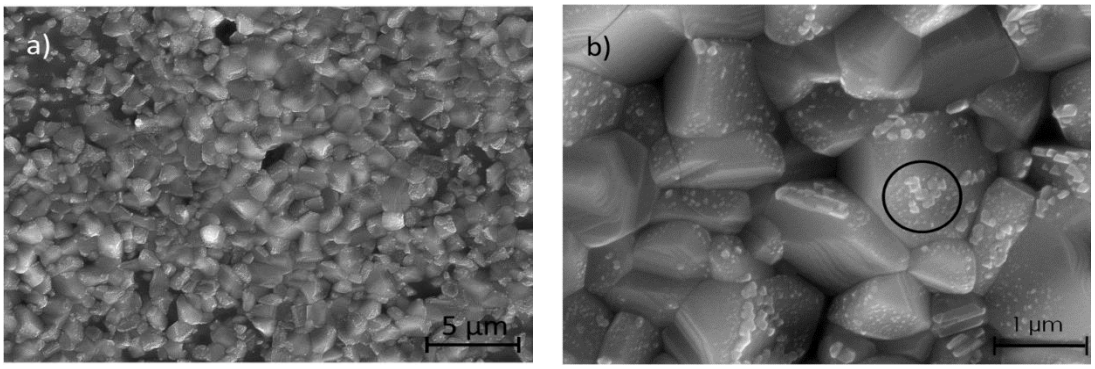

Fig. 1 SEM image of S1 film (a), SEM image of S1 film (b)

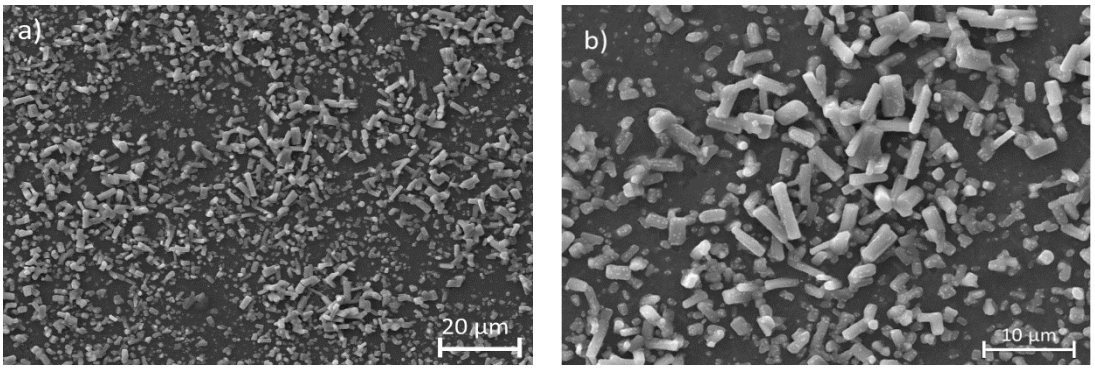

Fig. 2 SEM image of S2 film (a) SEM image of S2 film (b)

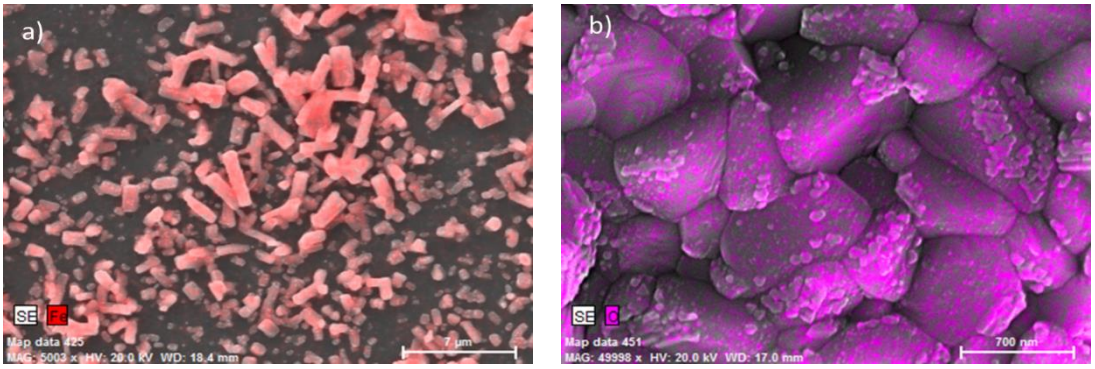

Fig. 3 EDX analysis of S1 film, Fe mapping (a), EDX analysis of S1 film, O mapping (b)

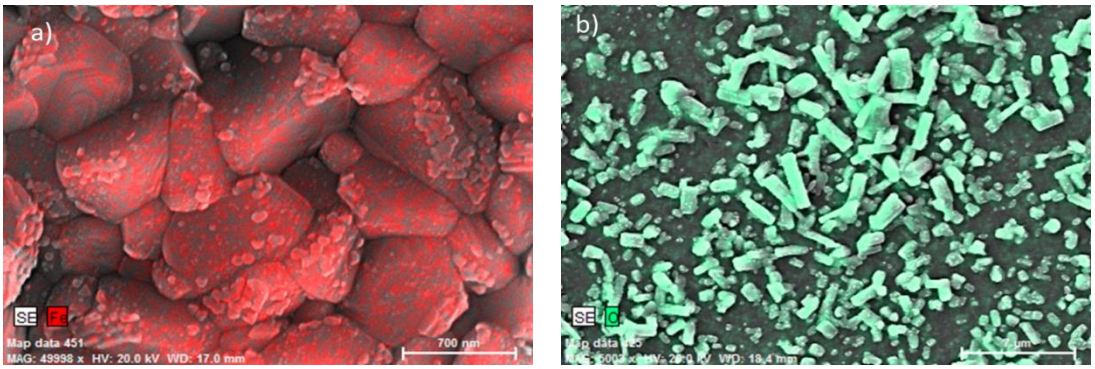

Fig. 4 EDX analysis of S2 film, Fe mapping (a) EDX analysis of S2 film, O mapping (b)

3.2. Composition and structure analyses

XPS analyses were made to explore the chemical composition of the films. Fig 5a shows the XPS spectrum of S1 film. The atomic percent of elements are 63.31% C, 24.38% O, 7.3% Si and 1.7% Fe. The XPS survey spectrum shows that the film consists of mainly carbon, with lesser percentages of oxygen, ferrum and silicium. From XPS survey spectrum of S2 film (Fig. 5b), the atomic percentages of elements are 61.2% O, 19.5% Si, 11.5% C and 7.8% Fe. Both of the films contain oxygen, silicium and ferrum in addition to carbon. The presence of oxygen is commonly seen in DLC films, as the XPS is a very surface sensitive technique (Li et al., 2009; Chen et al., 2007). The existence of ferrum and silicium could be explained by contamination from steel electrodes and the Si substrate. The content of oxygen and ferrum of S2 film is much higher than the S1 film. From the atomic percentages and EDX analysis, we suggest that the particles appeared on the surface of the S2 film are Fe-O compounds. As the S1 film contained lesser O and Fe, the sub-micron particles that appeared on the surface of the S1 film could also be defined as Fe-O compounds. However, the composition of the films will be determined more accurately by Raman spectroscopy.

C 1s peak of S1 film is seen in Fig. 5c. Deconvolution of the spectrum shows that the C 1s peak consists of three peaks, corresponding to sp^2 C (284.3 eV), sp^3 C (284.73 eV), and C-O (286.0 eV) bands. The shoulder at the higher binding-energy side of C 1s spectrum originates from carbon atoms bonded to oxygen. The sp^3/sp^2 ratio for S1 film was obtained as 0.55, which is higher than the value obtained for poly(phenylcarbyne) (Yan et al., 2005), a pre-ceramic polymer. Because of low carbon content, deconvolution was not made for C 1s peak of S2 film.

Raman spectroscopy is one of the most widely used techniques to investigate the chemical structure of carbon-based materials as well as other compounds because of its sensitivity to changes in translation symmetry (Yan et al., 2005; Ferrari et al., 2002). Fig 6a-b shows full Raman spectra of the S1 and S2 films, respectively. In the Raman spectrum of S1 film (Fig. 6a), D and G bands, which are characteristics bands of DLC films, appear at 1347 cm^{-1} and 1597 cm^{-1}, respectively. It is well known that crystallite graphite and diamond show a single sharp peak at 1582 cm^{-1} and 1332 cm^{-1}, respectively. Therefore, we believe that the structure of S1 film is amorphous. On the other hand, in the Raman spectrum of the S2 film (Fig. 6b) similar bands are observed with a small shoulder in between. Peak positions were defined at 1330 cm^{-1}, 1428 cm^{-1}, and 1602 cm^{-1} for D, shoulder, and G bands, respectively (see Fig. 6c).

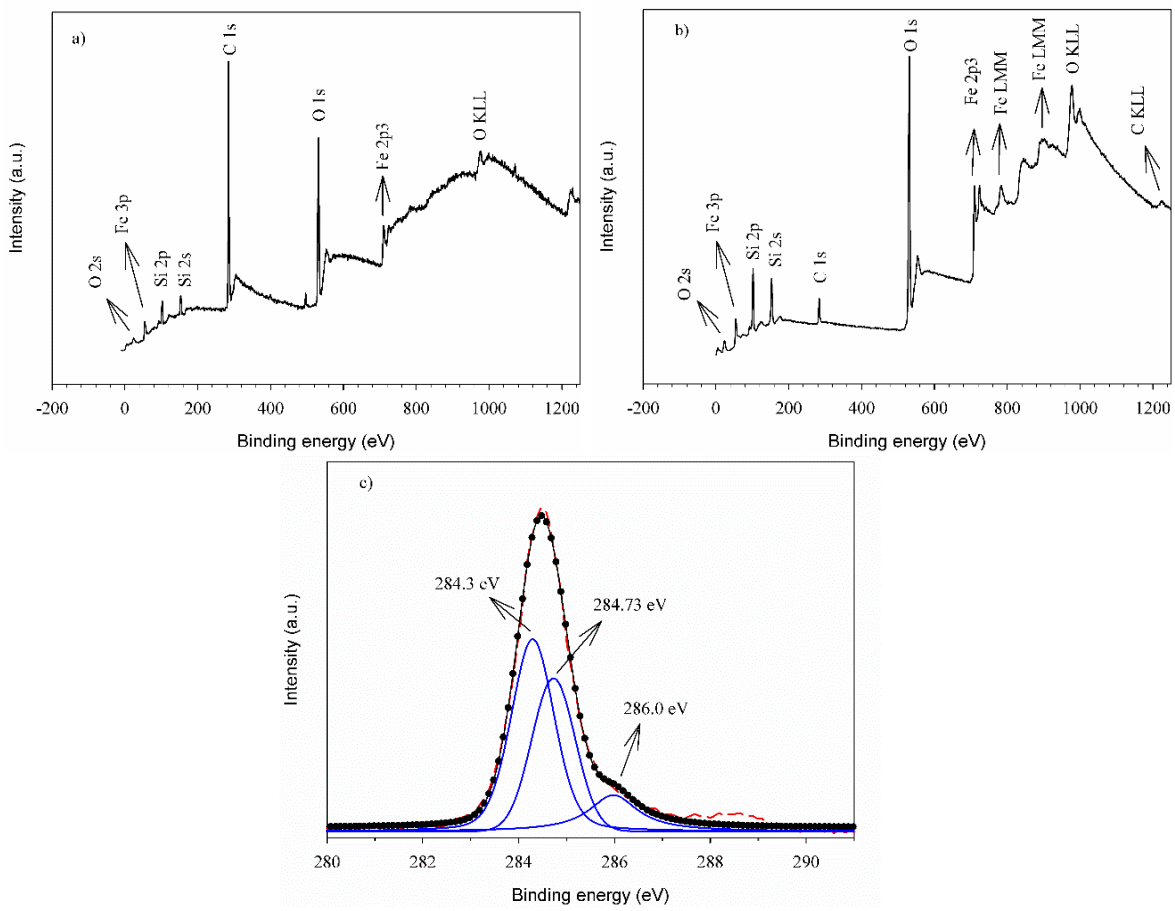

Fig. 5 XPS spectrum of S1 film (a), XPS spectrum of S2 film (b), Deconvoluted XPS spectrum of C 1s of S1 film (c)

The shoulder is attributed to the sp^3-bonded diamond precursor phase or to the converting polymer upon pyrolysis (Yan et al., 2004). In this spectrum, D and G bands are not clearly defined when compared with S1 film because of low content of carbon. The resonance of the substrate is seen at 521 cm^{-1} for both films. A split peak is appearing in the range of 910-1050 cm^{-1} for both S1 and S2 films in Fig 6a and 6b. Therefore, it was deconvoluted, and two peaks were obtained at 940 cm^{-1} and 970 cm^{-1} (Fig. 6d). These peaks were attributed to Si second-order and SiC, respectively (Bianconi et al., 2004; Ferrari, 2002; Xu et al., 1997; Chen et al., 2000; Liang et al., 2012). In both of the Raman spectra, some peaks appear at about 828 cm^{-1}, 667 cm^{-1}, 610 cm^{-1}, 400 cm^{-1}, 295 cm^{-1} and 220 cm^{-1}. Nur et al. (2011, 2009) also observed peaks in such regions. However, except the peak at 650 cm^{-1}, they did not match these peaks to any bound or structure. By considering SEM images, EDX and XPS analyses, we tried to match these peaks with iron and silicon compounds. Hereby, the peaks at 828 cm^{-1} and 400 cm^{-1} correspond to fayalite (Fe_2SiO_4) (Chopelas et al., 1991), while the peaks at 667 cm^{-1} and 220 cm^{-1} correspond to magnetite (Fe_3O_4) (Shebanova and Lazar 2003; Legodi and Waal, 2007; Jubb and Allen 2010). The feature at 295 cm^{-1} can be matched with both Fe_3O_4 and Fe_2SiO_4 (Chopelas, 1991; Jubb and Allen, 2010). Actually, these results are not surprising as the polymerization was made using stainless steel electrodes, and the polymer was coated on the Si substrate. The electrodes were eroded during the polymerization at -6 V. This erosion could be seen even with naked eye after the electrolysis. As a result of erosion, iron oxide is inevitably included in the polymer solution, and thus appears in the heat-treated films. Fe_2SiO_4 phases should be produced at the interface between the Si substrate and DLC film due to the reaction between iron oxide included in the polymer solution and Si substrate. It should be noted that most of the iron oxide particles remained in the polymer, which was

removed during the filtration. Similar micro-particles were observed by Nur et al. (Katzenmeyer et al., 2009). However, they did not define them as iron oxide particles but nano/micro crystalline graphite. On the other hand, Nur et al. (2008) observed some XRD peaks in their study which were unmatched with diamonds or derivatives. We concluded that their unmatched XRD peaks should belong to iron oxide derivatives. Hereby, we declare that diamond/diamond-like carbon obtained from electrochemically synthesized pre-ceramic polymers include iron oxide impurities. This matter was undiscovered by Nur et al. (2008, 2009, 2011) in their studies because of inadequate characterizations.

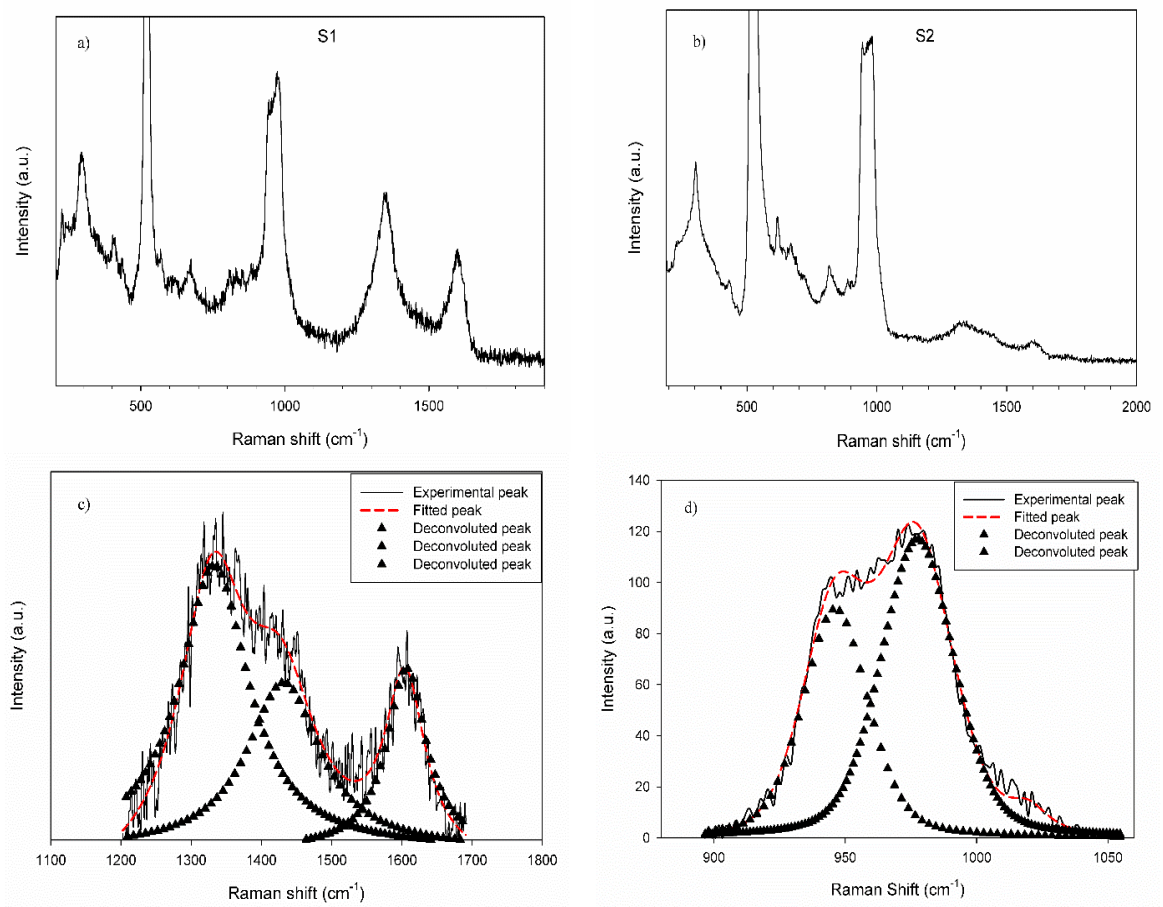

Fig. 6. Full Raman spectrum of S1 film (a), Full Raman spectrum of S2 film (b), Deconvoluted Raman bands appeared in the range of 1200-1700 cm^{-1} for S2 film (c), Deconvoluted Raman bands appeared in the range of 900-1050 cm^{-1} for S1 film (e)

4. Conclusion

In this study, we aimed to prepare diamond-like carbon film from the poly(hydridocarbyne) polymer and to investigate its surface, compositional and structural properties. More comprehensive characterizations than the previous studies revealed some new results. The following conclusions were derived from the present study:

- From SEM image, it was observed that the S1 film is rough and consists of micron sized particles. It was thought that these micro-particles arise due to aggregation of the polymer converting upon heating. Additionally, Fe-O impurities were also observed on the surface.

- X-ray photoelectron spectroscopy analysis revealed that the S1 film consists of mainly carbon, with lesser percentages of oxygen, ferrum and silicium.
- From the deconvolution of C 1s peak, sp^3/sp^2 ratio was found to be 0.55.
- Two broad peaks assigned to the D and G bands of DLC films appeared at 1347 cm^{-1} and 1597 cm^{-1}, respectively, which indicates the amorphous nature of the film.
- Several peaks which were matched with the Fe_3O_4 and the Fe_2SiO_4 phases also appeared in the Raman spectrum.
- The presence of the Fe_3O_4 and the Fe_2SiO_4 phases were explained as such, electrosynthesized polymer includes iron oxide due to erosion of electrodes, so these phases were also included in the DLC films produced from this polymer. Additionally, Fe_2SiO_4 is seen due to the reaction between iron oxide included in the polymer and silicon substrate at the interface.

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