Investigation into the structure and composition of Carbon/Carbon-SiC Composites

Tatiana Perova*[a], Karl Maile[b], Abram Lyutovich**[b], Karl Berreth[b], Daria Potapova[a], Gernot Zies[b] and Alan Moore[a]

[a]Dept. of Electronic & Electrical Engineering, Trinity College, Ireland; [b]MPA Stuttgart, Univ. of Stuttgart, Germany

ABSTRACT

In this work, pyrolytical carbon and C-Si_xC_y-SiC coatings were deposited by chemical vapour deposition (CVD) in a "Cold Wall" reactor. The C/C samples from "Schunk Kohlenstofftechnik GmbH", Germany were used as substrates. The pyrolytical carbon coatings were obtained by CH_4 cracking at 1200-1300°C. Si_xC_y and SiC coatings were deposited from $SiCl_4/H_2$ mixtures by varying the $H_2/SiCl_4$ ratio (α). Micro-Raman spectroscopy and X-ray diffraction have been used to determine the order grade for pyrolytical carbon coatings and to investigate the structure and composition of SiC coatings depending on the deposition conditions. In particular, the analysis of Raman spectra of carbon films in the region of 1200-1800 cm^{-1} allowed the determination of crystal size in a film, which varied from 2.6 to 8.5 nm depending on α. The presence of a strong narrow band at 2712 cm^{-1} in the second order Raman spectra region (2300-3400 cm^{-1}) indicated a high degree of perfection of the crystalline lattice and an onion like structure in some of the carbon films. XRD investigation of the SiC-peak showed a shift in frequency and a reduction in intensity when compared to the substrate. The peak shift corresponds to a crystal-geometric grading of the coating.

Keywords: Carbon/carbon composites; SiC; thermo CVD; micro-Raman spectroscopy; X-ray diffraction

1. INTRODUCTION

Carbon/Carbon (C/C) composites exhibit excellent structural characteristics including low density, high strength, high stiffness and high fracture toughness [1]. However, when these composite materials are used in oxidising and corrosive atmospheres, a surface protection is required. SiC is an excellent protective coating for C/C composites [2]. The protective properties of SiC are limited due to the difference in expansion coefficients of C/C and SiC and the formation of cracks. One way to overcome this problem is to grow graded layers of C-Si_xC_y-SiC. The residual stress results from the abrupt transition from one layer to another. This transition can be separated into so many layers as discrete atomic layers. Macroscopically it can be seen as a graded multi-layer structure. The fragmentation leads to gradual changes in both the macroscopic elastic modulus and, at the same time, in the expansion coefficients.

Raman spectroscopy is useful for the testing and control of this process and also for the characterisation of the morphology, grade of order and chemical composition of the C-graded Si_xC_y coatings. This is because the free carbon or silicon and SiC composition can be identified by their specific lines. Raman spectroscopy is also a suitable technique for monitoring the deposition conditions. The formation of new phases by C-SiC deposition can be checked easily by X-ray diffraction. As was also shown recently in Ref. [3], certain parameters of Raman spectra correlate with Young's modulus, tensile strength and micro-hardness. In this work the pyrolytical carbon and Si_xC_y coatings were deposited by the thermo CVD technique. Micro-Raman spectroscopy, X-ray diffraction and scanning electron microscopy (SEM) have been used in investigation of the structure and composition of Si_xC_y coatings, depending on the deposition conditions.

*perovat@tcd.ie; phone 353 1 608-3802; fax 353 1 677-2442; http://www.tcd.ie; Department of Electronic & Electrical Engineering, University of Dublin, Trinity College, Dublin 2, Ireland; **lyutovich@mpa.uni-stuttgart.de; phone +49-711-685-7667; fax +49-711-685-3053 Staatliche Materialpruefungsanstalt (MPA) Stuttgart, University of Stuttgart, D-70569 Stuttgart, Germany.

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This study is important from both fundamental and technological points of view. The study of physical phenomena in composite materials on a microscopic scale is important for understanding how this type of structure is related to the mechanical properties such as hardness, mechanical stability, tensile strength etc. The possibility to monitor the structure and composition of these films depending on the process conditions by *in-situ* Raman measurements is important from the technological point of view. In particular, SiC exhibits a large number of poly-types [4-7] with different structural and physical properties and it is important to establish the stoichiometry of the film during deposition.

2. EXPERIMENTAL

2.1 Sample description

C/C-SiC samples S1, S2 and S3, prepared in "Schunk Kohlenstofftechnik GmbH" (Germany), have different structures. Sample S1 is produced from carbon fibre filaments introduced in carbon resins by chemical processes. It is then infiltrated in molten silicon in order to form the SiC composition. Samples S2 and S3 are a special SKT siliconiced (20% free Si). The pyrocarbon layers and Si_xC_y coatings were deposited by chemical vapour deposition in a vertical "Cold Wall" reactor in atmospheric pressure. Sample S1 was used as the substrate for all coatings. The pyrolytical carbon coatings were obtained by the CH_4 cracking in a hydrogen atmosphere at 1200-1300°C. Si_xC_y and the SiC coatings were deposited from CH_4, $SiCl_4$ /H_2 mixtures by varying the $SiCl_4$ /H_2 ratio (α). The performance of the deposition process with a programmed precursor concentration with time and temperature parameters (taking into account the physical-chemical properties of the Si-C system) allows one to obtain Si_xC_y layers and multilayer structures with the preset composition distribution in the growth direction (graded systems).

The chemical reactions of these processes are as follows:

a) $CH_4 + H_2 \rightarrow C + H_2$ (for obtaining carbon films) and

b) $SiCl_4 + CH_4 + H_2 \rightarrow Si_xC_y + HCl$ for obtaining Si_xC_y films with different ratio of Si and C (including stoichiometric SiC). The process conditions together with sample's name are summarised in Table 1. The morphology of the coatings was studied using optical microscopy and scanning electron microscopy (SEM).

Table 1. Sample description and the crystallite size (L_a) evaluated from Raman G and D bands.

Sample name	Sample description and notation	L_a, nm
S1	Substrate C/C – SiC not coated	**-**
S2, S3	C/C – SiC substrate	**-**
G1	Graphite	**20.6 ±0.5**
F1	Carbon coated substrate S1 (T=1200°C, CH_4 at 60ml/min for 20'	**3.4±0.5**
F2	Carbon coated substrate S1 (T=1200°C, CH_4 at 25 ml/min for 20' (growth in vacuum)	-
F3	SiC coated substrate S1 (CH_4+$SiCl_4$ $\rightarrow$ SiC +HCl)	**9±1**
F4	Carbon coated substrate S1 (T=1200°C, CH_4-60 ml/min, H_2-60 ml/min duration 20')	**2.6 ± 0.3**
F5	Carbon coated substrate S1 (CH_4 - 30ml/min, H_2-30 ml/min, T=1200° C, duration 20')	**2.4 ± 0.3**

2.2 Raman measurements

Raman spectra were registered in backscattering geometry using a RENISHAW 1000 micro-Raman system equipped with a Leica microscope. The excitation wavelength was 514.5 nm from an Ar^+ ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical laser power of ~ 20 mW. An 1800 lines/mm grating was used in all measurements,

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which corresponds to a spectral resolution of ~ 2.5 cm^{-1}. The 100x magnifying objective of the Leica microscope focused the beam into a spot of about 0.7 μm in diameter. In order to define the position of the phonon lines with a higher accuracy, the spectral lines, used for the analysis, were fitted with a Lorentzian or Gaussian functions or a mixture of both.

Two different types of Raman measurements have been used in this study: i) single spot measurements and ii) line-mapping measurements. The former measurements were carried out using the 100x objective of the Leica microscope while the line-mapping experiment was performed using both the 20x and 100x objectives. During the line mapping measurements, Raman spectra were collected along 50 μm and 1 μm lines with steps of 2 μm and 0.1 μm respectively in order to monitor the microstructure of the studied carbon films. Spectra from graphite and 6H-SiC single crystals were also collected as references.

2.3 X-ray diffraction measurements

Studies with X-ray diffraction (XRD) were performed in backscattering geometry using a Siemens diffractometer D 5000 with monochromatic radiation of Cr-Kα, wavelength λ = 0,22897 nm. The Cr-Kβ radiation was suppressed by a vanadium filter. The X-ray beam is focussed on the surface of the specimen and the diffracted intensity is measured depending on the double angle 2θ in between the beam and the specimen surface. For the present studies, an angle range from 30° to 150° was scanned in steps of 0.02° with a dwell time of 10 s per step and a total time of 16 hours for one diffractogram.

A device specific software (DIFRAC AT) was used for controlling the diffractometer and for the evaluation of the diffractograms. The crystalline phases in the specimens were identified by matching of their characteristic peak systems to suitable known phases of standard peak systems for powder. The diffractogram obtained from the high purity SiC single crystal was used as a reference pattern for the diffraction analysis of films and for the verification of the changes of the film lattice compared with the SiC reference lattice.

2.4 SEM measurements

SEM measurements have been performed using a JSM-6400 scanning electron microscope. The parameters used were: accelerating voltage - 25 kV, working distance - 46 mm, tilt angle -0° and magnification 100:1/500:1.

3. RESULTS AND DISCUSSION

In order to get the exact position of certain vibrational bands such as C-C and Si-C for comparison we first measured a pure graphite sample of high quality and a SiC single crystal.

3.1 Graphite

The Raman spectrum of a graphite sample in the range of 1000-3500 cm^{-1} is shown in Fig. 1. This spectrum is in good agreement with previous measurements on polycrystalline graphite obtained in Refs. [8-10]. In the region 1200-1700 cm^{-1} (first order Raman region – some times called Carbon region), two main peaks are observed. The characteristic graphitic or G band with E_{2g} symmetry is observed at ~ 1581 cm^{-1}. This G band is assigned to the zone-centre LO phonon mode of the graphite lattice. It is close to the position of the single Raman line found at 1575 cm^{-1} on single crystals of graphite. This Raman line is present in all graphite samples. The second peak at ~ 1353 cm^{-1} is typically observed in Raman spectra of many graphitic materials (with its maximum ranging from 1390 to 1350 cm^{-1}) [10-12]. It is attributed to the interlayer "disorder mode" (D-mode) of microcrystalline graphite. This mode is only active for crystallites of finite size. Its intensity is inversely proportional to the crystallite size as was shown in Refs. [11,13-15]. In particular, for polycrystalline graphite the microcrystalline planar size L_a (which corresponds to in-plane dimensions) can be obtained from the ratio of the integrated intensities $R \propto I_G/I_D$ [11,13]. For the low crystalline degree carbons the following relationship can be used

$$L_a = 44 \cdot [I_D/I_G]^{-1} \tag{1}$$

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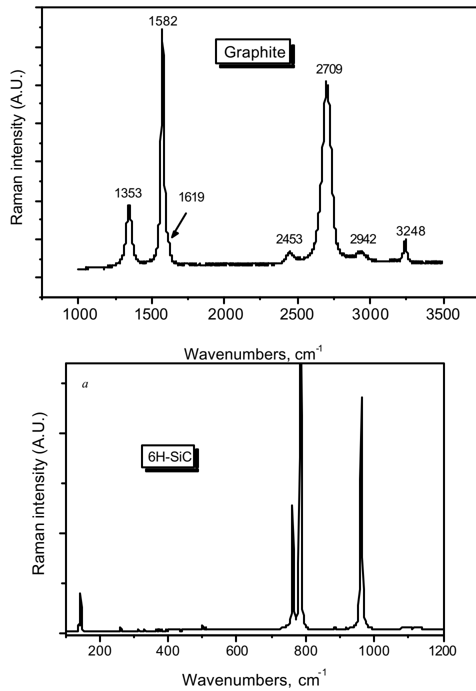


Figure 1. Raman spectrum of pure graphite shown in a spectral range 1000-3500 cm^{-1}.

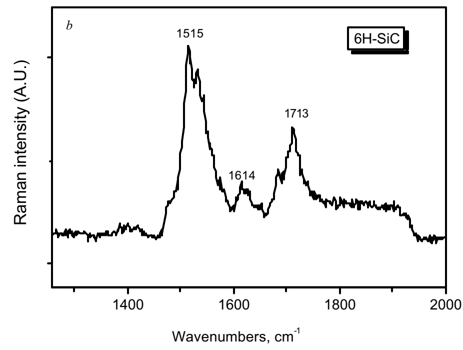
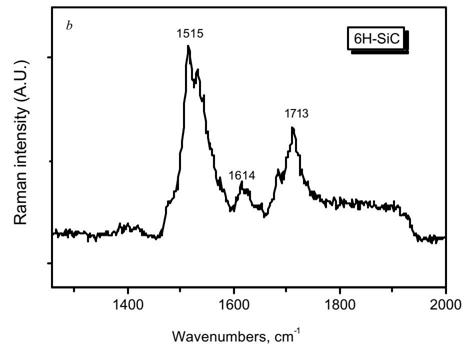
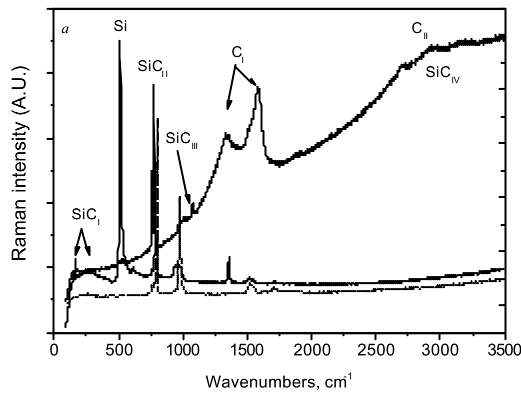
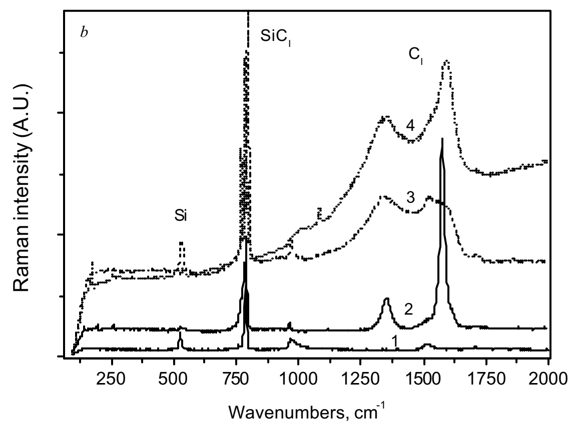



Figure 2. Raman spectra of 6H-SiC single crystal shown in spectral range 100-1200 cm^{-1} (a) and in the range 1300-2000 cm^{-1} (b).





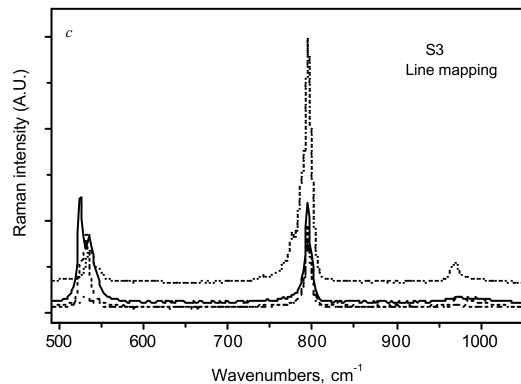


Figure 3. Raman spectra of C/C-SiC substrates: a) - S1 (thick solid line), S2 (thin solid line) and S3 (dotted line); b - spectra of substrate S1 obtained from different spots during single Raman measurements; c – line mapping experiment for S3 shown in Si and SiC_{II} regions.

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Both the peak Both the peak position and bandwidth of the G and D modes are sensitive to L_a. The calculations performed after the band fitting procedure in the range 1200-1700 cm^{-1} gives a value of L_a=20.6 nm, which is a reasonable result for this type of carbon material. The bandwidth for the G band is 24 cm^{-1} and 53 cm^{-1} for the D band.

The shift of G band from single crystalline graphite is ~7 cm^{-1} to the high frequency side. The shoulder at about 1600 cm^{-1} (sometimes in literature this shoulder is called the D' band) could be due to the presence of glassy carbon [16]. This is due to the fact that the position of the G band for glassy carbon is shifted to a longer wavenumber than for normal graphite [8,9]. It can also be the measure of structural disorder in SiC materials [17].

Furthermore, additional information on the structure of carbon materials can be also obtained from the analysis of the second order Raman spectra in the range 2500-3500 cm^{-1}. As can be seen from Fig. 1 *b* a strong band at 2709 cm^{-1} is surrounded by two satellite peaks. The position of the band at 2709 cm^{-1} is close to the highly oriented pyrolitical graphite at 2719 cm^{-1}. A similar band with 2 satellites at 2453 and 2945 cm^{-1} was observed by Obraztsova et al. [18] in the Raman spectrum of carbon onions.

Table 2 Peak assignment for spectra shown in Figs. 2 *a*

4H-SiC peak Raman shift [18] (cm^{-1})	Mode symmetry	6H-SiC peak Raman shift [18] (cm^{-1})	Mode symmetry	6H-SiC peak (our results) (cm^{-1})
195.5	E_2 planar acoustic	146.0, 150.5	E_2 planar acoustic	144.0, 149.3
203.5	E_2 planar acoustic	235.0, 240.0	E_1 planar acoustic	234.0, 240.0
266.0	E_1 planar acoustic	266.0	E_2 planar acoustic	265.0
610.5	A_1 axial acoustic	505.0, 513.5	A_1 axial acoustic	504.0, 513.4
777.0	E_2 planar optic	767.5, 788.0	E_2 planar optic	766.4, 788.0
797.5	E_1 (TO)	796	E_1 (TO)	796.7
		888.5	A_1 axial optic	888.4
967.0	A_1 (LO)	966.5	A_1 (LO)	965.6

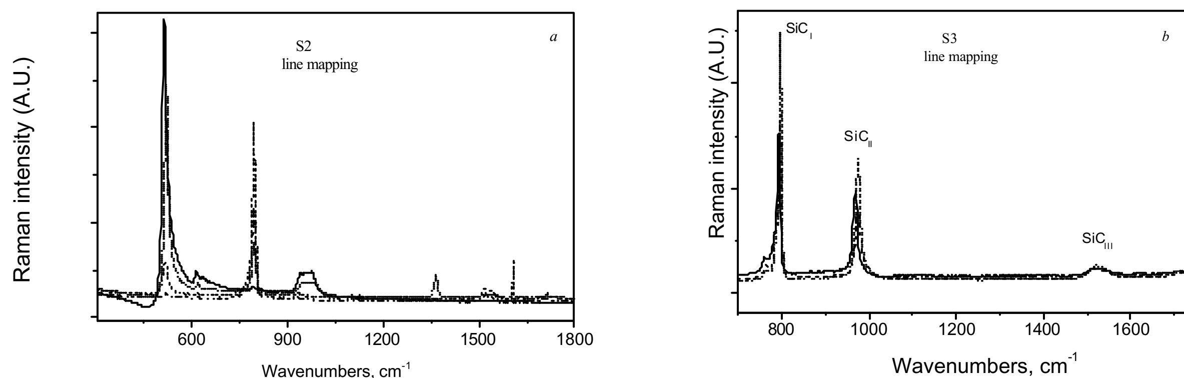

Figure 4. Raman spectra of samples S2 and S3 obtained during line mapping experiment.

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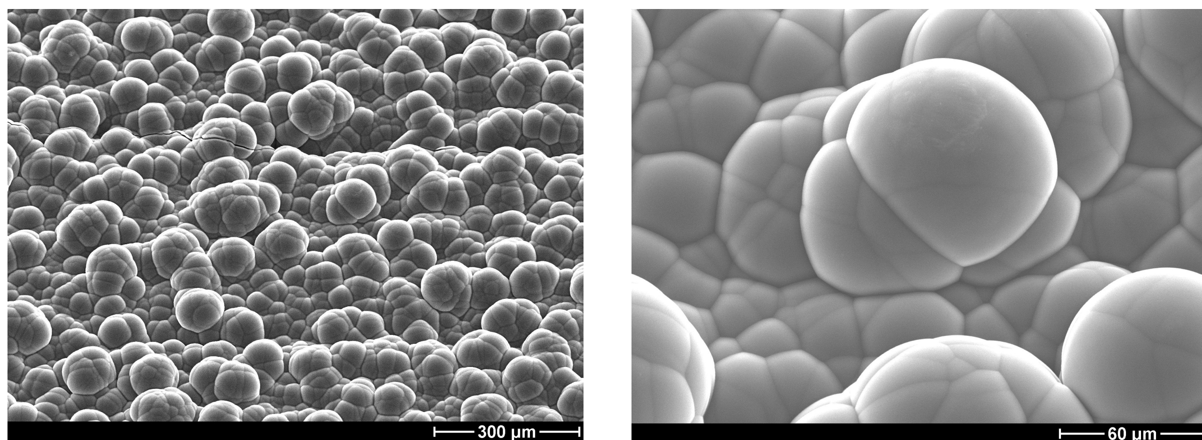

Figure 5. SEM micrograph of PyC film at low and high (b) magnification (the magnification factor shown at each plot).

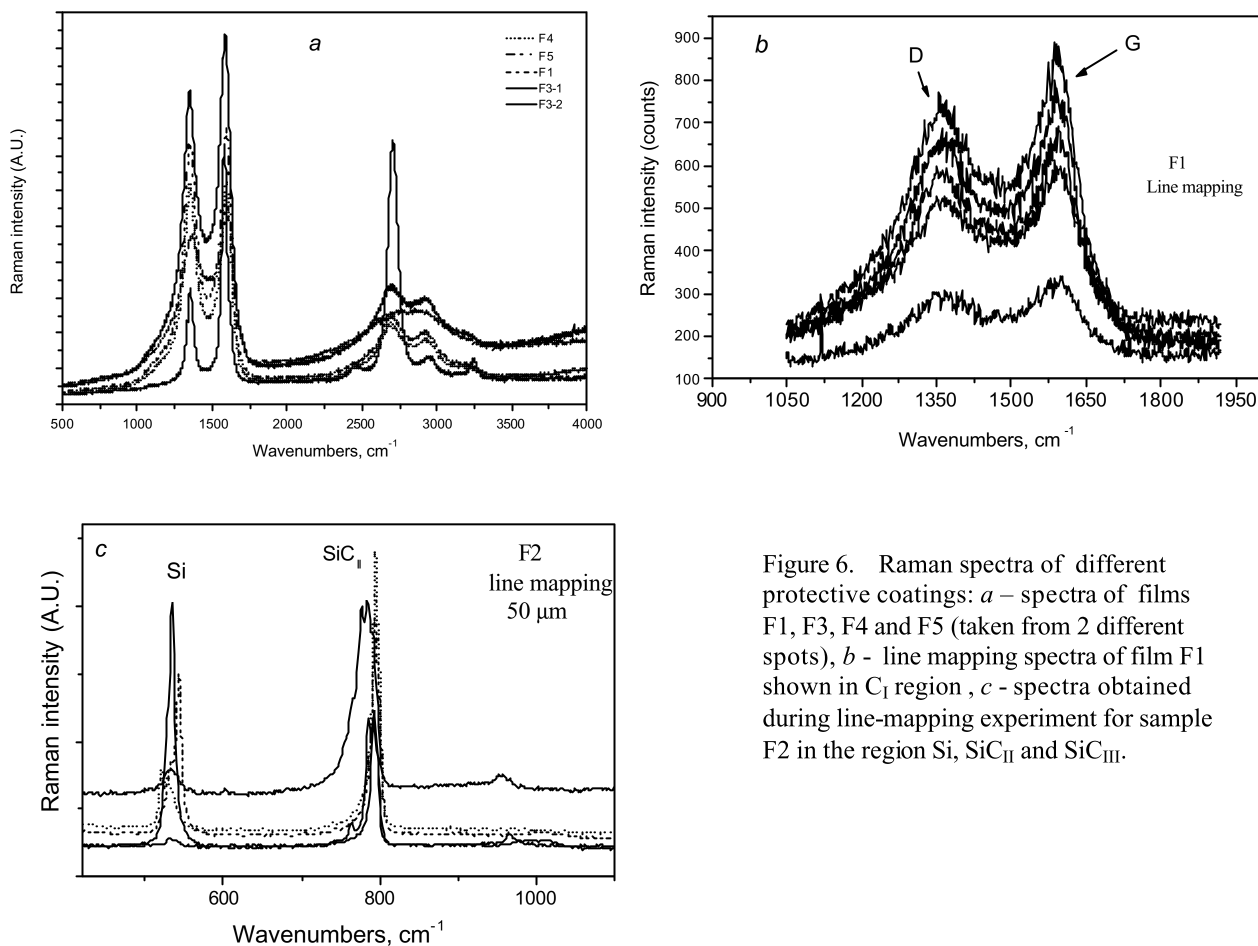

Figure 6. Raman spectra of different protective coatings: *a* – spectra of films F1, F3, F4 and F5 (taken from 2 different spots), *b* - line mapping spectra of film F1 shown in C_I region , *c* - spectra obtained during line-mapping experiment for sample F2 in the region Si, SiC_{II} and SiC_{III}.

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3.2 SiC

The Raman spectra obtained in this work for 6H-SiC single crystal in the regions of 100-1200 cm^{-1} and 1500-3000 cm^{-1} are shown in Figs. 2 *a* and *b*. These Raman spectra are similar to those published by Burton [19,20] for 6H-SiC crystalline substrates. The results of the peak position (together with band assignment) are summarised in Table 2, which show a good agreement with different measurements. The optical branch of the second-order Raman spectra for SiC was found [20] to be poly-type dependent and much more complex for 6H-SiC than for a cubic 3C-SiC structure (see Refs. [21,22]).

3.3 C/C-SiC substrate

In order to relate Raman spectra of composite materials to their mechanical properties, one must identify the fingerprints of all phases present in a material and assign their components to particular chemical bonds. Raman spectra obtained from various positions around the centre of different C/C-SiC substrates during single spot measurements are shown in Figs. 3*a* and *b*, while spectra obtained during the line-mapping experiment are shown in Figs. 3 *c* and 4 *a* and *b*. As we can see from these figures the spectra obtained for all three substrates differ in various spectral ranges. In order to simplify further discussion, we will divide the Raman spectrum into few different regions of interest and denote them in the following way: SiC_I (120-516 cm^{-1}), Si (range around 520 cm^{-1}), SiC_{II} (740-820 cm^{-1}), SiC_{III} (950-1200 cm^{-1}), C_I (1250-1650 cm^{-1}), SiC_{IV} (1450-1800 cm^{-1}) and C_{II} (2400-3400 cm^{-1}).

From the comparison of spectra shown in Figs. 3 and 4 we can conclude that all three substrates have different structure and uniformity (at least at the surface level). The best uniformity in composition is shown in the substrate S3, where only the SiC phase was found (see Fig. 4 *b*). In the substrate S2, both free Si and SiC phases were observed (see Fig. 4 *a*). Finally, in substrate S1, all three phases (Si, SiC and C) were found in different compositions and with different structures. We will discuss the results obtained for all three substrates in the details below.

Raman spectra obtained from certain positions on the C/C-SiC substrate S1 are shown in Fig. 3 b. As can be seen from this figure, free carbon or silicon can be identified by their specific lines at ~ 1580 cm^{-1} (G-line), ~1350 cm^{-1} (D-line) for carbon and ~ 520 cm^{-1} for silicon. SiC show four lines at 793 cm^{-1}, 965 cm^{-1} and also lines in the ranges 200-220 cm^{-1} and 410-420 cm^{-1}. Raman spectra collected from different spots on this substrate show quite substantial differences in the relative intensities and positions of bands observed in different spectral ranges such as Si, SiC_I, C_I and C_{II}. We will discuss these spectral regions separately for all spectra obtained during Raman line mapping session.

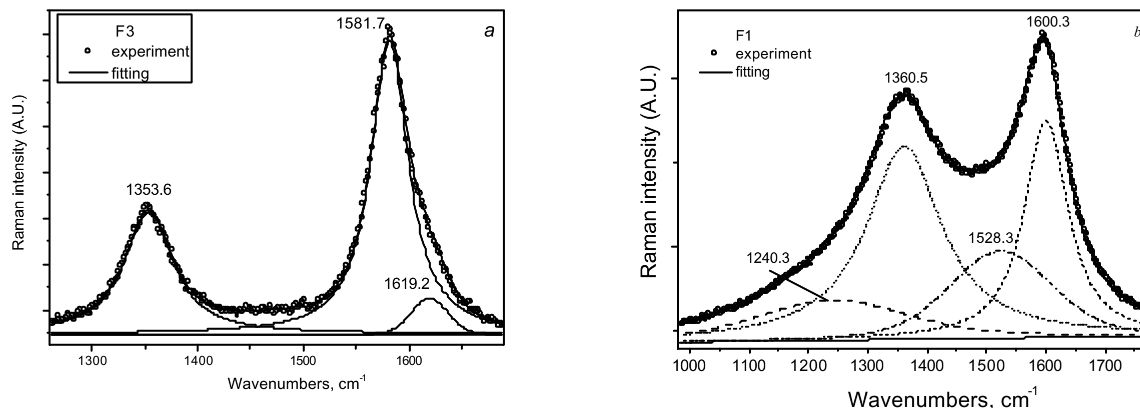

Figure 7. The example of the band fitting for samples F2 (a) and F3 (b).

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Spectral range 450-600 cm^{-1} (Si range)

As is shown in Fig. 3 c, the spectra obtained after the line mapping with a 2 μm step show quite a substantial difference in peak position ranging from 520 to 550 cm^{-1}. Two possible explanations of this observation are suggested: i) the existence of microscopic regions of compressively stressed Si around carbon fibres and ii) the existence of different poly-types of SiC with some vibrations which may show up in this region.

i) Stressed Si regions

The substrate S1 was obtained by dipping carbon fibres into melted silicon followed by cooling to room temperature. During the cooling stage, melted silicon froze around the material with higher thermal expansion coefficient and greater hardness. This can lead to strong compressive stress in free silicon micro-regions frozen in the vicinity of carbon fibres. We believe that the process mentioned above can create conditions similar to the indentation experiments performed on silicon recently [23-25]. In particular, Gogotsi et al. [25] have observed a local shift of the silicon band up to 529 cm^{-1} when a diamond probe was compressed into the silicon under the pressure of 5-12 Gpa. Thus, the Raman bands observed for the substrate S1 at 526, 535 and 545 cm^{-1} can be due to the strong silicon micro-compression around the hard carbon fibres.

ii) Existence of different SiC polytypes

From another point of view, as was shown in Refs. [4-7], SiC is a material which can have approximately 250 different poly-types. The poly-types have the same chemical composition but exhibit different crystallographic structures and stacking sequences along the principal crystal axis. This change in structure of different poly-types will be reflected in their Raman spectra. For example, in the region of 450-600 cm^{-1} two different type of crystals, 6H-SiC and 4H-SiC, show the A_1 axial acoustic mode at 505 and 513 cm^{-1} and at 610.5 cm^{-1} respectively. Thus, the different bands observed in the C/C-SiC substrate with micrometer spatial resolution may belong to pure Si regions (if observed at ~520 cm^{-1}) and to the different poly-types of SiC (if observed at higher frequencies 535-550 cm^{-1}). The existence of these different poly-types can also be determined from the behaviour of bands observed in the pure SiC region (700-1200 cm^{-1}), which will be discussed in the following section.

SiC_{II} regions (700-820 cm^{-1} and 900-1200 cm^{-1})

The importance of poly-types on the one-phonon Raman spectra of SiC was first noted by Choyke and collaborators [5] and also shown by Virag [6]. Raman spectroscopy has been shown to be a valuable probe of SiC grown by a variety of techniques [26,27]. The spectrum of SiC in the range of 750-820 cm^{-1} is very sensitive to the lattice structure. The cubic lattice structure is indicated by the single, transverse-optical (TO) peak and the longitudinal-optical (LO) peak (at 796 cm^{-1} (TO) and 973 cm^{-1} (LO) respectively), as was shown in Ref. ([4], p.298]). Non-cubic structures are indicated by the splitting of the TO mode into three peaks (TO_2 at 767 and 788 cm^{-1} and TO_1 at 798 cm^{-1}) and LO mode at 967 cm^{-1}. The micro-Raman spectra of SiC crystals with sizes ranging from a few μm to a maximum of 20 μm permitted the identification of both cubic and non-cubic poly-types as was shown in Ref. [8]. The comparison of the Raman spectra with isotope data obtained with an ion microprobe suggest that all SiC grains with anomalous isotopic compositions have a cubic structure, while isotopically normal grains have a non-cubic structure. Most of cubic the SiC grains showed a weak, broad LO band, indicating an imperfect structure.

Raman spectra obtained for S1 from the line mapping experiment in the region 700-1200 cm^{-1} are shown in Fig. 3 c as well. The presence of different poly-types of SiC (cubic and non-cubic) can be observed by the change in the relative intensities and peak positions for a set of bands in the regions of 750-820 cm^{-1}. The behaviour of the band at ~ 960 cm^{-1} is typically a measure of the SiC crystallite sizes. The behaviour of this band also changes quite substantially (in peak position, width and asymmetry) when spectra were collected from different spots on this sample.

We observed that the spectra obtained for the substrate S2 contained more free silicon when compared with S1. The number of different spectral variations for this substrate are shown in Figs. 4 *a* and *b*. It should also be noted that the fitting performed in the region 650-850 cm^{-1} shows that there are two intensive bands with frequencies 795 and 800 cm^{-1} for this substrate, while for the substrate S1 the dominant feature in this spectral range was band with a maximum at 796 cm^{-1}. Thus, we can conclude that the SiC in substrate S1 is present mainly in a cubic crystalline form and mainly non-cubic (in particular hexagonal) in substrate S2.

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Carbon (C_I) and SiC_{III} region

The region of 1200-1700 cm^{-1} belongs to a high ordered graphite band at ~1592 cm^{-1} (G band) and to a disordered carbon structure at 1352 cm^{-1} (D band) and an additional band at ~1530 cm^{-1}. As previously mentioned, the size of crystallites formed, the substrate and the films can be identified from this region. In order to determine the exact position and intensities of the G and D bands, the fitting procedure was performed using Grams Research software (see example of this fitting in the following section). We found that the fitting is more accurate if we used a mixture of Gaussian and Lorentzian functions for bands at 1592 and 1352 cm^{-1} and the pure Gaussian function for the band at ~1530 cm^{-1}. Furthermore, due to asymmetry of the band at 1352 cm^{-1} from the low-frequency side, an additional band with a frequency of 1170 cm^{-1} was added. The calculations of parameter La (Eq. (1)) leads to the conclusion that the most of the carbon in the substrate does not posses a highly ordered structure since the carbon crystallites size only range from 2 to 4 nm.

In addition to this, the bands from SiC vibrations at 1720 cm^{-1} (see Fig. 2 b for comparison) are also present for certain areas. In the region of the second order Raman spectrum 2400-3400 cm^{-1} of substrate S1 we can also see a few different spectral variations confirming not highly ordered graphitic structure as well.

Substrate S2 consist all aforementioned components (C, SiC and Si) arranged in a different way. In particular, there was more Si and SiC found on the substrate than C and SiC. The number of spectra collected from different spots on this substrate are shown in Figs. 4 a and 4 b. As these figures show, the variation in different bands are much smaller in this case. In particular, the low-frequency bands of SiC (in the region 100-500 cm^{-1}) are not present at all. In the region of 650-1200 cm^{-1} (SiC_{II}), mainly one poly-type of SiC is observed with two bands at 795 and 800 cm^{-1} (1 cm^{-1} shift to the low-frequency side when compared with substrate S1). Line mapping Raman measurements also show that pure silicon phases are present in this substrate with the Si phonon band located at ~518-519 cm^{-1}. This means that the Si lattice is under a small tensile stress. It is interesting to note that for these particular spots a quite strong and wide band was observed in the spectral range of 950-1150 cm^{-1}. This band is always present in Czrochalski grown Si wafers which contain a certain amount of interstitional oxygen. It is attributed to Si-O stretching vibrations. This band was not observed for substrates S1 and S3. In the C_{II}-SiC_{IV} region, the single vibrational band at 1366 cm^{-1} was found for some spots. This indicates the presence of highly ordered free carbon regions. In addition to this, the set of bands at 1520, 1622 and 1714, which belong to the second order Raman spectrum of crystalline 6H-SiC, was detected too. No bands have been observed in the second order Raman spectrum of carbon (C_{III} region).

3.4 Carbon and Si_xC_y coatings

In this section we will discuss the structure and composition of a number of carbon and Si_xC_y films deposited by CVD at different conditions onto substrate S1 as listed in Table 1. A typical SEM image, obtained from PyC films, is shown in Fig. 5 a for low magnification and in Fig. 5 b for high magnification (the scale or magnification factor is shown on each figure). From these figures one can see that the structure of this film is not uniform and contains grains of different sizes. The surface morphology appears to be pebble-like (botryoidal).

Examples of Raman spectra obtained for films F1, F3, F4 and F5 are shown in Fig. 6 a. One can see that the spectra for these films looks like typical PyC films, since the main spectral features are observed only in C_I (1200-1800 cm^{-1}) and C_{II} (2400-3400 cm^{-1}) regions. It should be also noted that the Raman spectra obtained for each of these samples during the line mapping session are almost the same (see example shown for F1 in Fig. 6b). However, the position and shape of the vibrational bands deviate slightly from one sample to another. The band fitting that was performed in the same manner as was described in the previous section for the substrates allows the crystallite size (L_a) to be obtained. The results of fitting the band parameters (see Fig. 7) and L_a calculations are shown in Table 1. From these results we can conclude that the crystallite size is larger at higher CH_4 flow and in the absence of H_2. If the process occurs in the presence of H_2, then the size of crystallite is larger for the higher flow of both CH_4 and H_2. These results can be explained as follows; the growth of PyC crystalline film occurs faster with the participation of chemical radicals. With addition of H_2, the crystallisation occurs via radicals. This speeds up the process and leads to the formation of a smaller size of crystallite than in the absence of H_2. This can be confirmed by the comparison of data presented in Table 1.

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For low CH_4 flows (see sample F2 shown in Fig. 6 c) the Raman spectra of the film looks more like a mixture of free Si and SiC. This is due to the fact that at low gas flows the film obtained is very thin and, possibly, the entire substrate is not covered by this film uniformly. For this reason, the spectra of this film sometimes look very similar to the spectra obtained from substrate S1.

Another interesting result has been observed for Si_xC_y coatings. From the Raman spectra of this film (F3) shown in Fig. 5 a for two different spots, one can conclude that the structure of this film is rather non-uniform and contains regions of highly ordered PyC (thick solid line) and less ordered graphitic structures (thin solid line). For the highly ordered PyC the crystallite size (L_a) ranges from 8 to 10 nm. SiC has not been observed in this film at all. We believe that the structure and composition of this film are due to the growth at very different conditions when compared with the other films. In particular, this film was grown in a vacuum.

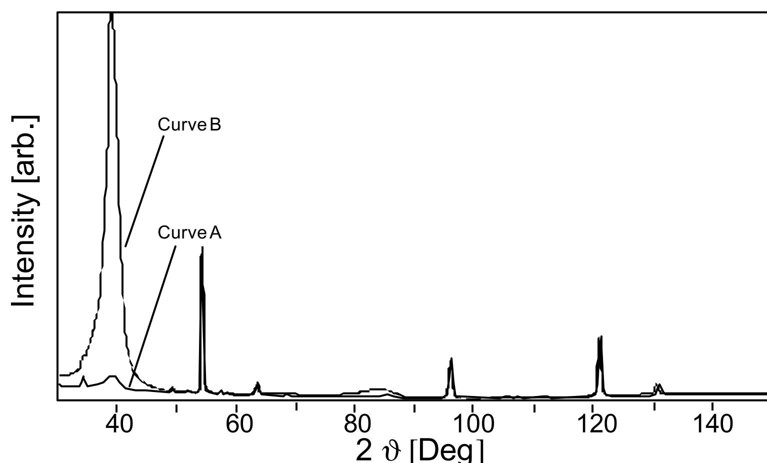

Figure 8a. X-ray diffractograms of the uncovered substrate (curve A) and of the PyC-SiC-film (curve B) superimposed to each other in a 2θ range of 30 to 150 °

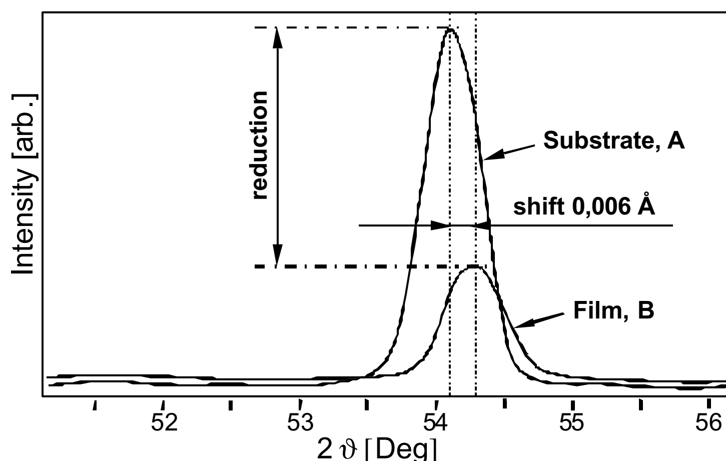

Figure 8b. Subsection from Fig. 8a for the 2θ range of about 51,1 to 56,1° showing shift and intensity reduction of the strongest SiC-peak of the film in comparison to that of the substrate.

3.5 Results of X-ray diffraction measurements

The diffractograms of the uncovered substrate (curve A) and of the PyC-SiC-film, F3, (curve B) are superimposed in Fig. 8a. Two broader peaks at angles of about 39° and 84° are striking especially in curve (B) of the film. These peaks can be identified with free carbon. The peak widening indicates that the carbon crystallites are very small (much less than 100 nm in size) and that an amorphous portion can not be excluded. Furthermore there are sharp peaks at angles 2θ of about 54, 54°, 96°, 121° and 131°. These peaks can be attributed to the rhomboedrical silicon carbide with crystal sizes above 100 nm. The crystallographic data of rhomboedrical Moissanite-33R also shows the fit to the measured

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diffraction peaks. Fig. 8b is a subsection of Fig. 8a in the region of the strongest (1 0 10) SiC peak beetween 51° to 56°. It shows that this peak for the film (curve B) is shifted in the 2θ scale by about 1/10° and has reduced intensity, compared to the substrate (curve A). The peak shift corresponds to a compression of the film lattice of about 0,0006 nm, the intensity reduction amounts 1/3.

It should be noted that the results obtained from XRD for F3 coatings are contradict the results obtained from Raman spectroscopy where only carbon structure was detected and no SiC. We believe that this is due to the difference in the depth of penetration for Raman and XRD experiments. Raman measurements are taken only from the external surface due to the strong absorption of carbon for visible light while XRD measurements are taken much deeper. It could also be some other reasons for this disagreement. The Raman spectra were taken from the same sample after XRD measurements. It is quite possible that the structure on the surface of the film changed during exposure to the monochromatic radiation of Cr-Kα.

4. Conclusion

A number of C/C-SiC substrates and those coated by carbon and Si_xC_y films were investigated by Raman spectroscopy. By analysing the different regions in the spectra we can obtain information on the presence of PyC, Si_xC_y or pure Si in films as well as extract information on the structure and quality of the substrate and films coated on top. This analysis can lead to establishing the growth conditions for obtaining different types of films with particular properties.

Raman spectra for C/C-SiC substrates, obtained by different methods, show substantial deviation in structure and composition. In particular, substrate S1contains more SiC and C and small regions of free Si under strong compressive stress. Substrate S2 contains large regions of Si (mainly under a small tensile stress), SiC and very small areas of free C with a high degree of perfection (diamond-like structure). Substrate S3 contains mainly SiC with hexagonal structure. The analysis of Raman spectra of carbon films in the range 1200 – 1800 cm^{-1} allows the determination of crystallite size in these films, which varied from 2.6 to 3.4 nm depending on the CH_4 and H_2 gas flow. We found that the maximum crystallite size in carbon films appeared at the following process conditions: T=1200°C, CH_4 flow 60 ml/min and duration 20 minutes.

The most unusual result obtained was for the sample marked as C/C-SiC substrate coated by SiC. However, from Raman experiment we detected only a free carbon film with a high degree of perfection of the crystalline lattice with an onion-like structure. This conclusion has been obtained from both the analysis of spectra in the region (2300 – 3400 cm^{-1}) and by calculation of the crystal size, L_a, which has the biggest value (9 nm) amongst all other films studied. However, these results differ from the X-ray diffraction data where the presence of C and SiC was shown. We presume that the difference between these two techniques is due to the different depth of penetration into the film, which may have a different structure on the top of the surface. This type of film composition was possibly due to different technological conditions for this film growth. The growth took place in a high vacuum.

Another interesting observation was found for sample F2 which was marked as a carbon coated C/C-SiC substrate at 1200°C with CH_4 flowing at 25 ml/min for 20'. This sample shows the spectra quite similar to the Raman spectra of the substrate itself. We assume that for the low CH_4 gas flow the coating is not uniform and is very thin. The Raman line mapping performed for this sample supports this assumption. The spectra collected from different spots on the sample are quite different. At the same time, line mapping performed for all other samples shows very similar results.

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