



JOINT RESEARCH CENTRE
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Biomedical Materials and Systems Unit

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Surface Characterisation and Processing Sector

TITLE:

ANALYSIS OF PECVD COATINGS USED FOR CELL CULTURE

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1. Introduction

In this document we report on the analysis carried out on samples provided by PLASMA ELETCRONIC GMBH, D. The work is part of collaboration with the Institute of Reference Materials and Measurements IRMM, (Geel, B) and is intended to be a starting point for a systematic investigation on the cell behaviour of different substrates in order to optimize a standardization process for In Vitro Testing.

2. Sample description

Four type of coatings (Table I) deposited by PECVD (Plasma Electronic GMBH, D) have been analyzed by different techniques, namely AFM (NT-MDT, Russia), XPS (ULTRA, Kratos Anal., UK), ToF-SIMS (ION TOF, D), FTIR (Bruker, D), Contact Angle (Digidrop, GMBX, FR) and Z-potential (EKA, Anton Paar, USA).

Coating	Precursor	Thickness (nm)
AQUACER	xxxxxxx	200-300
LIPOCER	xxxxxxx	100-150
CARBOCER N	C ₂ H ₂ + N ₂	1000-1500
CARBOCER S	C ₂ H ₂ + TMS	1000-1500

Table I: Coatings deposited by PECVD. (TMS=Trimethylsilane)

3. Results

- *Sample morphology (AFM)*

Scanning probe experiments were performed with a commercial Atomic Probe Microscope (SMENA head, Solver electronics, NT-MDT). A standard silicon cantilever has been used in contact mode ($K_{cl} = 10$ N/m). For each sample images at different scan size were acquired: 30 x 30 μm , 10 x 10 μm , 2 x 2 μm . The Root-Mean-Square (RMS) roughness values have been calculated using the controlling software of the instrument, following the equation:

$$R_{rms} = \sqrt{\frac{1}{N_x N_y} \sum_{i=1}^{N_x} (Z_i)^2 \sum_{j=1}^{N_y} (Z_j)^2}$$

where N_x and N_y are the number of pixels in the scan plane for the x and the y directions respectively (256 x 256 pixels) and $Z_{i,j}$ is the measured heights for each pixel. RMS roughness values were calculated for different scan sizes from 0.5 μm to 30 μm .

The saturation roughness was calculated with the average value of the RMS roughness that does not change with the scan size. The correlation length was taken as the scan size at which the RMS roughness reaches the saturation value

In Figure 1 AFM pictures of the coatings are presented. All coatings present a good uniformity and high scratch resistance indicative of good adhesion. In particular both ACQUACER and LIPOCER present a fully amorphous structure with saturation roughness of 0.22 and 0.30 nm and correlation lengths of 1.07 and 1.90 nm, respectively. On the other hand, the two CARBOCER coatings revealed an amorphous structure with randomly distributed granular inclusions with a diameter of the order of 0.1-0.2 μm . Those coatings also present higher saturation roughness (0.61 nm for CARBOCER-N and 1.03 nm for CARBOCER-S) with similar correlation lengths (2.90 nm).

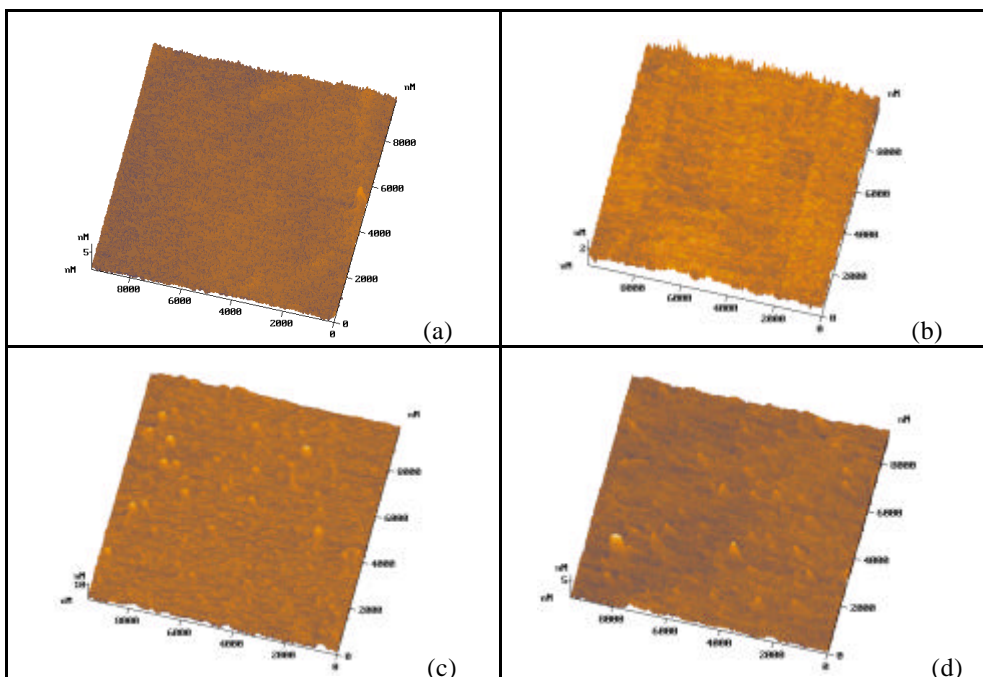


Figure 1: AFM picture of PECVD coatings: ACQUACER (a), LIPOCER (b), CARBOCER-S (c) and CARBOCER-N (d).

- *Sample Composition (FTIR, XPS, ToF-SIMS)*

FTIR spectra were acquired in dry air using a Bruker Vector 22 spectrometer working in transmission at a resolution of 4 cm^{-1} . In Figure 2 IR spectra of different coatings are illustrates.

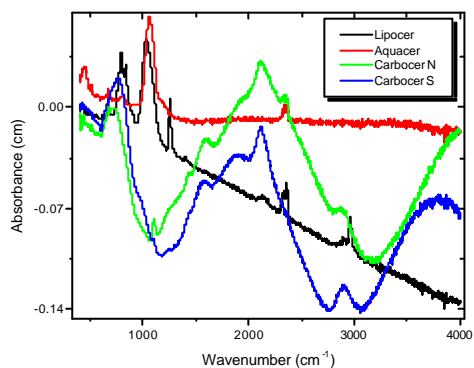


Figure 2: FTIR Spectra (row data) recorded in transmission on the PECVD coatings.

As we can be seen, the four samples present some very different infrared spectra. In particular, whereas comparison between CARBOCER-N and CARBOCER-S is possible, LIPOCER and AQUACER appear to

be quite different materials. Moreover all IR spectra are different from the typical spectra of diamond, graphite, silicone, amorphous carbon (a-C, a-C:H, a-C:H:N) or Si-C. For example, only few IR absorption peaks are observed in the case of the AQUACER film: the 600-1200 cm^{-1} band and a band centred on 2300 cm^{-1} . Since infrared measurements are sensitive to asymmetric bond vibrations, we can presume that symmetric bonds mainly compose the bonding structure of this film. However Raman measurements (sensitive to the symmetric bond) should be performed to confirm this hypothesis

In order to gain more information, a base line subtraction using a third order Airy function was performed, Figure 3, the IR spectra after the baseline subtraction are plotted.

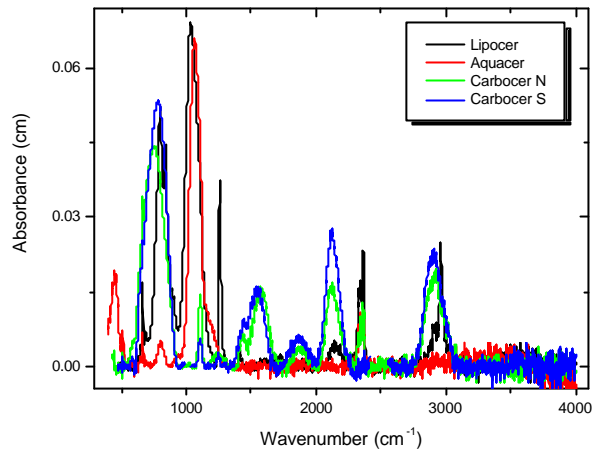
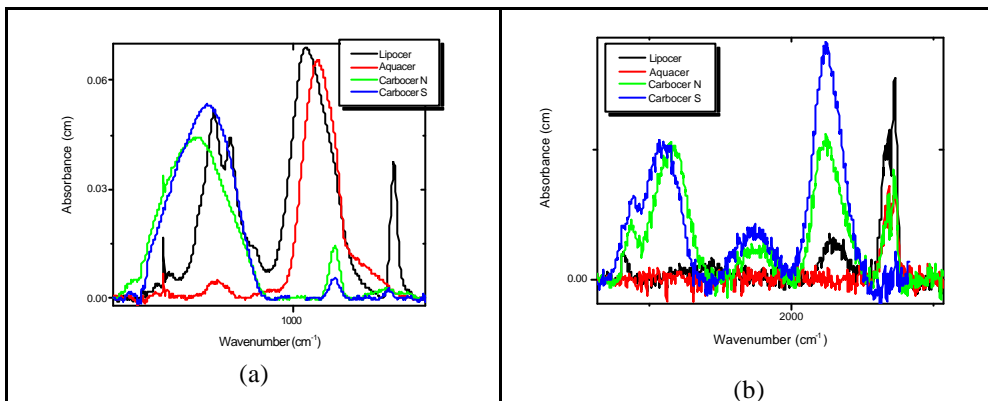


Figure 3: IR spectra after baseline subtraction.

Three main regions can be identified as illustrated in Figure 4 (a-c).



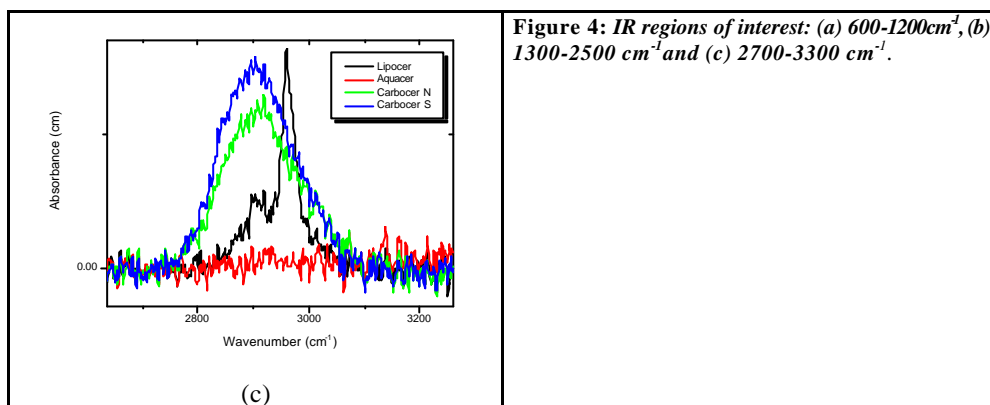


Figure 4: IR regions of interest: (a) 600-1200 cm^{-1} , (b) 1300-2500 cm^{-1} and (c) 2700-3300 cm^{-1} .

For LIPOCER film, we observe a doublet peak at 800 cm^{-1} and 840 cm^{-1} . These two contributions, in good agreement with the xxxxx precursor composition can be respectively attributed to the Si-C and Si-O-CH₃ bonds. In addition, the shoulder at 885 cm^{-1} can be due to the probable presence of Si-H bonds. The peak centred on 1032 cm^{-1} reveals the presence of oxygen in the sample. These oxygen atoms are linked with silicon atoms and probably with carbon atoms. The narrow peak centred at 1259 cm^{-1} shows the presence of Csp³ bonds. This very narrow and well-defined peak suggests the presence of a diamond structure with a good crystallinity. On the other hand, it is difficult to identify a unique structure for the band at about 2150 cm^{-1} . In fact, a band in this range is usually observed in amorphous carbon nitride sample (C≡N contribution) or in silicon thin films (Si-H₂ and Si-H₃ bonds). The doublet 2330 cm^{-1} - 2360 cm^{-1} is due to O=C=O (CO₂) vibrations, whilst the IR bands between 2800 cm^{-1} and 3050 cm^{-1} reveal the presence of C-H sp³. The main peak at 2960 cm^{-1} can be attributed to the CH₃ sp³ vibrations. These bonds can come from the CH₃ terminal bond of the O-Si-(CH₃)₃ (revealed by the peak at 840 cm^{-1}). The second apparent contribution at 2900 cm^{-1} can be due to C-H sp³ band.

The spectrum of AQUACER sample shows absorption bands at 804 cm^{-1} , 1066 cm^{-1} and 2340 cm^{-1} that can be attributed to Si-C, C-O and/or Si-O and CO₂ respectively. It is surprising to not observe the presence of hydrogen bonded to carbon or silicon atoms. Measurements of density and symmetric bonding structure (Raman, X-rays reflection) can in this case give more information.

One of the two main differences between CARBOCER-S film and CARBOCER-N is the apparent shift of a band at 600-950 cm^{-1} (Fig. 5(b)). But if we observe the base tail of these bands we do not observe major differences. Also the shift is mainly due to the increase (or decrease) of one of the contributions to the band. In our case, the decrease of the O-Si-CH₃ vibration centred at 840 cm^{-1} can induce a band shift to the low wavenumber. This explanation is in a good agreement with the deposition conditions. Indeed, the CARBOCER-N, deposited from acetylene i.e. without Si-CH₃ bonds, shows the most important shift to the low wavenumber.

Both CARBOCER-S and CARBOCER-N layers show low oxygen content because the bands at 1100 cm^{-1} and 2300 cm^{-1} have a low intensity.

The band between 1350-1700 cm^{-1} is due to the presence of carbon/carbon bonds and carbon/hydrogen bonds. The main peak is probably due to C-C and C=C, whereas the shoulder around 1450 cm^{-1} can be associated to C-H bonds. The presence of carbon/carbon bonds is also confirmed by the presence of the broad band around 1870 cm^{-1} . Indeed we can associate the vibration of carbon chains to this band.

The band around 2200 cm^{-1} can be attributed to the C-N, C≡N (for CARBOCER-N) and Si-Hx bonds (for CARBOCER-S). This reflect the difference between the layer deposited from XXXXXXX and from acetylene + nitrogen. However the presence of an important band in this range suggests also that the films are more porous (lower densities) than LIPOCER or AQUACER films. The band between 2800 cm^{-1} and 3100 cm^{-1} shows the presence of C-H_x sp³ bonds (FIG. 5(c)). The maximum shifted to the low wavenumber, suggests a high content of C-H sp³ bonds.

Finally comparison of CARBOCER-S and LIPOCER spectra lead to the following observations:

- incorporation of O-Si-CH₃ is lower in CARBOCER-S layer than in LIPOCER

- Si-O, Si-H and C-H bonds dominate the 600-950 cm^{-1} band for CARBOCER-S layer, contrary to the LIPOCER films.

XPS analyses have been carried out using an ULTRA system equipped with Al monochromatic source working at 225W. The base pressure was 6.5×10^{-10} Torr whilst the working pressure was below 4×10^{-9} Torr. Survey (0-1150eV BE) and high-resolution spectra were acquired at pass energy of 160 and 20eV respectively. All spectra were acquired at 90° take off angle (respect to sample surface) and with a spot size of $100 \mu\text{m}$. Ion etching was performed using an Ar ion gun (MINIBEAM I, Kratos Anal.) operated at 2KeV and with a chamber pressure of $\approx 2 \times 10^{-8}$ Torr. Spectra have been analyzed using Vision 2 software (Kratos). Sample compositions are calculated using tabulated Atomic Sensitivity Factors (ASF).

Survey spectra of the different films are presented in Figure 4 (a-d) whereas samples compositions are reported in Table II. Beside the expected elements, i.e. C, O, Si and N, traces of contaminants such as F, Cl and Na have been detected. However it must be noticed that the contamination level is below 1at% in all samples.

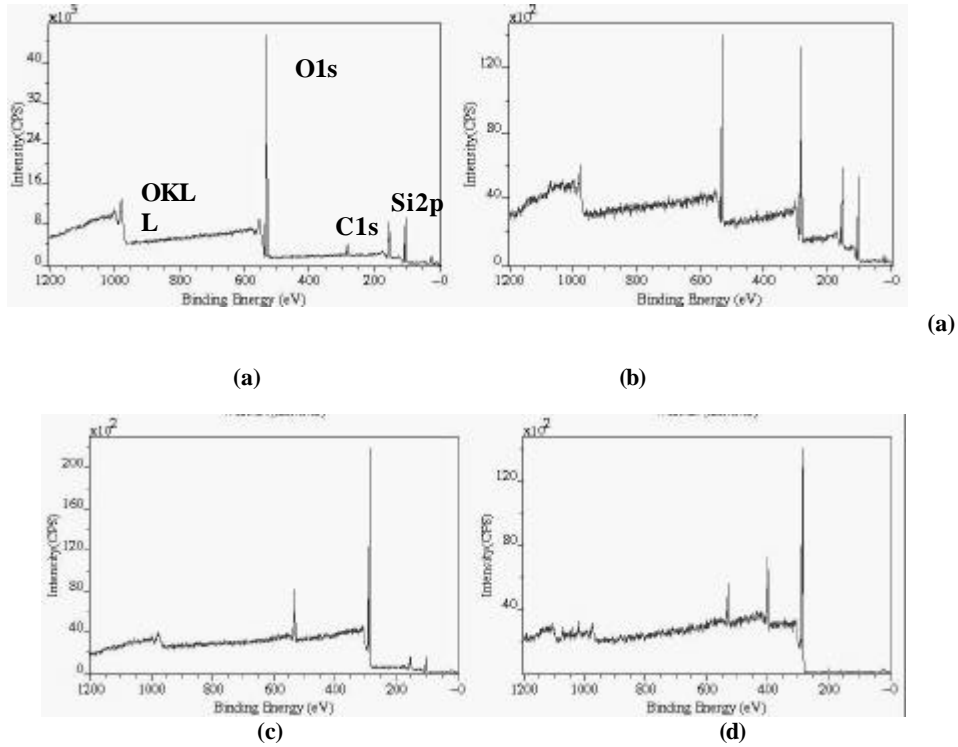


Figure 5: Survey spectra of the as deposited PECVD films: (a) AQUACER, (b) LIPOCER, (c) CARBOCER-S and (d) CARBOCER-N

	C	O	Si	N	F	Na	Cl
AQUACER	9.64	62.94	25.53	1.54	--	--	--
LIPOCER	58.75	19.30	21.95	--	--	--	--
CARBOCER-N	79.21	11.59	5.23	2.96	--	--	--
CARBOCER-S	74.92	8.64	0.5	15.57	--	--	--

Table II: Chemical composition (at%) of as deposited films

In order to reduce contamination all samples were etched with ion bombardment (Ar^+ at 2KeV). As can be seen in Table III, where chemical compositions after etching are reported, and contamination is almost completely eliminated after 120" etching time (corresponding to a depth of about 5.5 nm).

Moreover for AQUACER sample the C content is reduced of a factor of 2 and the O/Si ratio show also a slight decrease from 0.42 to 0.40. This indicates that AQUACER film consists of a SiO_x over-stoichiometric layer.

The composition of the LIPOCER coating almost reflects the composition of the plasma precursor as already indicated by FTIR measurements. In fact, the theoretical composition of the XXXXXX monomer is two Si atoms, one oxygen atom and six carbon atoms; that is $\text{C/O}=3$ and $\text{O/Si}=0.5$, respectively. If one assumes that there is no change in Si concentration, we can evaluate atomic concentrations by XPS. As can be seen in Table I the C/Si and O/Si ratios are 2.66 and 0.98 respectively, indicating a higher amount of oxygen and a lower amount of carbon in the LIPOCER film. This is due to possible reaction of surface free radicals with air following formation of cross-linked carboxilosane network.

In order to study the possible reaction in air, the LIPOCER sample has been fatherly etched with Ar ions. The variation of C/Si and O/Si as a function of etching time is reported in Figure 6.

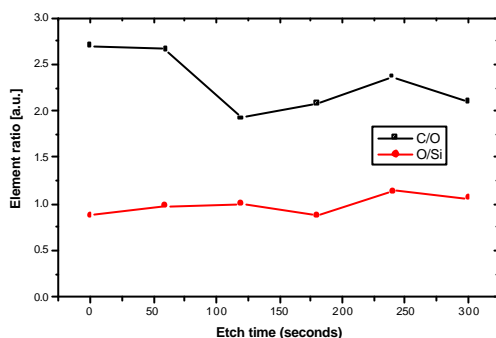


Figure 6: Element ratio depth profile for sample LIPOCER

As can be seen the oxygen level remains well above the theoretical value of xxxx also within the film indicating a strong reaction of the coating with air.

The CARBOCER-N and CARBOCER-S are carbon based materials doped with $\text{N}(\cong 10\text{at}\%)$ and $\text{Si}(\cong 6\text{at}\%)$ respectively. However, whilst the CARBOCER-N film is deliberately doped with N, the presence of Si in the CARBOCER-S is due to the precursors used (XXXXXX).

Analysis of the C1s high-resolution spectra (not shown) indicate the presence of C-N type bonding in the CARBOCER-N films as expected. However ToF-SIMS analysis revealed a strong surface contamination both films that can hinder the real coating surface. This contamination effect could also explain the similar wetting response of these two samples.

	C	O	Si	N	F	Na	Cl
AQUACER	4.05	67.53	27.67	0.75	--	--	--
LIPOCER	48.61	25.36	25.74	--	--	--	--
CARBOCER-N	89.27	0.85	0.18	9.56	--	--	--
CARBOCER-S	89.29	3.74	6.34	--	--	--	--

Table III: Chemical Composition (at%) after 120" ion etching.

In fact, as illustrated in Figure 7, positive SIMS spectra are quite similar and the main difference is related to the intensity of the silicon signal that is significantly higher in the CARBOCER-S material with respect to the CARBOCER-N..

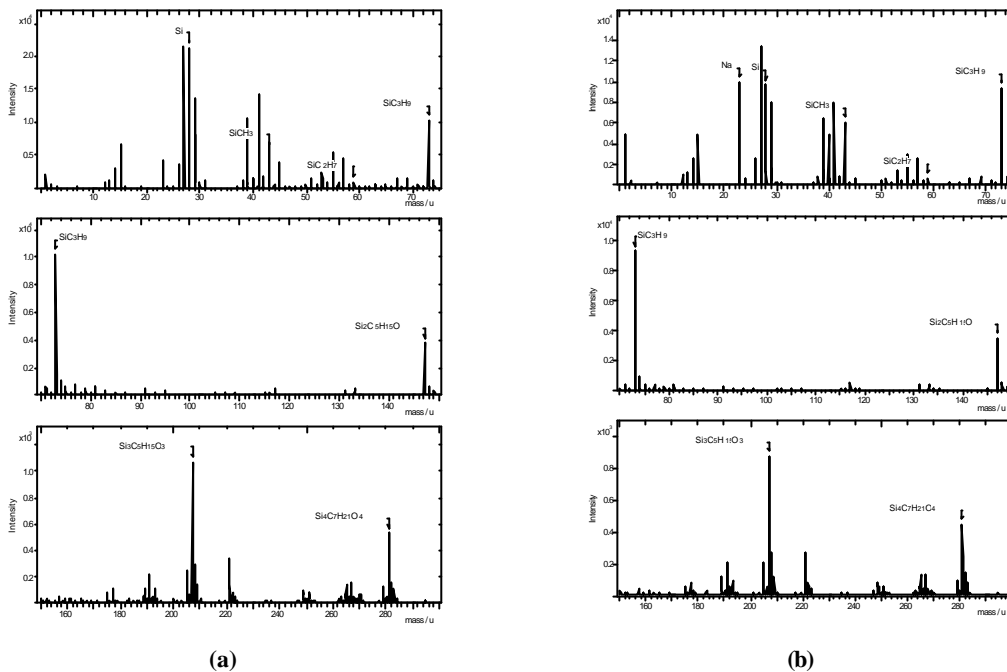


Figure 7: Positive SIMS spectra of CARBOCER-S (a) and CARBOCER-N (b)

The majority of the peaks in the positive spectra are attributable to PDMS (Polydimethylsiloxane)- a very commonly found contaminant in TOF-SIMS samples resulting from handling and transport using plastics where PDMS is used as release lubricant in the stamping/molding process. However, in these samples the presence of a PDMS type material may in part be the result of the precursor used in the coating process. At this time studies were conducted only on “as supplied “ samples without any washing or decontamination procedures that could reveal whether this material is a contamination or an integral part of the film. A possible solution to this problem could be a short hexane treatment before analysis

The results of the negative spectra, reported in Figure 8, clearly show the much greater inclusion of nitrogen (CN/CNO peaks) in the CARBOCER-N sample and higher silicon species in the CARBOCER-S sample. This findings are in agreement with the XPS measurements (Table II and III). Another difference noted was in the ration of oxygen/hydroxide, which the sample shows a higher OH in the CARS1 sample compared to the CARBOCER-N material. Apart from the common alkali/alkali earth elemental contaminants Na, K, Mg the only unusual elemental contamination observed on the surface was Cu.

Analysis of the LIPOCER films shows a very high sensitivity to the Ga⁺ ion beam used in the TOF-SIMS analysis with visible changes to the surface being seen after only one pass of the raster beam. This is clear indication that the surface is being modified during the analysis and more detailed study is necessary to assess whether the analysis procedure is significantly modifying the resultant spectra.

Finally also the AQUACER film seems to have a strong PDMS contamination with a SIMS spectrum similar to the one of CARBOCER(s) coatings. However, as in the case of CARBOCER-S, the PDMS-like materials can be also related to the plasma precursor. This makes almost impossible any type of conclusion about the true chemical composition of the coating surface with respect to a highly surface sensitive analysis method such as TOF-SIMS.

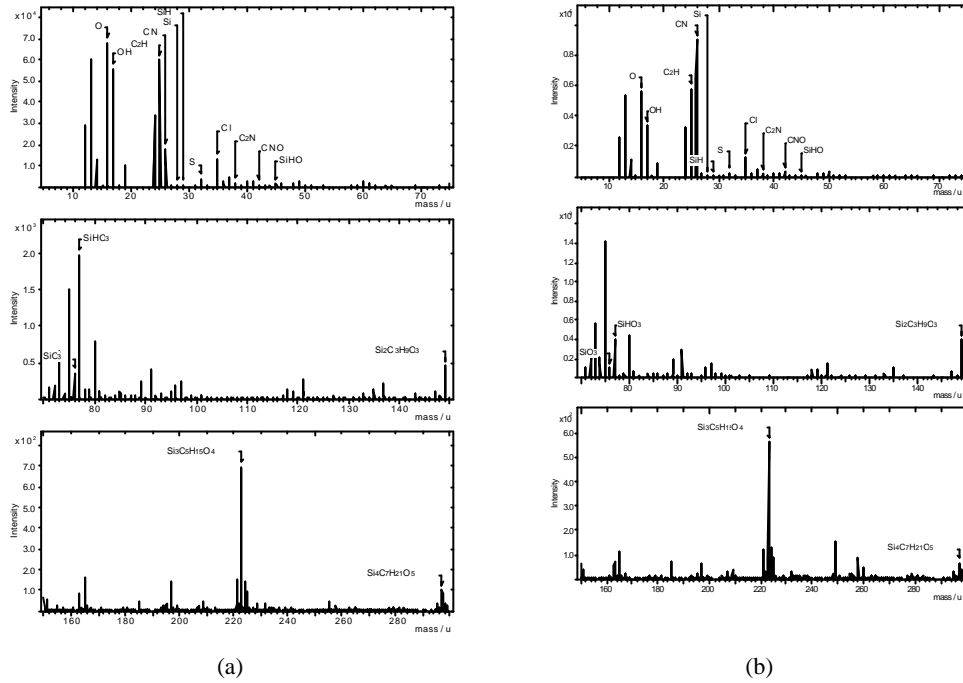


Figure 8: Negative SIMS spectra of CARBOCER-S (a) and CARBOCER-N (b) films.

- *Contact Angle and Zeta potential measurements*

The results of static Contact Angle (CA) measurements are presented in Figure 7(a) contact. Three liquids (pure water, ethyleneglycole, alphabromonaphtalene) were used in order to assess the surface responses to different acid character of the wetting agent. In case of water CA's both the hydrophilic and hydrophobic samples respect their behavior. Regarding these contact angles (figure 3.1), no conclusions can be extracted in terms of surface tension components on the basis of Good-Van Oss theory because of pressure spreading limit effects. The Si and N doped carbon films show relatively similar results to each other in both contact angle and Zeta potential curves (Figure 7(b)). In fact, in this measurement of surface charges only the hydrophilic film (AQUACER) shows a different behavior, which confirms the highly polar character of such a film as denoted by the very low contact angles with polar liquids.

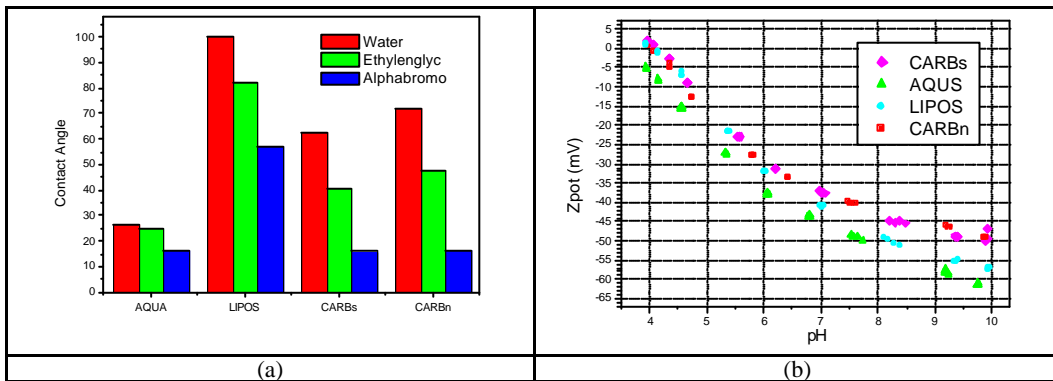


Figure 9: Contact angle measurements (a) and Z potential characteristics (b) of PECVD coatings

As already pointed out above, possible contamination of CARBOCER-N and CARBOCER-S coatings observed by ToF-SIMS could influence the wetting response of these two films.

4. Conclusions

Four different PECVD coatings used for cell culture have been analyzed.

FTIR analyses show a well-ordered structure with low oxygen content and a well-ordered carbon and silicon atomic network in case of the LIPOCER films with presence of O-Si-CH₃ bonds related to XXXXXX. This is also confirmed by XPS measurements. FTIR analysis of AQUACER sample is difficult due to the weak information deductible from the IR spectrum. In case of CARBOCER-S and CARBOCER-N, XPS analyses indicate a similar composition (carbon based materials); the major difference being the presence of nitrogen in CARBOCER-N, which result in C≡N and C-N bonds as also observed by FTIR. However ToF-SIMS analysis indicates the presence of contaminant layer (probably PDMS) that possibly influence the wetting behaviour of those coatings. A possible solution will be to repeat the coatings with a more careful sample handling or perform a treatment in hexane solution before surface characterization.

On the other hand, LIPOCER and AQUACER films reveal hydrophobic and hydrophilic character as declared by the manufacturer.

5. References

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