Optical characterization of composite layers prepared by plasma polymerization

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Abstract. Thin composite layers from polymer/nanoparticles (Ag-nanoparticles and detonation nanodiamonds) were prepared by plasma polymerization process on the base of hexamethyldisiloxane. The variation of the layer composition was achieved by changing the type of nanoparticles. The optical measurement techniques used were UV-VIS-NIR ellipsometry (SE), Fourier-transformed infrared spectroscopy (FTIR) and Raman spectroscopy. The values of the refractive index determined are in the range 1.30 to 1.42. All samples are transparent with transmission between 85-95% and very smooth. The change in Raman and FTIR spectra of the composites verify the expected bonding between polymer and diamond nanoparticles due to the penetration of the fillers in the polymer matrix. The comparison of the spectra of the corresponding NH₃ plasma treated composites revealed that the composite surface becomes more hydrophilic. The obtained results indicate that preparation of layers with desired compositions is possible at a precise control of the detonation nanodiamond materials.

1. Introduction

The producing of biomaterials that support appropriate cellular behavior and functions is critical for tissue engineering and cell therapy. There is a growing interest in functional organic/inorganic composites where a small amount of nanometer-sized material yields better physicochemical properties for cells [1, 2, 3]. Plasma polymers are easy to prepare by a well established technology of plasma polymerization. It has a long history of exploitation in a variety of applications, because it is non-toxic, transparent, with a very low surface tension, very good adhesion to any substrate, flexible, and it neither dissolves nor swells in a cell culture medium, insoluble in cold and hot solvents [4, 5, 6]. From the other hand nanodiamonds are of interest due to the combination of unique properties inherent to diamond and the specific surface structure of particles facilitating its functionalization [1].

In the present study the polymer/nanodiamond composite layers based on hexamethyldisiloxane and detonation-generated nanodiamond particles embedded into a polymer matrix, were prepared and characterized by UV-VIS-NIR ellipsometry, FTIR and Raman spectroscopy.

2. Materials

The substrates used were cover glass (CG) discs with a diameter of 15 mm.
In order to prepare composites with different properties we have used different types of nanoparticles. The detonation nanodiamonds (DND), synthesized by a detonation of carbon-containing explosives, are produced with particles of mostly 4 nm in size and can be easily modified by chemical reactions. In the present study the following diamond nanoparticles were used:

6-DND powder: The initial nanodiamond’s synthesis was carried out by use of carbon-containing explosive mixtures – conical cast charges consisting of TNT/RDX in ratio 70/30. The purification of the diamond powder was done as follows: boiling in a solution of stoichiometrically calculated amounts of potassium dichromate in sulfuric acid at 100-115°C, followed by several water washings and additional removal of metal impurities by HCl-treatment (80-100°C) and washing with water until pH=7.

Ag-DND powder: The ammonia complex of silver [Ag(NH₃)₂]⁺ was added to 6-DND-suspension under constant stirring at room temperature followed by adding of a dextrose solution. The temperature of the mixture was raised to 50°C until the Ag incorporation into the DND surface was finalized.

Si-DND powder: The silanization of 6-DND surface through an attachment of trimethylsilyl groups was done by mixing of a dehydrated 6-DND with ethyl acetate containing hexamethyldisilazane and trimethylchlorosilane[7].

Ag nanoparticles: “AgBion” (Ag-nano): prepared by bio-chemical synthesis in a form of colloidal solution of Ag-nano particles (3-16 nm in size), stable in various organic solvents (Dodecane and Octane) as well as in water and mixture of water-ethanol (stabilized by surface-active substances). “AgBion” have antibacterial, viral and fungus characteristics. Also it shows negative influence over mould and blue-green duckweed.

Plasma Poly-hexamethyldisiloxane (PPHMDS) films: prepared by plasma polymerization technology previously described [5]. The deposition of the composites was carried out in the same plasma polymerization equipment by the following procedure: the mixture of DND powder and HMDS was ultrasonically treated for 15 minutes before and during the plasma procedure.

In order to investigate the influence of chemistry of the composite surface on its properties the samples were subsequently treated by NH₃ plasma for 5 min in the same plasma reactor [7].

3. Characterization
The composite layers were characterized by UV-VIS-NIR ellipsometry (SE), FTIR and Raman spectroscopy.

3.1. UV-VIS-NIR ellipsometry (SE)
The measurements were performed using a variable angle spectroscopic ellipsometer (model VASE from the J. A. Wooman Co., Inc.) with 5 nm steps, in the spectral range of 190-1700 nm at the angles of incidence (AOI) for the composites of 56°, 57°, 58°. The model used for fitting the ellipsometric data is based on General Oscillator model and is composed of 2 Tauc - Lorentz and 6 Gauss oscillators.

3.2. Fourier-transformed infrared spectroscopy (FTIR)
FTIR spectra of the of PPHMDS and nanoparticles/PPHMDS composites were registered by Brucker FTIR spectrometer at ambient temperature in the range of 400 to 4000 cm⁻¹, using OPUS software, average of 64 scans and a resolution of 2 cm⁻¹. The assignment of the absorption bands was based on experience with organic compounds and the literature data.

3.3. Raman spectroscopy
Room temperature resonance Raman spectra of PPHMDS and DNDs/PPHMDS structures, grown on Si substrate were measured using a micro Raman spectrometer (Jobin-Ivon, HR 800) with a grating 600 gr/mm.

4. Results and Discussion

4.1. Optical transmission and refractive index
The optical transmission spectra of the composite films were measured with Woollam VASE ellipsometer in the wavelength range from 250 to 850 nm and the values are in the range of 85-95% as it is shown in figure 1. This is important for practical use when the coating needs to be seen transparent.

![Figure 1. Measured optical transmission spectra of the composite thin films as a function of wavelength.](image1)

An important optical characteristic of this type of materials is their refractive index. The highest refractive index belongs to the composite containing Ag nanoparticles as filler (figure 2, approximately 1.43 at 630 nm).

![Figure 2. The refractive index dispersion](image2)

The lowest refractive index is obtained for the samples where Ag modified nanodiamonds is (1.30 at 630 nm). It is shown that this physical property can be varied by changing the type of the particles used to fill the polymer network.

In table 1 summarized data of the experiments above as well as measurements for the thickness and roughness of the layers were shown. It is found that modification of the composite with ammonia plasma...
is possible to change its surface chemistry. This method for polymerization yields very smooth layers as shown in the table.

| No. | Samples Nomenclature | $d_{\text{film}}$ (nm) | $d_{\text{rough}}$ (nm) | MSE | Transmission, % | Refractive index |
|-----|----------------------|------------------------|-------------------------|-----|-----------------|-----------------|
| 1   | CG                   |                         | 3.14                    |      | 95              | 1.51            |
| 3   | PPHMDS               | 33.53                   | 0.0                     | 2.04 | 90              | 1.41            |
| 4   | PPHMDS_NH3           | 22.68                   | 0.0                     | 2.11 | 90              | 1.41            |
| 5   | Si_DND_PPHMDS        | 287.27                  | 2.2                     | 6.56 | 90              | 1.43            |
| 6   | Si_DND_PPHMDS_NH3    | 242.26                  | 1.1                     | 6.58 | 85              | 1.37            |
| 7   | Ag_DND_PPHMDS        | 106.51                  | 0.0                     | 2.70 | 89              | 1.32            |
| 8   | Ag_DND_PPHMDS_NH3    | 97.80                   | 2.1                     | 1.25 | 90              | 1.32            |
| 9   | Ag_nano_PPHMDS_Si    | 963.59                  | 20.5                    | 4.11 |                 | 1.43            |

4.2. FTIR spectra of the plasma polymer and composites.
For DND/PPHMDS films the characteristic peaks for sp$^3$ and sp$^2$ bonded C, new (C-Si-C) bonds and different CH$_3$ bonds proved the existence of both hydrophobic and hydrophilic centers. For Si-DND/PPHMDS composite definite peaks at around 500, 1200-1300, 1470 and 1600 cm$^{-1}$ pointed for an increased content of amorphous C. The appearance of an intensive peak at 550 cm$^{-1}$ in the spectrum of Ag-DND/PPHMDS, the splitting of the peak at 1550 cm$^{-1}$ into two peaks and the appearance of a broad band at 1800 cm$^{-1}$ confirmed the location of Ag ions at the grain boundaries of DND (figure 3a).

Figure 3. FTIR spectra of a) (1)PPHMDS; (2)6-DND/PPHMDS; (3) Si-DND/PPHMDS; (4) Ag-DND/PPHMDS; b) (1) PPHMDS/NH$_3$; (2) 6-DND/PPHMDS/NH$_3$; (3) Si-DND/PPHMDS/NH$_3$; (4) Ag-DND/PPHMDS/NH$_3$.

A change matrix of polymer characteristic bands is explained by the penetration of DND particles in the polymer. The comparison of the spectra of the corresponding NH$_3$ plasma treated composites revealed the decrease in intensity of the bands for methyl groups and the composite surface becomes more hydrophilic (figure 3b).
4.3. Raman spectra of the plasma polymer and composites.

For detailed analysis of characteristic bands, associated with bonding between the DNDs and PPHMDS, Raman microspectroscopy is used. In the figure 4a,b,c Raman spectra of DNDs/PPHMDS composites are presented.

![Raman spectra](image)

Figure 4. Raman spectra:

- **a)** (600 – 900 cm\(^{-1}\)):
  - 1) PPHMDS
  - 2) 6-DND/PPHMDS
  - 3) 7-DND/PPHMDS
  - 4) Ag-DND/PPHMDS
  - 5) Ag-DND/PPHMDS/NH\(_3\)

- **b)** (1200 – 1600 cm\(^{-1}\)):
  - 1) 6-DND/PPHMDS
  - 2) 7-DND/PPHMDS
  - 3) Ag-DND/PPHMDS
  - 4) Ag-DND/PPHMDS/NH\(_3\)

- **c)** (2800– 3000 cm\(^{-1}\)):
  - 1) PPHMDS
  - 2) 6-DND/PPHMDS
  - 3) 7-DND/PPHMDS
  - 4) Ag-DND/PPHMDS
  - 5) Ag-DND/PPHMDS/NH\(_3\)

The assignment of characteristic vibrational bands is based on a comparison with the results in [3, 8]. The repeating unit of PPHMDS is -(Si(CH\(_3\))\(_2\)-O)\(_{-}\) with an Si-O-Si backbone and methyl side group attached to Si atoms. The Raman shift related to CH\(_3\) vibration bands are as follows: 2967 and 2906 cm\(^{-1}\) (stretching) (figure 4c), 1413 and 1260 cm\(^{-1}\) (deformation) (figure 4b) and 865, 756, and 688 cm\(^{-1}\) (rocking) (figure 4a). Raman spectra related to the C-Si-C groups are 845 and 790 cm\(^{-1}\) (asymmetric stretching) and 706 cm\(^{-1}\) (symmetric stretching). All characteristic Raman vibration bands of PPHMDS are also present in DNDs/PPHMDS composites. A new relatively intensive band at 1450 cm\(^{-1}\) is observed in all composites containing DND (figure 4b). To appreciate the possibilities of DNDs to modify the structure and the nature of chemical bonding of the polymer matrix (PPHMDS) further
analysis of relative intensities of normal modes was performed following procedure described in [3].
The ratio of relative intensities \( \frac{I_{2967}}{I_{2985}} \) of CH\(_3\) was lower in the composites (DNDs/PPHMDS) in
comparison with PPHMDS. It was pronounced in the composites containing DND particles without any
modification (6-DND and 7-DND). Such a tendency of decreases was also present in the vibrations of
side chains (C-Si-C). The observed changes in Raman and FTIR spectra of DNDs/PPHMDS verify the
expected bonding between PPHMDS and DNDs nanoparticles.

5. Conclusion
Original technology for producing composites on the base of hexamethyldisiloxane and detonation
nanodiamond particles by plasma polymerization was developed. The characterization of the obtained
new materials proved that the nanoparticles were embedded in the polymer matrix. Moreover by varying
the type of diamond or silver nanoparticles in the polymer matrix and using ammonia plasma
modification, thin layers with desired properties could be obtained. The results are very promising for
applications of composites in biocompatible materials.

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