CARBON STRUCTURES AS EFFECTIVE MODIFIERS OF THE MATERIALS' BASIC PROPERTIES

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Abstract: Because of the unique energetic, refractive and photoconductive characteristics of effective nano-objects, especially carbon nanotubes, the modification of optical properties of the organic and inorganic materials can be considered as the preferable one via the use of the nanostructuration process. Emphasis has been given to the incorporation of nanoobjects directly in the materials' body and on their surface. Under the conditions of a surface treatment of the inorganic structures, an IR-laser at the wavelength of 10.6 micrometers was used to orientate carbon nanotubes deposited in the electric field of 100-600 V×cm^{-1}. Dramatic spectral and mechanical parameters changes have been found. Refractive features of the nanostructured organics have been studied via applying the second harmonic of the pulsed Nd-laser at different spatial frequencies and under the nanoparticles sensitization doping such as fullerenes, carbon nanotubes, shungites, quantum dots, and graphenes. A drastically obtained laser-induced refractive index has been established. A prediction has been proposed to extend the area of the application of the systems considered.

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Keywords: Carbon nanotubes, organics, inorganics, interface, refraction, laser-matter interaction

Introduction

It is well known that after the discovery of fullerenes (1985) and carbon nanotubes (1991), many scientific and research groups have conducted scrupulous studies on them and found different areas of applications of these nanoobjects and related ones (Bhattacharya et al., 2004, Yamamoto et al., 2004, Xu & Xiong, 2004, Yu et al., 2011, Taranko et al., 2012, Ciszewski et al., 2013, Asokan, 2013, Xi et al., 2014, Neyts & Erik, 2015,Guo et al., 2016). The peculiarities of the growth, the mechanisms of the sensitization, and the changes of the basic physic-chemical parameters have been tested. Our own steps in this direction occupy a significant place too (Kamanina, 2002, Kamanina, 2005, Kamanina & Uskokovic 2008, Kamanina et al., 2012, Kamanina et al., 2016). The main reason to use fullerenes, shungites, and quantum dots is connected with their unique energy levels and high value of electron affinity energy. The basic features of carbon nanotubes, graphene, graphene oxides are their branched surface, high conductivity, strong hardness of their C—C bonds as well as complicated and unique mechanisms of charge carrier moving. These features of the mentioned perspective nanoobjects can provoke, the discovery of new physical and technology ways to optimize the photorefractive, photoconductive and dynamic parameters of organic conjugated polymers, monomers and liquid crystal (LC) systems via nanoobjects sensitization. For example, due to its ability to enhance the polarization of the composites the sensitization process (connected with the activation of the intermolecular charge transfer complex formation) permits to increase the speed of the LC elements (from 8-16 ms to 1-2 ms and less for the structured nematic LC) and to improve the photorefractive features, such as can be seen in the laser-induced refractive index Δn from the value of 10^{-5} up to 10^{-3}-10^{-2}. It also increases the surface mechanical hardness, laser strength as well as the wetting angle of the inorganic materials.

In the current paper, some evidence will be shown of the increase of the transparency of some inorganic materials and their mechanical and wetting features will be discussed as well as the modification of the organics' refractive properties by checking the increase of the laser-induced refractive index.

Experimental conditions, materials and results: inorganic system modification

It should be mentioned that to modify the properties of the inorganic materials via their surface treatment, the carbon nanotubes have been deposited on the material surface using an IR CO_2-laser with *p*-polarized irradiation at a wavelength of 10.6 μm and power of 30 W. Moreover, when single wall carbon nanotubes (SWCNTs) have been placed at the materials interface, an electric field up to 100-600 V×cm^{-1} was applied in order to orient the nanotubes during the deposition process. The spectra of the nanotube-treated materials have been obtained using Perkin-Elmer Lambda 9 and

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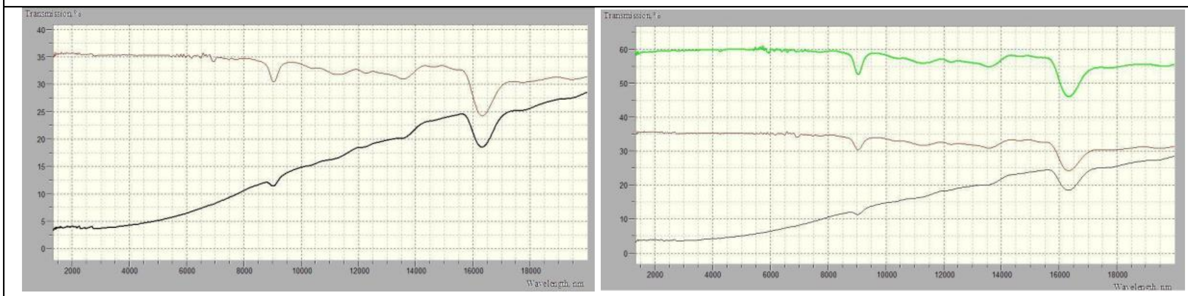
Furrier FSM-1202 instruments. Surface mechanical hardness was revealed using the CM-55 instrument as well as via using of the microhardness device PMT-3M (“LOMO,” Saint-Petersburg). The laser strength was checked with a pulsed nanosecond Nd-laser. The special accent was given to observe the relief at the material surface via checking the wetting angle. In this case the camera with parameters as Compact F1.6 1/3 CS Mount 6.0-60 mm Manual Focal Iris Zoom Lens for CCTV Camera (Black) was applied.

Si materials spectra and hardness

As an effective material in the application of solar energy and as the perspective photosensitive layer in the spatial light modulators operated in the reflective mode, the Si structure was treated. Using a laser deposition technique and as a method to orient the carbon nanotubes (Kamanina & Vasilyev, 2009, Kamanina & Vasilyev 2010), the essential increase of the transparency of the Si materials was obtained as well as the increase of the micro hardness was shown. The quantum chemical calculation based on the LAMMPS program (Plimpton, 1995, Tersoff, 1989) was made to support the different penetration of the CNTs depended on the different CNTs diameter and varied their speed. The data are shown in Figure 1 and 2 and in Table 1.

Figure 1: Transmittance spectra of the pure Si (lower curve) and Si covered with the vertically aligned CNTs (upper curve), *a*. Transmittance spectra of the pure Si (lower curve), Si covered with the vertically aligned CNTs (middle curve), and Si covered with the graphene (upper curve), *b*.



a *b*

Source: Authors

Analysing the spectral dependence (see Figure 1*a*), one can see that the transparency of the Si materials has drastically increased in the IR range from 2 to 16 micrometres. It should be noted that the refractive index, for example of CNTs, is close to 1.01-1.1 (Yang et al., 2007), thus the Fresnel loses are decreased dramatically. Furthermore, the spectral range of the inorganic materials which surfaces’ can be treated with carbon nanoparticles, such as CNTs, can be extended to the IR spectral range due to the fact that the imaginary part of the dielectric constant of the CNTs (responsible for absorption) is close to zero in the near IR and the middle IR-ranges. Moreover, based on the data in Figure 1*b*, the advances of the graphene layer as a promising coating can be suggested. It permits to propose that the graphene treated systems can be effective elements in optoelectronic devices when the transparency of the devices should be dramatically increased. Furthermore, this can be proposed for the laser technique too, for example, when the thickness of the key layers of the optically addressed spatial light modulators should be decreased and the mobility for the charge should be increased. It should be noticed that the increase of the charge carrier mobility is an important parameter for the solar energy elements and the battery as well.

Analysing the mechanical properties (see Table 1), one should take into account the fact that the coupling length between the Si-Si atom is large (0.23-0.235 nm), in comparison with the length of C-C bond in the carbon nanotubes (~ 0.139-0.143 nm), thus the hardness of silicon is much less than carbon nanotubes. This can be improved and optimized with the laser deposition of carbon nanotubes because of their unique physical and chemical properties and very high Young's modulus with the values placed in the range of some terra Pa (Namilae et al., 2004). Thus, a 7.7% increase of the micro hardness can be found. Moreover, the roughness of the pure Si sample (RMS, nm) was 0,206; 0.219; 0.200 in comparison to the optimized Si treated with CNTs: 0,160; 0.165; 0,169. In addition, the data for the Ge micro hardness improvement, for the comparison, has been presented (see Table 1).

Figure 2: Penetration depth change due to the CNTs diameter variation and the velocity of the CNTs deposition increase on the Si surface

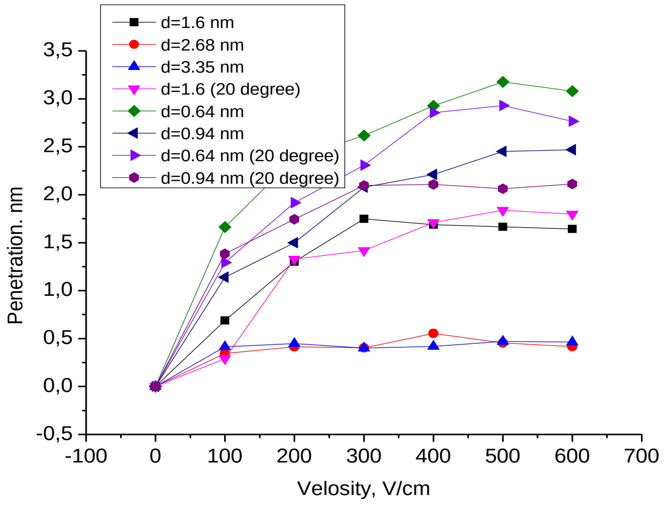


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Table 1: Micro-hardness of the pure and CNTs treated Si and Ge at the indenter force ~30g

Materials	Micro-hardness, Pa	Materials	Micro-hardness, Pa
Si	1.189×10^{9}	Ge	0.897×10^{9}
Si+CNTs	1.281×10^{9}	Ge+CNTs	0.943×10^{9}

Source: Author

ITO coating spectra, laser strength and hardness

In this paragraph, the emphasis was given on the modification of the ITO-conducting layers because these structures have a very broad area of application in the solar energy, biomedicine, display, laser, and general telecommunication systems areas (Vasilev et al., 1987, Kamanina & Vasilenko, 1997). Some problem with increase of the transparency, mechanical and laser strength have been existed. For example, the transparency connected with the annealing temperature, the laser strength coincided with the mechanical hardness, etc. Thus, the nanostructuration process permits us to find new ways to resolve the problem mentioned above. The data shown in Figures 3 and 4 as well as in the Tables 3 and 4 support the spectral evidence, the mechanical, laser, resistance and wetting features as well.

Figure 3: Transmittance spectra of the ITO-layer covered with the vertically aligned CNTs under the application of different electric fields.

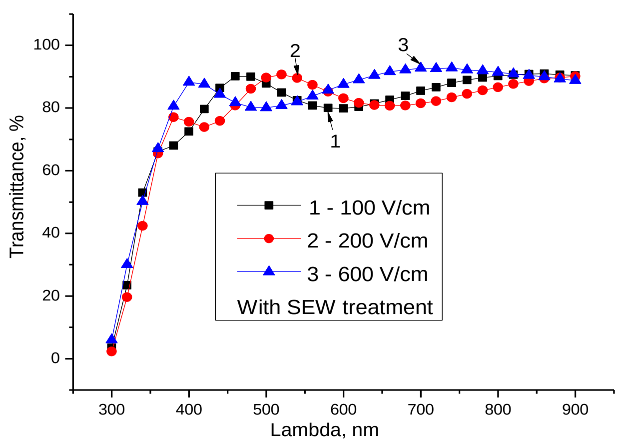

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Figure 4: Model picture of the CNTs-ITO surface obtained via a quantum-chemical simulation

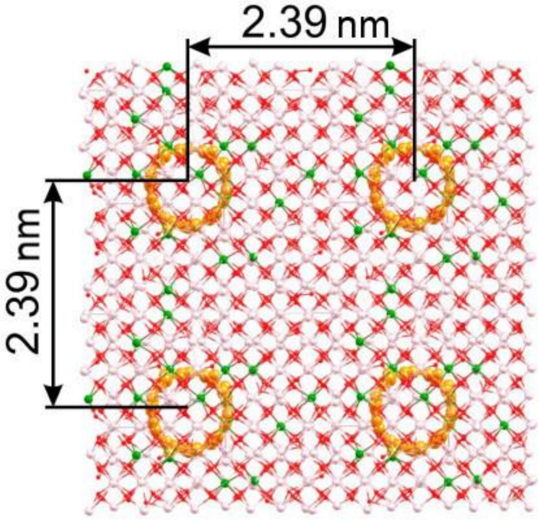

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Table 2: Comparative micro-hardness of the pure and CNTs treated ITO-conducting layers

Materials	Micro-hardness, Pa	Micro-hardness increase, times
ITO	2.2×10^{9}	0
ITO+CNTs	3.5×10^{9}	~1.6
ITO+CNTs+SEW	4.7×10^{9}	~2

Source: Author

One can see from the Figure 3 data that the structuration of the ITO surfaces with oriented CNTs provokes the shift of spectral parameters. Moreover, the data from Figure 4 shows that the effect has been coincided with the formation of the link between the carbon atom and the atomic layer of the ITO surface. It should be noted that the quantum chemical calculation was made based on the LAMMPS program (Plimpton, 1995, Tersoff, 1989). Moreover, it supports the dependence of the penetration depth on the diameter and the speed of the CNTs placed on the ITO surface via the oriented laser deposited technique. The ITO-relief obtained can be sufficiently used in the display technique due to the fact that the modified relief at the ITO surfaces can be considered as the conducting layer with the decreased resistivity, from one side. But, this relief can be used as the orienting one to align the LC-dipole with good advantage as well.

Analysing the data shown in Table 3 one can see that the strength of the ITO-conducting layer can be successfully increased via the CNTs treatment. It should be mentioned that traditionally the researchers have used the HfO_2-coatings deposited on the ITO surface to eliminate their roughness and increase the strength, but the CNTs modification can lead to better results.

Table 3: Comparative laser strength of the pure and CNTs treated ITO-conducting layers

Materials	Energy density, $J\times cm^{-2}$	Energy density provoked the destruction of the layer, $J\times cm^{-2}$
ITO	0.3-0.4	0.65
ITO+CNTs	0.6-0.7	~0.75
ITO+CNTs+SEW	0.9	~1.5

Source: Author

According to the change of the wetting angle of the pure and structured ITO-layers it should be noted that the wetting angle can be increased from 70-75 degrees up to 85-89 degrees.

Thus, using this consideration based on the Si and ITO materials study, the CNTs laser treatment can be proposed as an innovative way to modify the important physic-chemical characteristics of this type of the inorganic material.

III. Experimental conditions, materials and results: organic system modification

The laser-induced change of the refractive index has been studied at the wavelength of 532 nm under Raman-Nath diffraction conditions (Kamanina & Vasilenko, 1997, Kamanina & Vasilenko, 1995Kamanina et al. 2015). The Raman-Nath diffraction condition is realized in the case when the recorded grating period is larger than the thickness d of the treated sample. Beam energies incident on and transmitted through the sample in first-order diffraction can be measured. The experiments have been made at a nanosecond pulsed regime at the spatial frequency of 90–130 mm^{-1} and at the laser energy density ranged from 0.01 to 0.6 $J \cdot cm^{-2}$. The technical experimental scheme has been analogous to that it can be explained in detail (Kamanina & Vasilenko, 1997, Kamanina & Vasilenko 1995) and was recently shown in (Kamanina et al., 2015) in the modified variant.

3.1. Polyimides, pyridines, LC structures laser-induced change of the refractive index

It should be mentioned that in order to analyze the refractive processes of the organic materials spatially, one it should take into account that when the electric field of the laser wave is less than the intra-atomic electric field correlated with the electron charge and with the Bohr radius, we should estimate the linear effect. But, when the electric field of the laser wave is larger than the intra-atomic electric field, we should draw attention on the nonlinear optical features. Using this aspect, the values of optical susceptibility play important roles in thr nonlinear optical effect. Really, the most important optical characteristic in this case is the induced dipole, whose can be expressed through dipole polarizabilities $\alpha^{(n)}$. These are in turn related to the proportional dependence to the nonlinear susceptibility $\chi^{(n)}$ and to the local volume υ of the materials (media). Thus, laser-matter interaction provokes the change in polarization of the media and predicts the change in such properties as dynamic, photorefractive and photoconductive ones.

To predict the change of the cubic nonlinearity $\chi^{(3)}$, as the minimum media local volume polarizability (Kamanina, 2005, Kamanina & Uskokovic, 2008, Kamanina et al., 2012, Kamanina et al., 2008), the laser-induced change of the refractive index Δn_i can be calculated from the diffraction efficiency η (Kamanina et al., 2015, Kamanina et al., 2008, Akhmanov & Nikitin, 1997) via realization of the Raman-Nath diffraction conditions ($\Lambda^{-1} \geq d$) using the equation (1):

$$\eta = \frac{I_1}{I_0} = \left(\frac{\pi \Delta n_i \mathrm{d}}{2\lambda} \right)^2 \quad . \tag{1}$$

Here Δn_i is the induced change of the refractive index, I_1 is the intensity in the first diffraction order, I_0 is the input laser intensity, d is the thickness of the medium, λ is the wavelength of the light incident on the medium, Λ is the spatial frequency.

The basic data of the laser-induced change of the refractive index of the materials studied are shown in Table 4.

According the studied nonlinear features of the polyimide, etc. materials with different nanosensitizers, it can be predicted that new composite materials can be considered in order to establish the dramatical nanoparticles influence on the photorefractive features of the organic conjugated matrixes and to apply the organic materials to the holographic recording, laser frequency conversion, switching, as well as for the testing of the dynamic properties of the modified composites and their possible application in general telecommunication systems and in biomedicine instead of the volumetric inorganic materials.

Conclusion To summarize the results, one can state that:

- Structuration of the inorganic material surfaces (based, for example, on the Si and ITO structures) has predicted the change in the spectral, mechanical and wetting features. The increase of the transparency, hardness, and wetting angle has been revealed.

- Structuration of the inorganic material surfaces based on ITO has shown and supported the essential decrease of the resistivity. It can incite the decrease of the applied voltage when these ITO coatings are considered as the transparent conducting layers in the spatial light modulators.
- Structuration of the inorganic material surfaces based on ITO via the CNTs oriented laser deposition technique can form possible quasi-graphene layers which can explain the change of the ITO resistivity due to the large charge from the core of the CNTs and their donor-acceptor properties.
- Sensitization of the organic materials by the studied nanoparticles has revealed the change of the laser-induced refractive index that is larger than the ones obtained for the pure matrixes.
- Sensitization of the organic materials by the studied nanoparticles has provoked the change of the laser-induced refractive index that is compared or larger than the ones obtained for the classical inorganics matrixes.
- The area of the applications of the materials which body and interface can be modified with effective nanoparticles can be extended essentially.

Table 4: Change in the refractive index Δn_i of the studied sensitized organics

Materials	Nano-object content, wt.%	Energy density, J×cm^{-2}	Δn_i
Pure polyimide	0	0.5-0.6	10^{-4}-10^{-5}
Polyimide +QDs CdSe(ZnS)	0.003	0.2-0.3	2.0×10^{-3}
Polyimide+graphene oxide	0.05	0.2	2.7×10^{-3}
Polyimide+graphene oxide	0.1	0.2	3.4×10^{-3}
Polyimide+C_{60}	0.2	0.5-0.6	4.2×10^{-3}
Polyimide+C_{70}	0.2	0.6	4.68×10^{-3}
Polyimide+shungite	0.1	0.5	3.46×10^{-3}
Polyimide+shungite	0.2	0.1	5.3×10^{-3}
Polyimide+CNTs	0.1	0.5-0.6	5.7×10^{-3}
2-cyclooctylamino-5-nitropyridine (COANP)+C_{60}	5	0.9	6.21×10^{-3}
COANP+C_{60}	5	0.9	6.89×10^{-3}
LC+polyimide+C_{70}	0.2	0.1	1.2×10^{-3}
LC+COANP+C_{70}	5	17.5×10^{-3}	1.4×10^{-3}
LC+COANP+C_{70}	1	30×10^{-3}	1.45×10^{-3}

Source: Author

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