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STUDY OF MECHANICAL AND SPECTRAL PROPERTIES OF ORGANIC AND INORGANIC NANOOBJECTS

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Abstract— **This article presents new results in the directions: improvement of the mechanical and spectral properties of the inorganic materials via covering them with nanotubes; improvement of the photorefractive and photoconductive features of the organic structures doped with fullerenes and carbon nanotubes. The first direction is connected with dramatic increase in mechanical hardness and laser strength as well as in decrease of roughness of the UV and IR-soft materials, some oxides based on In and Sn, some metals, etc., when these materials have been covered with oriented nanotubes. The second one is regarded to correlation of the nonlinear optical and photoconductive characteristics of the organics doped with fullerenes or nanotubes. The data presented in the paper testified that these nano-objects-containing materials could be used as new transparent optical elements, new laser window for the UV and IR spectral range, and new 3D-media for the broad spectral range. Moreover, the materials studied can be used as new structures for automobile, medicine and information processing systems.**

Keywords— **Inorganic materials, Fluorides, Nanotubes, Fullerenes, Conjugated Structures, Laser-matter interaction**

I. INTRODUCTION

Optoelectronics, telecommunication systems, aerospace, and correction of amplitude-phase aberration schemes, as well as laser and display techniques have revealed the fullerenes and carbon nanotubes features to be apply as good candidate for the modifications of the characteristics of the inorganic and organic materials. At present time so many scientific and research groups have found different aspects of strong hardness of nanotubes C—C binding and the unique energetic levels and high electron affinity energy of fullerenes [1-3].

In the present paper new mechanical and laser properties have been observed when inorganic soft materials of the UV and IR spectral range or some oxides and metals have been treated with carbon nanotubes. The structures without interface between matrix materials and coatings have been obtained. The dramatic increase in surface mechanical hardness (this parameter can be improved in 2-10 times) has been found. Moreover, the mechanical and laser features have been observed under conditions of saving or improvement of the spectral range. Moreover, the correlation between photoconductive and nonlinear optical parameters of the organic conjugated systems has been revealed. As an additional, the nonlinear refraction and cubic nonlinearity (the last parameter is responsible for the change in the local volume polarizability) of the organic materials doped with nanoobjects have been studied via laser four-wave mixing technique.

II. EXPERIMENTAL CONDITIONS

As the inorganic matrixes, the MgF_2, LiF, silicon glass, ITO coatings, Ta, Ti, etc. materials have been considered. As effective nanoobjects, the single wall carbon nanotubes (SWCNT) have been used. It should be mentioned that the carbon nanotubes have been placed on the material surface using IR CO_2-laser with *p*-polarized irradiation at wavelength of 10.6 μm and power of 30 W. Moreover, when SWCNT have been placed at the materials interface, the electric field up to 100-200 $V\times cm^{-1}$ has been applied in order to orient the nano tubes during the deposition process. The relief obtained after carbon nano tubes deposition is shown in Fig.1. After that some structures have been additionally treated with surface electromagnetic waves (SEW) in order to obtain homogeneous surface with promising roughness. The relief of the surface after SEW treatment is shown in Fig.2. The spectra of the nano tubes-treated materials have been obtained using Perkin-Elmer Lambda 9 instrument. Surface mechanical hardness has been revealed using the CM-55 instrument. The test has been made using silicon glass K8 as etalon. This etalon permits to obtain abrasive hardness close to zero at 3000 cycle with forces on indenter close to 100 g. The scheme to treat the nano structured inorganic in order to estimate the surface hardness is shown in Fig.3.

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As the organic matrix, the conjugated polymer and monomer materials have been chosen. Polyimide (PI), 2-cyclooctylamine-5-nitropyridine (COANP) compounds, polyaniline (PANI), as well as fullerenes C_{60}, C_{70} and carbon nanotubes have been studied. Fullerenes thin solid films have been made by laser vacuum deposition technique. Polyimide and other organics films have been prepared from 3–6.5% solutions in tetrachloroethane, chloroform, or benzene by centrifugal method. The films have been modified by adding fullerenes C_{60}, C_{70}, and carbon nanotubes with the concentrations varied from 0.05 to 0.5 wt % relative to the photosensitive polymer component. The organics conjugated films have been placed onto glass substrates covered with transparent conducting layers based on ITO contacts. For the electric measurements, gold contacts have been applied to the upper side of the film surface. The bias voltage applied to the photosensitive polymer layers has been varied from 0 to 70 V. The current–voltage characteristics have been measured for the samples with various concentrations of fullerene and nanotubes under the conditions from dark to variable illumination intensity. The photorefractive characteristics have been studied using four-wave mixing technique. The second harmonic of pulsed Nd-laser at wave length of 532 nm has been used. The energy density has been chosen in the range of 0.1-0.9 $J{\times}cm^{-2}$. The nanosecond laser regimes have been applied. The amplitude-phase thin gratings have been record under Raman-Nath diffraction conditions at spatial frequency of 90 and 150 mm^{-1}. The experimental scheme has been analogous to that presented in paper [4].

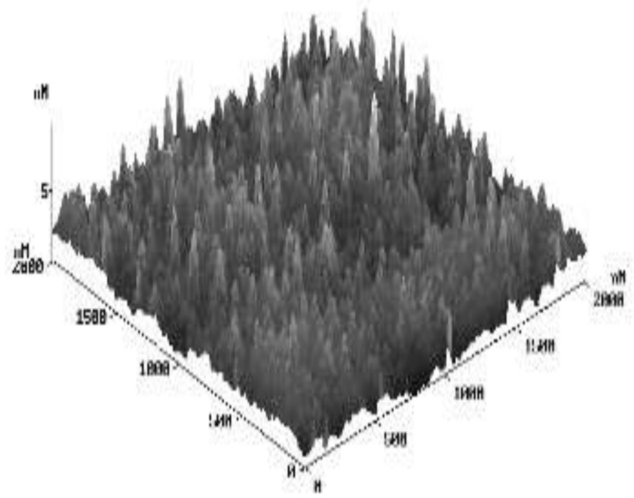

Fig.1. AFM-image of the nanotubes-covered silicon glass

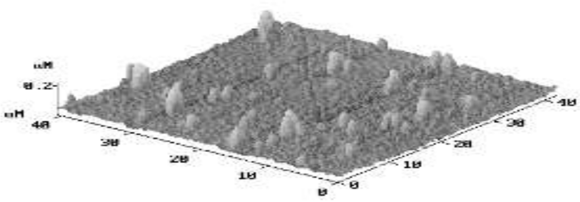

Fig.2. AFM-image of the surface relief after SEW treatment

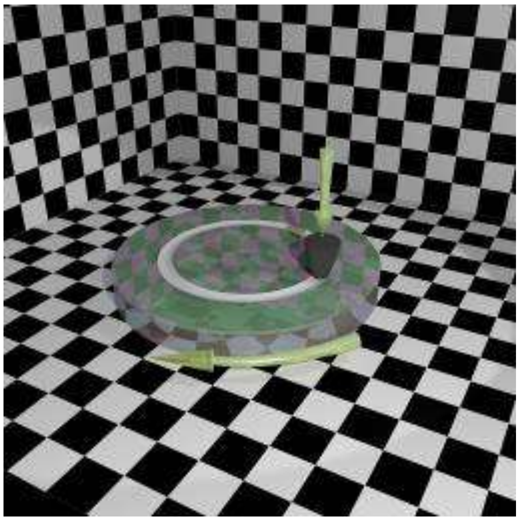

Fig.3. The general view of the principle to obtain the abrasive surface hardness of the materials

III. EXPERIMENT AND RESULT

It should be noticed that search for the new nanostructured compounds operated in the broad spectral range, including deep UV and middle IR, and having good mechanical and laser properties is the complicated task of the scientific and technological research. Some steps to reveal the improved characteristics of such type of the materials have been shown in paper [3].

Let us consider the magnesium fluoride as the model systems. For this structure the spectral characteristics, atomic force microscopy data, measurements to estimate the hardness and roughness have been found in good connection. The main aspect has been made on interaction between nanotubes (their C—C bonds) placed at the MgF_2 surface via covalent bonding [3]. As the results of this process, the refractive index can be modified that explains the increase in transparency in the UV.

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Moreover, the spectral range saving or increasing in the IR range can be explained based on the fact that the imaginary part of dielectric constant of carbon nanotubes, which is responsible for the absorption of the nanoobjects, is minimum (close to zero) in the IR range. The UV-VIS and near IR-spectra of the magnesium fluoride is shown in Fig. 4. One can see from Fig. 4, that some defects can be eliminate after SEW treatment (please see curve 1 and 2) and better transmission can be observed in the UV range (please see curves 3 and 4) for the magnesium fluoride covered with nanotubes. Moreover, the nanostructured samples reveal the better surface hardness. Really, after nanotubes placement at the MgF_2 surface the surface hardness has been better up to 3 times in comparison with sample without nanotreatment. The data is shown in Table 1.

Table 1. AFM results to estimate the roughness of nanostructured magnesium fluoride

	Roughness before nanotreatment	Roughness after nanotreatment	Remarks
R_a	6.2	2.7	The area of 5000×5000 nm has been studied via AFM method
S_q	8.4	3.6	

Table 2. Surface mechanical hardness of some materials after nanotubes deposition

Structures	Abrasive surface hardness (number of cycles before visualization of the powder from surface)	Remarks
Pure organic glasses	200-400 cycles	CM-55 instrument has been used. The test has been made using silicon glass K8 as etalon. This etalon permits to obtain abrasive hardness close to zero at 3000 cycle with forces on indenter close to 100 g.
organic glasses +nanotubes	1500-3000	
BaF_2	200	
BaF_2 + nanotubes	3000	
CaF_2	500	
CaF_2 + nanotubes	2500-3000	
MgF_2	1000	
MgF_2+ nanotubes	3000	

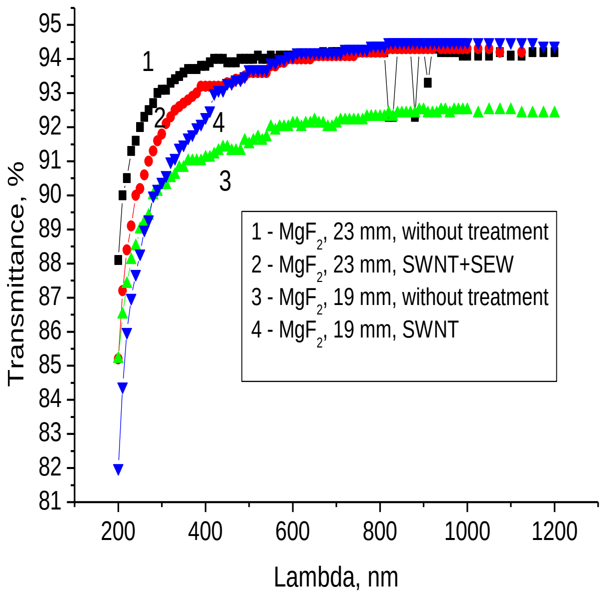

Fig.4. UV-VIS and near IR spectra of MgF_2 structures

Fig.5. The diffraction orders recorded under Raman-Nath diffraction conditions

It should be mentioned, that as an additional, the laser strength of the ITO contacts (which can be used as conductive coatings for solar energy cell or as the contacts of spatial light modulators and display elements) has been increased from 0.3-0.5 to 1.2-1.5 J×cm^{-2}. The experiment has been made using the pulsed Nd-laser. The results testified that the laser strength of the ITO coatings covered with nanotubes in 5 times larger than the ones estimated for the ITO without nanotreatment. Moreover, some metals, such as Ta and Ti have revealed the better roughness after nanotubes depositions and treatment with SEW. The R_a and S_q parameters have been increased up to 2-3 times.

III Study the properties of the organic materials with fullerenes and nanotubes

Table 3 presents the comparative data (Ref.5, etc.) of laser-induces change in the refractive index for the previous experiments (with fullerenes sensitization) and the current ones (with nanotubes sensitizations) of organics based on polyimides. Laser-induced change in the refractive index Δn_i has been calculated via equation (1). It has been based on measurement of the diffraction efficiency η [6]:

$$\eta = I_1/I_0 = (\pi \Delta n_i d/2\lambda)^2, \quad (1)$$

where I_0 and I_1– intensity in the zero and in the first diffraction orders, d – thickness of the media, λ – the wavelength of the laser irradiation. Fig.5 demonstrates the distribution of the diffraction orders in the focal plate of the lens behind the sample.

One can see from Table 3, that at less value of energy density (0.3 J×cm^{-2} in comparison with previous ones of 0.6 J×cm^{-2}) and at lager spatial frequency (Λ=150 mm^{-1} in comparison with spatial frequency of Λ=90 mm^{-1}) the following values of laser-induced change in the refractive index Δn_i have been obtained: 5.0×10^{-3} – for the sample with concentration of the nanotubes of 0.07 wt.%; and 5.5×10^{-3} – for the sample with concentration of the nanotubes of 0.1 wt.%. This fact can be explained by the additional mechanism involved in photorefractive processes and connected with the charge carrier moving of odd nanotubes electrons in comparison with fullerenes ones. Really, we should taken into account the 7 ways for the charge carrier moving: 1 – along the nanotubes, 2 – across the nanotubes, 3 – between the nanotubes, 4 – inside the nanotubes if they are the multiwall ones, 5 and 6 – between the organic conjugated molecules and nanotubes under the conditions of different relation of electron affinity energy of the organic molecules and nanotubes, 7 – inside the organic molecules, when the donor-acceptor interaction have been revealed. It should be noticed that the photoconductive parameters of the PI structures with fullerenes and nanotubes have been correlated with the nonlinear optical ones. It should be noticed that the increase in the dark and photocurrent for the PI with concentration of the nanotubes close to 0.07 wt.% has been larger than that studied before for the pure PI or PI with fullerenes. The value of the dark current for the pure PI film is close to 10^{-13} A. Thus, more than 10^{4}-10^{5} times increase in the current has been found for the PI structures doped with nanotubes. A little bit larger value of the current has been revealed for the PI with 0.1 wt.% of the nanotubes. It should be mentioned, that current-voltage dependences have been connected with the laser induced change in the refractive index for the PI systems doped with nanotubes.

Table 4 presents the basic results regarded the nonlinear refraction n_2 and third order nonlinearity (cubic nonlinearity $\chi^{(3)}$). The data show the nonlinear parameters estimated by scientist in papers [7-19] and data of the current experiments. It should be mentioned, that in the current experiments made using four-wave mixing technique, the nonlinear refraction coefficient and cubic nonlinearity have been estimated via equations (2) and (3):

$$n_2 = \frac{\Delta n_i}{I} \quad (2)$$

$$n_2 = \frac{16\pi^2}{n_0 c}\chi^{(3)}, \quad (3)$$

where I – is the irradiation intensity, n_0 – is the linear refractive index of the media, c – is the speed of the light.

One can see from the data of Table 4 that nonlinear optical parameters of the nanoobjects-doped conjugated structures are larger than those obtained for traditional nonlinear systems that permit to apply these materials as effective holographic recording element in passive and active mode, as spatial light modulator, as switchers, as nonlinear absorber in the visible and in the near-infrared spectral ranges, as new 3D-media.

IV CONCLUSION

To summarize the results, it should be taken into account, that influence of the nanoobjects based on fullerenes and carbon nanotubes on mechanical, spectral, photoconductive, and nonlinear optical characteristics have been studied. The correlation between photorefractive and photoconductivity has been observed. Moreover, based on four-wave mixing technique the comparative studies of the nonlinear refraction and cubic nonlinearities have been found for the pure fullerenes films, nanotubes films and some conjugated nanostructured organic films. As the results of comparative investigations, the area of applications of the materials treated can be found in the optoelectronics and laser optics, for example, for gas storage and solar energy accumulation, for automobile area and medicine, as well as in nonlinear optical field and search for 3D-media.

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Table 3. Comparative data of laser-induced change in the refractive index

Structure studied at the spatial frequency	Nano-objects content wt.%	Wavelength, nm	Energy density, J×cm^{-2}	Spatial frequency, mm^{-1}	Laser pulse width, ns	Laser-induced change in the refractive index, Δn	References
Pure polyimide	0	532	0.6	90	20	10^{-4}-10^{-5}	[5]
Polyimide+C_{70}	0.2	532	0.6	90	10-20	4.68×10^{-3}	[5]
Polyimide+nanotubes	0.07	532	0.3	150	10	5.0×10^{-3}	Current
Polyimide+nanotubes	0.1	532	0.3	150	10	5.5×10^{-3}	Current

Table 4. Nonlinear optical characteristics of the materials studied

Structure	n_2, cm^2 W^{-1}	$\chi^{(3)}$, cm^3 erg^{-1} (esu)	Ref.
CS_2 SiO_2	3×10^{-14} 3×10^{-16}	10^{-12} 10^{-14}	[7] [7]
C_{60} film		2×10^{-10}	[8]
C_{70} film		2.6×10^{-11}	[9]
C_{60} film	0.43×10^{-9}	1.2×10^{-8}	Cur.1
Carbon nanotubes film	0.6×10^{-9}	0.125×10^{-7}	Cur.2
Cu - phthalocyanine		$2.1\pm0.2\times10^{-12}$	[10]
Pb - phthalocyanine		2×10^{-11}	[11]
α-TiO-phthalocyanine		1.59×10^{-10}	[12]
Polyimide - C_{70}	0.78×10^{-10}	2.64×10^{-9}	[13,14]
Polyimide - C_{70}	-1.2×10^{-9}	1.9×10^{-10}	[15]
Polyimide+nanotubes	0.114×10^{-10}	0.39×10^{-9}	[16]
Polyimide+nanotubes	0.17×10^{-10}	0.6×10^{-9}	Cur.3
Polyimide+nanotubes	0.18×10^{-10}	0.62×10^{-9}	Cur.4
2-cyclooctylamine-5-nitropyridine (COANP)- C_{60}	$0{,}69\times10^{-10}$	$2{,}14\times10^{-9}$	[17]
COANP - C_{70}	$0{,}77\times10^{-10}$	$2{,}4\times10^{-9}$	[17, 18]
PDLC based on COANP- C_{70}	1.6×10^{-9}	4.86×10^{-8}	[19]
Si	10^{-10}	10^{-8}	[7]
Liquid crystal	10^{-4}	10^{-3}	[7]