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1. Introduction

After discovery of the fullerenes, carbon nanotubes and quantum dots, many scientific and research groups have found different area of applications of these nano-objects. The main reason to use the fullerenes and quantum dots is connected with their unique energy levels and high value of electron affinity energy. The basic features of carbon nanotubes are regarded to their high conductivity, strong hardness of their C—C bonds as well as complicated and unique mechanisms of charge carrier moving. These peculiarities of carbon nanotubes and their possible optoelectronics applications will be under consideration in this topic with good new advantage.

In this section of the book the features of some nano-objects have been considered in order to apply and to recommend them in the extended area of laser, display, telecommunications, medicine, etc. technique.

1.1 Homeotropic alignment of nematic liquid crystals elements using carbon nanotubes

It is well known that mostly liquid crystal (LC) cells, which can be considered as display pixel, operate in S and T configurations that realize a planar orientation of the LC mesophase on the aligning substrate surface. However, the solution of some problems, where the initial black field is necessary for the regime of light transmission through the cell structure, requires a homeotropic alignment of LC molecules on the substrate. Homeotropic alignment is frequently obtained using surfactants, such as lecithin, fused quartz, etc. [1,2]. A new alternative method for obtaining a surface nanorelief that favors the homeotropic alignment of an LC mesophase is offered by the so-called nanoimprinting technology [3].

Realization of this method, while making possible the formation of a surface relief with a good optical quality, requires the use of toxic substances, in particular, acids. Recently a new method for the homeotropic alignment of LC molecules has been proposed [4]. It is based on a contactless technique of relief formation on the surface of a glass (quartz) substrate using the deposition of carbon nanotubes (CNTs) and their additional orientation in an electric field. The procedure can be briefly shown as follows. This treatment has been made when glass or quartz substrates have been used. These substrates have been covered with ITO contact and then with CNTs using laser deposition technique. As an additional, CNTs have been oriented at the electric field close to 100-250 V×cm⁻¹. To decrease the
roughness of the relief the surface electromagnetic wave (SEW) treatment has been used. SEW source was a quasi-CW gap CO\textsubscript{2} laser generating \(p\)-polarized radiation with a wavelength of 10.6 micrometers and a power of 30 W. The skin layer thickness was \(\sim\)0.05 micrometers. The relief obtained before and after SEW treatment of the CNTs layers is shown in figure 1a and b.

![Figure 1](image)

**Fig. 1.** New orientation relief obtained after laser deposition oriented CNTs: before (a) and after (b) SEW treatment.

The homeotropic alignment of LC molecules was studied using two sandwich type cells with an nematic LC mesophase confined between two glass plates. The reference cell represented a classical nematic LC structure, in which the alignment surfaces were prepared by rubbing of polyimide layers. In the experimental cell, both alignment surfaces were prepared using CNTs as described above. Experiments with the second cell confirmed that a homeotropic alignment of the LC molecules was achieved. The results of these experiments are presented in the table 1. The spectral data in a 400–860 wavelength range were obtained using an SF-26 spectrophotometer. Reference samples with planar alignments and homeotropically aligned samples prepared using the new nanotechnology of substrate surface processing were mounted in a holder and the transmission of both cells was simultaneously measured at every wavelength in the indicated range. It should be noted that the two cells had the same thickness of 10\(\mu\)m and contained the same nematic LC composition belonging to the class of cyanobiphenyls. The experimental data were reproduced in several sets of cells. The spectral results are shown in table 1. Thus, the new features of CNTs have been demonstrated in order to obtain the initial black field of LC cells using a homeotropic orientation of LC molecules on CNTs relief. The results of this investigation can be used both to develop optical elements for displays with vertical orientation of NLC molecules (for example, in MVA-display technology) and to use as laser switcher.

### 1.2 Polarization elements for visible spectral range with nanostructured surface modified with carbon nanotubes

The functioning of various optoelectronic devices implies the use of polarization elements. As it is known, the operation of polarization elements is based on the transverse orientation of fields in electromagnetic waves. Polarization devices transmit one component of the natural light, which is parallel to the polarizer axis, and retard the other (orthogonal) component. There are two main approaches to create thin film polarizers. The first method employs metal stripes deposited onto a polymer base. The metal layer reflects the incident light, while the polymer film transmits and partly absorbs the light, so that only the light of a certain polarization is transmitted. Another method is based on the creation of...
Carbon Nanotubes Influence on Balk and Surface Properties of the Optical Materials

| Wave-length, nm | Transmission, % | Wave-length, nm | Transmission, % |
|----------------|----------------|----------------|----------------|
|                | reference cell (planar) | experimental cell (homeotropic) | reference cell (planar) | experimental cell (homeotropic) |
| 400            | 0               | 0              | 460            | 11.1             |
| 420            | 2.8             | 0              | 440            | 23.2             |
| 430            | 19              | 0              | 450            | 25.6             |
| 440            | 23.2            | 0              | 460            | 26.7             |
| 470            | 27.3            | 0.5            | 480            | 27.6             |
| 490            | 27.5            | 0.5            | 500            | 27.4             |
| 510            | 27.2            | 0.5            | 520            | 27.0             |
| 530            | 26.8            | 0.5            | 540            | 26.6             |
| 550            | 26.3            | 0.4            | 560            | 26.1             |
| 570            | 25.8            | 0.4            | 580            | 25.6             |
| 590            | 25.2            | 0.4            | 600            | 24.9             |
| 610            | 24.5            | 0.4            | 620            | 24.1             |

Table 1. Optical transmission of LC cells prepared using different methods of alignment at the substrate–LC interface

polymer-dispersed compositions, e.g., iodinated poly(vinyl alcohol) (PVA) films, which transmit the parallel component of the incident light and absorb the orthogonal component. Thus, the principle of operation of the iodinated PVA film polarizer is based on the dichroism of light absorption in PVA–iodine complexes.

This paragraph briefly considers the possibility of improving the optical and mechanical properties of iodine–PVA thin film polarizers by the application of modern nano-objects - carbon nanotubes (CNTs). The polarizers structures comprising iodinated PVA films with a thickness of 60–80 µm, which were coated from both sides by ~0.05 µ thick layers of single walled CNTs have been studied. The polarizers contained polarization films with either parallel or mutually perpendicular (crossed) orientations, depending on the need to obtain the initial bright or dark field. It was found that the modification (nanostructuring) of the surface of polarization films by CNTs led to some increase in the optical transmission for the parallel component of incident light (see. curves 1 and 2 in the figure 2), while retaining minimum transmission for the orthogonal component (cf. curves 3 and 4).
It should be mentioned that CNTs were laser deposited onto the surface of polarization films in vacuum using p-polarized radiation of a quasi-CW CO\(_2\) laser. During the deposition, the CNTs were oriented by applying an electric field with a strength of 50–150 V\(\times\)cm\(^{-1}\). For the first time the method of laser deposition of CNTs onto iodine-PVA structures has been described in paper [5]. The optical transmission measurements were performed using an SF-26 spectrophotometer operating in a 200–1200 nm wavelength range. The results of spectral measurements were checked using calibrated optical filters. The error of transmission measurements did not exceed 0.2%.

![Graph showing the dependence of percentage transmission versus wavelength of parallel and orthogonal polarized light for iodinated PVA film polarizers without and with CNTs modified nanostructured surfaces.](https://www.intechopen.com)

Fig. 2. Dependence of percentage transmission versus wavelength of (1,2) parallel and (3, 4) orthogonal polarized light for iodinated PVA film polarizers without (1, 3) and with (2, 4) CNTs modified nanostructured surfaces.

The nanostructuring of the surface of polarization films by CNTs led to a 2–5% increase in the optical transmission in the visible spectral range for the parallel component of incident light, while retaining minimum transmission for the orthogonal component. This result is evidently related to the fact that the deposition of CNTs onto the surface of iodinated PVA films modifies the properties of air–film interface and reduces the reflection losses. The losses are decreased due to the Fresnel effect, which is related to a small refractive index of CNTs (\(n \sim 1.1\)). In a spectral interval of 400–750 nm, the CNT-modified iodinated PVA films ensured the transmission of the parallel component on a level of 55–80%.

As an additional feature of a new method to deposit the CNTs onto both surfaces of polarization films are based on the improved mechanical protection of the films. Really, the standard approach to mechanical protection of polymeric polarization films against scratching and bending consists in gluing polarizers between plates of K8 silica glass or pressing them into triacetatecellulose. The proposed method of surface nanostructuring increases the surface hardness, while retaining the initial film shape that is especially important in optoelectronic devices for reducing aberrations in optical channels and obtaining undistorted signals in display pixels. The increase in the surface hardness is apparently related to the covalent binding of carbon nano-objects to the substrate surface, which ensures strengthening due to the formation of a large number of strong C–C bonds of the CNTs, which are difficult to destroy.

The CNT-modified thin film polarizers can be employed in optical instrumentation, laser, telecommunication, and display technologies, and medicine. These polarizers can also be
1.3 Carbon nanotubes influence on the photorefractive features of the organics materials

In the present paragraph the emphasis is made on the improving of the photorefractive characteristics of conjugated organic materials doped by fullerenes, CNTs, and quantum dots. The possible mechanism to increase the laser-induced change in the refractive index, nonlinear refractive index and cubic nonlinearity has been explained in the papers [6-8]. Regarding CNTs it was necessary to take into account the variety of charge transfer pathways, including those along and across a CNT, between CNTs, inside a multiwall CNT, between organic molecules and CNTs, and between the donor and acceptor moieties of an organic matrix molecule. The possible schemes of charge transfer are schematically depicted in figure 3 (middle part).

The systems have been studied using a four-wave mixing scheme analogous to that described previously [9]. By monitoring the diffraction response manifested in this laser scheme, it is possible to study the dynamics of a photoinduced change in the refractive index of a sample and to calculate the nonlinear refraction and nonlinear third order optical susceptibility (cubic nonlinearity). An increase in the latter parameter characterizes a change in the specific (per unit volume) local polarizability and, hence, in the macroscopic polarization of the entire system. The experiments were performed under the Raman–Nath diffraction conditions in thin gratings with spatial frequencies of 100 and 150 cm$^{-1}$ recorded at an energy density varied within 0.1–0.5 J/cm$^2$.

The organic compositions were based on polyimide (PI), prolinols, and pyridines, including N-(4-nitrophenyl)-L-prolinol (NPP), 2-(N-prolinol)-5-nitropyridine (PNP), and 2-cyclooctylamine-5-nitropyridine (COANP). The thicknesses of thin film samples were
within 2–4 μm. The organic matrices were sensitized by doping with commercially available fullerenes (C\textsubscript{60} and C\textsubscript{70}) and CNTs (purchased from Alfa Aesar Company, Karlsruhe, Germany). The concentration of dopants was varied within 0.1–5 wt % for fullerenes and below 0.1 wt % for CNTs.

The main results of this study are summarized in the table 2 in comparison to the data of some previous investigations. An analysis of data presented in the table 2 for various organic systems shows that the introduction of fullerenes as active acceptors of electrons significantly influences the charge transfer under conditions where the intermolecular interaction predominates over the intramolecular donor–acceptor contacts. Indeed, the electron affinity of the acceptor fragments (which is close to 1.1–1.4 eV in PI-based composites and 0.4–0.5 eV in pyridine-based systems) is 2.5–5 times that of fullerenes (2.6–2.7 eV). Redistribution of the electron density during the recording of gratings in nanostructured materials changes the refractive index by at least an order of magnitude as compared to that in the initial matrix. This results in the formation of a clear interference pattern with a distribution of diffraction orders shown in figure 4. The diffusion of carriers from the bright to dark region during the laser recording of the interference pattern proceeds in three (rather than two) dimensions, which is manifested by a difference in the distribution of diffraction orders along the horizontal and vertical axes. Thus, the grating displacement takes place in a three dimensional (3D) medium formed as a result of the nanostructirization (rather than in a 2D medium).

![Fig. 4. The visualization of the diffraction response in the organics doped with nano-objects](image)

In addition, data in the table 2 show that the introduced CNTs produce almost the same change in the refractive properties as do fullerenes, at a much lower percentage content of the CNTs as compared to that of C\textsubscript{60} and C\textsubscript{70} and for the irradiation at higher spatial frequencies (150 mm\textsuperscript{-1} for CNTs versus 90–100 mm\textsuperscript{-1} for fullerenes). This implies that the possibility of various charge transfer mechanisms in the systems with CNTs is quite acceptable and may correspond to that depicted in figure 3. Using the obtained results, we have calculated the nonlinear refraction \( n_2 \) and nonlinear third order optical susceptibility (cubic nonlinearity) \( \chi^{(3)} \) for all systems using a method described in [10]. It was found that these parameters fall within \( n_2 = 10^{-10}–10^{-9} \text{ cm}^2/\text{W} \) and \( \chi^{(3)} = 10^{-10}–10^{-9} \text{ cm}^3/\text{erg} \).

It should be noted that classical inorganic nonlinear volume media (including lithium niobate) exhibit significantly lower nonlinearity, while bulk silicon based materials have

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nonlinear characteristics analogous to those of the organic nano-objects-doped materials under consideration.

| Structure         | Content of dopants, wt.% | Wavelength, nm | Energy density, J/cm² | Spatial frequency, mm⁻¹ | Laser pulse duration, ns | Laser-induced change in the refractive index, Δn |
|-------------------|--------------------------|----------------|-----------------------|-------------------------|--------------------------|-----------------------------------------------|
| NPP               | 0                        | 532            | 0.3                   | 100                     | 20                       | 0.65×10⁻³                                      |
| NPP+C₆₀           | 1                        | 532            | 0.3                   | 100                     | 20                       | 1.65×10⁻³                                      |
| NPP+C₇₀           | 1                        | 532            | 0.3                   | 100                     | 20                       | 1.2×10⁻³                                       |
| PNP*              | 0                        | 532            | 0.3                   | 100                     | 20                       | *                                             |
| PNP+C₆₀           | 1                        | 532            | 0.3                   | 100                     | 20                       | 0.8×10⁻³                                       |
| PI                | 0                        | 532            | 0.6                   | 90-100                  | 10-20                    | 10⁻⁴·10⁻⁵                                     |
| PI+malachite green dye | 0.2                 | 532            | 0.5-0.6              | 90-100                  | 10-20                    | 2.87×10⁻⁴                                     |
| PI+C₆₀           | 0.2                      | 532            | 0.5-0.6              | 90-100                  | 10-20                    | 4.2×10⁻³                                       |
| PI+C₇₀           | 0.2                      | 532            | 0.6                  | 90-100                  | 10-20                    | 4.68×10⁻³                                     |
| PI+C₇₀           | 0.5                      | 532            | 0.6                  | 90-100                  | 10-20                    | 4.87×10⁻³                                     |
| PI+CNTs          | 0.1                      | 532            | 0.5-0.8              | 90-100                  | 10-20                    | 5.7×10⁻³                                       |
| PI+CNTs          | 0.05                     | 532            | 0.3                  | 150                     | 20                       | 4.5×10⁻³                                       |
| PI+CNTs          | 0.07                     | 532            | 0.3                  | 150                     | 20                       | 5.0×10⁻³                                       |
| PI+CNTs          | 0.1                      | 532            | 0.3                  | 150                     | 20                       | 5.5×10⁻³                                       |
| PI+quantum dots based on CdSe(ZnS) | 0.003               | 532            | 0.2-0.3              | 100                     | 20                       | 2.0×10⁻³                                       |
| COANP            | 0                        | 532            | 0.9                  | 90-100                  | 10-20                    | 10⁻⁵                                           |
| COANP+TCNQ**     | 0.1                      | 676            | 2.2 W/cm²            | 2×10⁻⁵                  | 2×10⁻⁵                  |
| COANP+C₆₀        | 5                        | 532            | 0.9                  | 90-100                  | 10-20                    | 6.21×10⁻³                                     |
| COANP+C₇₀        | 5                        | 532            | 0.9                  | 90-100                  | 10-20                    | 6.89×10⁻³                                     |

* The diffraction efficiency has not detected in pure PNP system at this energy density
** Dye TCNQ - 7,7,8,8-tetracyanoquinodimethane – has been used in the paper [11]

Table 2. Laser-induced change in the refractive index in some organic structures doped with nano-objects

1.4 Carbon nanotubes use to modify the surface properties of the inorganic materials

It is the complicated complex task to modify the optical materials operated as output window in the UV lamp and laser resonators, as polarizer in the telecommunications, display and medicine systems. Many scientific and technological groups have made some steps to reveal the improved characteristics of optical materials to obtain good mechanical hardness, laser strength, and wide spectral range. Our own steps in this direction have been firstly shown in paper [12]. In order to reveal the efficient nano-objects influence on the materials surface it is necessary to choose the model system. It should be noticed that magnesium fluoride has been considered as good model system. 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 MgF2 surface via covalent bonding [13]. Table 3 presents the results of surface mechanical hardness of MgF2 structure after nanotubes placement; Table 4 shows the decrease of MgF2 roughness.

| Structures                           | Abrasive surface hardness (number of cycles before visualization of the powder from surface) | Remarks                                                                 |
|-------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| MgF2                                | 1000 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. |
| MgF2+nanotubes                      | 3000 cycles                                                                                   |                                                                          |
| MgF2+vertically oriented CNTs       | more than zero hardness                                                                        |                                                                          |

Table 3. Abrasive surface hardness of the MgF2 structure before and after CNTs modifications

One can see from Table 3 that the nanostructured samples reveal the better surface hardness. For example, after nanotubes placement at the MgF2 surface, the surface hardness has been better up to 3 times in comparison with sample without nano-objects. It should be noticed that for the organic glasses this parameter can be increased up to one order of magnitude. Moreover, the roughness of the MgF2 covered with nanotubes and treated with surface electromagnetic waves has been improved essentially. Really, \( R_a \) and \( S_q \) roughness characteristics have been decreased up to three times. One can see from Table 4 that the deposition of the oriented nanotubes on the materials surface and surface electromagnetic waves treatment decreases the roughness dramatically. Indeed this process is connected with the nature of the pure materials; it depends on the crystalline axis and the defects in the volume of the materials.

In order to explain observed increase of mechanical hardness we compared the forces and energy to bend and to remove the nanotubes, which can be connected with magnesium fluoride via covalent bond MgC. Thus, the full energy responsible for destruction of the surface with nanotubes should be equal to the sum of \( W_{\text{rem}} \) (energy to remove the layer of nanotubes) and of \( W_{\text{destr}} \) (energy to destroy the magnesium fluoride surface).

| Parameters | Materials | Roughness before nanotreatment | Roughness after nanotreatment | Remarks |
|------------|-----------|--------------------------------|------------------------------|---------|
| \( R_a \)  | MgF2      | 6.2                            | 2.7                          | The area of 5000×5000 nm has been studied via AFM method |
| \( S_q \)  | MgF2      | 8.4                            | 3.6                          |         |

Table 4. Roughness of the MgF2 structure before and after CNTs modifications

Due to the experimental fact that nanotubes covering increases drastically the surface hardness of MgF2 [13], the values of \( W_{\text{rem}} \) and \( W_{\text{destr}} \) can be close to each other. Under the conditions of the applied forces parallel to the surface, in order to remove the nanotubes from MgF2 surface, firstly, one should bend these nanotubes, and secondly, remove these nanotubes. In this case \( W_{\text{rem}} \) are consisted of \( W_{\text{elast}} \) (elasticity energy of nanotube) plus \( W_{\text{MgC}} \) (energy to destroy the covalent MgC binding). The energy of elasticity can be estimated as follow [14]:


\[ W_{\text{elast}} = F_{\text{rem}} \times \frac{L^3}{6E \times l} \]  

(1)

where \( E = 1.5 \) TPa [15] is the modulus of elasticity, \( l = \pi \cdot r^2 \cdot \Delta r \) is the moment of inertia of the nanotube cross section at its wall thickness \( \Delta r = 0.34 \) nm, \( r = 4 \) nm; and \( L = 50 \) nm is the nanotube length. The force \( F_{\text{rem}} \) can be estimated as follows:

\[ F_{\text{rem}} = F_{MgC} \times \frac{2r}{L} \]  

(2)

where \( F_{MgC} \) is close to 2 \( \mu N \).

Based on our calculation we should say that in order to break the relief with nanotubes, we should firstly bend the nanotubes with energy that is 5 times more than the one, which can be applied to simply remove the nanotubes from the surface after the destroying MgC binding. This fact is in good connection with the experimental results. This calculation can be used to explain the results of dramatically increased mechanical surface hardness of the MgF\(_2\) covered with nanotubes. The experimental data testified that the surface mechanical hardness of MgF\(_2\) materials covered with nanotubes can be compared with the hardness of etalon based on silicon glass K8. As a result of this process, the refractive index can be modified which explains the increase in transparency in the UV. 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 nano-objects, is minimum (close to zero) in the IR range. The UV-VIS and near IR-spectra of the magnesium fluoride is shown in Fig. 5.

![UV-VIS-near IR spectra of MgF\(_2\) before (curve 1) and after single wall nanotubes deposition (curve 2). The thickness of the sample close to 2 mm.](image)

**Fig. 5.** UV-VIS-near IR spectra of MgF\(_2\) before (curve 1) and after single wall nanotubes deposition (curve 2). The thickness of the sample close to 2 mm.

It should be noticed that the drastic increase in the transparency at wavelength of 126 nm has been observed. Really, for the 5 units of MgF\(_2\) sample, the transparency \( T \) has been changed after nanotubes deposition as follows: sample No1. \( T = 61.8\% \rightarrow T = 66.6\% \) 1 \( \rightarrow T = 69\% \); No2. \( T = 54.5\% \rightarrow T = 65.8\% \); No4. \( T = 58.1\% \rightarrow T = 67.5\% \); No5. \( T = 50.9\% \rightarrow T = 65\% \).

It should be mentioned that the CNTs are the good candidate to modify the surface properties of the materials in order to obtain the good advantage in the hardness and spectra.

1.5 Conclusion

In conclusion, the influence of the nano-objects, such as carbon nanotubes, on alignment ability, polarization features, dynamic, photoconductive and photorefractive characteristics...
as well as on mechanical hardness and spectral parameters has been shown. CNTs can modify bulk and surface properties of the materials with good advantage. As the result of this discussion and investigation, new area of applications of the nanostructured materials can be found in the optoelectronics and laser optics, medicine, telecommunications, display, microscopy technique, etc. Moreover, the nanostructured materials can be used for example, for development of transparent UV and IR window, for gas storage and solar energy accumulation, as well as in airspace and atomic industry.

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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This book focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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