A nanostructuring approach for modification of the features of optical materials: lithium fluoride

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Abstract. It is well known that different technical methods and physical-chemical approaches can be used to improve the basic properties of optical materials operated in the UV-VIS-IR spectral range. Laser-based equipment and a nanotechnology approach can be jointly applied with good advantage. In this paper, the advantage of the laser-oriented deposition technique is discussed. Promising nanoobjects based on carbon nanotubes and LiF structures were considered, and their spectral, mechanical and wetting properties were evaluated. It was found the modification of the LiF with the carbon nanotubes improves the optical properties of the former. The quantum chemical simulations confirmed the experimental results obtained. Besides, the changes in the properties of the other classical materials (such as KCl, KBr, MgF₂, etc) were comparatively shown.

1. Introduction
Optical materials are promising and widely applied in the general optoelectronics, especially, in the laser schemes, in space and automobile industry as well as in the biomedicine. These materials are efficiently operated in the UV-VIS-IR wavelength ranges and at the extended range of the energy density [1-5]. At present, the laser structuring of the material surface allows to modify the physical and chemical properties of the matrix material with good advantage [6,7]. From this point of view, carbon nanotubes (CNTs) can be considered as the perspective nanoobjects due to their unique atomic structure, strong bonding between the carbon atoms and very small value of the refractive index as well [8-10].

Using CNTs for surface modification of optical materials may drastically tune its properties, causes with the fact that the atomic structure of such materials includes the substances that can provoke the different features against the radiation, such as: transmission, scattering, reflection, absorption, refraction, etc. These processes can be activated and modified via the propagation of the electromagnetic waves through the nanostructured optical media. Using structuration approach the
spectral, refractive, mechanical properties, wetting phenomena, etc. can be essentially changed. For example, as the good evidences, the Fresnel losses can be changed, which can be easy shown based on the glass substrate. Indeed, using the classical method (PDV, CVD, etc.) one can deposit many layers of the thin coatings in order to reduce the losses at the reflection process and thus to improve the light transmission (aperture ratio) of the optics, the surface of the glass can be exposed to special treatment, which is called “enlightenment of optics”. On the surface of the matrix materials (glass), the thin film should be deposited, the refractive index of which \( n_{film} \) should be less than the refractive index of glass \( n_{glass} \): 
\[
\frac{n_{film}}{n_{glass}} < 1
\]
In order to achieve the minimal reflection losses and maximum of the transmittance, the film should have the thickness determined by equation (1):
\[
h = \frac{d}{n_{film}},
\]
where \( h \) is the geometric thickness of the film, \( d \) is an optical thickness of the film defined as \( d = \frac{\lambda}{4} \) (\( \lambda \) is wavelength of the light in exact part of spectrum).

It is well known that the film with the thickness of \( \frac{\lambda}{4} \) from the substance with the refractive index of \( \sqrt{n_{glass}} \) decreases the reflective coefficient dramatically. If one considers the interface such as the air-glass with the reflective index of the glass material close to 1.5, the reflection from one surface of the substrate is approximately 4%, and from two surfaces, it is approximately 8%.

Using the innovative laser structuration approach and forming the covalent bonding between the carbon nanotubes with the small refractive index \( n \approx 1.1 \), the Fresnel loses via the reflection can be changed in one order of magnitude, at least.

Lithium fluoride [11] is the unique colourless cubic optical crystal with the unit cell parameter \( a \) close to 0.40279 nm. It has a very high transparency from the UV to the IR wavelength (from 0.12 to 6 microns), and already applied in the vacuum ultraviolet region and in the IR spectral range. Such advantages lead to using LiF for measuring the radiation doses by the method of the thermoluminescent dosimetry. Single crystals of lithium fluoride are used for X-ray monochromators and for the manufacture of the high-performance laser with the free colouring centres. Furthermore, in addition, the lithium fluoride crystals with colour centres are commonly used as the passive laser gates for the transfer of the total power generation in the monopulse one.

It should be mentioned that the refractive index \( n \) of the LiF materials can be changed by altering the wavelength as follows [12]: 1.77 (at 112.7 nm), 1.3978 (at 420 nm), 1.39 (at 620 nm), and 1.29 (at 6200 nm). The nanostructuration of the LiF surface makes it possible to change their optical and mechanical parameters, such as transparency, wetting angle and mechanical hardness.

In the present paper, the change in the Fresnel losses via transparency improving and the increase in the hardness and wetting angle are presented for the classical optical material based on the lithium fluoride (LiF). It should be noted that the use of the oriented laser-based deposition of carbon structures on the surface of the materials favorably differs from the CVD and PDV methods shown in the recently published works [13-15].

2. Methods and materials

Structural modification of the LiF surface was carried out with IR \( \text{CO}_2 \)-laser with \( p \)-polarized irradiation at the wavelength of 10.6 \( \mu \text{m} \) and the power of 30 W. The laser system was connected to a vacuum hood containing the fixing unit samples and the device for placing substances deposited on the substrate. CNTs were placed at the materials interface under an additional electric field of 100-600 \( V/cm \) in order to orient the nanotubes in the vertical position during the deposition process. Thus, the laser-oriented deposition (LOD) method was realised.

The spectra of the CNTs-treated materials were obtained using a Fourier FSM-1202 instrument as well as a VIS SP-26 spectrophotometer operated in the spectral range of 250-1200 nm. A POLAM-
P312 microscope was applied to make the image of the treated materials. Surface mechanical hardness (abrasive strength) was revealed using a CM-55 instrument, and the microhardness was measured via using the PMT-3M device produced by “LOMO” (Saint-Petersburg, Russia) with the ability to vary an indenter force as well. Moreover, the OCA 15EC device from LabTech Co. (Saint-Petersburg-Moscow, Russia) was applied to careful control the wetting angle change too. The modified surface analysis was carried out using a Solver Next atomic force microscope AFM (NT MDT Co., Zelenograd, Moscow Region, Russia).

To modify the LiF properties via their surface treatment, single-walled carbon nanotubes (SWCNTs), type #704121, with the diameter varied from 0.7-1.1 nm (Sigma-Aldrich Co., Steinheim, Germany) were used. The dimension of the nanotubes is important in order to combine their diameter directly with the unit cell of the model material. Moreover, Russian CNTs and nanofibers, type “Taunit-MD” (NanoTechCenter Ltd., Tambov, Russia) were applied as well.

All calculations were performed at the level of density functional theory as implemented in the VASP package [16,17] within the augmented plane-wave basis set [18]. Due to the large size of considered system the plane-wave cutoff energy was set to 250 eV, and the density of states was calculated only in the \( \Gamma \)-point. Several test calculations show that decreasing the cutoff energy from 400 to 250 eV leads to relatively small changes in the total energy of the system. Studied system consists of 200 lithium atoms, 200 fluorine atoms and 110 carbon atoms, which is the CNT together with 10 hydrogen atoms (passivation of the upper end).

3. Results, calculation and discussion

The spectral features of the modifications of the LiF surface are shown in figure 1 for the spectral range of 225-350 nm. It is important to note that the essential transmittance changes can be established in the UV range. It should be mentioned that the curve 1 (black line) indicates transmittance for the pure LiF (without modification), whereas curve 2 (red line) is related to the nanostructured one.

![Figure 1. Transmittance of pure LiF surface (curve 1, black) and modified by CNTs (curve 2, red) in the UV-VIS spectral range.](image)

It should be taken into account that the transparency and the reflective characteristics are coincided with each other. Thus, the decrease in the reflectance was found at the operated wavelength. One should note that the change in the reflectance is connected with the modified Fresnel losses. It was testified that the Fresnel losses (assigned to the relation between the refractive index of the CNTs and the matrix material) from the nanostructured surfaces can be decreased by using the laser oriented deposition technique as well as by the implantation of CNTs into the voids in the LiF surface layer. The fact of the possible strong binding of the CNTs with the LiF surface can be supported by the theoretical simulations.
In order to obtain more deep understanding of the influence of CNT deposited on LiF surface on its physical and chemical properties, the theoretical calculations within the density functional theory were performed. In figure 2 the studied atomic structure of the CNT/LiF interface is shown. The LiF (100) surface was considered, since it has termination containing two types of the atoms (Li, F) on the surface. Then, the CNT was deposited on the surface (figure 2, side and top views, respectively). Due to the large number of atoms in the considered unit cell of the substrate, the CNTs has the length of 1.2 nm, which is long enough to describe the effects related to the binding with LiF surface. The upper end of the tube was passivated by hydrogen atoms, since after the deposition of the CNT on the LiF surface, the main changes appear in the region close to the CNT/LiF interface.

![Figure 2. An atomic structure of the considered CNT/LiF interface.](image)

The geometry relaxation of the interface structure shows that the deposition of the CNTs on the (100)-LiF surface does not lead to significant changes in the interface structure. The distance between the lower atoms of the CNTs and LiF surface was found to be 3 Å, which corresponds to the general van der Waals distance. Indeed, the calculations of the binding energy confirm it with the very small value of -0.66 meV/Å². Thus, to achieve the best binding between the CNTs and the substrate, it is necessary to deposit the former with some finite velocity to force them to penetrate into the latter.

Besides, the study of the electronic properties was performed, in particular, the electronic density of states (DOS) was calculated (figure 3). Only a tiny redistribution in the electronic density in the CNTs/LiF interface was found (see upper panel of figure 3). Moreover, the dependence of DOS on the energy also manifests about the weak interaction between the tube and substrate (see the bottom panel in figure 3). The deposition of the CNT leads to the shift of the main peak in the valence band towards the red region of visible spectra (~2 eV). The deposition of the CNTs also leads to the appearance of a certain number of energy levels close to the Fermi level, which can be seen from figure 3.
Figure 3. Distribution of the electronic density and a dependence of the electronic density of states on the energy for the CNT/LiF system.

This calculation (for example, the shift of the main peak in the valence band towards the red region of visible spectra) supports the transmittance and reflection spectral changes as well. According to the decreased Fresnel losses, one can expect for the change in the reflection parameters (figure 4).

Moreover, the wetting angle and the mechanical hardness can be successfully modified. The increase in the LiF material wetting angle after the LOD technique application was obtained. It was found that the wetting angle changes from 97.5-97.8° up to 107.3-107.5° after treating one side of the LiF substrate with the CNTs. It is worth noting that after processing on one side of the lithium fluoride sample, a Lotus effect, preventing water droplets from penetrating into the surface layers of the composite material, can be demonstrated. However, it remains possible to penetrate the water droplets from the other side of the sample, as well as from the ends. Therefore, the use of the laser oriented CNTs deposition in two-sided processing, as well as in view of the protection of the lateral surfaces of the sample, is more significant. It should be noticed that in order to study the structuration process influence on the physical and chemical characteristics of the LiF materials, the substrates with polished surfaces and the thickness of 5 mm are used.

The change in the mechanical characteristics is presented in table 1. Based on these data, one can testify that a 10-% increase in the microhardness can be found after treating the material surfaces with the CNTs through the laser oriented deposition technique. The data for the other optical materials are shown in table 1 for comparison. It should be remarked that increasing the mechanical strength of the LiF even by 10 % is very important from the point of view of using this crystal in passive mode generation when converting the total generation of laser radiation into a monopulse one.
4. Conclusion

It was found that the laser oriented approach can be used with good advantage in order to deposit the CNTs in the vertical position on the surface of optical materials such as LiF. This approach allows to arrange the covalent bonding between the carbon atoms and the near interface matrix material atoms. The experimental data were related to the theoretical explanation. The quantum chemical calculations showed the changes in the electronic properties (red shift of the valence band) of the LiF after the CNTs deposition, thereby supporting this bonding evidence. Moreover, the spectral and mechanical properties, as well as the wetting angle change, were found to be in good agreement with the modelling performed. Furthermore, there were no purpose to compare the LiF materials directly with the KBr, KCl and the other crystals because they have different applications. For example, potassium bromide is a key element of Fourier spectroscopy; potassium chloride can be used as a mirror when working with a CO₂-laser. Thus, the advantage and effective application of the laser-oriented processing for a large class of optical materials including lithium fluoride were demonstrated.

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