ADVANTAGES OF MATERIALS SURFACE STRUCTURATION WITH CARBON NANOTUBES: ZnS OPTICAL CERAMIC

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Abstract

One of the important optical ceramics is material based on the zinc sulphide – ZnS. In the current paper the change of the main characteristics of these types of the materials is shown. The transmittance spectral change and increase of the micro hardness as well as the increase of the wetting angle are discussed due to the covalent bonding of the carbon nanotubes with the near-surface layers of the matrix materials. Quantum chemical simulation has supported the data presented. The data established for the ZnS materials are connected with the other ones observed for the different inorganic structures, such as BaF_2, KBr, Si, etc. These data are related to the direct tendency, such as: correlation between spectral, mechanical and wetting parameters can be provoked via nanostructuration of the materials surfaces.

Keywords: optical ceramics, ZnS structures, carbon nanotubes, surface, spectra, mechanical hardness, wetting angle, basic parameters modification via laser-oriented deposition method.

Introduction

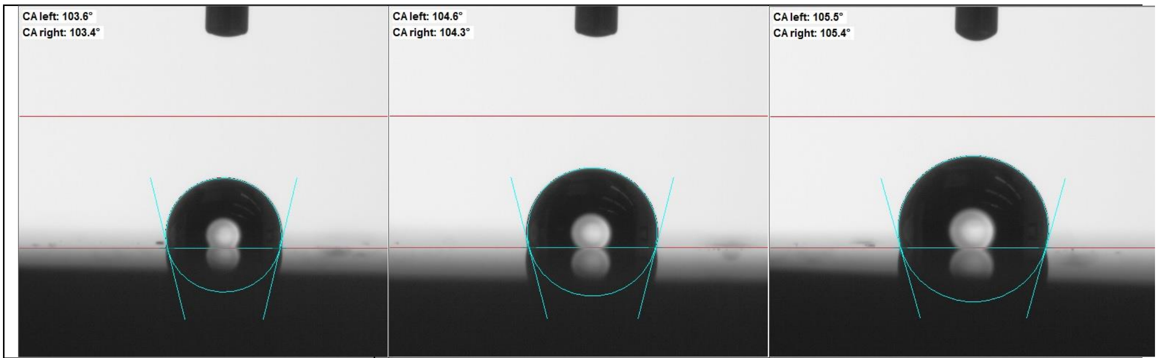
At the present time the perspective materials, namely carbon nanotubes (CNTs), reinforce the materials properties with good advantage [1]. It should be noticed that in this direction among the different technical approaches [2-4] used in the materials science area in order to modify the physical-chemical properties of the structures the laser oriented deposition (LOD) technique occupies a certain unique place [5-7]. In the last case the CNTs have been placed on the materials surface in the vertical position. The carbon nanotubes features regarded to their branched surface, high conductivity, strong hardness of their C—C bonds, little value of the refractive index as well as to their complicated and unique mechanisms of charge carrier moving [8-10] have been taken into account. From one side, it is possible to organize the covalent bonding between the carbon atoms and the surface atoms of the matrix material; from the other side, it should be mentioned that at the nano-scale level it so easy to establish a correlation between changes of the spectral, mechanical, and hygroscopic characteristics. This approach has been previously applied to modify the above indicated properties of the MgF_2, BaF_2, KBr, conducting ITO layers, etc. materials [11-13]. In the current paper the optical ceramic based on the ZnS structure is shown as the perspective material, which can be successfully treated by the nanotechnology approach.

Experimental condition

It should be mentioned that in order to modify the properties of the zinc sulphide materials via their surface treatment, the SWCNTs type #704121 with the diameter of ~0.5-0.7 nm purchased from Aldrich Co. have been used. These nanotubes have been deposited on the material surface using the IR-CO_2-laser with the *p*-polarized irradiation at the wavelength of 10.6 μm and with the power of 30 W. Moreover, the CNTs have been placed at the materials interface under the conditions when an additional electric field of 100-600 V×cm^{-1} has been applied in order to orient the nanotubes in the vertical position during the deposition process. The spectra of the nanotubes-treated materials have been obtained using the Furrier FSM-1202 instruments as well as using VIS SF-26 device operated in the range of 250-1200 nm. The device PMT-3M (produced by "LOMO", Saint-Petersburg, Russia) with the ability to vary an indenter forces has been used to estimate the micro-hardness. The special accent has been given to observe the relief at the material surface via checking the wetting angle. In this case the device OCA-15E (LabTech Co., Moscow) have been applied. The modified surface analysis has been additionally made using Solver Next AFM (purchased from NT MDT Co., Zelenograd, Moscow region, Russia).

Results and discussion

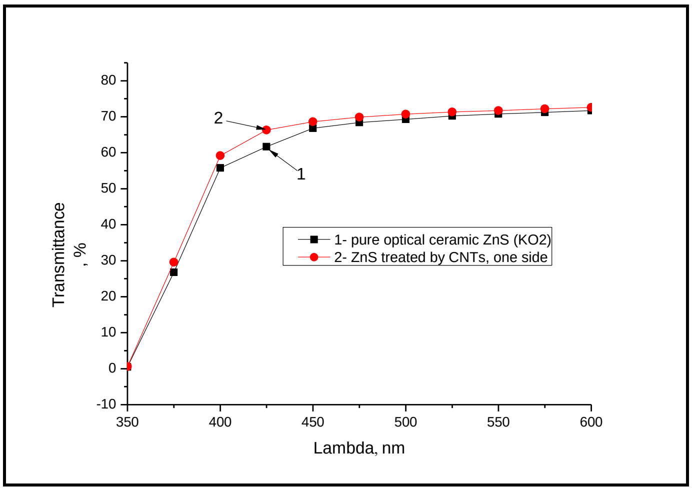
It should be remarked that ZnS semiconductor materials is included in the optical ceramics groups (KO2) with the classical magnesium fluoride MgF_2 structures (KO1). Both types of these ceramics are widely used in the optoelectronics technique. Thus, the studied the properties of these materials can be useful in order to accept the knowledge about the influence of the nanostructuration process on the basic physical parameters. With the accent on the ZnS materials, the micro hardness estimation reveals the increase of this parameter up to 5-7 percent. Thus, for the ZnS ceramic the micro hardness has been increased substantially. It should be mentioned that the indenter with the forces of 20 g has been used to treat this type of the optical ceramics. Moreover, the tendency to increase the wetting angle for the ZnS structure after the nanostructuration of their surfaces has been established as well. The supporting data are shown in Fig.1.



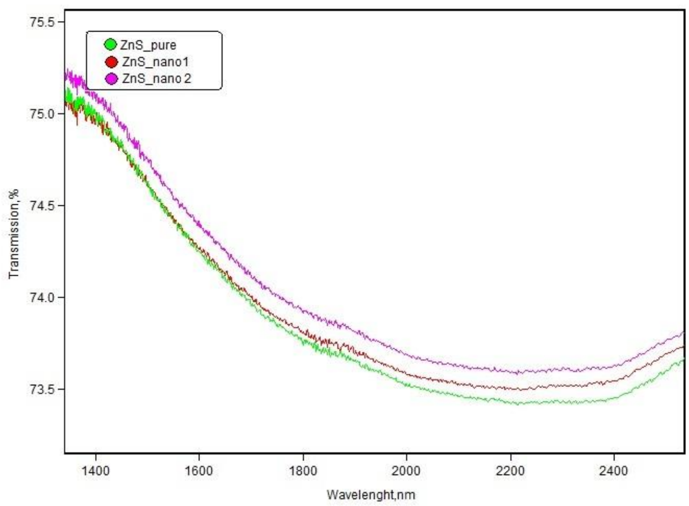
a	*b*	*c*

Figure 1. Wetting angle parameters of the ZnS substrate: pure (*a*), structured from one side (*b*), structured from the both sides (*c*)

The spectral data in the VIS and in the near and middle IR-range are shown in Fig.2, *a,b*. It should be noticed that in the case of the analysis of the spectra one take into account the change of the transmittance spectrum with the one-sided processing of the material and with the processing from two their sides. It should be mentioned that the substrate thickness was 5 cm.



a



b

Figure 2. Spectral parameters of the pure and of the nanostructured ZnS sample: in the VIS (*a*) and in the near and middle IR spectral range (*b*)

The quantum chemical simulation has supported the results of the spectral and the mechanical properties changing due to the incorporation of the CNTs into the materials surfaces and due to form the possible bonding between the carbon atom and the original material surface atoms of the ZnS material. It should be mentioned that the penetration depth has been depended on the velocity of the CNTs and their diameters. The part of the quantum-chemical results is shown in Fig.3. The analysis has been made using the procedure in the framework of the LAMMPS program [14,15]. For example, behavior of the ZnS substrate at finite temperature has been described with the many-body Tersoff potential. To describe the interaction between the CNT and the ZnS substrate the 12/6 potential $E = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ has been used. The interaction parameters have been chosen as: $\varepsilon = 0.011$ eV, $\sigma = 1.80$ Å. Considered ZnS substrate is included about ~47000 atoms and had a height about 14 nm. Such height of the ZnS substrate is enough to avoid the penetration through the substrate. The molecular dynamics simulations have been carried out at constant temperature, which was about 300 K. The total time of the simulation has been of 60 ps with the time step of 1 fs. The velocities of the tubes have been varied from 100 to 600 m×s^{-1} according to the experiments. It should be noticed that dependence of the penetration depth on the CNTs velocity for the studied ZnS materials under the laser oriented deposition process using the different diameter of the CNTs has been previously shown in the paper [7]. Now the additional results are presented. They are shown the penetration of the CNT into the surface layers of ZnS at the rate of the CNTs of 200 m/s using the different their diameter close to 0,64 nm (Fig.3, *left figure*) and to 2,68 nm (Fig.3, *right figure*).

Thus, using the consideration based on the ZnS materials, the current study can propose the CNTs laser treatment as the innovative way to modify the important physical and chemical characteristics of this type of the optical ceramics.

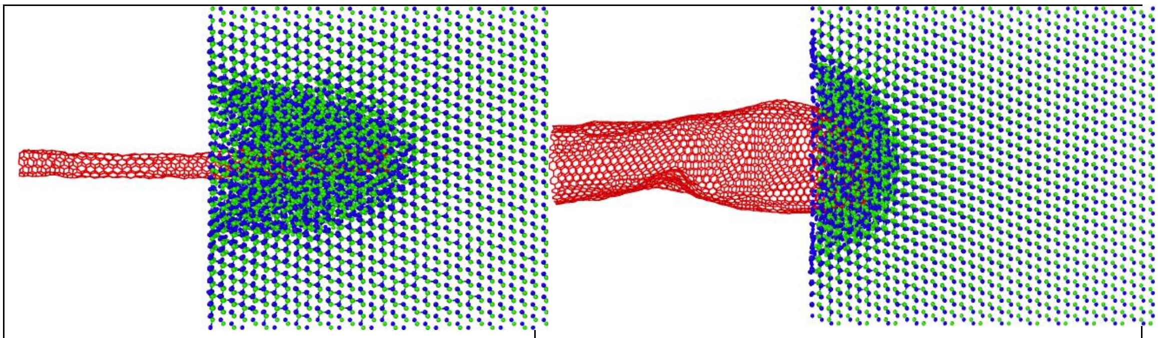


Figure 3. The penetration of the CNT into the surface layers of zinc sulfide at a rate of 200 m/s: the diameter of nanotubes was 0,64 nm (*left figure*) and 2,68 nm (*right figure*)

It should be noticed that the ZnS materials have been use, for example, for the manufacture of the space components and the devices of the technical sensors, etc. Thus, all of the mentioned above area of the application of the materials under the current consideration can be essentially exceeded via using the LOD technique with good advantage.

Conclusion

The optical ceramics based on the ZnS structures has been studied to reveal the advantage of their surface structuration. The spectral and mechanical parameters, as well as the wetting phenomena features have been improved. It is imported to note that the tendency to increase the transparency, the mechanical parameters, and the wetting angle of the ZnS materials after the application of the nanostructuration process, which has been shown before for the other optical materials, has been supported once again. The area of the use of this type of the optical ceramics can be extended in the practical optoelectronics to develop the photosensitive layers of the electrically or/and optically-addressed spatial light modulators, mirrors, prisms, etc. electronic elements. Moreover, the obtained data can be used in the education process with good advantage.

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