ITO conducting coatings properties improvement via nanotechnology approach

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Abstract

In this paper the investigation devoted to study and development of the optimized ITO conducting layers are presented and discussed under the conditions of the materials surfaces laser structuration in order to apply the modified conducting materials in the optoelectronics, virus protection, solar energy, microscopy, biomedicine, etc. area. Based on our knowledge and expertise it is established the dramatic change of the main characteristics of the ITO matrix, which surface is modified by the carbon nanotubes (CNTs), and additionally treated by surface electromagnetic waves (SEW) as well. The transmittance and reflection spectral change, increase of the micro hardness and laser strength as well as the increase of the wetting angle and refraction change are discussed due to the covalent bonding between the carbon nanotubes and the near-surface atoms of the matrix materials. As the unique point of the study the effective decrease of the resistivity is established and presented. Quantum chemical simulations are supported the data presented.

1. Introduction

It is known that at present time different approaches can be used in order to modify the physical-chemical properties of the materials including the ITO ones. The physical methods of deposition of the coatings (Physical Vapour Deposition or PVD process) and chemical methods of deposition of the coatings (Chemical Vapor Deposition or CVD-process) is widely used \cite{1–7}. The PVD technology is made in vacuum from the gas phase, in which the coating is obtained by the direct condensation of the coating material. The coating material passes from the solid state to the gas phase by an evaporation under the influence of heat or in the spraying. Physical methods also include the laser ablation of the target and the epitaxial method of the films growing. The CVD methods of the film deposition are carried out through the use of one or more volatile precursors on the substrate, where they decompose or react, forming the desired coating. The CVD method has some significant advantages compared to the PVD one. Possibility of an uniform composition and the film thickness on parts of the complex configuration and a large area; the ability to achieve the high deposition rate (up to several millimeters per hour) while maintaining the high quality of the films.

Some years ago we have proposed the unique contactless method to improve the properties of the inorganic matrix. It is based on the laser oriented deposition (LOD) of the carbon nanotubes on the materials surfaces \cite{8,9}. Developed and optimized our coating nanotube-based flesh can withstand heating up to 1500 °C (due to the fact that CNTs themselves are destroyed at a temperature of 2000 °C and above) do not require the use of the toxic solvents, is applied to a noncontact method by the laser deposition. The carbon nanotubes are oriented in the varied electric field in the range from 50–100 up to 500–600 V cm\textsuperscript{−1}. This enables one to create the homogeneous layers with the controlled depth of the penetration of the CNTs in the near-surface atomic layers of the matrix of the materials. The thickness of the developed carbon-based coatings is 10–100 nm; with such a relatively small thickness due to the covalent binding on a surface layer of the matrix material, allowing one to use the strength of C-C bonds, coating withstand mechanical loading: from a few tenths to a few tens of GPa, and
also negate the media interface: material-air, water vapor, excluding, therefore, the contact with the atmosphere of a matrix of the hardened material. Vertical deposition of the CNTs provides the effect of ‘Lotus’, consequently, increases the hydrophobicity of the coatings and their laser resistance. Moreover, homogenization of the boundary allows to enlighten the surface of the optical materials due to the small refractive index of the CNT at the level of 1.05–1.1 \[10, 11\] using minimizing Fresnel losses. It is important to note that the CNTs are incorporated on the substrate practically at room temperature; subfloors rotating carousel vacuum post as radially and along the axis of the rotation of each clamping unit. Subsequent surface approach. It is well known that the ITO conducting structure reduces the surface roughness and creates a controlled relief. Part of the features of our method are patented note that the CNTs are incorporated on the substrate practically at room temperature; subfloors rotating carousel vacuum post as radially and along the axis of the rotation of each clamping unit. Subsequent surface treatment of the surface electromagnetic wave (SEW), which has been predicted in the classical papers \[12, 13\] reduces the surface roughness and creates a controlled relief. Part of the features of our method are patented in \[14, 15\].

In the current paper the special accent is given on the ITO conducting layer structuration via the LOD approach. It is well known that the ITO conducting structure (heterostructure of two oxides: \(\text{In}_2\text{O}_3\) and \(\text{SnO}_2\)) are widely used in the display technique, telecommunication and gas storage systems, solar energy, laser switching, modulation schemes, biomedicine instruments, etc. technique with good advantage. Sometimes it can be required to apply these conducting materials in the specific temperature and pressure conditions.

2. Experimental conditions

In order to modify the properties of the studied conducting materials via their surface treatment, the single wall carbon nanotubes (SWCNTs) type #704121 with the diameter placed in the range of 0.7–1.1 nm purchased from Aldrich Co. have been used. It is important in order to combine the CNTs diameter directly with the elementary lattice of the material. Moreover, the Russian CNTs and nanofibers type ‘Taunit-MD’ from the Tambov Company ‘Nanotech-Centre’ production have been applied as well.

To modify the studied material surface the IR \(\text{CO}_2\)-laser with \(p\)-polarized irradiation at the wavelength of 10.6 \(\mu\)m and with the power of 30 W has been used. The general view of the block scheme is shown in figure 1.

It is seen that the laser system is connected with a vacuum hood, which contains the fixing unit samples and the device for placing substances deposited on the substrate. Moreover, the nano-objects, such as, the CNTs have been placed at the materials interface under the conditions when an additional electric field of 100–600 V \(\times\) cm\(^{-1}\) has been applied in order to orient the nanotubes in the vertical position during the deposition process and to vary the velocity of the CNTs. Thus, the laser oriented deposition (LOD) method can be realised. This procedure permits to form the covalent bonding between the carbon atom and an interface atom of the studied materials.

Moreover, the same \(\text{CO}_2\)-laser has been used to produce the surface electromagnetic wave (SEW) in order to make the gratings on the ITO surface. The speed of the laser beam was approximately of 2–12 cm s\(^{-1}\), the polarization of the beam was orthogonal. The intensity of the beam in this case was \(10^3\) W cm\(^{-2}\), the width of the beam was 5 mm.

The spectra of the nano-object-treated materials have been obtained using the Furrer FSM-1202 instruments as well as using the VIS SF-26 spectrophotometer operated in the spectral range of 250–1200 nm. POLAM-P312 microscope has been applied to make the image of the materials treated. Surface mechanical hardness (abrasive strength) has been revealed using the CM–55 instrument and the microhardness has been measured via using the PMT-3M device produced by ‘LOMO’ (Saint-Petersburg, Russia) with the ability to vary an indenter forces as well. The laser strength has been checked with the pulsed nanosecond Nd-laser at the lambda of 1064 and 532 nm and with Er-laser at the wavelength of 1.54 microns as well. The special accent has been 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 Iris Zoom Lens for CCTV Camera (Black) has been used. Moreover the OCA 15EC device has been purchased from LabTech Co. (Saint-Petersburg-Moscow, Russia) and has been used to control the wetting angle change too. The modified surface analysis has been made using Solver Next AFM (purchased from NT MDT Co., Zelenograd, Moscow region, Russia).
It should be mentioned that it permits to register the homogeneity of the surfaces and to estimate their roughness as well.

3. Results and discussion

New orientation relief obtained after the laser oriented deposition of the CNTs on the ITO surface is shown in figure 2 for to mode: before (left) and after (right) the SEW treatment. It can be seen that the regular relief has been obtained after processing the CNTs relief with a surface electromagnetic wave. As the results, this conducting structure can be used not only to apply the bias voltage, but also to orient the liquid crystal (LC) molecules or polymer layers to predict the elimination of the high resistive alignment layers.

The evidence of the resistivity decrease of the structured ITO coating is shown in figure 3. Seven randomly selected samples have been examined for the changes in the resistance.
It should be mentioned that the spectral parameters of the ITO layers measured in the VIS spectral range can be changed and shifted to the IR spectral region after the LOD procedure when the orienting electric field has been changed from the value of \(100 \text{ V cm}^{-1}\) up to the value of \(600 \text{ V cm}^{-1}\). The obtained data are shown in figure 4.

Thus, the devices with the modified ITO conducting coatings can be applied in the specific spectral conditions, including, for example, light-addressed and electrically-addressed spatial light modulators used in the complex laser schemes operated in the near and possibly in the middle IR spectral ranges.

Moreover, the microhardness of these ITO modified with CNTs has been increased as well. The established data are shown below in table 1. It should be remarked that the data sample have been made from 10 samples of each batch. It should be noticed that that the load on the samples has been the same. The value of microhardness has been determined by dividing the normal load applied to the diamond tip by the conditional area of the studied material surface of the resulting print. The experimental error has been \(\sim 0.5\%\). Analysing the table 1

![Figure 5. Some variant of the wetting angle change for the ITO coating with CNTs placement.](image1)

![Figure 6. Possible CNTs placement on the ITO surfaces with the dimension. Yellow color—carbon atom, red color—oxygen, pink color—In, green color—Sn.](image2)

| Type of the sample | Micro-hardness, \(10^9 \text{ Pa}\) | Increase of the micro-hardness |
|-------------------|------------------|-------------------|
| ITO               | 2.2–2.4          | 0                 |
| ITO + CNTs        | 3.5              | 1.5               |
| ITO + CNTs + SEW  | 4.2–4.8          | 1.9–2             |

Table 1. The ITO microhardness increasing data.

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data one can testify that a ∼1.5-fold increase in microhardness is observed for the samples with CNTs; a ∼1.9–2-fold increase in microhardness is observed for the samples with CNTs and additional treatment with SEW.

Furthermore, the wetting angle of the modified ITO conducting coating can be changed from the 80–85 (for pure ITO) to 100–120 degrees (for the ITO covered with the CNTs). It can provoke the Lotus effect and can propose the use of the materials treated with the CNTs for the biomedicine to protect the medical instruments from the virus placement. Some change of the wetting angle is shown in figure 5.

Some quantum-chemical calculation has supported the obtained results and formation of the proposed covalent bonding between the carbon atoms and the ITO surface atoms. The simulated data are shown in figure 6.

It should be mentioned that the quantum-chemical calculation has been made based on the LAMMPS program [16, 17]. Thus simulation is in good coinciding with the spectral shift shown in figure 4 due to the fact that the velocity of the CNTs is correlated with the petentarion depth of the CNTs into the ITO surface. Thus, it provokes the better reconstruction of the surface layer of a conductive substance under the action of the laser treatment with carbon nanotubes.

Considering the obtained results it can be proposed the following qualitative model shown in figure 7.

Remembering that the CNTs can display the donor and acceptor features [18], using their unique transport properties [18–20] one can taken into account the large numbers of the electrons from the core of the CNTs, which can dramatically increase the conductivity of the surfaces covered with CNTs. Some quasi-graphene layers can be formed, that leads to decrease dramatically the resitvivity. In this case the ITO covered with the carbon nanotubes can be effectively used in the gas storage systems, at which the change of the resistivity plays the role of determining the amount of the stored gases.

Of course, it is worth noting that many scientific and technical groups in the world study the properties of the ITO conductive coatings, since they compete with the ZnO conductive contacts. It is due to the fact that ITO has better conductivity parameters, lower refractive index, and other advantages, which leads to their wide application in various optoelectronics and biomedicine devices. In the present work an effective laser method is used for modifying the ITO properties via CNTs vertically deposited on the materials surface. Different experiments are supported the established results and the proposed area of the applications.
4. Conclusion

Analysing the obtained results one can testify the following: (1). The bathochromic spectral shift can be found after the CNTs deposition on the ITO surface via the LOD technique. It can extend the area of the applications of the ITO conducting layers in the devices, which can be used at the special conditions. Recently the IR-shift has been shown by us in the LC-based devices doped with LnS nanoparticles, when the interface has been modified with the CNTs. It extends the types of the sensitized LC with the novel relief for the orientation of the large molecules under the external fields [21]. (2). The dramatic decrease of the resistivity can be established, which corresponded to the change of the resistivity values from 700–100 Ohm to 400–40 Ohm. It can be useful in the electroooptical devices to decrease the level of the bias voltage in all electro-optical devices, for example, in the solar cells, gas storage systems and in the modulation technique, which use the spatial light modulators in the electro-addressed and light-addressed modes. Recently the modified ITO coatings has been used by us to decrease of the bias voltage of the LC-cells doped with the WS2 nanoparticles [22]. (3). The obtained ITO + CNTs + SEW relief can be useful in order to be applied in the display technique to orient the LC molecular according the dominant direction without the application of the direct alignment layer. Thus, the number of the technological operations can be decreased. Moreover, the novel relief without the high toxical polymide layers used by the different display companies can be useful in the biomedicine to visualise the erythrocytes, DNA, etc. bio-objects. (4). The increase of the wetting angle, from one point of view can be considered as the forerunner to propose the novel method for the LC molecular orientation in the vertical position, in comparison with the well-known MWVA technology. It can be connected with the increase of the transparency in the LC-cells with the modified ITO by CNTs deposition. From the other side, it can be useful for the biomedicine to protect the medical instruments from the virus. Recently the modified ITO coatings has been proposed and shown by us to protect the medical instruments from the viruses [23]. (5). Due to the effective electron outflow from the CNT core it can be possible to propose the qualitative model in order to explain the dramatic change of the resistivity. (6). It should be noticed that the same experiments have been made for the ITO coatings coated with the reduced graphene oxides, in order to compare these data with the ones established and controlled for the ITO treated with the CNTs under the same LOD procedure. But the results should be explained in details and will be presented in future paper.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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