Creation of ZnO-based nanomaterials with use synergies of the thermal action and laser-induced vibrations

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Abstract. Synthesis of metallic-semiconductor nanocomposite based on ZnO nanowires under pulse-periodic laser action with a pulse frequency of 3 Hz was performed. By analyzing the results of the samples’ responses to the laser-induced vibroexcitation, it was found that the vibration rate increases in the case of frequencies that are divisible by the frequency of initial oscillation, during the amplitude decrease with the frequency increase. The determination of sample heating features by laser action was performed. Analysis of the X-ray diffraction image showed that thermal oxidation by the pulse-periodic laser treatment leads to the ZnO oxide formation on the substrate of porous Cu–Zn alloy. It is shown that a non-stationary local deformation, caused by a highly-powered external action, is a condition for the intensification of mass transfer in the solid phase of a metallic material. Thus, for the first time it is shown that the use of synergies of thermal effects and laser-induced vibrations in the sound frequency range of pulse-periodic laser beam allow the implementation of a new approach for the creation of structures of composite nanomaterials based on zinc oxide. Results of study are the basis for creating software to controlling laser systems.

1. Introduction

As one of the most promising semiconductor compounds with n-type conductivity and interesting piezo- and ferro-electric properties, zinc oxide attracts the attention of researchers in connection with the extensive field of practical applications [1]. Particular attention is paid to the production of structures based on nanoelements (nanowires, nanorods, nanofibers, nanofilms, etc.) [2-4]. Such structures can be used as sensor devices, and show clear advantages in comparison to commercially available sensors. For example, sensors based on nanoelements could possibly combine an increase in selectivity with lower energy consumption [5]. Besides the production of gas sensors, ZnO offers a chance for manufacturing of LEDs and lasers in the ultraviolet range of the spectrum, as well as for the production of solar cells, scintillators, piezoelectric devices and so on. Highly dispersed ZnO with a high specific surface area has attracted particular attention [6]. Among the possible technical applications of these forms are composite metals / oxide materials which are of interest as functional electric contact materials, and, in particular, a metallic-semiconductor nanocomposite ZnO / Cu. Ordered periodic compositions of nanostructures based on wurtzite ZnO and monoclinic CuO find potential application in nanoelectronics, nanooptics, nanocalysis, bioengineering et al. [7-9]. However, there are currently no effective methods available on which an industrial technology for a controlled production of periodic structures of metallic-semiconductor ZnO / Cu nanocomposites based on the metal matrix and semiconductor nanomaterial, and the oxide semiconductor nanocomposite ZnO / CuO could be founded.
In earlier Ref. [10–14], possibilities for the generation of nanomaterials have been evaluated and a synthesis of nanoporous as well as composite nanomaterials based on ZnO by pulse-periodic laser action has been performed. For the first time, a significant increase (several times in comparison with only the thermal action) of the diffusion coefficient in a metallic material has been described caused by synergies of the thermal action and laser-induced vibrations (mainly in the sound frequency range) evoked by a pulse-periodic laser beam with pulse durations in the micro- and millisecond range [15-17]. In this case, laser-induced vibrations were performed mainly in the sound frequency range [18-21]. A condition for an intensification of mass transfer in the solid phase of selectively oxidizable copper-zinc metallic materials has been identified as a non-stationary stressed-deformed state caused by laser induced sound waves. The use of this synergistic effect, which we are studying, allows the implementation of a new approach for the creation of structures of composite nanomaterials based on zinc oxide: metallic-semiconductor ZnO / Cu nanocomposites and oxide semiconductor nanocomposites ZnO / CuO. It can also serve as a basis for the development of new creation methods for promising semiconductor heterostructures n-ZnO / p-CuO. Such methods open the possibility to achieve excellent results in the area of creating new functional nanomaterials. In this context, for the creation of nanomaterials based on ZnO the actual task is the problem of researching the synergy of thermal action and vibration in the infrasonic range near the lower boundary of the sound frequencies caused by pulse-periodic laser action.

2. Synthesis of metallic-semiconductor nanocomposite ZnO / Cu based on ZnO nanowires under laser action

For the experiments, samples of brass L62 with a thickness of 50 micrometers and dimensions of 30×20 were used. A diffusion-cooled and radio frequency excited CO₂-laser ROFIN DC 010 with single pulse duration of 0.026–125 ms was used. A diffractive optical element [22-25] within an optical system has been used for beam forming. The laser action was performed by using a pulse frequency of 3 Hz. Laser power of Gaussian energy density distribution was varied in the range of 150–305 W, and a laser spot diameter on the sample surfaces is 16 mm. A three-component scanning laser vibration-measuring instrument Polytec® PSV-400-3D was used to measure the vibration rate. Spectra of the samples’ responses to external vibroexcitation caused by pulse-periodic laser action have been measured and their wave forms have been determined and registered.

Figure 1 shows a typical range of the vibration rate \( V \) of the sample during the laser action with a pulse frequency \( f = 3 \) Hz. By analyzing the results of the samples’ responses to the described laser-induced vibroexcitation, it was found that the vibration rate increases in the case of frequencies that are divisible by the frequency of initial oscillation, during the amplitude decrease with the frequency increase. In the study of the forced oscillations it was revealed that the maximum values of vibration rate occur at frequencies close to the natural vibration frequency. For selected sample dimensions, this value is approximately 48.5 Hz. Figure 2 shows images of the sample, which have been re-established with the use of PSV Presentation software. The shape of the oscillations corresponds to frequencies close to the upper boundary of the infrasonic range, namely: 3 Hz, 6 Hz, 9 Hz, 12 Hz, and 15 Hz. It has been defined that maximum vibration rate occurs on the periphery of the sample.

For researching the heating of the samples via laser action, a FLIR SC7300 thermovision camera was used. The determination of sample heating features by laser action with a pulse frequency \( f = 3 \) Hz was performed with the help of laser radiation of 165 W. This provided an opportunity to ensure conditions for slower heating of the samples. For example, the centre area of the heat affected zone of the samples to the temperature 500°C was heated no faster than 150 s. An increase of the laser action time led to a rise of the centre area temperature in a greater degree than on the periphery. Figures 3, 4 show the time dependence of the temperature for the central point of the heat affected zone of the sample at laser action for 168 s. The power of the laser action was 165 W. The temperature difference at growth of action time is increases and reaches 80°C at the last cycle (minimum temperature 435°C, maximum temperature 515°C). Figure 5 shows the temperature distribution along the sample at pulsed-periodic laser action. The highest temperature was registered at the centre of the heat affected zone. Figure 6 shows the temperature field of the sample. Laser action time is 168 s.
Figure 1. Spectrum of vibration rate averaged over the entire surface of the sample during laser action with pulse frequency 3 Hz.

Figure 2. The sample images per quarter of the oscillation period, obtained using the PSV Presentation software and corresponding to the frequency of 3 Hz (a), 6 Hz (b), 9 Hz (c), 12 Hz (d), 15 Hz (e).

Figure 3. The time dependence of the temperature for the central point of the heat affected zone of the sample at laser action for 168 s. The power of the laser action was 165 W; time interval 50–168 s.

Figure 4. The time dependence of the temperature for the central point of the heat affected zone of the sample; time interval 165–168 s.
Figure 5. The temperature distribution along the sample.

Figure 6. The temperature field of the sample at pulsed-periodic laser action. Laser action time is 168 s.

The surface of the material after the pulse-periodic laser treatment that realized on the air was researched by using a scanning electron microscope VEGA\ SB, Tescan. In this case, on the surface of the brass the formation could be observed of an oxide coating of lemon-yellow colour, which with increasing laser treatment time passed into the whitish-gray that is typical of zinc oxide, and consisted of elongated needle-shaped crystals. An analysis of the elemental composition of this coating was performed by using a system of electron-probe energy-dispersive microanalysis INCA Energy SEM Oxford Instrument as part of microscope VEGA\ SB, Tescan. It was found that the proportion of zinc of the metal elements reached up to 99 %. This demonstrates that on the surface of Cu–Zn alloys mainly zinc oxide ZnO is formed. On the surface of metallic material pores are formed in sub-micron and micron ranges. The image of the surface of the metal-semiconductor nanocomposite ZnO/Cu that obtained with using a scanning electron microscope, which is a ZnO film on the surface of a metallic porous material with a copper content of up to 90%, is shown in Figure 7.

The dimensions and shapes of nanopores distributed over the surface are relatively stable. After laser action on the sample surface the structure is formed that contained evenly distributed on area the openly micropores with different forms: from oval to irregular. Sub-micropores with a characteristic size not exceeding 1 μm are detected, as well as micropores. Connecting with each other through constrictions, the pores also formed micropores branches. At the center area of laser pulse-periodic action, the pore density is higher than at periphery. Figure 8 shows pores of the sub-micrometer and micrometer ranges formed on the surface of the processed material. Figure 9 shows the images of ZnO nanofibers formed on the surface of brass L62.

Figure 7. Metal-semiconductor nanocomposite ZnO/Cu: 1 – area of whitish-gray films forming; 2 - sub-micron range pores on the surface of metallic material.

Figure 8. Pores of the sub-micrometer and micrometer ranges formed on the surface of the processed material.
Figure 9. The images of ZnO nanofibers formed on the surface of brass L62.

Since the diffusion coefficient is related exponentially to the temperature, a temperature rise is an effective way to increase the mobility of atoms. However, a non-stationary local deformation, caused by a highly-powered external action, is a condition for the intensification of mass transfer in the solid phase of a metallic material. At that, laser action with pulse-periodic radiation allows a persistent stress condition to develop on the surface of the samples. However, the intensity of the nanofibers formation of zinc oxide much higher in centre than on the periphery, as the highest temperature during heating was in the central zone.

An X-ray structural analysis of the samples of the copper–zinc alloy was performed. The X-ray diffraction method based on the ability of the X-rays to be reflected from the planes of the crystal lattice of the material makes it possible to determine in polycrystalline objects: the size of coherent scattering regions; the lattice parameters of the separate fractions; and the presence of chemical compounds. Analysis of the X-ray diffraction image showed that thermal oxidation by the pulse-periodic laser treatment leads to the ZnO oxide formation on the substrate of porous Cu–Zn alloy. Thus, for the first time it is shown that the use of synergies of thermal effects and laser-induced vibrations in the sound frequency range of pulse-periodic laser beam allow the implementation of a new approach for the creation of structures of composite nanomaterials based on zinc oxide in pure metallic-semiconductor ZnO / Cu nanocomposite.

3. Conclusion
Synthesis of metallic-semiconductor nanocomposite ZnO / Cu based on ZnO nanowires under laser action of a diffusion-cooled and radio frequency excited CO₂-laser was performed. The laser action was realized with a pulse frequency of 3 Hz. Spectra of the samples’ responses to external vibroexcitation caused by pulse-periodic laser action have been measured and their wave forms have been determined and registered. By analyzing the results of the samples’ responses to the described laser-induced vibroexcitation, it was found that the vibration rate increases in the case of frequencies that are divisible by the frequency of initial oscillation, during the amplitude decrease with the frequency increase. The determination of sample heating features by laser action was performed at power of 165 W.

The surface of the material after the pulse-periodic laser treatment that realized on the air was researched by using a scanning electron microscope. In this case, on the surface of the brass the formation could be observed of an oxide coating. It was found that the proportion of zinc of the metal elements reached up to 99 %. This demonstrates that on the surface of Cu–Zn alloys mainly zinc oxide ZnO is formed. Under the oxidized layer, on the surface of metallic material pores were formed in sub-micron and micron ranges. The dimensions and shapes of nanopores distributed over the surface were relatively stable. After laser action on the sample surface the structure was formed that contained evenly distributed on area the openly micropores with different forms: from oval to irregular. Analysis of the X-ray diffraction image showed that thermal oxidation by the pulse-periodic laser treatment leads to the ZnO oxide formation on the substrate of porous Cu–Zn alloy.
Since the diffusion coefficient is related exponentially to the temperature, a temperature rise is an effective way to increase the mobility of atoms. However, a non-stationary local deformation, caused by a highly-powered external action, is a condition for the intensification of mass transfer in the solid phase of a metallic material. At that, laser action with pulse-periodic radiation allows a persistent stress condition to develop on the surface of the samples. Thus, for the first time it is shown that the use of synergies of thermal effects and laser-induced vibrations in the sound frequency range of pulse-periodic laser beam allow the implementation of a new approach for the creation of structures of composite nanomaterials based on zinc oxide in pure metallic-semiconductor ZnO/Cu nanocomposite. Results of study are the basis for creating software to controlling laser systems that provide the required processing modes. This is important to solve the problems of laser information technologies.

4. References
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