Creation of zinc oxide based nanomaterials by repetitively pulsed laser treatment

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Abstract. By repetitively pulsed laser treatment with a frequency of 500 Hz was metal/semiconductor nanocomposite on a basis of zinc oxide nanowires created. An analysis of results made it possible to find that with described laser-induced vibroexcitation of samples, vibration speed increases for frequencies multiple to frequency of the initial oscillation, and when frequency is increasing the amplitude is decreasing. Samples heating particularities in consequence of laser irradiation were determined. Analysis of X-ray diffraction images showed that the zinc oxide creation on the porous copper-zinc alloy substrate occurs as a result thermal oxidation by the repetitively pulsed laser treatment. It is shown that intensification condition of mass transfer in a solid state of a metal material is a local non-stationary deformation that is produced by a highly-powered outer action. Using of synergies of thermal action and vibrations in a sound frequency range caused by laser irradiation, provides opportunity of a new approach realization for the structures creation of composite nanomaterials on a basis of zinc oxide in metal/semiconductor Cu/ZnO nanocomposite.

1. Introduction
Special attention of researchers attracts the zinc oxide as a very interesting n-type semiconductor material with fine ferro- and piezoelectric properties, due to the extensive field of application [1]. Structures that are based on nanofilms, -fibers, -wires and etc. [2, 3] can be used in detector devices [4-6], and this focused special attention to their production, since such devices demonstrate clear advantages compared with commercially available sensors. Such sensors are characterized by lower power consumption and increased selectivity [7]. ZnO provides an opportunity for manufacturing of scintillators, piezoelectric devices, solar cells, ultraviolet lasers and LEDs, as well as a production of gas sensors. Specific attention is provided by highly dispersed state of zinc oxide that has a high specific area of surface [8]. Composite metal/oxide materials can contain ZnO in such a state for possible technical applications of this state and present interest as electrical contact materials, especially a metal/semiconductor nanocomposite Cu/ZnO. Nanostructure compositions based on monoclinic copper oxide and wurtzite zinc oxide have a potential application in bioengineering, nanocatalysis, -optics, -electronics, and others [9-11]. However, at the present time doesn’t exist the technology for nanocomposite structures manufacturing of the oxide semiconductor CuO/ZnO and metal/semiconductor Cu/ZnO.
Synthesis of porous Cu-Zn nanomaterials and later of composite nanomaterials on a basis of zinc oxide by repetitively pulsed laser treatment was considered in Ref. [12]. For the first time a thermal action and vibrations that are caused by a repetitively pulsed laser beam having a pulse duration in milli- or microsecond ranges were researched. Was registered an increase in several times of the diffusion coefficient compared with only thermal action on metal materials [13]. In this case, vibrations caused by laser effect occurred in infrasound and sound frequency ranges [14-16]. It was determined that caused by laser effects sound waves to conditional a non-stationary stress-strain state are conditions for intensification of mass transfer processes in selectively oxidizable Cu-Zn metal materials. This synergistic effect can be as base for development of new methods for creation prospective heterostructures p-CuO/n-ZnO. It allows the realize of a new approach for a manufacturing of zinc oxide based composite nanomaterial structures: oxide semiconductor CuO/ZnO and metal/semiconductor Cu/ZnO nanocomposites. Such creating methods of new functional nanomaterials present an opportunity to achieve great results in this area. Therefore, problem of researching synergies of thermal action and vibrations that are caused by repetitively pulsed laser treatment is actual for the formation of zinc oxide based nanomaterials.

2. Creation based on zinc oxide nanowires of metal/semiconductor nanocomposite Cu/ZnO in consequence of laser irradiation

Samples of the brass L62 with dimensions of 30×20 mm$^2$ and a thickness of 0.05 mm were used for experiments. The effect on samples was performed by CO$_2$ Slab laser ROFIN DC 010, where a pulse frequency was 500 Hz. Laser power was 330 W, and a diameter of the laser spot which has been formed on the samples surface was 16 mm. A diffractive optical element [17-20] has been used for the beam shaping. A 3D scanning vibration-measuring unit Polytec® PSV-400-3D has been used to register the vibration rate and record oscillation forms of samples.

Figure 1 shows a resulting spectrum of vibration rate $V$ while performing the laser treatment of the sample with a pulse frequency $f = 500$ Hz. During analysis of results was found that with described laser-induced vibroexcitation of samples, vibration speed increases for frequencies multiple to frequency of the initial oscillation, and when frequency is increasing the amplitude is decreasing. It was found that at frequencies in the vicinity to the frequency of natural oscillations, the maximum value of the oscillation frequency is reached. That value was approximately 48.5 Hz for selected sample dimensions. Images of the sample corresponding to initial frequency of 500 Hz that were recreated with the use of the PSV Presentation software is shown Figure 2. The oscillations shape that was obtained corresponds to frequencies of the sound range, namely: 500 Hz, 1000 Hz, 1500 Hz, etc. It was determined that on the sample periphery occurs the maximal vibration rate.

![Figure 1. Resulting spectrum of vibration rate while performing the laser treatment with a pulse frequency 500 Hz.](image-url)
To study the samples heating in consequence of laser irradiation, the thermal imaging camera FLIR SC7300 was used. The definition of samples heating particularities by repetitively pulsed laser treatment with a frequency $f = 500$ Hz and a power of 330 W was performed. The centre of the heat affected zone was heated to 500ºC in less than 12 s. In the process of laser treatment, the temperature in the centre increased more than at the periphery. Figure 3 shows the distribution of temperature along the sample, where the temperature reached maximum value in the centre of the heat affected zone by repetitively pulsed laser treatment. Figure 4 shows the distribution of temperature on the sample, where laser treatment time was 16 s.

A scanning electron microscope VEGA/SB, Tescan was used for an investigation of the surface morphology of the material after a repetitively pulsed laser processing, which was realized in air. In this case, the formation of oxide coating on the brass surface could be observed composed of needle shaped crystals and having a lemon-yellow colour. When increasing laser treatment time, the colour became white-gray that is characteristic for ZnO. As a result of an analysis of the chemical composition of this coating using an electron-probe energy-dispersive analysis system, it was found that mostly zinc oxide was formed on cooper–zinc alloys. Since the proportion of Zn came up to the value of 99 % from all metal materials. Micro- and submicropores were formed on the metal material. Was obtained the scanning electron microscope image that demonstrates the nanocomposite surface of the metal/semiconductor Cu/ZnO. Figure 5 shows formed a zinc oxide film on the porous metal material with content a copper up to 90%.

Figure 2. Images of sample corresponding to the frequency of 500 Hz(a), 1000 Hz(b) and 1500 Hz(c) that are obtained by use the PSV Presentation software.

Figure 3. Distribution of temperature along the sample.
Figure 4. Distribution of temperature on the sample by repetitively pulsed laser treatment, with 16 s exposure time.

Figure 5. Metal/semiconductor nanocomposite of Cu/ZnO: 1 – zone of white-gray coating; 2 – submicropores on the material surface.

Figure 6. Micro- and submicropores formed on the material surface.

Figure 7. Zinc oxide nanowires on the surface of treated material.
After laser irradiation, a structure is formed on the sample surface, containing micropores of various shapes uniformly distributed over the area: from oval to nonregular. Micropores with a typical size bigger than 1 μm were detected, as well as sub-micropores. At periphery of the heat affected zone, the density of pores is smaller than in the central area. Pores also formed micropores branches, which are connected through constrictions. Figure 6 shows micro- and submicropores formed on the material surface. Figure 7 shows zinc oxide nanowires on the surface of treated material.

Temperature increase is an effective measure to raise atoms mobility, because a diffusion coefficient is exponentially growing with the temperature raising. However, intensification condition of mass transfer in a solid state of a metal material is a local non-stationary deformation that is produced by a highly-powered outer action. In this case, on the sample surface appears stress-strain state that is caused by repetitively pulsed laser treatment. But, the formation intensity of zinc oxide nanowires on the periphery is much lower than in the central area insofar as the higher heating temperature was in the centre. The study of samples of the copper–zinc alloy was performed with the method of X-ray diffraction, which is based on X-rays reflecting from planes of the material crystal lattice. This analysis showed that the zinc oxide formation on porous copper–zinc alloy occurs as a result is thermal oxidation by repetitively pulsed laser treatment. Thus, using of synergies of thermal action and vibrations in a sound frequency range caused by laser irradiation, provides opportunity of a new approach realization for the structures creation of composite nanomaterials on a basis of zinc oxide in metal/semiconductor Cu/ZnO nanocomposite.

3. Conclusion
Creation based on zinc oxide nanowires of metal/semiconductor nanocomposite Cu/ZnO in consequence of laser irradiation was performed. Spectrum of vibration rate while performing the laser treatment was registered and their oscillation forms was determined. An analysis of results made it possible to find that with described laser-induced vibroexcitation of samples, vibration speed increases for frequencies multiple to frequency of the initial oscillation, and when frequency is increasing the amplitude is decreasing. The definition of samples heating particularities by repetitively pulsed laser treatment with a frequency \( f = 500 \) Hz and a power of 330 W was performed.

A scanning electron microscope VEGA//SB, Tescan was used for an investigation of the surface morphology of the material after a repetitively pulsed laser processing, which was realized in air. In this case, the formation of oxide coating on the brass surface could be observed composed of needle shaped crystals and having a lemon-yellow colour. When increasing laser treatment time, the colour became white-gray that is characteristic for ZnO. It was found that mostly zinc oxide was formed on cooper–zinc alloys. Since the proportion of Zn came up to the value of 99 % from all metal materials. Micro- and submicropores were formed on the metal material. After laser irradiation, a structure is formed on the sample surface, containing micropores of various shapes uniformly distributed over the area: from oval to nonregular. Subsequent analysis showed that the zinc oxide formation on the porous cooper–zinc alloy occurs as a result is thermal oxidation by repetitively pulsed laser treatment.

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