Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Study of the action of a femtosecond laser beam on samples of a Cu-Zn alloy

Study of the action of a femtosecond laser beam on samples of a Cu-Zn alloy

S P Murzin[1], G Liedl[2], R Pospichal[2] and A A Melnikov[1]

[1]Samara National Research University, Moskovskoe Shosse 34, Samara, Russia, 443086
[2]Vienna University of Technology, Institute for Production Engineering and Laser Technology, Getreidemarkt 9, Vienna, Austria, 1060

e-mail: murzin@ssau.ru, gerhard.liedl@tuwien.ac.at, pospichal, melnickov.alex@yandex.ru

Abstract. We performed experimental researches of the action of a femtosecond laser beam on samples of a Cu-Zn alloy with 50 μm thick. We observed at the time of the laser action, the change in the maximum deflection of the cantilevered samples, which indicated their stressed-deformed state. We performed a metallographic study of the treatment zone. In the multipulse mode at an energy density below the multipulse ablation threshold on the samples surface nanostructures were formed which had ridgelike, one-dimensional lattice structure. These ridges had an average periodicity of 0.68 μm. On the surface of the brass the formation could be observed of a zinc oxide. It is highly probable that superficial zinc extraction which as the more active material is oxidized predominantly can be a result of the acceleration of the diffusion due to the frequency action and the action of the ultrafast laser pulses. Obtained results are important for problems solving of laser information technologies and are the basis for a creating of software for the aim of a controlling of lasers that provide required modes of material processing.

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. Particular attention is paid to the production of structures based on nanoelements (nanowires [1-3], nanorods [4, 5], nanofibers [6, 7], nanofilms, etc.). 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 [8]. 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. 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, nanocatalysis, bioengineering et al [9-11]. 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 Refs. [12-14], possibilities for the generation of nanomaterials have been evaluated and a synthesis

IOP Conf. Series: Journal of Physics: Conf. Series **1096** (2019) 012138 doi:10.1088/1742-6596/1096/1/012138

of composite nanomaterials based on ZnO by pulse-periodic laser action was performed. 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 [15-19]. This 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 [20-24]. In this context, the actual task is the formation of such composite materials with periodic modulation of the chemical composition. An ultrafast laser system could be used to create such spatially ordered, periodic nanostructures on the surface of a material.

Ultrafast lasers have created a new path in laser processing of materials by increasing the capabilities of ultrahigh precision micro- and nanofabrication [25, 26]. Usually, the pulses width of ultrafast lasers ranges from several tens of femtoseconds up to tens of picoseconds. In most cases, pulses shorter than picoseconds are typically used for fundamental research, while longer pulses are used for commercial and industrial applications. The action of a femtosecond laser beam allows the creation of laser-induced periodic surface structures. Such regular single- or two-dimensional structures are caused by a local material removal due to laser ablation after each ultrashort pulse from the areas of interference maximums at the surface of the material and can be generated practically on any opaque material. This process is often accompanied by oxidation, alloying with elements or complex compounds from the environment, thus giving the surface new optical and physical-chemical properties. Additionally, the chemical composition can be changed because of non-uniform evaporation of the surface when it is intensively heated by laser beam. For example, some two- and multicomponent materials evaporate evenly over a wide range of exposure regimes, while others, like different alloys, preferentially lose a more volatile component [27, 28]. As a consequence, the creation of periodic structures on the surface of two- and multicomponent materials typically raises the question of the spatial distribution of chemical elements. And for ultrashort pulses, due to the possibility of more localized heating, it is possible to produce a precise chemical modification of the surface. The purpose of the article is to study a possibility of forming laser-induced periodic surface structures with surface oxidation by the femtosecond laser beam action, which is a new approach to the creation of functional nanomaterials based on zinc oxide.

2. Material under study and laser equipment

Experimental studies of the action of a femtosecond laser beam on samples of a Cu-Zn alloy with 50 μm thick were performed. Parameters of the femtosecond laser action in the scheme without scanning were: average pulse power 500–680 mW, pulse frequency 1 kHz; pulse number 1000, sample position 45 mm, treatment area 0.8 mm^2, and average specific energy in pulse 0.6–0.8 J/mm^2. Figure 1 shows the experimental setup with ultrafast laser.

3. Results and discussion

First, the samples were cantilevered in the fixture. At the time of the laser action with a total duration of 1 s, the change in the maximum deflection of the cantilevered samples was observed by about 1 mm, which indicated their stressed-deformed state. After the end of laser action, the samples immediately themselves were returning to their initial position. A metallographic study of the treatment zone was performed. On the surface of the brass the formation could be observed of an oxide coating of lemon-yellow colour, which passed into the whitish-gray that is typical of zinc oxide. Figure 2 shows an image of the area of laser treatment of the samples of brass L62 with a thickness of 50 micrometers and with the formation of the whitish-gray coating on the surface. Even using an optical microscope, there was an opportunity to distinguish areas of periodic structures formation.

The action of a femtosecond laser in a multipulse mode leads to a change in the morphology of the surface of the material, which was studied by scanning electron microscopy. For the examination of laser processed structures, an analytical scanning electron microscope VEGA \\ SB, Tescan was used, whose accelerating voltage range is between 0.2–30 kV; the electron source is a tungsten cathode with thermionic emission.

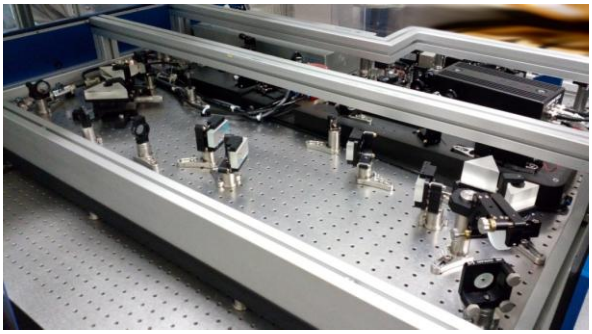

Figure 1. The experimental setup with ultrafast laser.

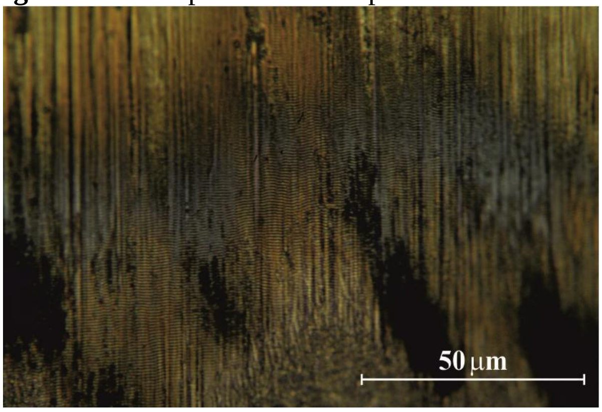

Figure 2. Image of the central (at the bottom) and peripheral (at the top) areas of the laser treatment zone of the samples of brass with a thickness of 50 micrometer with formation on the surface of whitish-gray coating.

Figure 3 shows nanostructures formed on the samples surface at an energy density below the multipulse ablation threshold. For the normal incidence of ultrafast laser pulses in the multipulse mode show a ridgelike, one-dimensional lattice structure. These ridges have an average periodicity of 0.68 μm. Use of a damping device caused some decrease in the intensity of treatment with reduction in size of characteristic zones. Only the increase in the average pulse power from 630 mW to 680 mW (i.e. 8 %) allows compensating this effect. Thus, the possibility of forming a stressed-deformed state in samples under the frequency action of a femtosecond laser is demonstrated. In addition, periodic nanostructures were obtained and surface oxidation was performed.

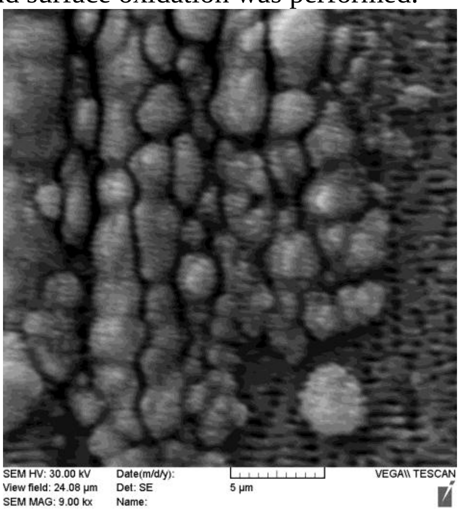

Figure 3. The image of nanostructures formed on the samples surface at an energy density below the multipulse ablation threshold.

To obtain information about the surface structure, the images in the secondary and back-scattered electrons were studied that shown in Figure 4. It is known that the contrast in secondary electrons depends most strongly on the surface contour, and images in back-scattered electrons, in addition to information on the morphology of the surface, contain additional information on the composition of the sample. The intensity of the back-scattered electrons is practically independent of the topography of the sample surface, and the resulting images characterize the elemental chemical composition. For example, the brighter areas on Figure 4b correspond to larger oxygen content that indicating on surface oxidation during processing. In these areas on treated sample surface, the content of copper is decreased. In this case, it is not talking about the replacement of copper atoms by oxygen atoms, as it may seem at first glance. Very likely is the following mechanism. Initially, on the material surface is occurs the predominantly oxidized of zinc as a more active material. The content of non-oxidized zinc is reduced. A concentration gradient is created in the material, which causes diffusion of zinc atoms to the surface. Diffusion becomes a limiting factor of the process. As the result of the frequency action and the action of ultrafast laser pulses, there is an acceleration of diffusion, occurs a more intensive release of zinc onto the surface, which then oxidizes. The content of copper on the surface is decreases (Figure 4c).

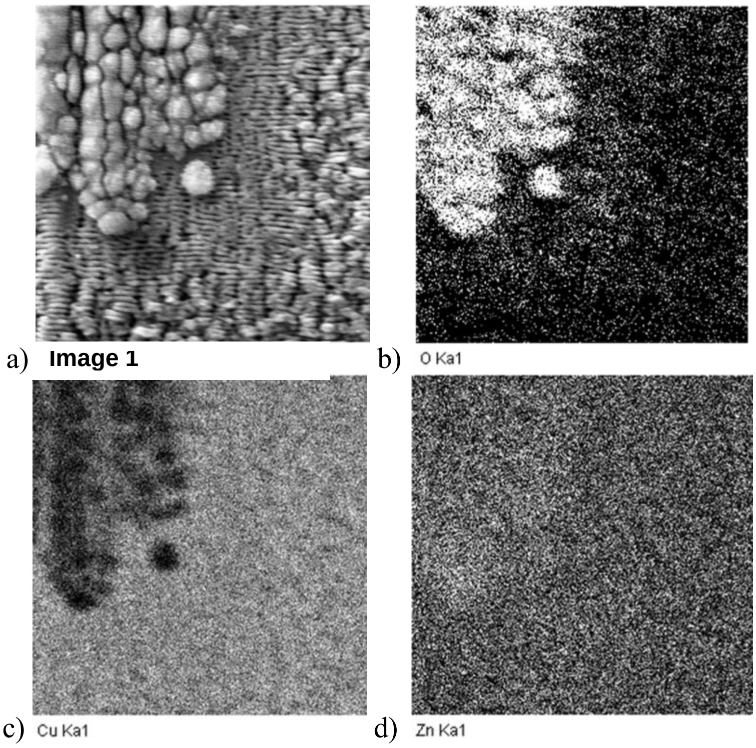

Figure 4. Obtained by means of an analytical scanning electron microscope VEGA \\ SB images in the secondary (a) and back-scattered electrons (b), (c), (d).

Elemental chemical analysis of microvolumes of the sample surface was performed. Figure 5 shows the designation of study areas of the elemental composition, and Table 1 presents the results of the analysis. It should be noted on the samples surface that in addition to copper, zinc and oxygen, the presence of carbon was recorded, the content of which varied from 3 to 5 % by weight in various microvolumes of the treatment zone.

Table 1. Results of elemental composition analysis in the zones on the sample surface (weight %).

Research area	*Cu*	*Zn*	*O*
1	38.3	39.0	22.7
2	58.5	38.1	3.4
The initial state	61.6	37.3	1.1

IOP Conf. Series: Journal of Physics: Conf. Series **1096** (2019) 012138 doi:10.1088/1742-6596/1096/1/012138

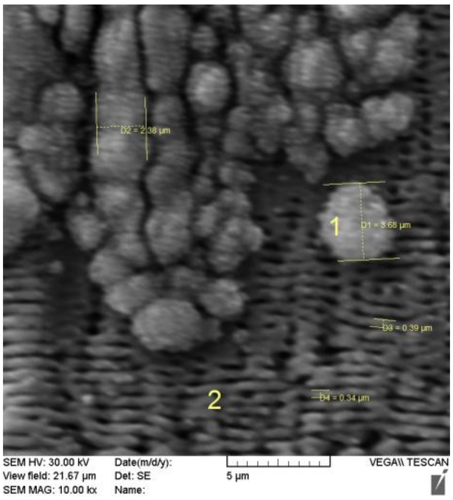

Figure 5. Image of nanostructures formed on the samples surface with the designation of study areas of the elemental composition.

4. Conclusion

The possibility of forming laser-induced periodic surface structures with surface oxidation by the femtosecond laser beam action is studied, which is a new approach to the development of functional nanomaterials based on zinc oxide. Experimental researches of the action of a femtosecond laser beam on samples of a Cu-Zn alloy with 50 µm thick were performed. At the time of the laser action, the change in the maximum deflection of the cantilevered samples was observed, which indicated their stressed-deformed state.

A metallographic study of the treatment zone was performed. In the multipulse mode at an energy density below the multipulse ablation threshold on the samples surface nanostructures were formed which had ridgelike, one-dimensional lattice structure. These ridges had an average periodicity of 0.68 µm. On the surface of the brass the formation could be observed of a zinc oxide. It is highly probable that due to predominantly zinc oxidation as more active material, a concentration gradient is created in the near-surface layer that causes the diffusion of zinc atoms to the surface. As the result of the frequency action and the action of ultrafast laser pulses, there is an acceleration of diffusion, occurs a more intensive release of zinc onto the surface, which then oxidizes. The content of copper on the surface is decreases. Obtained results are important for problems solving of laser information technologies and are the basis for a creating of software for the aim of a controlling of lasers that provide required modes of material processing.

5. References

[1] Zhu C L, Chen Y J, Wang R X, Wang L J, Cao M S and Shi X L 2009 Synthesis and enhanced ethanol sensing properties of α-Fe_2O_3/ZnO heteronanostructures *Sens. Actuator B-Chem.* **140(1)** 185-189

[2] Goris L, Noriega R, Donovan M, Jokisaari J, Kusinski G and Salleo A 2009 Intrinsic and doped zinc oxide nanowires for transparent electrode fabrication via low-temperature solution synthesis *J. Electron. Mater.* **38(4)** 586-595

[3] Kwon J, Hong S and Lee H 2013 Direct selective growth of ZnO nanowire arrays from inkjet-printed zinc acetate precursor on a heated substrate *Nanoscale Res. Lett.* **8(1)** 1-6

[4] Lv Y, Guo L, Xu H and Chu X 2007 Gas-sensing properties of well-crystalline ZnO nanorods grown by a simple route *Physica E* **36(1)** 102-105

[5] Wu C, Shen L, Yu H, Zhang Y-C and Huang Q 2012 Solvothermal synthesis of Cu-doped ZnO nanowires with visible light-driven photocatalytic activity *Mater. Lett.* **74** 236-238

[6] Song X and Liu L 2009 Characterization of electrospun ZnO-SnO_2 nanofibers for ethanol sensor *Sens. Actuator A-Phys.* **154** 175-179

[7] Song X, Wang Z, Liu Y, Wang C and Li L 2009 A highly sensitive ethanol sensor based on mesoporous ZnO-SnO_2 nanofibers *Nanotechnology* **20(7)** 075501
[8] Ge C, Xie C and Cai S 2007 Preparation and gas-sensing properties of Ce-doped ZnO thin film sensors by dipcoating *Mater. Sci. Eng. B-Solid State Mater* **137** 53-58
[9] Luo X, Morrin A, Killard A J and Smyth M R 2006 Application of nanoparticles in electrochemical sensors and biosensors *Electroanalysis* **18(4)** 319-326
[10] Li Y, Qian F, Xiang J and Lieber C M 2006 Nanowire electronic and optoelectronic devices *Mater. Today* **9(10)** 18-27
[11] Gao P-X, Ding Y and Wang Z L 2009 Electronic transport in superlattice-structured ZnO nanohelix *Nano Letters* **9(1)** 137-143
[12] Murzin S P 2014 Method of composite nanomaterials synthesis under metal/oxide pulse-periodic laser treatment *Computer Optics* **38(3)** 469-475
[13] Murzin S P 2015 Determination of conditions for the laser-induced intensification of mass transfer processes in the solid phase of metallic materials *Computer Optics* **39(3)** 392-396 DOI: 10.18287/0134-2452-2015-39-3-392-396
[14] Murzin S P and Kryuchkov A N 2017 Formation of ZnO / CuO heterostructure caused by laser-induced vibration action *Procedia Engineering* **176** 546-551
[15] Murzin S P 2011 The research of intensification's expedients for nanoporous structures formation in metal materials by the selective laser sublimation of alloy's components *Computer Optics* **35(2)** 175-179
[16] Murzin S P 2015 Formation of nanoporous structures in metallic materials by pulse-periodic laser treatment *Opt. Laser Technol.* **72** 48-52
[17] Murzin S P, Shakhmatov E V, Igolkin A A and Musaakhunova L F 2015 A study of vibration characteristics and determination of the conditions of nanopores formation in metallic materials during laser action *Procedia Engineering* **106** 266-271
[18] Murzin S P, Kostriukov E E, Glushchenkov V A, Afanasiev S A and Blokhin M V 2016 Influence of initial surface condition on intensity of porous structure formation in a metallic material during laser action *CEUR Workshop Proceedings* **1638** 83-88
[19] Murzin S P, Prokofiev A B and Safin A I 2017 Study of Cu-Zn alloy objects vibration characteristics during laser-induced nanopores formation *Procedia Engineering* **176** 552-556
[20] Murzin S P 2016 Formation of structures in materials by laser treatment to enhance the performance characteristics of aircraft engine parts *Computer Optics* **40(3)** 353-359 DOI: 10.18287/2412-6179-2016-40-3- 353-359
[21] Murzin S P and Liedl G 2017 Laser welding of dissimilar metallic materials with use of diffractive optical elements *Computer Optics* **41(6)** 848-855 DOI: 10.18287/2412-6179-2017-41-6-848-855
[22] Kazanskiy N L, Moiseev O Yu and Poletayev S D 2016 Microprofile formation by thermal oxidation of molybdenum films *Technical Physics Letters* **42(2)** 164-166
[23] Murzin S P, Kazanskiy N L, Liedl G, Otto A and Bielak R 2017 Laser beam shaping for modification of materials with ferritic-martensitic structure *Procedia Engineering* **201** 164-168
[24] Bolotov M A, Pechenin V A and Murzin S P 2016 Method for uncertainty evaluation of the spatial mating of high-precision optical and mechanical parts *Computer Optics* **40(3)** 360-369 DOI: 10.18287/2412-6179-2016-40-3-360-369
[25] Sugioka K 2017 Progress in ultrafast laser processing and future prospects *Nanophotonics* **6(2)** 393-413
[26] Sugioka K and Cheng Y 2013 *Ultrafast laser processing: from micro- to nanoscale* (Singapore: Pan Stanford Publishing)
[27] Bulgakov A V, Evtushenko A B, Shukhov Y G, Ozerov I and Marine W 2010 Pulsed laser ablation of binary semiconductors: Mechanisms of vaporisation and cluster formation *Quantum Electronics* **40(11)** 1021-1033
[28] Pershin S M, Colao F and Spizzichino V 2006 Quantitative analysis of bronze samples by laser-induced breakdown spectroscopy (LIBS): A new approach, model, and experiment *Laser Physics* **16(3)** 455-467