Powerful ultraviolet laser pulse impact on polished metals and semiconductors

Yu V Khomich¹, T V Malinskiy¹, S I Mikolutskiy¹, V E Rogalin¹, V A Yamshchikov¹, I A Kaplunov²* and A I Ivanova²

¹Institute for Electrophysics and Electric Power RAS, 191186, Russia, Saint-Petersburg, 18, Dvorzovaya Naberezhnaya
²Tver State University, 170100, Russia, Tver, 33, Zhelyabova st.

*E-mail: kaplunov.ia@tversu.ru

Abstract. Laser treatment for samples of copper, its alloys and gold was carried out with a UV pulse of nanosecond duration. After irradiation at subthreshold values of the energy density (E ~ 0.2 - 0.8 J/cm²) the noticeable changes in the surface layer were revealed. These are traces of thermoplastic deformation resulting from laser exposure. They appear as uneven rise of the irradiated sample surface area up to 1 μm. The effect is cumulative, because the height of the uplifts increases with increasing number of impact pulses. In addition, the characteristic features of high-temperature plastic deformation were observed in the form of crystallographic slip and grain-boundary slippage. At E ~ 1 J/cm² or more the optical breakdown occurred with the formation of a crater on the metal surface, that precludes the detection of described effects. The mechanical impulse of a laser plasma, when exposed to a metal surface, prevents the thermomechanical expansion of the material, and therefore, similar effects have not been previously observed. On the surface of materials with a significantly larger elastic limit (single crystals of germanium and silicon, a tungsten carbide) this phenomenon was not observed, because the generated thermomechanical stresses were insufficient to create conditions of plastic deformation.

1. Introduction

Micro- and nanostructuring of the surface has found such wide application in science and technology due to the improvement of the electrical, thermal, radiative, and tribological properties of materials [1-3]. At surface treatment by laser radiation [4–7] micro- and nanostructures are formed, that largely determines surface morphology and physicochemical properties, in particular, adhesion, which is based on diffusion phenomena [8]. It is known from [9–10] that pulsed laser irradiation contributes to a sharp change in the diffusion coefficient with the possibility of increasing it by six orders of magnitude. A direct laser nanostructuring due to its comparative ease of use and high efficiency [5-7] can become a promising method for implementing such a laser exposure. The method has only one stage of processing the material, which consists in irradiating the surface with a focused laser beam, and does not require the use of additional devices.

Despite the fact that the basic amount of the works on direct laser nanostructuring was previously carried out using picosecond and femtosecond lasers [11-14], for practical applications it is interesting to use more reliable and easy-to-use sources, such as nanosecond lasers generating UV radiation and providing higher output energies [15-17].
2. Materials and methods
Polished samples of oxygen-free copper, Cu-Zr and Cu-Cr-Zr alloys, gold sprayed on a lithium niobate crystal, single crystals of silicon (Si) and germanium (Ge) were exposed to laser nanosecond pulses. In addition, polished samples of tungsten carbide were investigated.

The experimental setup is similar to the setup in [14], but in our case, a solid-state pulse-periodic NdYAG-laser is used as the main source of laser radiation. What is more, we use a third harmonic of NdYAG-laser with a wavelength of $\lambda = 355$ nm, a pulse duration of $\tau = 10$ ns, a frequency of $f = 10$ Hz and a pulse energy of up to 8 mJ. The processing parameters were varied by changing the energy density of the laser pulse and the number of pulses in the irradiation spot. For revealing thermoplastic deformation processes, the energy density was preferably near a subthreshold value.

The morphology of the samples was studied using an optical three-dimensional profilometer Zygo NewView 7300 and a scanning electron microscope (SEM) JEOL JSM 6610LV. Using the prefix to the SEM, the elemental composition of the samples was studied before and after laser exposure.

3. Results and discussions
It was found that along with the traditionally studied phenomena of melting, evaporation, and ablation, which are processes associated with the substance transition to another aggregate state [17, 18], a new phenomenon was observed in some materials for exposure regime investigated. It is an irreversible uneven rise in the surface of a number of metals (copper; Cu-Zr and Cu-Cr-Zr alloys; gold). The upper temperature limit of the samples was determined by the condition of preservation of the studied metal in a condensed state [19].

Figure 1 shows primary visually observed traces of laser impact obtained at a pulse energy density of $E \approx 0.15$ J/cm$^2$ on samples of copper and its alloys. In this zone, the sample surface was cleaned of impurities and acquired a characteristic light shade (Figure 1a). The surface uplifts with the height of 20–30 nm and a maximum in the centre of the spot were indicated (Figure 1c). Small scratches passing through the irradiated zone were usually not observed in it.

![Figure 1](image_url)

**Figure 1.** Surface of Cu-Zr sample after irradiation by 1 pulse of NdYAG-laser ($E = 0.15$ J/cm$^2$): (a) photograph by optical microscope; (b) image by three-dimensional profilometer; (c) surface profile.
It is quite possible that with a higher quality polishing of the samples (with a lower initial surface roughness) we could observe the effect of surface rising even with a lower value of pulse energy density. It is interesting to note that the effect is cumulative. An increase in the number of laser pulses led to an increase in the height of the surface uplift. At subthreshold energy densities ($E \sim 0.6 \text{ J/cm}^2$) in the absence of noticeable traces of ablation, an increase in the height of surface uplift by approximately 100 nm was observed in the impact zone [20].

Near the optical breakdown threshold of approximately 1 J/cm$^2$, traces of melting and boiling of thin surface metal layer, which then rapidly solidified, were observed in the area of the irradiation spot. Figure 2 shows the surface of a sample of the Cu – Cr – Zr alloy irradiated by 25 laser pulses with energy density $E \sim 0.8 \text{ J/cm}^2$. In this case, against the background of a general uplift of the spot zone, the geometry of which was comparable with the distribution of laser radiation in the beam, individual numerous spike-like uplifts were observed. The height of such structures was up to 1 μm, or sometimes more (Figure 2d). On copper samples, the traces of melting were less noticeable. We assume that this is due to the higher thermal conductivity of copper as compared to alloys.

![Figure 2](image)

**Figure 2.** Surface of Cu-Cr-Zr alloy sample after irradiation by 25 pulses of NdYAG-laser ($E = 0.8 \text{ J/cm}^2$, $f = 10 \text{ Hz}$): (a) photograph by optical microscope; (b) SEM image; (c) image by three-dimensional profilometer; (d) surface profile.

In some cases, grain-boundary slippage was detected. Different grains reacted differently to laser exposure: a peculiar phenomenon of laser etching was revealed, and it provides appearing individual grains of metal. Also the appearance of slip bands that change orientation during the transition of the grain boundary was indicated (Figure 3). In other words, there were characteristic features of high-temperature plastic deformation. In contrast to the results of [21], a restudy of the sample surfaces, carried out 6 months after laser irradiation, showed no changes. With an increase in the number of impact pulses, a certain accumulation effect was observed.
Figure 3. SEM image of copper surface after irradiation by 16 pulses of NdYaG-laser (E ~ 0.3 J/cm², f = 10 Hz).

At the same time, this phenomenon was not observed on the surface of a number of materials studied (single crystals of germanium and silicon, tungsten carbide). These materials have a significantly larger elastic limit and, therefore, the generated thermomechanical stresses are insufficient to create conditions for plastic deformation. After reaching the optical breakdown threshold the intense evaporation of the surface layer occurred with the formation of a crater. The mechanical impulse of the laser plasma restrained the movement of the sample material to the surface and, therefore, the effect of expansion did not appear. In this case, ultrafast melting, evaporation, and cooling of a thin surface layer of metal took place [5, 7, 17].

4. Conclusions
After irradiating the samples of copper and its alloys, as well as gold, with a UV nanosecond laser pulse at energy densities below the ablation threshold (0.2 - 0.8 J/cm²), noticeable changes in the morphology of the surface layer were detected. These are traces of thermoplastic deformation that occurred as a result of the action of a laser pulse. They appear as uneven rise of the irradiated sample surface area up to 1 μm. In the irradiation spot, the characteristic features of high-temperature plastic deformation were observed in the form of crystallographic slip and grain-boundary slippage. The effect of surface rise has a cumulative nature, that is, the height of the uplifts increases with increasing number of impact pulses.

The dissipation of the laser pulse energy in such a short time should lead to a sharp increase in the concentration of nonequilibrium point defects in the near-surface layer. Along with this, the resulting significant distortions of the crystal structure of the surface layer of the metal should significantly affect the processes of surface diffusion. It is assumed that such preliminary laser heat treatment should significantly improve the diffusion welding of metals.

At the energy density of 1 J/cm² or more, an ablation crater was formed and an optical breakdown occurred on the metal surface. The mechanical impulse of a laser plasma, when exposed to a metal surface, prevents the thermomechanical expansion of the material, therefore similar effects have not been previously observed. In addition, the formation of a laser crater with the depth significantly exceeding the height of the rise eliminates the possibility of detection of such effects. Also on the surface of materials with a significantly larger elastic limit (single crystals of germanium and silicon, a tungsten carbide), the phenomenon of surface rising was not observed. The generated thermomechanical stresses were insufficient to create conditions of plastic deformation.
Acknowledgments
This work was carried out using the resources of the Centre for Collective Use of Tver State University as part of the state assignment for scientific activity (N 0057-2019-0005, N 0817-2020-0007).

References
[1] Wan Y and Xiong D S 2008 J. Mater. Process. Technol. 197 96
[2] Wu Z, Deng J X, Chen Y, Xing Y Q and Zhao J 2012 Int. J. Adv. Manu. Technol. 62 943
[3] Bhushan B 2008 Phil. Trans. R. Soc. A 366 1499
[4] Makarov G N 2013 Phys. Usp. 56 643
[5] Khomich V Yu and Shmakov V A 2015 Phys. Usp. 58 455
[6] Tokarev V N, Shmakov V A, Khasaya R R, Mikolutskiy S I, Nebogatkin S V, Khomich V Yu and Yamshchikov V A 2010 Proc. Int. Cong. on Applications of Lasers and Electrooptics (Anaheim, USA) pp 1257–1265
[7] Tokarev V N, Khomich V Yu, Shmakov V A and Yamshchikov 2008 Doklady phys. 53 206
[8] Lee L H 2013 Fundamentals of adhesion (New York: Springer Science+Business Media) pp 325-348
[9] Gurevich M E, Larikov L N, Mazanko V F, Pogorelov A E and Falchenko V M 1978 Metallophysics (In Russian) 73 80
[10] Rovinskii R E, Rogalin V E, Rozenberg V M and Teplitskii M D 1980 Physics and Chemistry of Material Treatment (In Russian) 3 7
[11] Vestentoft K, Olesen J A, Christensen B H and Balling P 2005 Appl. Phys. A 80 493
[12] Vorobyev A Y and Guo C 2005 Phys. Rev. B 72 195422
[13] Ostendorf A, Koch J, Korte F and Chichkov B N 2004 Proc. SPIE 5448 1
[14] Mikolutskiy S I, Khasaya R R, Khomich Yu V and Yamshchikov V A 2018 J. Phys. Conf. Ser. 987 012007
[15] Guillemot F, Prima F, Tokarev V N, Belin C, Porte-Durrieu M C, Gloriant T, Baquey C and Lazare S 2004 Appl. Phys. A 79 811
[16] Ganin D V, Mikolutskiy S I, Tokarev V N, Khomich V Yu, Shmakov V A and Yamshchikov V A 2014 Quantum Electron. 44 317
[17] Khasaya R R, Khomich Yu V, Malinskiy T V, Mikolutskiy S I, Yamshchikov V A and Zheleznov Yu A 2014 Letters on materials (In Russian) 4 45
[18] Vashukov Yu A, Demichev S F, Elenev V D, Khomich Yu V, Malinskiy T V, Mikolutskiy S I, and Yamshchikov V A 2019 Appl. Phys. 1 8
[19] Mirzade F H 2009 Nonlinear deformation waves interacting with laser induced carriers of local disorder Laser Technologies of Material Treatment (In Russian) ed. Panchenko V Ya (Moscow: Fizmatlit) chapter 7 pp 220-278
[20] Malinskiy T V, Mikolutskiy S I, Rogalin V E, Khomich Yu V and Yamshchikov V A 2019 Thesis of Reports of Scientific-practical Conference of Russian and Croatian Scientists (Moscow: NUST “MISIS”) pp 171-173
[21] Vasil’ev S V, Ivanov A Yu, Liopo V A and Sitkevich A L 2019 Proc. of 13th Int. Conf. IRS-2019 (Minsk, Belarus) pp 221–223