SELF-ORGANISED VORONOI DIAGRAMS GENERATED BY SINGLE-SHOT FEMTOSECOND LASER ABLATION OF METAL SURFACES.

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Abstract
Here we report on experimental studies of self-assembled Voronoi diagrams observed on the surface of laser-induced craters. The craters are left by means of single-shot femtosecond laser ablation of metal samples. The Voronoi cells appear in the melt layer which undergoes transition to overheated liquid, i.e. represents a system driven far from equilibrium. The pattern properties and mechanisms leading to its appearance are discussed. A possibility to control the position of the nodes of the Voronoi diagram is demonstrated.

Key words
Voronoi Diagram, femtosecond laser ablation, nonequilibrium systems, pattern formation

System driven far from equilibrium are known to demonstrate large variety of self-organised patterns (Cross and Hohenberg, 1993). Nice examples of pattern formation phenomena can be observed in chemical (de Wit, 1999), biological (Murray, 1993), optical (Arecchi *et al.*, 1999), granular (Ristow, 1995) and other systems; among the frequently-observed structures one can mention fronts, periodical stripes, hexagonal arrangements, solitons, spirals, and many others. However some types of patterns are seldom observed in experiments. Among them are e.g. concentric ring pattern observed only in hydrodynamic (Thompson *et al.*, 2002) and in gas-discharge systems (Gurevich *et al.*, 2003) (Gurevich *et al.*, 2005) and self-organised Voronoi diagrams (Voronoi, 1908) reported only in chemical (de Lacy Costello *et al.*, 2004) and gas-discharge (Zanin *et al.*, 2002) systems, or by aggregation of crystalline Ge during annealing of an Al/Ge bilayer film deposited on a SiO_2 substrate (Doi *et al.*, 1998).

A Voronoi diagram (VD) is a partition of an area to a number of domains corresponding to a given set of reference points (nodes). Each domain corresponding to a node consists of points for which the distance to the particular node is less than to all other nodes. They are interesting for practical applications in different branches of sciences from pattern recognition till partitioning of a city into areas of responsibility for public facilities (Okabe *et al.*, 1992).

In this manuscript we report on the experimental observation of self-organised Voronoi diagrams observed in the craters left on metal surfaces after ablation by means of single femtosecond laser pulses. Comparing to the common nanosecond laser ablation, the femtosecond one can be characterised by more complicated physical processes triggered in metals by the incident laser field. On the other hand these processes happen on different time scales; that simplifies the analysis of the mechanisms responsible for the formation of the structures. The laser pulse duration for typical femtosecond lasers is $\tau \sim 10^{-13}$ s; on this time scale free electron gas absorbs electromagnetic wave and the electron temperature in the surface layer increases with the rate of $\gtrsim 10^{14}$ K/s and exceeds 10^3 K (Ivanov and Zhigilei, 2003). Due to such a quick increase of the surface temperature a thin surface layer undergoes transition to overheated liquid which boils explosively (Povarnitsyn *et al.*, 2008). The depth of the liquid layer according to Molecular Dynamic Simulations (MDS) is approximately several tens of nanometers (Ivanov and Zhigilei, 2003) and 100-200 nm according to simulations based on the Two-Temperature Model (TTM) (Povarnitsyn *et al.*, 2008); the lateral dimension is close to the crater radius, i.e. several tens of micrometers. Thus the pattern-forming system is a thin two-dimensional layer of overheated liquid which undergoes rapid boiling and resolidification.

Although pattern formation in overheated liquid layers has not been explored jet, there are several publications reporting pattern formation by laser ablation of solids: One can observe random splashing pattern (Vorobyev and Guo, 2006) or periodic stripes or localized structure there (Varlamova *et al.*, 2006). However

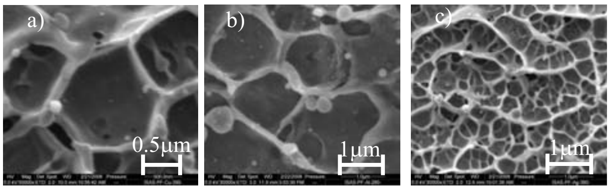

Figure 1. Typical laser crater. a) Cu, F=127 kJ/cm^2; b)Al, F=93 kJ/cm^2; c)Ag, F=127 kJ/cm^2.

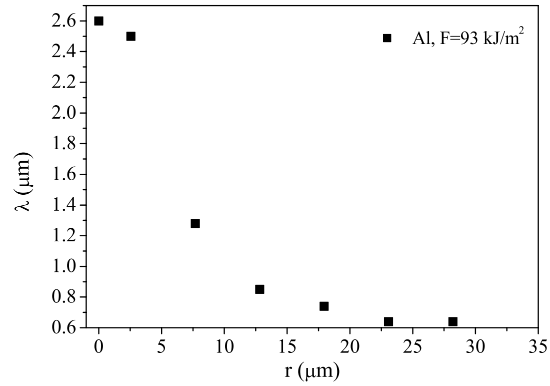

Figure 2. Dependence of the cell size along the crater radius.

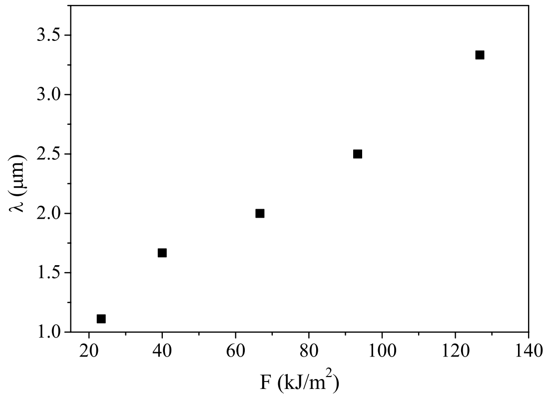

Figure 3. Dependence of the maximal cell size (in the centre of the crater) for aluminium sample on the pulse fluence.

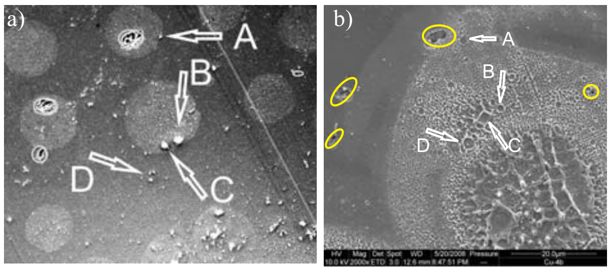

Figure 4. Copper sample a) before and b) after fs-laser ablation. Nanoparticles present on the surface before the ablation and corresponding Voronoi cells are marked with arrows. The cavities on the surface are marked in the both figures for the orientation. The figure size is approximately 70 μm

the physical mechanisms of the pattern formation in such systems are not clear. Indeed, in the cited papers the self-organised patterns are ascribed to interaction of the incident laser wave with surface defects or with waves of other origin excited on the surface (Akhmanov *et al.*, 1985). Moreover, in most experiments on pattern formation in laser craters, each surface unit is treated by a large number of laser pulses, see e.g. (Varlamova *et al.*, 2006). This suggests application of mode-competition models. In the experiments reported in this paper the solids are ablated with a single laser pulse in order to simplify the analysis of the underlying physics and exclude mechanisms based on the interaction between consequent laser pulses.

A thin layer of overheated liquid is generated by means of femtosecond laser ablation of metallic samples by means of ”*Hurricane*” near infrared femtosecond laser produced by *Spectra Physics*. The laser pulse energy E_p is changed from 70 to 400 μJ, pulse duration is approximately 10^{-13} s, wavelength 800 nm. The laser beam is focussed on the sample surface by means of ”*UP-XP*” femtosecond optical microscope produced by *New Wave*. The sample is exposed by single laser pulses. The number of pulses is controlled by adjusting the open time of the shutter with the repetition rate of the laser. Samples made of Ag, Al, Au, Cu, W were studied.

After the exposure the resolidified sample surface is studied by means of Scanning Electron Microscope (SEM) *Quanta FEI 200*. Typical crater patterns can be found in Fig. 1. One can see that the cells appear in different metals by different ablation conditions. They are edged by thin walls of resolidified metal. The wall height in the centre of the crater is approximately several hundred nanometers and thickness of 20-30 nm.

The size of the cells λ depends on the local laser fluence on the sample surface. The cells in the middle of a crater are larger than in the periphery, due to the Gaussian intensity profile of the laser pulse, see Fig. 2. The dependence of the sell size in the centre of the crater on the average pulse fluence F for aluminium sample can be found in Fig. 3. The size of Voronoi cells increases linearly with the pulse fluence.

We can influence the position of some nodes in the self-assembled VD by introducing defect such as nanoparticles on certain positions before the laser ablation. In Fig. 4 (a) one can see surface of a diamond-cut copper sample with spread copper nanoparticles. Some large nanoparticles are marked with signed arrows. The same place after the laser ablation is shown in Fig. 4 (b). One can see that the positions of nanoparticles on the peripheral part of the laser crater correspond to large cells, which are marked as well.

We suppose that the observed pattern is a self-assembled Voronoi diagram, which appears in a thin layer of overheated metal melt. The bubbles spontaneously formed in the liquid overheated metal are the nodes of the Voronoi cells. The bubbles grow but the rate decreases due to decrease of the Laplace pressure in the bubble. Simultaneously the temperature in the crater decreases and the melt pressed between the nodes solidifies. A two-dimensional metal foam formed in this way is an example of self-assembled Voronoi diagram formed by bubbles which appear by explosive boiling of overheated melt. Artificial introduction of defects on the metal surfaces suggests a possibility to control the nodes of the Voronoi diagram.

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