On thermophysical effects on the surface of functional nanostructured materials obtained with the application of femtosecond laser pulses

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Abstract. In recent years, a great scientific and practical interest is caused by functional energy surfaces, modified for certain technological problems. The urgency of the work is to develop promising technologies for thermal and nuclear power engineering, methods for converting solar energy, cooling low-current and high-current electronics devices, energy storage and transport systems on the basis of studying and developing new ways of creating and modifying the functional surfaces of heat exchange and other devices. Modified functional surfaces must have a number of new mechanical and thermophysical properties, including mechanical strength, a new surface morphology for controlling the processes of wetting and spreading working fluids on them, and have high efficiency from the viewpoint of thermohydrodynamic processes of flow and heat and mass transfer of working fluids to them. Among the various ways of modifying surfaces, recently, the method of surface exposure to femtosecond laser pulses (FLI) has become widespread. The technology of femtosecond laser surface treatment (FLSPT) of solid materials has shown high efficiency, reliability, high productivity and a huge variety of modification methods.

The paper presents new results on the study of thermophysical phenomena - the wetting and spreading of drops of various liquids, the study of the hysteresis of the contact angle, the study of evaporation and boiling processes on functional energy surfaces modified by femtosecond laser pulses. It is shown that in the majority of cases the presence of regular or stochastic nanostructures on the surface leads to a very strong change in the basic properties of the surface, which makes it possible to use such a technology to quickly and efficiently modify and obtain functional energy surfaces for certain predetermined purposes.

1. Introduction
Recently the functional surfaces produced by femtosecond laser pulses (FLPs) for a wide range of solid materials are heavily emphasized. And the principal reason is due to its particular hydrodynamic, thermal, and optical properties attributed to surface multiscale structures and physico-chemical changes of a surface layer [1–8]. Generally, the surfaces of metals and semiconductors are processed with multiple FLPs that results in formation of well examined periodic surface structures, cone- and moundlike microstructures, and edge micro-crown structures. However, a rather scant coverage has
been given to investigation of surface morphology of semiconductors exposed to single FLPs [4,5,8,9].

2. Material and methods

The amplified Ti:Sapphire laser system (Coherent, USA) that provides linearly polarized laser pulses of $\tau_p = 40$ fs duration at a central wavelength of $\lambda = 800$ nm with a maximum pulse energy $E = 1.5$ mJ and at 1 kHz repetition rate was used in the experiments [7]. The laser pulse energy was controlled through a combination of a half-wave plate and a Glan prism. The sample was mounted on a three-axis computer-controlled translation stage placed at an angle of 45° to the incident laser beam. The sample surface was monitored with an imaging system coupled to a CCD detector. The threshold laser fluences for the c-Si sample were measured to be of $F_{\text{mel}} = 0.16$ J/cm$^2$ for melting, $F_{\text{abl}} = 0.34$ J/cm$^2$ for ablation. They agree with values in other works. The laser beam was focused with a 300 mm lens to an ellipse with diameters of 44 $\mu$m (minor axis) and 66 $\mu$m (major axis) at a level of 1/e. Thus, the estimated laser fluence on the silicon surface was 1.5 $F_{\text{abl}}$ which gives the intensity of $\sim1$ TW/cm$^2$. The desired number of laser pulses incident on the same spot of the sample was controlled by the translation speed of the sample (0.78 mm/s) and the pulse picker device (Avesta, Russia).

Irradiation of the silicon surface with femtosecond laser pulses made it possible to obtain in a scanning mode a structured substrate, the location of the craters on which is schematically shown in Fig. 1. Parameters of laser radiation: wavelength of laser radiation 800 nm, pulse duration 40 fs, energy density $F = 0.54$ J/cm$^2$ (1.07 $F_{\text{abl}}$), the pulse repetition frequency is 10 Hz. At the speed of movement Of the translator equal to 0.75 mm/s, on which the target was attached, for Structuring of this site took 37 minutes (with increasing pulse repetition rate up to 100 Hz, and the speed of the translators up to 7.5 mm/s, it takes $\sim4$ minutes).

In total, two different in structure were constructed. The structure of the sites corresponds to the scheme in Figure 1a, the difference is only in the number of laser pulses per unit area. The first stage is performed when the laser pulse interacts twice with the surface of the substrate. The second, with a three-fold action of the laser pulse along the same region. Thus, only the morphology of the craters themselves, from which the site is formed, differs (Figure 1b). The area of the structuring region is 10 mm$^2$, the distance between the craters along the abscissa axis is 75 $\mu$m, along the ordinate axis is 60 $\mu$m. The total number of craters on this site is 166x133 = 22078.

In this work samples are used: No. 1 - polished silicon with a crystallographic orientation (111), No. 2 - silicon modified with two femtosecond laser pulses, No. 3 - silicon modified with three femtosecond laser pulses. Measurements of contact angles and evaporation rate and evaporation of working fluid were carried out at normal atmospheric pressure and humidity of 58-62%. Distilled water was used as the working fluid in these measurements. In the first series of experiments for samples No. 1 and No. 3, measurements were made in the temperature range 21-350 °C, in steps of 10 °C. For sample No. 2, measurements were made only at room temperature. Between 3 and 5 measurements were carried out for each temperature, depending on the temperature. The second series of experiments completely repeated the measurements of the first series, but after heating the samples to 350 °C and their subsequent cooling in air to room temperature.
Figure 1. The structure of the silicon surface

Scanning electron microscopy of craters at 2 and 3 times the action of a laser pulse is shown in Figure 2. The morphology of the structured substrate allows to decompose the incident sunlight into the spectrum.

Figure 2. Scanning electron microscopy of craters at 2 and 3 times the action of a laser pulse

3. Investigation of the contact angle on silicon surfaces.

In Figure 3, the dynamics of the contact angle during evaporation from the surfaces of polished and modified silicon at room temperature is shown. From the graphs, the increase in the contact angle on the modified surfaces is clearly seen in comparison with the polished sample. It should be noted that on samples with a less explicit structure (after a double exposure), the wetting angle is greater than on samples after three-fold exposure. When considering each surface before and after heating, from the results obtained, we note that after heating the contact angle increases by approximately 20 degrees.
In the process of evaporation, two different mechanisms can be distinguished (Figure 4). The first - with a constant contact line (CCL: constant contact line), in this case the angle of contact decreases, but the length of the contact line remains unchanged. The second - with a constant angle of contact (CCA: constant contact angle), it is characterized by a decrease in the contact line, with a constant angle of contact. In this process, as a rule, both mechanisms are involved in the evaporation process, but one predominates over the other. During the measurement of contact angles, these mechanisms manifested themselves in different ways, even on one surface at the same temperature. Now consider the differences in the dynamics of the contact angle. On the surface of silicon modified by three pulses before and after heating. In general, the nature of the change in contact angle with time is the same, except for one fact. On the surface prior to heating, to achieve certain droplet radius begins to shrink and the contact angle sharply increases. This process is shown in detail in Figure 5. If we consider the initial stage of the process, it may be noted that at the surface to heat the initial contact angle depends on the surface temperature, and with increasing the angle decreases the temperature. In turn, on the surface after heating, the contact angle at the beginning of the process is almost the same. With regard to the behavior of the curves (contact angle dependency of time), they are identical.
Two models were proposed to describe the effects of surface roughness on hydrophobicity [4]. In the Wenzel model, the liquid is assumed to be in contact with every part of the rough surface, and the increase in contact angle is simply a result of the increase in surface area. Wenzel proposed that the contact angle, $\theta^*$, on the roughened surface is given by

$$\theta^* = r \theta$$

where $r$ is the ratio between the actual and projected surface areas and $\theta$ is the contact angle measured on the equivalent flat surface. Because $r$ is always greater than 1, this model predicts that the contact angle of a liquid that wets a surface ($\theta < 90^\circ$) always decreases when that surface is roughened ($\theta^* < \theta$). Likewise, the contact angle of a liquid that does not wet the surface ($\theta > 90^\circ$) always increases when that surface is roughened ($\theta^* > \theta$). Indeed, roughening a nonwetting surface increases its hydrophobicity. In contrast, the Cassie-Baxter model assumes that the liquid does not completely wet the roughened substrate. Air pockets are trapped in the crevices of the rough surface, and the liquid interacts with the composite surface made of substrate material and air. In this configuration, the measured contact angle on a roughened surface ($\theta^*$) is given by

$$\theta^* = \cos^{-1}\left(\frac{1}{r}\right)$$

Shifts in the Leidenfrost temperature were attributed to reductions in contact angle and substantial capillary wicking due to nanoporosity during intermittent contacts of the droplet with the heated surface. The greatest shift was seen on NC-pyramid structures, which are characterized by 14 μm tall surface features separated by 25 μm that were blanketed with a thick layer of self-assembled nanoparticles. This combination of feature spacing and nanoporosity resulted in significant intermittent contact of the droplet with the surface near film boiling regime, which promoted capillary wicking and nucleate boiling. Further research is needed to determine the limits of the self-assembled nanoparticles on shifting the Leidenfrost temperature and their durability in austere environments.

4. Leidenfrost effect

In the experiments carried out, the dependence of the evaporation time of a 5-μl drop of water for the surfaces of polished silicon and silicon modified by two and three pulses, respectively, was studied. As a result of the measurements, it was found out that the properties of the surface before and after heating are different, which clearly shows the dependence of the static wetting angle. In these experiments, the surface was heated to 350 degrees, then cooled to room temperature in air. Because the modified surfaces were on the same substrate, the evaporation time of the droplet with the modified surface impulses was not measurable.

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Figure 6. The dependence of the evaporation time on the substrate temperature of the modified samples of silicon, in comparison with the polished sample: a) for sample No. 3; b) for sample No. 2

It can be seen from the graphs presented in Fig. 6 that, after heating, the heat transfer efficiency decreased somewhat, but the temperature of Leidenfrost decreased by 10 degrees, in comparison with polished silicon. At the same time, before heating on a surface modified by three pulses, we observe the opposite effect: the evaporation time decreased compared to polished silicon, and the temperature of Leidenfrost increased by ten degrees. It turns out, on more hydrophobic surfaces the temperature of Leidenfrost is lowered, and on more hydrophilic the temperature is lowered. A similar phenomenon was investigated in [4,5], which means that the results of our observations confirm once again the nature of the change in the Leidenfrost temperature.

In Figure 7 the dependence of the change in evaporation time on temperature in relative units is shown. In [5], a linear dependence was obtained on such surfaces. And the nonlinear dependence obtained by us in the experimental part of this work can be explained by the long storage of samples in contact with the surrounding medium.

As the temperature increases up to 100°C, the droplet lifetime decreases on both surfaces, but for the modified surface this dependence is more flat. Within the temperature range of 100–130°C transient regimes are observed for both surfaces, but again for the modified surface this change occurs more abruptly and dramatically (see an inset in Figure 7). We suppose this is due to involvement of another heat transfer mechanism, namely of boiling. And for the modified surface this effect is more pronounced. With temperature increasing, the formation of more vapor in the vicinity of the surface gradually insulates the heated surface, a stable vapor film is formed and a heat flux considerably reduces up to its minimum value. The temperature that corresponds to this phenomenon is referred to as the Leidenfrost temperature [4]. As a general trend, rendering a material more hydrophobic decreases the Leidenfrost temperature. This was also proved for the femtosecond laser processed c-Si surface subsequently exposed to thermal heating.
The Leidenfrost temperature for this modified surface was reduced by about 20–30°C. The scattered data for the droplet lifetime on the polished c-Si surface at temperatures above 140°C is associated with droplet vapor explosion and jet generation due to the rising of a vapor bubble to the droplet surface. When a liquid droplet is placed on a rather hot surface it evaporates with vapor bubbles generation inside the droplet. These vapor bubbles then coalesce and form a big one. When it rises to the surface, a droplet fragmentation occurs. Some small droplets fall back onto the surface and continue to evaporate in the Leidenfrost regime. As a visual field of the CCD is limited, tracing the evaporation time of each small droplet is rather complicated. That is the reason for a dramatic drop of the droplet lifetime on the polished surface for temperatures above 150°C.

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