NEW PROSPECTS OF APPLICATION OF LIQUID CRYSTAL POLYMER CANTILEVER

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The manufacturing technique of a millimetric sizes cantilever from photodriven azobenzene polymer is described. The cantilever oscillations under the influence of laser radiation are studied. The possibility of making a micron-sized cantilever by a femtosecond laser initiated two-photon polymerization technique is shown. Such cantilever can become the basis for a high sensitive sensor, controlled directly by light.

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Introduction. In connection with the enormous pollution of the environment, the wide spread of various viral diseases and the active development of biological weapons, the need for highly sensitive and fast-acting sensors is a very urgent task. And the efforts of scientists today are actively directed to resolve it.

Today in a big variety of different types of sensors the most sensitive ones operate on the principle of resonance frequency shift. The modern nanotechnologies allow creating a super sensitive sensor on the basis of cantilever (bar, one end of which is rigidly fixed and the other one can oscillate). The cantilever oscillating at frequency of 106 Hz is able to capture in real time the appearance of a mass of particles of a few kDa (one Dalton – about the mass of a proton or a neutron, and a few thousand Daltons match the weight of single molecules of proteins or DNA). Such sensor allows diagnosing the disease long before they become available for detection by any other modern methods. Covering cantilever by antibodies of specific viruses it is possible to selectively catch the viral particles in analyzed bio-object (e.g. saliva, blood, etc.).

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Obviously, in order to achieve high sensitivity, it is necessary to ensure high oscillation frequency of cantilever. In [1] the compact, high sensitive nano-mechanical sensor for analyzing the chemical composition of various substances is described. Mechanical oscillations can be excited and detected using electrostatic [2, 3], magnetomotive [4], thermal [5–7], piezoresistive [8] and piezoelectric [9] techniques. However, all these methods have significant disadvantages [10]. For the magnetomotive actuation, a very high magnetic field is needed, which increases the size of device and its price and makes it difficult to operate [4]. Electrostatic schemes are rather inefficient at high resonant frequencies and small dimensions of nano-electromechanical systems (NEMS) [6, 10].

Thermal actuation and piezoresistive transduction induce heating, which changes the kinetics of bio-molecular reactions and consequently decreases the accuracy of measurements. Furthermore, the operating frequency is significantly limited by the finite thermal conductance of the cantilever [6, 11]. Piezoelectric actuation at high resonant frequencies requires complex multilayer nanostructures with a thin piezoelectric layer. This impairs mechanical characteristics of the cantilever and affects the chemical properties of its surface [12].

As it follows from the foregoing discussions, only optical approach can eliminate these drawbacks, simplify the design of sensors and ensure its high sensitivity. In [1, 5] such a sensor was made on silicon using standard CMOS technology. The sensitivity of this sensor is strictly dependent on the oscillation frequency of cantilever, causing its nano-metric size. Since silicon is one of the hardest materials with cubic lattice, in which the atoms are strongly bounded by covalent bonds, the maximum amplitude of oscillations of such cantilever is no more than 20 nm, which significantly complicates the registration. Furthermore, the sensitivity of described sensor is fundamentally limited by thermo-mechanical noise of cantilever and the noise of the probe optical signal. Moreover, photonic nano-waveguide is actually an optical resonator, parameters of which are strongly dependent on external factors, particularly on temperature.

On the other hand, there are a great number of cantilevers based on other materials, particularly on polymers. The oscillation property is in the very nature of the polymers, as polymer molecules form long, flexible chain. It should be emphasized that the liquid crystal polymers are photoactive and their swinging can be realized directly by light, i.e. these polymers are photo-driven materials. The creation of cantilever in micron or submicron dimensions on these materials will become the base for super-sensitive sensor fabrication.

In this paper the prospects for using a cantilever made from a photo-driven azobenzene polymer as a basis for a high sensitive biosensor are investigated.

Experimental Part.

Cantilever Making Technology. To make a cantilever from azobenzene containing liquid crystal (LC) polymer (BEAM Co., https://www.beamco.com) the cell is assembled using two glass substrates, coated by a photo-orienting material, on which the planar orientation was been formed by UV irradiation. After checking ori-
entation quality between crossed polarizers, the assembled cell heats up to 60–70 °C. Then, LC polymer is introduced into the cell, the temperature of which maintained to ensure slow and uniform melting of the LC polymer. When the cell is completely filled, the LC polymer polymerize under the radiation of green LED for 30 min, at that the cell retains on the heater. After complete polymerization the cell is disassembled, the polymerized layer is peeled off and cantilever of necessary dimensions is cut.

**Observation of Cantilever Oscillations under the Influence of Laser Irradiation.** To study the cantilever oscillations under the influence of light radiation, the scheme is assembled, shown in Fig. 1. The laser radiation (450 nm) through a system of lenses (1) by an optical fiber (2) is directed to an LC cell located between crossed polarizers (3), serving as a light attenuator. LC cell is controlled by “LC Driver” (device, allowing generate the control signals of various shapes and amplitudes and register the signal from the photodiode). Then by a lens (4) and semitransparent mirror (5) the beam is focused on the fixed on a rigid base LC cantilever (6), while part of the light is directed to the photodiode to measure the relative intensity. To register the angle of cantilever deflection from the initial position, a microscope with 5× magnification was used.

![Fig. 1. Scheme of experiment: 1 – lenses; 2 – optical fiber; 3 – polarizers; 4 – focusing lens; 5 – semitransparent mirror; 6 – cantilever.](image)

In the course of the experiment, the intensity of the laser irradiation, incident on the cantilever, was changed using attenuator. The images of the cantilever in the absence (a) and under the influence (b) of laser irradiation obtained under the microscope are shown in Fig. 2, and the results of experiment are shown in Fig. 3.

The cantilever considered above can become the basis for a high sensitive sensor. Covering cantilever by corresponding antibody will provide selective adsorption of material under detection, which will lead to a change in the amplitude of the cantilever oscillations and, therefore, to register the presence of substance in the studied environment. However, in this case, to increase the sensitivity of the system, it is necessary to significantly reduce the size of cantilever, making it submicron. The manufacturing of cantilever in micron or submicron dimensions on these materials will
become the base for high-sensitive sensor fabrication. But at first glance it seems that to make a cantilever of submicron size on LC polymer is not an easy task. However, for this case there is a standard technology – a well-known femtosecond laser initiated two-photon polymerization technique, described above.

**Making of Micron-size Cantilever.** To make a cantilever of submicron sizes on LC polymer, the setup is assembled and two-photon polymerization technique is mastered. A three-dimensional micro-fabrication workstation has been used, located at DELTA laboratory of Synchrotron Research Institute of Candle (https://www.candle.am). The scheme of experimental setup is given in Fig. 4. As a light source a femtosecond laser is used, parameters of which are controlled in wide range (pulse duration 400 fs – 10 ps, pulse frequency 1–100 kHz, average power up to 8 W, pulse energy up to 2 mJ). The principle element is high-precision controlled three-axis stage.
with 50 nm positioning accuracy. Laser beam polarization changing is realized by Glan-Thompson polarizer and wave plate. The lens system (objective) used in optical scheme allows focusing the laser beam with diameter less than 2 mm. CCD camera is foreseen for visualization and control of the recording process.

The experiments have been provided by using OrmoComp® (Microresist Technology GmbH, Germany) polymer. OrmoComp® is organic-inorganic hybrid polymer, which can be locally converted to a solid phase immediately after laser irradiation. Though OrmoComp® is not a photo-orienting material, the physical and optical properties of this polymer are very close to the LC polymer from the point of view of the technological features of the two-photon polymerization process. In addition, the difference in refractive indices of liquid and polymerized OrmoComp® is large, which makes it easier to control the polymerization process by a microscope. Samples of various sizes and shapes were obtained by moving the focus of the acting laser radiation along pre-programmed trajectories (Fig. 5).

Technological parameters of the presented microstructures obtaining process are presented in Table.

<table>
<thead>
<tr>
<th>No table name</th>
<th>515 nm</th>
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<tbody>
<tr>
<td>Wavelength</td>
<td>515 nm</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>450 fs</td>
</tr>
<tr>
<td>Laser repetition frequency</td>
<td>1 kHz</td>
</tr>
<tr>
<td>Scanning speed</td>
<td>1000 um/s</td>
</tr>
<tr>
<td>Optimal pulse energy</td>
<td>56—75 nJ</td>
</tr>
<tr>
<td>[Estimated polymerization threshold]</td>
<td>[20 nJ]</td>
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</table>

Thus, two-photon polymerization technique make it possible making a cantilever of micron dimensions.

**Conclusion.** The azobenzene-containing liquid crystal polymers are ideal candidates for sensor applications as they are capable of strong and efficient mechanical
actuation powered remotely by light energy, without the need for additional components such as batteries or wires. Creating a cantilever of micron or submicron sizes from these materials will be a serious alternative to the sensors presented on the modern market. Such a sensor will have huge advantages – there are no strong restrictions on the amplitude and frequency of oscillations, control is carried out directly by light (polarization or wavelength), easy to manufacture, easy to use, etc.

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COMPARISON AND VALUATION OF MECHANICAL SENSORS AND ACTUATORS USING LIQUID CRYSTAL POLYMER CANTILEVER TECHNOLOGY

A new method for the design of millimeter-sized photoreactive azobenzene polymer has been proposed for the fabrication of micro- and nanoscale cantilever sensors. The method involves the use of photoreactive polymer layers with a thickness of several micrometers, which can be further modified by applying a laser radiation. The method allows for the fabrication of nanometric cantilever sensors, which can be used as the basis for high-sensitive optical sensors.