Acta Technica 62 No. 4B/2017, 1–8

Investigation of hydrophobic nanostructured film for its application in MEMS industry[1]

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Abstract. The variants of technologies for the development of hydrophobic nanostructured self-assembling films for the use in MEMS are considered in the article. The technology of a hydrophobic film development on the surface of polysilicon using the gaseous phase of the organic compound FOTS is described. The results of these films hydrophobic properties study are presented. It is shown that the contact angle of wetting on the surface of polysilicon modified by this method makes about 120 °.

Key words. Hydrophobic film, MEMS elements, wetting contact angle.

1. Introduction

The adhesion of moving parts of elements (membranes, consoles, beams) can occur for a number of MEMS converters operating under the conditions of high humidity at high relative humidity or as a result of specific factor influence under the action of capillary forces, which in its turn will lead to the device failure. In order to minimize the effect of capillary forces, a nanostructured coating that substantially reduces the amount of adhesion of the moving elements can be developed at the final stage of device fabrication on MEMS surfaces. In addition, nanostructured coatings cannot prevent the adhesion of elements, but also they cannot protect them from contamination. Thus, the research of technological methods for the development of

[1]The performed work is provided by the financial support of the Ministry of Education and Science of the Russian Federation within the framework of State order No. 16.1.18.2259.01 on Project No. 8.8624.2017/BC. The study of parameters concerning produced hydrophobic nanostructured films was performed with the help of the measuring instruments by "Functional Control and Diagnostics of Micro- and Nanosystem Technics". Center based on Scientific-Manufacturing Complex "Technological Centre".

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a hydrophobic nanostructured film is an actual task. At present, silicon (polysilicon) membranes are widely used in highly sensitive MEMS. Such membranes are used in acoustic transducers, accelerometers, pressure sensors and a number of other MEMS devices [1–3]. This paper studied various versions of the technology concerning the application of hydrophobic films to silicon crystals with a polysilicon layer of 1 μm formed on their surface.

2. Hydrophobic film development methods

During the development of a hydrophobic film, both the liquid phase and the gaseous phase of organic solvents were used. In order to form hydrophobic films on silicon, it is necessary to have a well-cleaned surface. The removal of impurities from the surface of all samples was carried out by ozone treatment for 10 minutes using UV Ozone Cleaner-ProCleaner purification system. In order to modify the surface of polysilicon films and the provision of hydrophobic properties for them, organic silane compounds were used, in particular: 1H, 1H, 2H, 2H-perfluorooctyl trichlorosilane (FOTS), octadecyl trichloro silane (OTS) and octyl-trimethoxylan (OTMS) by Sigma-Aldrich Company.

OTMS and OTS silanes were used to form hydrophobic films from the liquid phase. In order to deposit OTMS film, the samples were incubated for 2 hours without the stirring in a freshly prepared 3 % solution of silane in methanol. In order to deposit the hydrophobic film from OTS, the samples were placed without mixing into a freshly prepared 3 % silane solution in toluene for 2 hours. After incubation, the samples were washed three times with excess toluene and were dried with dry nitrogen if necessary.

3. Measurements of hydrophobic film parameters

The main parameter of material surface hydrophobicity is the value of the contact angle of wetting. The measurements were carried out using the device for the contact angle of wetting OCA15EC measuring using the Young-Laplace method. To form a droplet, 1 μl of freshly prepared deionized water was applied to the test surface. Figure 1 and Table 1 show the results of these measurements. In order to form a droplet, 1 μl of freshly prepared deionized water was applied to the test surface.

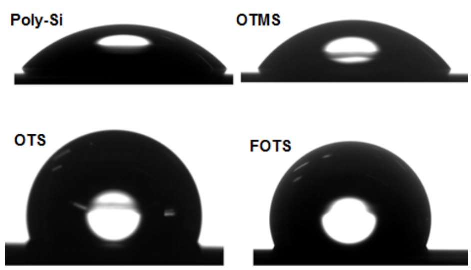

Fig. 1. The image of the contact angle of wetting for various surfaces of polysilicon

Table 1. The value of the contact angle of wetting for different polysilicon surfaces

Poly-Si	$51.05\,^\circ \pm 5,48\,^\circ$
OTMS	$66.45\,^\circ \pm 5.01\,^\circ$
OTS	$110.85\,^\circ \pm 1.25\,^\circ$
FOTS	$112.02\,^\circ \pm 2.58\,^\circ$

Table 1 shows that the modification with OTMS use results in an insignificant increase in the wetting angle in comparison with the initial surface of polycrystalline silicon, which roughly coincides with the data of the work [4]. Despite the fact that the boiling point of FOTS makes 192 °C, it was found experimentally that the optimum temperature at which the injection into the chamber occurs is 260 °C. This temperature was required to provide the above 192 °C throughout the chamber. Thus, because of the high temperature, we had to refuse from the use of dishes made of polystyrene and polytetrafluoroethylene because of the destruction temperatures for these polymers. The Petri dish from the calcined glass was pretreated with 20 *upmu*l of FOTS for 2 hours. The processing allowed to modify the surface with the fluoroorganic layer, which will avoid the loss of reagents in future due to the reactions with glass on the chamber walls.

Initially, the deposition process from FOTS was carried out for 2 hours with the injection of about 15 µl per silicon wafer. After the processing, the angle of wetting on the crystal was approximately 118–122 °, which indicates the formation of a film on the surface. However, a metallized contact wiring is present in most cases on MEMS elements of devices requiring the creation of hydrophobic layers. Figure 2 shows the flow pattern of the FOTS reaction with the silicon oxide surface, given that there is SiO_2 layer on the silicon surface. Figure 3 shows the contact angle of crystal surface wetting, modified by FOTS

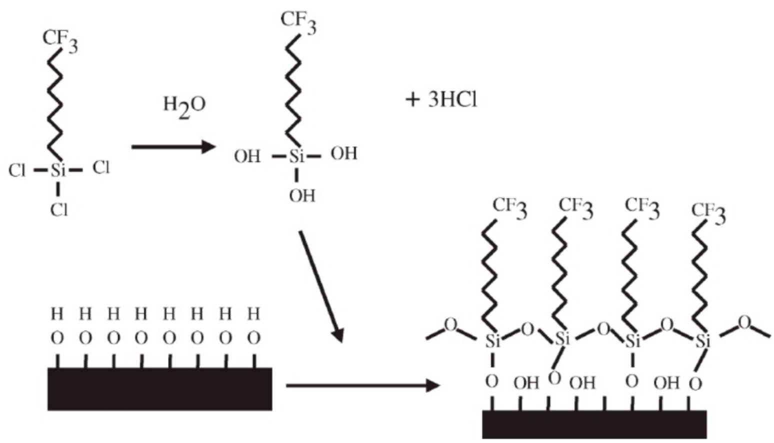

Fig. 2. FOTS reaction scheme with the surface of silicon oxide

At a prolonged contact of non-washed samples with the atmosphere, a complete corrosion of aluminum occurs and the condensation forms from the organic fluorine polymer, covalently attached to the surface. This condensate has a chemical resistance to almost all washing and plasma etching. Due to the etching of metallization, it becomes pointless to use the deposition of the desired film from FOTS and the organic solvent, since the minimum film deposition time established from the experiment makes 30 minutes. The complete corrosion of the metallization may occur during such a period.

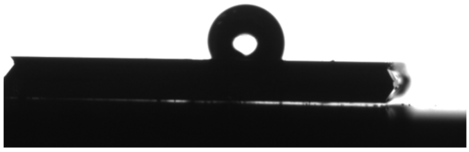

Fig. 3. The contact angle of crystal surface wetting, modified by FOTS

4. Optimization of deposition process for hydrophobic film

Summarizing the above mentioned, it is possible to identify several key factors that need to be taken into account in order to optimize the technological sequence of the hydrophobic film formation process: to minimize time and amount of the reagent introduced to prevent or minimize the metallization etching reaction during surface modification; to minimize the amount of water in the system during the reaction and until the complete removal of excess reagent from the surface. The samples of such silicon, oxidized in ozone beforehand, experienced the optimization of the process concerning the formation of hydrophobic FOTS film with the control of surface morphology after treatment was carried out by the method of scanning probe microscopy. In the course of experimental studies, the conditions were selected that make it possible to obtain an incomplete monolayer on an oxidized surface. It was shown experimentally that during the injection onto a hot surface, the formation of the first layer occurs within the first 5 minutes, and a significant effect on the film morphology begins to appear only after 1–2 hours of reaction. Considering that the etching of metallic wiring occurs during such long periods, the increase of reaction time for more than 5 min does not make any practical sense for this protocol. The variance of injected volume of FOTS was performed from the original 450 µl to 10 µl for a selected period. With the concentration decrease, the decrease in the number of aggregates on the surface is observed, until an incomplete monolayer is developed.

4.1. SA algorithm

4.1.1. A description of the SA algorithm. SA is a meta-heuristic algorithm utilized to overcome large issues having a large solution space and producing results close to the global optimum amount in a short time. The SA algorithm was first created by Metropolis et al. in 1953 to generalize the Monte Carlo method to determine the equations of state and also to determine frozen states of n-body systems in the field of metallurgy [5].

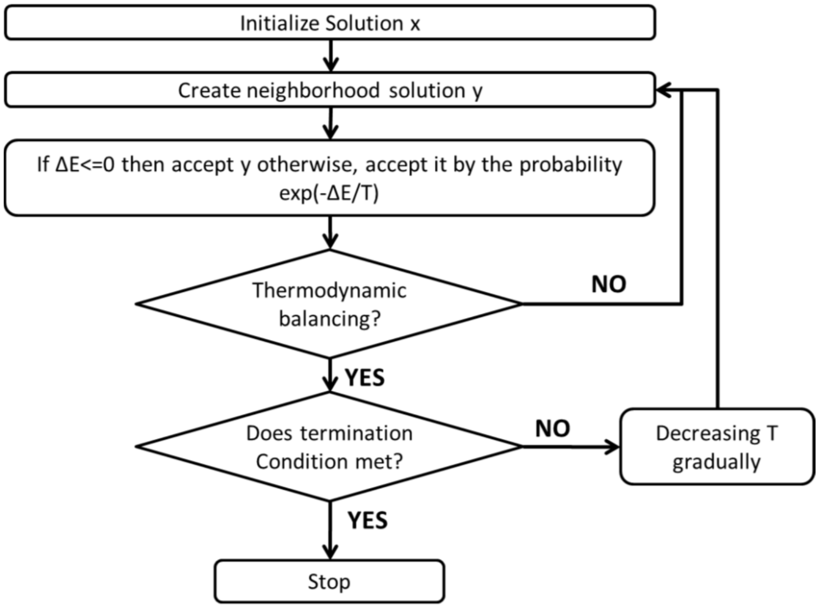

Fig. 4. The standard SA procedure

4.1.2. Operators of algorithm SA.

A. Cooling scheme

In cooling scheme, an exponential approach has been used, and in each diversification, the temperature in a fixed number smaller than one is multiplied. Since there are only two temperatures in the algorithm, only one of the temperatures decreases in this method, and other temperature with the aim of increasing Diversification in the whole process of solving algorithm will be fixed.

B. Acceptance probability

The possibility of choice of an inferior solution X_{new} is provided by the next equation, where T_i and X_i are the temperature and real solution amounts in iteration i.

$$p(T_i, X_{\mathrm{new}}, X_i) = \exp \frac{\Delta}{T_i}\,, \tag{1}$$

where

$$\Delta = \frac{f(X_{\mathrm{new}}) - f(X_i)}{f(X_i)} \times 100$$

is a dimensionless parameter; it shows the relative rate of deviation of the perturbed solution X_{new} from the real one X_i.

C. Temperature settings

Temperature controls diversification of the algorithm. In SA, the standard of temperature was great at first (the Diversification is high) and with continue of the solution gradually decreases. In this paper, two different algorithms of SA are designed, and results obtained by solving the problem by these two algorithms were compared with each other. In the first algorithm, a standard SA is considered, and the initial temperature is determined according to conventional methods of setting parameters. The second algorithm is designed with the aim of increasing diversification in times that algorithm in several consecutive times cannot improve the answer. Here it is assumed that non-improvement in the answer can be occurred due to the algorithm stop at a local optimum solution. On the basis, in this algorithm is considered two temperatures. The first temperature continuously and based on the cooling scheme at different stages of solving is reduced and appropriate to it the chance of accepting bad answers and Diversification reduces. If the algorithm during several periods (N) is not able to improve the best answer obtained, the second temperature is activated and leads to the increase of Diversification algorithm. This action causes that algorithm to be out of local optimal solution and resume the path to recovery. If the answer is improved, again the first temperature activated and this process continues continuously. In this algorithm, exist two different temperatures create this opportunity that in initial stages consider temperature lower and therefore increase the speed of recovery.

D. Termination condition

Since in this paper the findings got off the algorithms of the solution are compared with each other, so stop condition of algorithms is to reach a specified time. This method causes the comparison of algorithms only to be possible through investigating the quality of their answers.

5. Results

Two groups of random problems are used in this research. The first group includes small-scale numerical problems that have been used to verify the authenticity of the results of metaheuristic algorithms which contains 15 problems. The second group, which included 21 medium and large-scale issues, has been solved by metaheuristic algorithms and produced responses to assess the effectiveness of changes created by algorithms and also comparing algorithms with each other are used.

5.1. Tuning the parameters of algorithms

In this section, it is necessary to set the parameters of the algorithms considered. One of the common approaches in this regard is the use of numerical examples and methods of Design of Experiments [5]. The method of Central Composition Design (CCD) is selected for this purpose, and MINITAB software is used for calculations. In this approach, for each factor, five levels are considered and by considering the midpoints, the possibility of detecting curve is provided. In this part, a mathematical model with 50 customers and five warehouses are used, and the problem is solved in 20 time periods.

The number of solutions vicinity created in each degree It-num [30 50] and the number of successive answers that in the case of failure of improvement in the optimal answer, the temperature range changes N [100 200] is considered. The results in equation 34 and optimization plot of this algorithm is presented in Fig. 5. On this basis, the optimal amount of temperature1 and temperature2 is calculated to equal to 50 degrees and 375 degrees, It-num equal to 53 and N equal to 159.

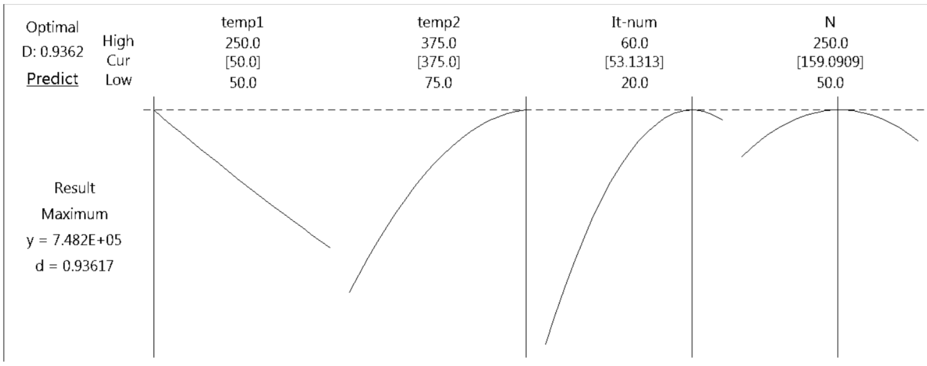

Fig. 5. Optimization plot of objective function

In order to minimize moisture in the system, the chamber glass was calcined initially for at least one hour at the temperature of 60 °C, after which the samples were introduced and the chamber with samples was calcined for at least one hour at 260 °C to remove moisture from the samples and stabilize temperature in the chamber. Then the injection of FOTS was performed in the amount of 10–15 µl of substance and the samples were incubated for 5 minutes. In order to clean the samples, hexane was chosen, which, on the one hand, dissolves the excess of FOTS, on the other hand, it practically does not gain moisture from the atmosphere (in contrast to toluene). Figure 3 shows the image of the contact angle of wetting after the modification of surface according to the above mentioned technology, its value was 120 °.

Figure 6 shows the influence of the static contact angle on the jumping speed, and a critical amount of the static contact angle has been reached $\theta_c = 140\,°$, for droplets with radius of 100 µm. Jumping happens for all values of θ_s between 140 ° to 180 °. But, for a surface with static contact angle $\theta_c = 160\,°$.

6. Conclusion

Based on the foregoing, it can be concluded that the use of organic compounds both in the liquid phase and in the gaseous form allows to create hydrophobic nanostructured films for the use in MEMS. Studies showed that the use of such organic solvents as FOTS, OTS, and OTMS, both in the liquid phase and in the gaseous phase, can be used to form hydrophobic nanostructured films. The contact angle of wetting made $51.05\,° \pm 5.48°$ for the initial polysilicon and $66.45\,° \pm 5.01°$ for the modified polysilicon. The wetting angle of the modified polysilicon OTS and FOTS with reagents was $110.85\,° \pm 1.25°$ and $112.0\,2° \pm 2.58°$, respectively. The technology which uses the gaseous FOTS phase at 260 °C for 5 minutes allows to avoid negative

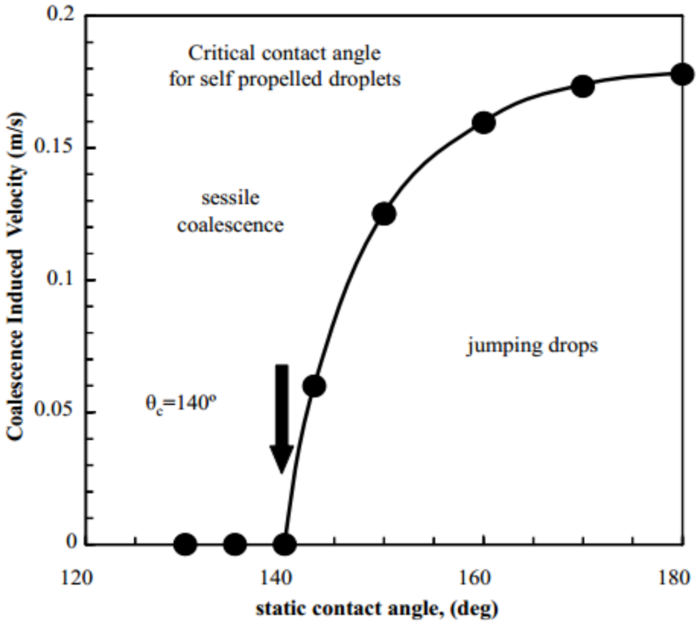

Fig. 6. Effects of the static contact angle on the droplet jumping speed, and determination of critical contact angle for jumping phenomenon ($\theta_c = 140\,^\circ$)

consequences, while the contact angle of the polysilicon surface wetting is about 120°.

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Received October 12, 2017