ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 15, No. 3. 2009

Hydrophobic Diamond Like Carbon Film for Surface Micromachining

Algirdas LAZAUSKAS[1*], Viktoras GRIGALIŪNAS[1,2], Šarūnas MEŠKINIS[2], Vitoldas KOPUSTINSKAS[2], Asta GUOBIENĖ[2], Angelė GUDONYTĖ[2], Mindaugas ANDRULEVIČIUS[2], Tomas TAMULEVIČIUS[2]

[1]*International Study Center, Kaunas University of Technology, Mickeviciaus 37, LT-44244 Kaunas, Lithuania*
[2]*Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, LT-50131 Kaunas, Lithuania*

Received 27 November 2008; accepted 22 May 2009

SiO_x doped diamond like carbon (DLC) film was applied as effective barrier for protecting microstructures against stiction during fabrication of surface micromachined electrostatically actuated microelectromechanical switch. Hydrophobic properties of the SiOx doped DLC film were determined using Zisman method (average critical surface tension 42.0 mN/m) and the average surface roughness was determined by atomic force microscope (R_a = 2.1 nm). The SiO_x doped DLC film surface properties were compared with actual Si <100> and Au film surface properties under the same investigation procedures. The X-ray photoelectron spectroscopy (XPS) showed typical chemical structure of SiO_x doped DLC film. High resolution scanning electron microscopy showed that microelectromechanical switch was successfully fabricated using SiO_x doped DLC film, the defects caused by stiction phenomenon were not observed.

Keywords: diamond like carbon (DLC), surface micromachining, microelectromechanical (MEMS) switch, stiction.

1. INTRODUCTION

Recently, the surface micromachining technology was introduced for the development of various modern devices and equipment (i. e. new generation laser TV's, microrobotics etc.) [1 – 3]. Differently from bulk micromachining technology, where structures are formed in the substrate (usually silicon) volume, in surface micromachining technology the structures are built by adding materials layer by layer on the surface of substrate [4]. In such a way, the substrate properties are not so important in surface micromachining technology comparing it with the bulk micromachining. Typically, the thickness of films does not exceed several micrometers when films are formed using electrochemical, vacuum evaporation, plasma or ion beam deposition techniques. Basically the two types of material layers are used, one carry out the structural functions, another – sacrificial functions, so it is very important to selectively choose appropriate materials and their combinations [5, 6]. For the topographical microdetail separation the dry plasmochemical and ion etching methods are used, while wet etching is performed to release the structural layers from the substrate by etching the supporting sacrificial layer [7, 8]. At the beginning of this work we faced up the wet etching problems using surface micromachining technology to fabricate microelectromechanical switch [9]. After the wet etching, during which the supporting sacrificial layer is removed, the meniscus created by the receding liquid/air interface tends to pull the structure against the substrate, the intimate contact gives rise to other surface forces like van der Walls force (also capillarity force), which irreparably pins the structure to the substrate after the drying, effectively destroying the device.

Different methods are used to prevent stiction phenomenon. The first category aims at preventing stiction by eliminating the capillarity force of the rinsing liquid. This is achieved by either drying the rinsed wafer with superficial CO_2, or by freezing and then sublimating the rinsing liquid. The second category aims at reducing the structural/ substrate contact area, in order to minimize the interface surface energy. This is achieved by introducing reduced contact area structures like dimples and mesas, and by texturizing the substrate (e. g., roughening it). Finally, the third category aims at replacing the liquid rinsing solution by a vapor phase etching (VPE), in which, the sacrificial silicon dioxide is etched with hydrofluoric acid (HF) vapor instead of the conventional aqueous HF solution [21, 22].

In the present study an attempt was made to prevent wet etching problem by using hydrogenated DLC film for protection of microstructures from stiction phenomenon. The contact angle with water of direct ion beam deposited DLC film can reach 69° [10] or even 72° – 78° [11]. By using CH_4/H_2 gas mixture instead of hydrocarbon gases the contact angle can be increased up to 94° [12, 13]. For non hydrogenated DLC synthesized using magnetron sputtering method the contact angle reaches just 40°, as for hydrogenated DLC the angle increases up to 65° [14]. However [15◦– 17] the obtained results show that for on hydrogenated DLC, synthesized using magnetron sputtering method the contact angles are comparatively large (76°...81°). It seems, that hydrogen stream can increase contact angle only in the case when the low energy (<10 eV) is passed to the carbon atom during the process of synthesis. By doping DLC with SiO_x or Si the contact angle can be considerably increased. By synthesizing the DLC using plasma activated chemical vapour deposition, for doped SiO_x and Si films the 100° and 90° contact angle were obtained respectively. As for non hydrogenated DLC films the contact angle was only 70° [18].

---

[*] Corresponding author. Tel.: +370-671-73375; fax.: +370-37-314423.
E-mail address: *algirdas.lazauskas@stud.ktu.lt* (A. Lazauskas)

In this work the surface micromachined electrostatically actuated microelectromechanical switch was successfully fabricated using SiO$_x$ doped DLC film.

2. EXPERIMENTAL TECHNIQUE

In this work the SiO$_x$ doped DLC film was deposited by direct ion beam from hexamethyldisiloxane vapour $[(CH_3)_3SiOSi(CH_3)_3]$ and hydrogen (H_2) gas mixture at ion beam energy $E = 800$ eV and ion beam current density $j_s = (50 \div 150)$ μA/cm^2. For removal of the SiO$_x$ doped DLC film, the oxygen ion beam etching technique was used [19]. Fig. 1 shows the modified microelectromechanical switch technology, where the SiO$_x$ doped DLC film is used.

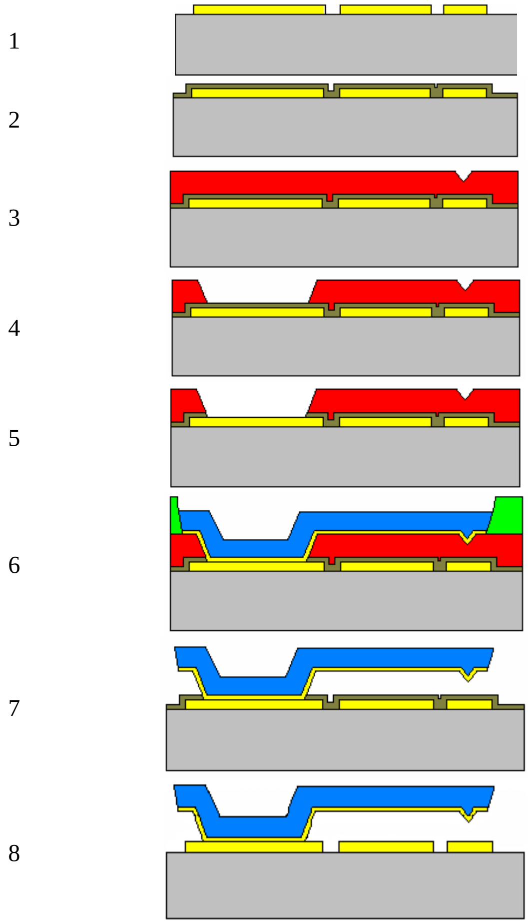

Fig. 1. The modified microelectromechanical switch technology using SiO$_x$ doped DLC film: 1) Cr/Au electron beam evaporation and "lift-off" lithography; 2) Direct ion beam deposition of the thin SiO$_x$ doped DLC film; 3) Electron beam evaporation of Cu film and contact tip fabrication using chemical etching; 4) Cantilever beam support opening using deep Cu etching; 5) Oxygen ion beam etching of SiO$_x$ doped DLC film for cantilever beam support opening; 6) Cantilever beam patterning using Au electron beam evaporation, "lift-off" lithography and Ni electrochemical deposition; 7) Selective Cu chemical etching; 8) SiO$_x$ doped DLC film removal using oxygen ion beam etching

Firstly the Si <100> wafer was treated using O_2/N_2 gas mixture plasma. For the improvement of surface adhesion properties the thin (thickness 30 nm) Cr layer was deposited using electron beam. Next, the Au layer (thickness 200 nm) was deposited using electron beam and the source, gate and drain electrodes were formed using lift-off lithography. Then SiO$_x$ doped DLC film (thickness 50 nm) was deposited using direct ion beam. Then a sacrificial copper layer was deposited using electron beam (thickness varied from 1500 nm to 3000 nm). Patterning of the copper layer was performed in two steps. Firstly, the copper layer was partially etched (etchant: $H_2SO_4 : CrO_3 : H_2O$) to define the contact tips for the cantilever beam and etching duration directly determined the spacing between contact tip's top and drain electrode. Next, the copper layer was etched away to uncover the source cantilever support area. Latter, oxygen ion beam etching of SiO$_x$ doped DLC film was performed to open the cantilever beam support. Again, the Au layer (200 nm) was deposited using electron beam and patterned using lift-off lithography (to make golden the bottom side of the microcantilever in order to improve the contact resistance). Next, a thick photoresist layer was formed and the sectors were defined using nickel electrochemical deposition. Nickel layer was electroplated using sulfamate electrolyte ($Ni(NH_2SO_3)_2 : 4H_2O$) fabricating cantilever beam structure. The sacrificial Cu layer was removed away using selective copper etchant to release the free-standing cantilever beam. Finally, SiO$_x$ doped DLC film, which served just for microdetail protection against stiction, was removed using dry oxygen ion beam etching technique.

The effect of SiO$_x$ doped DLC film for the Cu sacrificial layer and support (Si, Au) interaction was investigated by comparing the hydrophobic properties, surface morphology and chemical composition of these surfaces.

Hydrophobic properties and critical surface tension were determined using Zisman method. The method according to Zisman uses this relationship by plotting $\cos\theta$ against the surface tension for various liquids and extrapolating the compensation curve to $\cos\theta = 1$. The corresponding value for the surface tension is known as the critical surface tension σ_{crit}. A drop of four chemical liquids – glycerol (GLY), polyethylene glycol 200 (PEG 200), ethylene glycol (EG), water (WA) were placed on flat SiO$_x$ doped DLC, Si and Au probe surfaces. Each of the four contact angles was measured using a contact angle measurement system. A procedure was repeated with three probes for each material. A graph of the cosine of the contact angle against the surface tension of the liquids was constructed. The critical surface tension σ_{crit} was determined. Water and other hydrogen-bonding liquids usually appreciably deviate from linearity when the surface that is measured contains functional group, which can establish hydrogen bonding with the liquid. For SiO$_x$ doped DLC water measurement results deviated from linearity, therefore to obtain more precise results water (WA) was partially emitted for determination of critical surface tension [20].

Surface morphology was investigated using contact mode atomic force microscope NT-206 (maximum scanning area 30 μm × 30 μm, maximum measurement height 4 μm, maximum lateral resolution 2 nm and vertical resolution 0.1 nm).

Surface chemical composition was determined using X-ray photoelectron spectrometer XSAM800 Kratos

Analytical (dual X-ray Al/Mg anode, X-ray beam energy: MgK_{α} = 1253.6 eV (line width at the average height 0.7 eV); AlK_{α} = 1486.6 eV (line width at the average height 0.85 eV)).

The removal of sacrificial layer and "stiction" was investigated using high resolution field emission gun scanning electron microscope FEI Quanta 200 FEG (accelerating voltage can be varied from 0.2 kV to 30 kV; resolution 1.2 nm).

3. EXPERIMENTAL RESULTS

Figs. 2 – 4 presents the relevant surfaces of microelectromechanical switch (Si <100>, Au and SiO_x doped DLC), where critical surface tension was determined according to Zisman method. One can see, that Si <100> (critical surface tension 32.5 mN/m) and Au (critical surface tension 32.0 mN/m) are less hydrophobic than SiO_x doped DLC surface (critical surface tension 42.0 mN/m. Therefore, the assumption that SiO_x doped DLC will reduce surface wetability and increase the liquid leakage can be made and thus it can effectively protect microdetails by removing Cu sacrificial layer using wet etching.

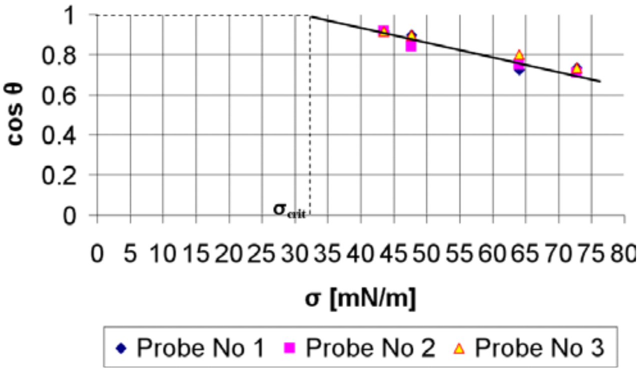

Fig. 2. Si <100> critical surface tension 32.5 mN/m determined using Zisman method

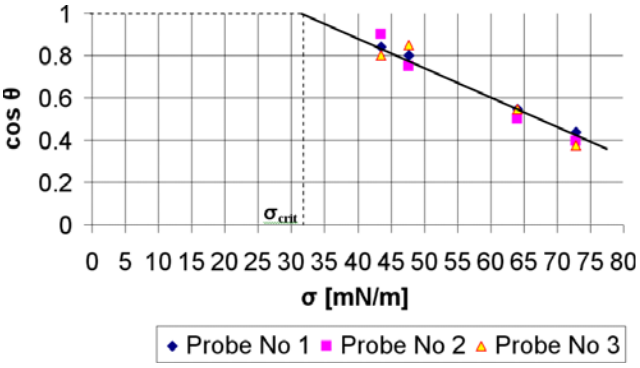

Fig. 3. Au critical surface tension 32.0 mN/m determined using Zisman method

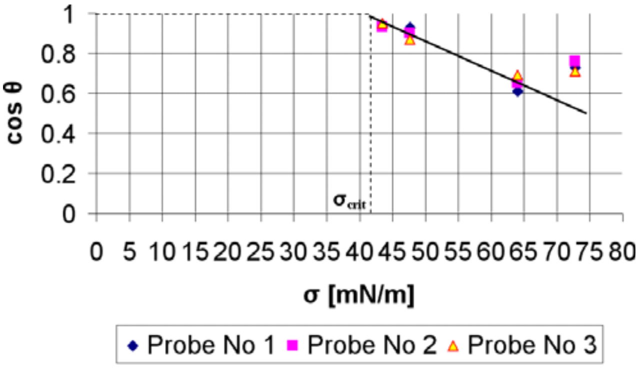

Fig. 4. SiO_x doped DLC critical surface tension 42.0 mN/m determined using Zisman method

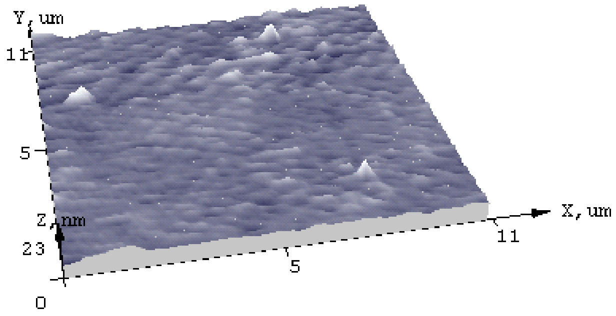

Fig. 5. Atomic force microscope view of the Si <100> surface (average roughness R_a = 0.72 nm)

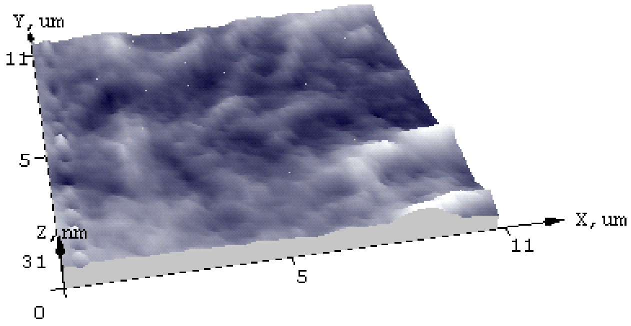

Fig. 6. Atomic force microscope view of the Au surface (average roughness R_a = 3.2 nm)

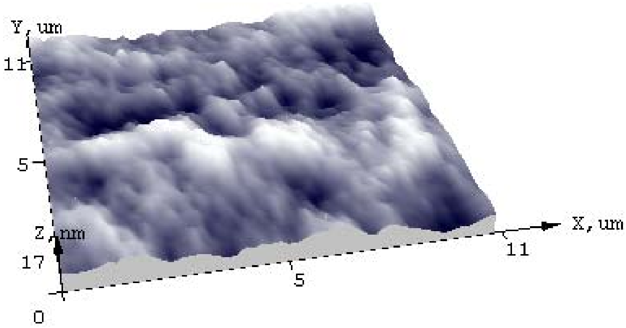

Fig. 7. Atomic force microscope view of the SiO_x doped DLC film surface (average roughness R_a = 2.1 nm)

The roughness of Si, Au and SiO_x doped DLC surface was investigated using atomic force microscope. Fig. 5 shows the Si <100> 3D view analysis (average roughness R_a = 0.72 nm). Fig. 6 shows the Au 3D view analysis (average roughness R_a = 3.2 nm). Fig. 7 shows the SiO_x doped DLC 3D view analysis (average roughness R_a = 2.1 nm). Once can see that Si <100> surface is more even than of electron beam evaporated Au film, and SiO_x doped DLC has slightly more even surface than of Au film. Due to the fact that surface inequalities differ only slightly, we can make the assumption that SiO_x doped DLC will not only improve the hydrophobic properties but will also make the balanced and more even surface for deposition of sacrificial layer. Therefore, SiO_x doped DLC can be even more effective for release of microdetails.

Fig. 8 shows the X-ray photoelectron spectrum of SiO_x doped DLC film, which indicates that oxygen and carbon (O1s, peak and C1s peak) are dominating in the film. The ratio of peak intensities shows typical chemical structure of SiO_x doped DLC film (increased amount of oxygen is present due to the SiO_x compounds formation, influencing the hydrophobic properties of the film). Atomic concentration for O1s is 24.11 %, for C1s is 54.71 % and for Si 2p is 21.18 %.

The quality of removal of sacrificial layer and possible stiction of microcantilever was investigated using the high resolution scanning electron microscope. The microphotograph shown in Fig. 9 illustrates the quality of removal of the sacrificial layer. Once can see that a gap between the microcantilever and contact electrodes is successfully fabricated. A size of the gap well matches to the thickness of the used sacrificial layer.

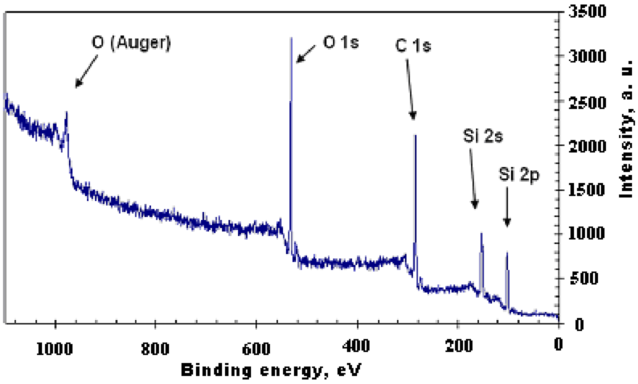

Fig. 8. X-ray photoelectron spectrum of SiO_x doped DLC film

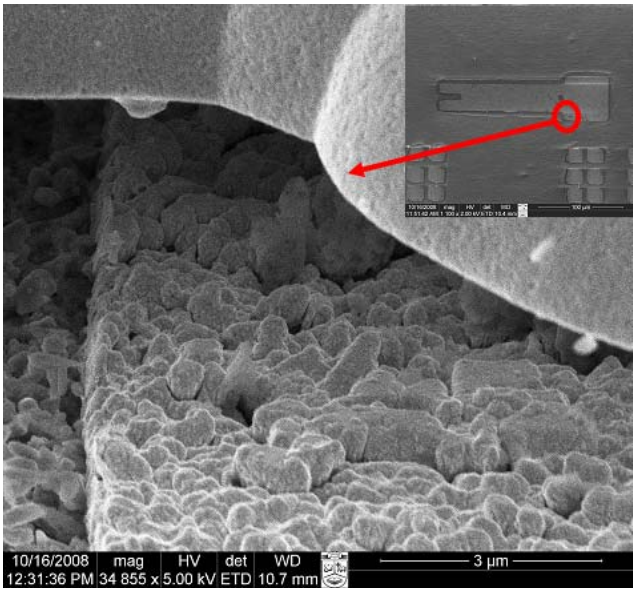

Fig. 9. Scanning electron microscope microphotograph (×34855) illustrating the quality of microcantilever Cu sacrificial layer removal

Microelectromechanical switch, fabricated using surface micromachining technology, due to its particularly small dimensions can be successfully used in integrated circuits, even in the same microchip with electronic scheme. Comparing the microelectromechanical switch with the analogous semiconductor devices one can see that it has much lower contact resistance in the "on" state and effectively higher resistance in the "off" state (see Fig. 10), also it can be characterized by considerably higher switching frequency, and uses less energy due to the electrostatic actuation.

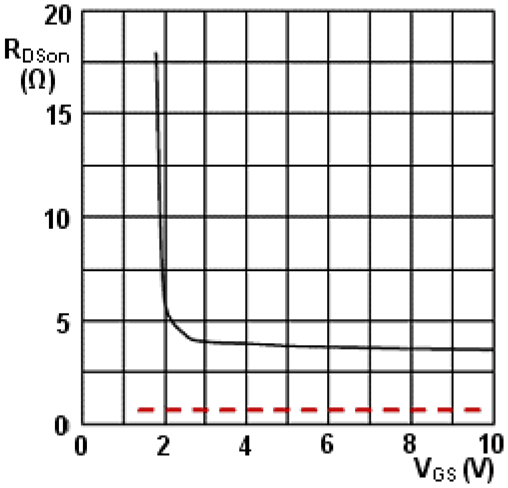

Fig. 10. "Typical n-type channel field transistor drain-source on-state resistance as a function of gate-source voltage." The doted line presents the value of resistance of the microelectromechanical switch [23]

4. CONCLUSIONS

The surface micromachined electrostatically actuated microelectromechanical switch was successfully fabricated using SiO_x doped DLC film. The Si <100> (critical surface tension 32.5 mN/m) and Au (critical surface tension 32.0 mN/m) were observed as less hydrophobic than SiO_x doped DLC (critical surface tension 42.0 mN/m). The Si <100> surface (average roughness $R_a = 0.72$ nm) was observed as more even than of Au film (average roughness $R_a = 3.2$ nm), and SiO_x doped DLC (average roughness $R_a = 2.1$ nm) as slightly more even surface than of Au film. The chemical structure of SiO_x doped DLC film showed that O 1s (atomic concentration 24.11 %) and C1s (atomic concentration 54.71 %) peaks are dominating in the film. Investigation with high resolution scanning electron microscope showed, that a gap between the microcantilever and contact electrodes matching to the thickness of the sacrificial layer was successfully achieved.

Acknowledgement

Support of Lithuanian State Science and Studies Foundation is gratefully acknowledged.

This work was partly supported by the Lithuanian Science Council Student Research Fellowship Award (A.L.).

REFERENCES

1. **Hornbeck, L. J., Nelson, W. E.** Bistable Deformable Mirror Device, OSA Technical Digest Series *Spatial Light Modulators and Applications* 8 1988: p. 107.
2. **Nathanson, H., Newell, W., Wickstrom, R., Davis, J.** The Resonant Gate Transistor *IEEE Transactions on Electron Devices* ED-14 (3) 1967: pp. 117 – 133.

3. **Trimmer, W.** Microrobot and Micromechanical Systems *Sensors and Actuators* 19 (3) 1989: pp. 267 – 287.
4. **Madou, M.** Fundamentals of Microfabrication. 2nd ed., CRC Press, Boca Raton, 2002.
5. **Nagaoka, S.** Compact Latching Type Single-mode Fiber Switches Fabricated by a Fiber Micromachining Technique and Their Practical Applications *IEEE Journal of Selected Topics in Quantum Electronics* 5 (1) 1999: pp. 36 – 45.
6. **Akiyama, T., Shono, K.** Controlled Stepwise Motion in Polysilicon Microstructures *Journal of Microelectromechanical Systems* 2 (3) 1993: pp. 106 – 110.
7. **Comtois, J., Bright, V., Phipps, M.** Thermal Microactuators for Surface Micromachining Processes *Proceeding SPIE 2642* 1995: pp. 10 – 21.
8. **Chollet, Ed. F.** *SU-8*: Thick Photo-Resist for MEMS, 14 Jan. 2006: http: //memscyclopedia.org/su8.html.
9. **Ostaševičius, V., Tamulevičius, S., Grigaliūnas, V., Kopustinskas, V., Palevičius, A., Gudonytė, A., Daukševičius, R.** Design and Fabrication of a Microelectromechanical Switch *Materials Science* (*Medžiagotyra*) 10 (4) 2004: pp. 313 – 316.
10. **Han, H., Ryan, F., McClure, M.** Ultra-thin Tetrahedral Amorphous Carbon Film as Slider Overcoat for High Areal Density Magnetic Recording *Surface and Coatings Technology* 120 – 121 1999: pp. 579 – 584.
11. **Gopinathan, N., Robinson, C., Ryan, F.** Characterization and Properties of Diamond-like Carbon Films for Magnetic Recording Application *Thin Solid Films* 355 – 356 1999: pp. 401 – 405.
12. **Grischke, M., Hieke, A., Morgenweck, F., Dimigen, H.** Variation of the Wettability of DLC-coatings by Network Modification Using Silicon and Oxygen *Diamond and Related Materials* 7 1998: pp. 454 – 458.
13. **Kim, J., Lee, K., Kim, K., Sugimura, H., Takai, O., Wu, Y., Inoue, Y.** Characteristics and High Water-repellency of a-C:H Films Deposited by Radio Frequency PECVD *Surface and Coatings Technology* 162 2003: pp. 135 – 139.
14. **Kim, J., Sugimura, H., Takai, O.** Water-repellency of a-C:H films Deposited by Radio Frequency Plasma-enhanced CVD *Vacuum* 66 2002: pp. 379 – 383.
15. **Leezenberg, P. B., Johnston, W. H., Tyndall, G. W.** Chemical Modification of Sputtered Amorphous-carbon Surfaces *Journal of Applied Physics* 89 2001: pp. 3498 – 3507.
16. **Chua, D. H. C., Teo, K. B. K., Tsai, T. H., Milne, W. I., Sheeja, D., Tay, B. K., Schneider, D.** Correlation of Surface, Mechanical and Microproperties of Tetrahedral Amorphous Carbon Films Deposited Under Different Magnetic Confinement Conditions *Applied Surface Science* 221 2004: pp. 455 – 466.
17. **Tay, B. K., Sheeja, D., Lau, S. P., Guo, J. X.** Study of Surface Energy of Tetrahedral Amorphous Carbon Films Modified in Various Gas Plasma *Diamond and Related Materials* 12 2003: pp. 2072 – 2076.
18. **Chen, L., Hong, C. F.** Surface Tension Studies of (Si, N)-Containing Diamond-like Carbon Films Deposited by Hexamethyldisilazane *Diamond and Related Materials* 12 2003: pp 968 – 973.
19. **Meškinis, Š., Kopustnikas, V., Šlapikas, K., Gudaitis, R., Guobienė, A., Tamulevičius, S.** Oxygen Ion Beam Etching of Diamond Like Carbon Films *Materials Science* (*Medžiagotyra*) 13 (4) 2007: pp. 282 – 285.
20. **Deshmukh, R. R., Shetty, A. R..** Comparison of Surface Energies Using Various Approaches and Their Suitability, *Journal of Applied Polymer Science* 107 2008: pp. 3707 – 3717.
21. **De Los Santos, H.** Introduction to Microelectromechanical Microwave Systems. Second Edition. Norwood, MA, USA: Artech House, Incorporated, 2004: pp. 6 – 8.
22. **Chollet**, **Ed. F., Liu, H. B.** A (Not So) Short Introduction to Microelectromechanical Systems. MicroMachines Centre, School of MAE, Nanyang Technological University, Singapore, version 2.0, 2006-08.
23. Philips Semiconductors, BSN304 N-channel Enhancement Mode Vertical D-MOS Transistor, data sheet, Product specification 2001-11.