EFFECT OF THE DECAMETHYLTETRASILOXANE FILMS DEPOSITION PARAMETERS ON THEIR PROPERTIES

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Introduction

Many critical systems in spacecraft or vacuum technology involve relative motion of contacting surfaces. Most of the applications require the use of low friction rate lubricants, taking into account the need for low power consumption and extreme reliability in a wide range of environments[1].

The increased interest in MEMS has raised the request for long-term stable micro actuators. However, the requirements on reliability, durability and local pressure will be comparable to macroscopic applications. One major problem is the lack of tribological optimized surfaces for micro parts. As a solution, microtribological coatings are used[2–4].

The plasma deposition of thin films with low friction coefficient have been intensively investigated in recent years[5–7]. The most known examples are the plasma deposited DLC diamond-like coatings[8–12].

An increasing interest in plasma deposition of thin films under atmospheric pressure, with the use of alkylsiloxanes compounds as the precursors[13,14,1] is observed. The interest stems not only from economic reasons, as compared with the low pressure methods used up to now, but also from the steadily increasing role of surface and demand of new utility properties of materials, as well as from the exhaustion of possibilities of the traditional technologies[15–17].

The goal of the investigations was to study the process of thin film deposition from decamethyltetrasiloxane (DMTOS) mixtures with argon and oxygen, which can be applied in MEMS (micro electro mechanical systems).

Experimental

The aim of the work was to determine the optimal conditions of depositing films in DBD (dielectric barrier discharge) under atmospheric pressure[1,2]. The process was carried out for 15 minutes at 1.5 kV voltage and 3–4 kHz frequency. Decamethyltetrasiloxane (DMTOS) of $C_{10}H_{30}Si_4O_3$ formula was the precursor. The films were deposited on monocrystalline silicon <100> surfaces, at 100–400 °C from 0.04 % DMTOS + O_2 +Ar mixtures at overall gas flow of 12 $dm^3 h^{-1}$ and oxygen concentration in the range of 0–1.42 %.

The obtained films were studied by:

– Composition: Infrared Spectroscopy with Fourier Transformation (FT-IR).
– Friction coefficient: Linear tribometer (designed at Łódź University, with a ¼" ball of ZrO_2 modified with Y_2O_3, under the loads of 30–90 mN. Rate of ball shift with respect to the surface studied − 10 mm min^{-1}, number of repetitions 4.
– Composition: Auger Electron Spectroscopy (AES) using a MICROLAB-350, produced by Thermo Fischer, using electron energy of 10 kV.
– Surface topography: Atomic Force Microscopy (AFM) produced by Park Scientific Instruments.
– Film thickness was measured by ellipsometry at 632.8 nm wavelength using Ellipsometr II (Applied Materials).

Results and discussion

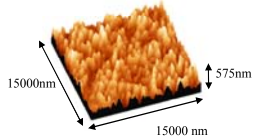
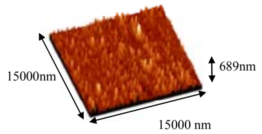
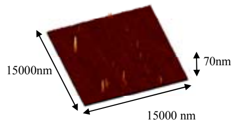
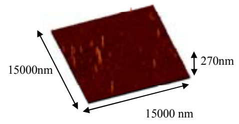
In the studies carried out attention has been put on the effect of the surface temperature and oxygen content in the mixture on the properties of films.

On the basis of IR studies, for mixtures 0.04 % DMTOS + O_2 + Ar comprising 0–0.18 % of oxygen it was found that with an increase in the surface temperature a decrease in the intensity of absorption bands characteristic of Si-CH_3, Si-

Table I
Characteristics of thin films deposited from the mixture of 0.04% DMTOS +Ar

Sample	Temperature [°C]	Thickness [nm]	Composition			Fiction coefficient
			C [%]	O [%]	Si [%]	
29 KR	100	85.5	42.4	18.9	38.7	0.048 ± 0,006
30KR	200	55.8	36.4	22.1	41.5	0.123 ± 0,014
32KR	300	37.0	26.7	27.3	46.0	0.262 ± 0,028
31KR	400	41.8	30.4	27.2	42.4	0.442 ± 0,044
Si						0.072 ± 0,014

Table II
Topography of the surface of films deposited at various temperatures form the 0.04 % DMTOS + 1.42 % O_2 + Ar mixture

40KR	43KR
	
temp.100°C RMS=32.4 nm	temp.200°C RMS=16.6 nm
42KR	**41KR**
	
temp.300°C RMS=16.5 nm	temp.400°C RMS=2.3 nm

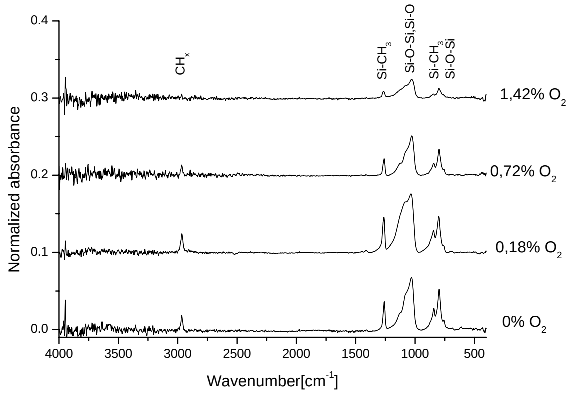


Fig. 1. **FTIR spectra of films deposited at 100 °C from the 0.04 % DMTOS + O_2 + Ar mixture with different oxygen content**

$(CH_3)_3$, Si-O-Si, Si-O and Si-O-C groups occurs, as well as that of the CH_x group decays. The results of FTIR studies of films deposited from mixtures containing from 0.72 % to 1,42 % of oxygen show a decrease in the intensity of bands characteristic of Si-CH_3 and Si-$(CH_3)_3$ groups, as well as an increase in that of Si-O-Si linkages with an increase in the surface temperature. XPS studies of thin films deposited from the mixture of 0.04 % DMTOS +Ar (films deposited from the mixture of 0.04 % DMTOS +Ar) revealed that with an increase in the surface temperature the carbon content in the layer decreases from 42 % to about 27 % (tab. I).

Topographic studies of the surface of films showed that with a rise of the surface temperature, the roughness (RMS) of films deposited from the 0.04 % DMTOS + 1.42 % O_2 + Ar mixture decreases (tab. II).

In the case of films deposited from other mixtures no such relation was found. The value of the friction coefficient for layers deposited from 0.04 % DMTOS + Ar mixtures shows a clear increasing tendency with a rise of the surface temperature. The lowest friction coefficient of 0.048 was obtained at 100 °C. It was also found that an increase in the surface temperature as well as increase in the oxygen content in the mixture caused a decrease in the rate of the deposition of films.

Studies carried out by means of infrared spectroscopy showed differences in the composition of films deposited at 100 °C from the 0.04 % DMTOS + (0–1.42 %) O_2 + Ar mixtures (Fig. 1).

With an increase in the oxygen concentration in the mixtures, a decrease in intensity of the absorption bands characteristic of Si-O-Si and Si-O-C groups (800 cm^{-1}) as well as of Si-CH_3 and Si-$(CH_3)_3$ ones (1260 cm^{-1}) has been observed. For films deposited at 200 °C no relationship between the films' composition and oxygen content in the mixture was found.

XPS studies revealed that an increase in the oxygen content in the gas mixture caused a decrease in the carbon content of the film from 42 % to about 23 % and an increase in the silicon content from 39 % to 47 % (tab. III). The silicon to oxygen ratio in the films was 2:1 and was analogous as in Si-O-Si linkages, despite an increase in the oxygen concentration in the mixture from 0 % to 0.72 %. For oxygen concentration of 1.42, the Si : O ratio decreases and is equal to 1.57. The friction coefficient of these films is equal to 0.225 and is larger than that for films deposited from mixtures with (0.72 %) oxygen (0.082) and without oxygen (0.048).

In coatings 29KR and 44KR the presence of CH(CH3) OCH(CH3)OCH(CH3)O- linkages was observed. The pres-

Table III
Characteristics of thin films deposited from the 0.04 %DMTOS + O_2 + Ar mixture with different oxygen content

Sample	O_2 content [%]	Thickness [nm]	Composition			Fiction coefficient
			C [%]	O [%]	Si [%]	
29 KR	0	85.5	42.4	18.9	38.7	0.048 ± 0,006
34KR	0.18	176.6	36.5	21.2	42.3	0.251 ± 0,007
44KR	0.72	74.8	36.9	20.1	43.0	0.085 ± 0,010
40KR	1.42	35.8	22.6	30.1	47.3	0.225 ± 0,016
Si						0.072 ± 0,014

Table IV
Concentration of carbon linkages in coatings with small friction coefficients

Sample	O_2 content [%]	Binding energy [eV]	Content [at. %]	Assigned group
29KR	0	286.64	9.5	$(CH_3CH_2)_2O$
		287.60	30.2	$CH(CH_3)OCH(CH_3)OCH(CH_3)O$-
		288.92	2.7	$(-CH_2C(O)O-)_n$
44KR	0.72	283.73	7.9	C
		284.69	16.1	C
		285.84	9.3	C
		287.06	3.6	$CH(CH_3)OCH(CH_3)OCH(CH_3)O$-

Table V
Friction coefficient of layers deposited on various surfaces at 100°C, from 0.04 % DMTOS +Ar and 0.04 % DMTOS + 0.72 % O_2 + Ar mixtures

Type of surface	Friction coefficients		
	Pure surface	Film deposited from mixture	
		0.04 % DMTOS +Ar	0,04 % DMTOS 0.72 % O_2+ Ar
Polycrystalline silicon	0.580 ± 0.031	0.160 ± 0.016	0.162 ± 0.018
Aluminum	0.499 ± 0.054	0.237 ± 0.024	0.206 ± 0.013
Silicon nitride	0.203 ± 0.016	0.181 ± 0.011	0.241 ± 0.019
Polisiloxane	0.4 – 0.75	1.151 ± 0.097	0.263 ± 0.011
Parilene	0.450 ± 0.013	0.058 ± 0.006	0.310 ± 0.022

ence of these groups in the film is probably responsible for the low friction coefficient value (Tab. IV).

Topographic studies of the films surface carried out by means of an atomic forces microscope did not show a relationship between the addition of oxygen and surface structure and roughness of the deposited films. Tribologic studies did not show a correlation between the addition of oxygen, substrate temperature and the friction coefficient value. In order to check the tribologic properties of films of selected parameters, they were deposited on other surfaces, such as polycrystalline silicon, aluminum, silicon nitride, polysiloxane and parilene (tab. V).

Conclusions

The films deposited at 100 °C from a 0.04 % DMTOS + Ar mixture had a from 2 to 8 times smaller friction coefficient than that of the surfaces used. A two-fold smaller friction coefficient was also obtained for films deposited at 100 °C from a 0.04 % DMTOS + 0.72 % O_2+ Ar mixture on an aluminum bed and from polysiloxane.

Films deposited from these mixtures have promising tribologic properties and can be utilized in micromechanics as films decreasing the friction coefficient.

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In the barrier discharge under atmospheric pressure, thin surface films were obtained from decamethyltetrasiloxane (DMTOS) as a precursor. The experiments were carried out in a laboratory reactor of controlled surface temperature (100–400 °C), at 3.3 kHz frequency. The films were deposited on surfaces of monocrystalline silicon <100> from mixtures of 0.04 % DMTOS + O_2 +Ar; oxygen concentration in the range of 0–1.42 %. The films obtained at 100 °C from mixtures of 0.04 % DMTOS + Ar, 0.04 % DMTOS + 0.72 % O_2 + Ar showed a smaller friction coefficient than that of silicon, and, therefore, they were applied as self-lubricating films on other surfaces used in MEMS .