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Dielectric Properties of the Ion Beam Deposited SiO_x Doped DLC Films

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In the present study SiO_x doped DLC thin films were synthesized from hexamethyldisiloxane vapor and hydrogen gas mixture by direct ion beam deposition. Dielectric properties of the films were evaluated by measuring breakdown field strength and dielectric permittivity. Chemical composition and structure of the deposited films were investigated by X-ray photoelectron spectroscopy and FT-IR spectrometry. Breakdown field strength of the samples was in (0.39 – 1.86) MV/cm range and dielectric permittivity – in 2.8 – 4.5 range. Dielectric properties of the deposited films are dependent on the substrate material, top electrode diameter as well as the ion beam current density and hydrogen flux during deposition.

Keywords: SiO_x doped diamond like carbon films, ion beam synthesis, dielectric properties.

1. INTRODUCTION

Diamond like carbon (DLC) remains at the top of the interest due to their outstanding mechanical, chemical, optical and electrical properties [1]. Particularly dielectric properties of the DLC and related hydrogenated amorphous carbon films received considerable interest in last decade [2 – 5]. Due to the possibility to grow high quality DLC layers at room temperature, the application of the diamond like carbon films in organic light emitting diodes as electron injection layer has been already considered [6, 7]. The properties of the DLC films can be controlled by doping with both metallic and non-metallic elements and compounds. In such a way problems of the adhesion with ferrous substrates, high internal stress and thermal stability can be avoided. Above all, SiO_x doped DLC films deposited by plasma enhanced chemical vapor deposition or hydrocarbon ion beam deposition would have some advantages over conventional hydrogenated DLC films as a dielectric (insulating) layers such as reduction of the internal stress [8], better adhesion with different metallic substrates [9], higher optical transmittance [10] and higher thermal stability [11]. However, there are few studies on dielectric properties of the SiO_x doped DLC films [12]. While organo-silicate glass (also known as a-SiOC:H or carbon doped silicon oxide) films already received considerable interest as a possible new low-k dielectric materials [3, 13, 14].

In the present research, dielectric properties of the SiO_x doped DLC films synthesized by direct ion beam deposition using different hydrogen fluxes and ion current densities were investigated. The dielectric properties of the films were analyzed in terms of structure and chemical composition of the synthesized SiO_x doped DLC layers.

2. EXPERIMENTAL

SiO_x doped DLC films were deposited at room temperature by direct 800 eV energy ion beam using a hollow cathode closed drift direct current ion source. Mixture of the hexamethyldisiloxane vapor with hydrogen ($HMDSO + H_2$) has been used as a hydrocarbon, silicon and oxygen source. Hexamethyldisiloxane was introduced into the technological chamber from a bubbler using H_2 as a feed gas. In some cases (experiments No 1 and 2 in Table 1) additional H_2 gas flux has been introduced. Base pressure was $2 \cdot 10^{-4}$ Pa, work pressure – $(1 \div 2) \cdot 10^{-2}$ Pa. Other technological parameters of deposition process are shortly presented in Table 1.

Table 1. Technological conditions of the SiO_x doped a-C:H films deposition process

Exp. No	$(HMDSO + H_2)/H_2$ gas flow ratio	Current density (mA/cm^2)	Ion beam energy (keV)
1	1 : 1	0.1 ±0.01	(0.8 ±0.1)
2	1 : 1.5	0.1 ±0.01	(0.8 ±0.1)
3	Only HMDSO + H_2	0.1 ±0.01	(0.8 ±0.1)
4	Only HMDSO + H_2	0.05 ±0.01	(0.8 ±0.1)
5	Only HMDSO + H_2	0.15 ±0.01	(0.8 ±0.1)

Samples for measurement of the FTIR and XPS spectra has been synthesized on commercially available monocrystalline n-Si wafers. Before deposition Si substrates were washed by dimethylformamide and acetone.

Three kinds of the substrates were used for evaluation of the dielectric properties of DLC films: DLC films deposited on monocrystalline Si substrates with vacuum evaporated Al bottom electrode on the other side of the wafer (Si-DLC-Al), DLC films on Al thin film (Al-DLC-Al), DLC films on Cr thin film (Cr-DLC-Cr). Substrates with vacuum evaporated Al and Cr films were loaded from vacuum evaporation chamber into the DLC film synthesis chamber within few minutes without any additional surface treatment. After the synthesis of the SiO_x doped diamond like carbon films, fabrication of the samples was completed by vacuum evaporation of the top electrode metallization layer. Circular dot shaped top electrodes of

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the necessary diameter (300 μm, 500 μm, 1 mm) were formed using evaporation through the mask. Top electrode metal was Al for first the two kinds of the samples and Cr for the third.

Dielectric properties of silicon oxide doped diamond like carbon films were evaluated by measuring breakdown field strength and dielectric permittivity (ε).

Thickness of the deposited films was measured by a laser ellipsometer Gaertner L115 (λ = 633 nm). FTIR spectra were measured by a spectrometer Spektrum GX (Perkin Elmer) in the range of 400 cm^{-1} – 4000 cm^{-1}. Influence of the Si(100) substrate on IR absorption spectra was evaluated and eliminated. The X-ray Photoelectron spectra were recorded with the KRATOS ANALYTICAL XSAM800 XPS analyzer. The Al K_α radiation ($h\nu$ = 1486.6 eV) was used. The energy scale of the system was determined according to Au4f 7/2 peak, the analyzer being in the constant transition mode. All spectra were determined at the 20 eV pass energy and 0.1 eV energy increment. Atomic concentrations were calculated using original KRATOS XSAM800 software. Raman spectra of the synthesized films were typical for diamond like carbon [10].

3. EXPERIMENTAL RESULTS

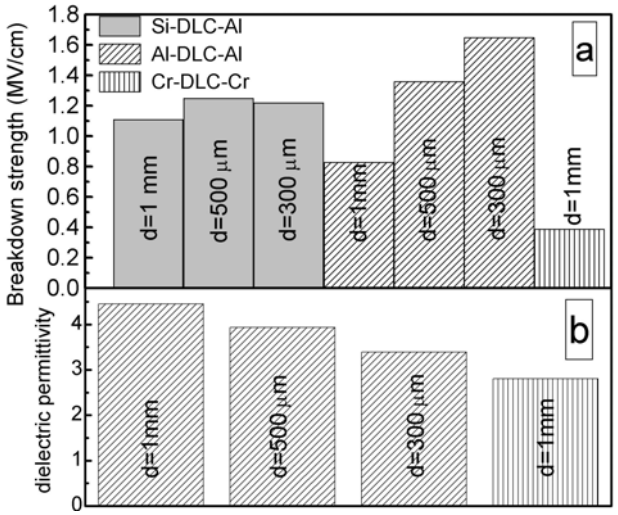

Fig. 1. Dielectric properties of SiO_x doped DLC films deposited on the different substrates: breakdown strength (a) and dielectric permittivity (b)

It can be seen in Fig. 1, that dielectric properties of the SiO_x doped DLC films deposited by 100 μA/cm^2 current density ion beam from hexamethyldisiloxane and hydrogen gas mixture depend on the substrate material used. The lowest breakdown field exhibited metal-insulator metal structure synthesized on Cr substrate. Breakdown field of the Al-DLC-Al and Al-DLC-Si structures was substantially higher. Yet dependence on the top electrode diameter was very different for these two cases. Only weak dependence on electrode diameter was observed for SiO_x doped DLC film deposited onto Si(111) substrate. While in the case of the SiO_x doped DLC film deposited onto Al substrate this dependence was much more stronger: breakdown field increased twice with decrease of the electrode diameter from 1 mm to 300 μm. Therefore breakdown field of the Al-DLC-Al structure with 1 mm electrode diameter was lower than the breakdown field of the Al-DLC-Si structure, while in the case of the 300 μm electrode diameter samples breakdown field of the DLC film deposited onto Al substrate was higher. It can be mentioned, that similarly to the present study in [2] contact area effect on the breakdown strength was much more weaker for the DLC films deposited on monocrystalline substrate than for DLC films deposited on metal substrates. The breakdown field of DLC films deposited on Cr was lower than breakdown field of DLC films deposited on Si and Al. However, in [2] breakdown strength of DLC films deposited on Si was several times larger than breakdown strength of films deposited on Al.

Dielectric permittivity of SiO_x doped DLC films was dependent on the type of the substrate as well (Fig. 1, b). Dielectric permittivity of films deposited on Al was 4.46 in comparison with 2.81 for the films deposited on Cr substrate.

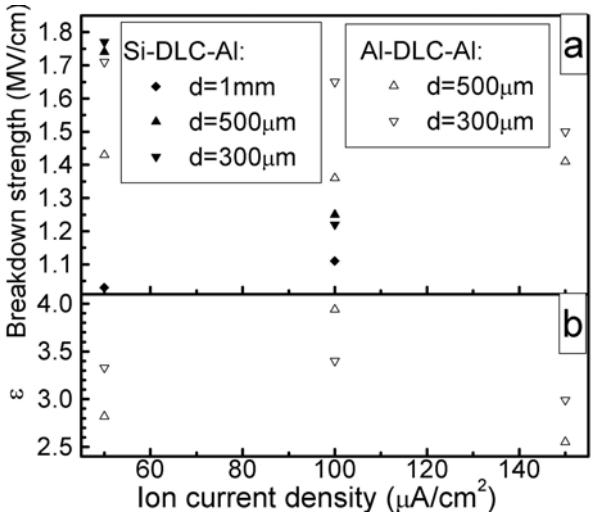

Fig. 2. Breakdown field strength (a) and dielectric permittivity (b) vs ion beam current density

It was found, that ion current density has more essential influence on the properties of the SiO_x doped DLC films deposited on Si substrate as compared to the films deposited on Al. It can be seen in Fig. 2, that in the case of the DLC films deposited onto the Si, increase of the ion current density results in ~1.5 times decrease of the breakdown field for the samples with electrodes of 300 μm and 500 μm diameter. While in the case of the samples with electrode diameter 1 mm, the breakdown field slightly increased with the current density. On the other hand increase of the ion current density in (50 – 150) μA/cm^2 range resulted in decrease of the breakdown strength from 1.71 MV/cm to 1.5 MV/cm for SiO_x doped DLC films deposited on Al substrate with electrode diameter 300 μm. While for the samples with electrode diameter 500 μm no dependence of the breakdown strength on ion current density was observed.

Dielectric permittivity in all cases was highest for the DLC films synthesized using 100 μA/cm^2 current density ion beam (Fig. 2, b). The lowest values of the dielectric permittivity were observed in the case of the films deposited using 150 μA/cm^2 current density ion beam. It can be mentioned, that in the case of the samples synthesized by

100 μA/cm^2 current density ion beam dielectric permittivity decreased with electrode diameter. While for samples deposited by 50 μA/cm^2 and 150 μA/cm^2 current density ion beams dielectric permittivity increased with decrease of the electrode diameter.

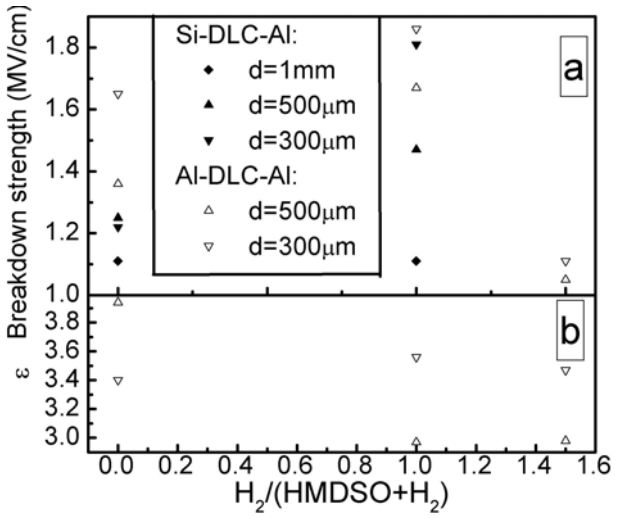

Fig. 3. Breakdown field strength (a) and dielectric permittivity (b) vs ratio between the additional hydrogen flux and hexamethyldisiloxane vapor – hydrogen gas flux

Additional hydrogen flow during the synthesis process resulted in increase of the dielectric strength of the SiO_x doped DLC film. However, dielectric strength decreased as a result of the further increase of the H_2 flux. It must be mentioned, that in the case of the DLC films deposited using additional H_2 flux, part of the samples were conductive ("short"). Dielectric permittivity (ε) of the synthesized films decreased with additional H_2 flux for samples with electrodes of 500 μm diameter. Surprisingly, in the case of the samples with top electrode diameter 300 μm, H_2 flux increased dielectric permittivity of the films.

Table 2. Chemical composition and structure of the SiO_x doped DLC films

Sample No	DLC film thickness (nm)	Composition related to Si (XPS)	Si-O / Si-$(CH_3)_x$ peak intensity ratio (FTIR)
1	180	$SiO_{1.14}C_{2.62}$	1,39
2	170	$SiO_{1.23}C_{2.32}$	1,22
3	200	$SiO_{1.15}C_{2.85}$	0,97
4	182	$SiO_1C_{2.55}$	1,08
5	190	$SiO_1C_{2.55}$	1,28

FTIR absorption spectra of the all samples were similarly shaped: the main peaks at ~2900 cm^{-1} (C-H bond stretching in CH_3 [1,15]), 2140 cm^{-1} (Si-H stretching in SiH_x [15,16]), 1000 – 1010 cm^{-1} (Si-O bond stretching in Si-O-Si) [15], 800 – 840 cm^{-1} (CH_3 in Si-$(CH_3)_x$ [16])) can be seen. Surprisingly intensity and area of the C-H related FT-IR peaks were the largest in the case of the DLC film deposited by 150 μA/cm^2 current density ion beam. While additional hydrogen flow did not caused increase of that parameters. Therefore, in the case of the films deposited using additional hydrogen flow presence of the large amount of the unbound hydrogen can be supposed. Table 2 presents atomic concentrations of thin DLC films defined by XPS. One can see, that atomic concentrations of the C, Si, O differ only for several percents for samples deposited under different synthesis process conditions. Position of the resultant Si2p peak is the same for DLC films deposited by 50, 100, 150 μA/cm^2 ion current density beam (101.5 eV). Summarizing presented FTIR and XPS data, structure of the synthesized SiO_x doped DLC films can be described using model suggested by [17] for SiO_x doped DLC films: two random interpenetrating amorphous networks of a-C:H and a-SiO_x .

4. DISCUSSION AND CONCLUSIONS

It can be seen, that in the case of the DLC-SiO_x films deposited using 10 μA/cm^2 and 150 μA/cm^2 current density ion beam chemical composition (according to XPS) is the same. While for film deposited using lower ion beam current density higher breakdown strength and lower Si-O / Si-$(CH_3)_x$ FTIR absorption peak intensity ratio can be seen. It can be seen in Table 2, that for films deposited without the additional hydrogen flow dielectric permittivity decreases with decrease of the Si-O / Si-$(CH_3)_x$ peak intensity ratio. The lowest ε between the all investigated samples observed for DLC-SiO_x films deposited using 150 μA/cm^2 current density ion beam is in good agreement with the highest intensity and area of the C-H related FT-IR peaks mentioned above. It can be mentioned, that dependence of Raman spectra of the undoped DLC films deposited by closed drift ion source on ion current density was observed [18]. Therefore, possible changes of the structure of a:C-H network in SiO_x doped DLC films such as increased size of the sp^2 clusters as well as decrease of the sp^3/sp^2 bond ratio with ion beam current density should be taken into account as well.

In the case of the experiment with additional hydrogen flow no correlation between the breakdown strength and Si-O / Si-$(CH_3)_x$ peak intensity ratio (Table 2) was observed. In this case rather Si/O ratio in deposited film must be taken into account. It can be seen in Table 2 and Fig. 3, that increased Si/O ratio in sample No 2 corresponds to decreased breakdown strength.

It seems, that substrate material has the same or even bigger influence on the dielectric properties of the deposited films than ion beam current density or additional hydrogen flow (Figs. 1 – 3). It can be mentioned, that in [2] dependence of the breakdown field of undoped DLC films on the substrate material was explained by dependence of the growing DLC structure on substrate.

It should be mentioned, that for all the samples investigated, the breakdown field increased with decrease of the top electrode diameter. It seems, that in the case of the samples deposited on Al substrate this dependence is most pronounced. However, for some samples breakdown strength of the DLC films deposited on Si substrate increased with the electrode diameter as well. In some cases differences between the dielectric properties of the structures Al-DLC-Al (Si-DLC-Al) deposited under the same technological process conditions (ion beam current density, reagents composition, substrate) with different top electrode diameter were of the same order or even larger than the differences between the samples of the same

electrode diameter deposited under different technological process conditions. Effect of dependence of the dielectric breakdown strength and time to breakdown on the electrode area was observed in different inorganic and organic didelectrics [19 – 21]. That effect was explained by increased overall number of the different defects with increase of the contact area [21]. Therefore, spacial homogeneity of the structure of deposited DLC films as well as homogeneity of the surface morphology must be considered.

In conclusion dielectric SiO_x doped diamond like carbon films deposited from hexamethyldisiloxane and hydrogen gas mixture were synthesized on Si, Al and Cr substrates without any interlayer. Breakdown field strength and dielectric permittivity of the most samples were in the range of (1 – 1.8) MV/cm and 2.8 – 4.5 respectively. The lowest dielectric strength and dielectric permittivity exhibited DLC films deposited on Cr substrate. While breakdown field strength of SiO_x doped DLC films deposited on Al and Si substrates varied in 0.83 – 1.86 and (1.11 – 1.86) MV/cm ranges respectively. Some increase of the breakdown field strength was achieved by decrease of the ion beam current density or introduction of the additional hydrogen flux. Yet chemical composition of the all samples established by XPS was similar. Therefore, the results concerning dielectric properties can be associated with change of the structure of a:C-H network of SiO_x doped DLC films. Substrate material and top electrode diameter had substantial influenceon dielectric properties of the investigated structures. It was explained by inhomogeneity of the DLC films as well as by dependence of the DLC film structure on the substrate material.

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