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Chemical structure of silicon-, oxygen- and nitrogen-containing a-C:H films prepared by RF plasma beam CVD

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Abstract

Si-, SiO_x- and SiN_x-containing a-C:H films (denoted as DLCSi, DLCSiO and DLCSiN) were deposited respectively from tetramethylsilane, hexamethyldisiloxane and hexamethyldisilazane precursors onto silicon wafer and aluminium substrates by electron cyclotron wave resonance (ECWR) RF plasma beam CVD. The chemical composition and the bonding states of the constituent elements were characterised by X-ray photoelectron spectroscopy and X-ray induced Auger electron spectroscopy.

Compared to the composition of the precursors, significant loss of C for each layer and some loss of N for the DLCSiN layers were obtained, while the O/Si ratios for the DLCSiO layers remained practically unaltered. The modified Auger parameter of Si (Si α) decreased with increasing oxygen content and increased with increasing N content for the DLCSiO and DLCSiN layers. Si α was proposed to reflect the degree of crosslinking. For the DLCSiO and DLCSiN layers Si α could be altered by the deposition conditions (self-bias). The appearance of Si–O bonds was inferred from the valence band analysis of an Ar^+ ion bombarded DLCSi layer containing O-contamination.

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Keywords: Diamond-like carbon; Silicon; XPS; Auger parameter

1. Introduction

Si-incorporation into a-C:H films is known to reduce its friction, wettability, residual internal stress, to improve its thermal stability and adhesion [1,2], and to modify its optical and electrical properties as well as hemocompatibility and biocompatibility [3]. SiO_x- and SiN_x-containing variants are considered to have further advantageous properties, e.g., reduced surface tension and compressive stress, improved adhesion to metals, fracture toughness, thermal stability and oxidation resistance [4,5]. A number of papers have been published on the preparation of such layers, applying various activation and deposition methods [4–9].

In this work we describe the preparation of a series of Si-, SiO_x- and SiN_x-containing a-C:H films (hereinafter referred to as DLCSi, DLCSiO and DLCSiN films) using an electron cyclotron wave resonance (ECWR) plasma-beam source and the results of their comparative quantitative analysis by X-ray photoelectron spectroscopy and X-ray induced Auger electron spectroscopy, including the chemical composition and the bonding modes between the constituent elements. In a follow-up paper [10] we characterise the nanomechanical properties of the films and establish relationships between the chemical structural and nanomechanical parameters.

2. Experimental

DLCSi, DLCSiO and DLCSiN films with 300–600 nm thicknesses were deposited at room temperature from tetramethylsilane (TMS), hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSA) precursors, respectively, using an electron cyclotron wave resonance (ECWR) radio frequency (RF) plasma beam source (PSQ 100, IPT,

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Table 1
List of samples and preparation conditions

Sample	Precursor	Pressure, Pa	Flow rate, $cm^3\ min^{-1}$	RF power, W	Self-bias, V
DLCSi-1	TMS	0.15	6	100	195
DLCSi-2		0.24	11	100	160
DLCSi-3		0.40	11	100	136
DLCSi-4		0.30	9	100	345
DLCSi-5		0.20	4	100	420
DLCSi-6		0.20	4	150	520
DLCSiO-1	HMDSO	0.40	25	80	270
DLCSiO-2		0.37	6	100	95
DLCSiO-3		0.34	6	100	130
DLCSiO-4		0.62	10	100	45
DLCSiO-5		0.26	4	100	300
DLCSiN-1	HMDSA	0.56	6	100	75
DLCSiN-2		0.58	5	150	95
DLCSiN-3		0.58	10	100	56
DLCSiN-4		0.28	4	100	320

Germany). Pieces of polished (100) silicon wafer with its native oxide and Al foils were used as substrates. The vapour of the analytical grade liquid-phase materials was introduced into the plasma beam source directly from an evaporator, or from a bubbler type saturator with 5N purity He carrier gas. The vessels were kept at room temperature (300 K). The flow rate was varied between 4 and 25 cm^3(STP)/min to reach an operation pressure of 0.1–0.6 Pa in the deposition chamber (base pressure 2×10^{-4} Pa). The RF power varied between 80 and 150 W, resulting in a self-bias ranging from 45 to 520 V between the plasma and the coupling electrode. Deposition lasted 30–50 min. Under the above conditions a relatively high growth-rate of 6–20 nm/min was achieved, as determined by a profilometer (Tencor AlphaStep). The main deposition parameters are given in Table 1.

The samples were analysed by X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES). Samples were mounted on stainless steel sample holders using double-sided adhesive tape. The spectra were recorded by a Kratos XSAM 800 spectrometer using Mg $K\alpha_{1,2}$ radiation in fixed analyser transmission mode (the wide scan and the detailed spectra with 80 and 40 eV pass energy, respectively). The bremsstrahlung component was applied to record the Si $KL_{23}L_{23}$ region. The pressure in the sample analysis chamber was lower than 10^{-7} Pa. The electrons originating from the Al window (interposed between the anode and the sample) prevented the samples from excessive electrostatic charging. The spectra were referenced to the C 1s line set to a binding energy of 284.4 eV, the value published for C–Si bonds in polydimethylsiloxane [11] and some similar organosilicon polymers [12]. Data acquisition and peak fitting was performed by the Kratos Vision 2000 software. Quantification was undertaken with the recently developed XPS MultiQuant program [13].

3. Results and discussion

The XPS results of compositional analysis are reported in Table 2. The binding energy (BE) values of the characteristic photoelectron peaks, the kinetic energy (KE) values of the Si $KL_{23}L_{23}$ peaks and the modified Auger parameters for silicon (Si α) are collected in Table 3.

Comparing the results of compositional analysis of the deposited layers (last column in Table 2) to the stoichiometric values of their respective precursors (SiC_4, Si_2C_6O and Si_2C_6N for TMS, HMDSO and HMDSA, respectively), the following compositional deviations can be obtained: significant loss of C for each layer, some loss of N for the N-containing samples and the appearance of O-contamination for the DLCSi and DLCSiN layers. The O/Si ratio of the DLCSiO films remained practically the same as that of the precursor HMDSO.

The two-dimensional chemical state plot for Si of the samples studied is depicted in Fig. 1. For comparison, the points corresponding to Si [14], SiC [15], SiO_2 [12,16] and Si_3N_4 [14,17], as well to the model polymers polydimethylsiloxane (PDMS) and polyvinyltrimethylsilane (PVTMS)

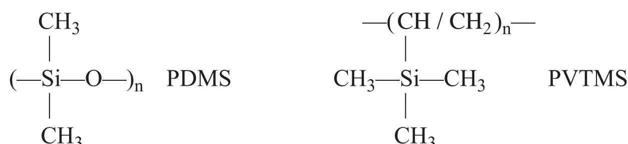
Table 2
Composition of the films as determined by XPS

Sample code	N, at.%	O, at.%	C, at.%	Si, at.%	Composition related to Si
DLCSi-1		4.7	70.6	24.7	$Si_1C_{2.9}O_{0.19}$
DLCSi-2		4.3	64.6	31.1	$Si_1C_{2.1}O_{0.14}$
DLCSi-3		9.3	63.9	26.8	$Si_1C_{2.4}O_{0.35}$
DLCSi-4		5.3	69.2	25.5	$Si_1C_{2.7}O_{0.21}$
DLCSi-5		5.1	71.9	23.0	$Si_1C_{3.1}O_{0.22}$
DLCSi-6		6.9	70.4	22.7	$Si_1C_{3.1}O_{0.30}$
DLCSiO-1		14.3	55.7	30.1	$Si_1C_{1.9}O_{0.48}$
DLCSiO-2		17.2	49.4	33.4	$Si_1C_{1.5}O_{0.51}$
DLCSiO-3		16.8	50.0	33.2	$Si_1C_{1.5}O_{0.51}$
DLCSiO-4		15.1	54.7	30.2	$Si_1C_{1.8}O_{0.50}$
DLCSiO-5		13.0	56.5	30.5	$Si_1C_{1.9}O_{0.43}$
DLCSiN-1	10.3	9.0	51.5	29.2	$Si_1C_{1.8}O_{0.31}N_{0.35}$
DLCSiN-2	10.5	4.8	53.9	30.8	$Si_1C_{1.8}O_{0.16}N_{0.34}$
DLCSiN-3	8.6	10.7	54.2	26.5	$Si_1C_{2.0}O_{0.40}N_{0.32}$
DLCSiN-4	10.8	5.9	53.0	30.4	$Si_1C_{1.7}O_{0.19}N_{0.36}$

Table 3
Peak energies and modified Auger parameters for Si

Sample code	N 1s, eV	O 1s, eV	Si 2p, eV	Si KLL, eV	Si α, eV
DLCSi-1		532.5	100.8	1613.7	1714.6
DLCSi-2		532.5	100.8	1613.6	1714.4
DLCSi-3		532.5	100.8	1613.9	1714.6
DLCSi-4		532.5	100.8	1613.8	1714.6
DLCSi-5		532.4	100.8	1613.8	1714.6
DLCSi-6		532.3	100.9	1613.9	1714.8
DLCSiO-1		532.3	101.4	1612.9	1714.4
DLCSiO-2		532.3	101.6	1611.9	1713.4
DLCSiO-3		532.3	101.6	1612.1	1713.7
DLCSiO-4		532.1	101.6	1611.0	1712.6
DLCSiO-5		532.2	101.4	1612.7	1714.2
DLCSiN-1	397.9	532.4	101.5	1612.0	1713.5
DLCSiN-2	397.9	532.4	101.3	1612.5	1713.8
DLCSiN-3	397.9	532.1	101.5	1611.2	1712.7
DLCSiN-4	397.9	532.3	101.2	1613.1	1714.3

[12] are also indicated, where the two polymers have the following repeat units:



It can be seen in Fig. 1 that the points corresponding to the DLCSi, DLCSiO and DLCSiN samples studied fall in the area situated between the points of SiC, Si_3N_4, PDMS and PVTMS. The points of the DLCSi samples are close to that of SiC, suggesting the predominant presence of Si–C bonds. There is no sign of presence of a significant amount of Si–Si bonds.

The points of DLCSiO and DLCSiN samples are situated at higher BE values of Si 2p and lower KE values of Si $KL_{23}L_{23}$, occupying positions between the points of PDMS and DLCSi samples. The value of Si α increases for the DLCSiO and the DLCSiN samples, when moving on the Auger plot in the direction from PDMS to SiC. Based on the relationship found previously between Si α and crosslinking of organosilicon polymers [12] in can be stated that the degree of crosslinking for the DLCSiO and the DLCSiN samples increases in this direction. The physical background is that a change in α is proportional to the change in the extra-atomic relaxation or screening the final state ion in the Auger transition by electrons from the neighbouring atoms. The increasing crosslinking in the direction from PDMS to SiC is backed up also by the facts that PDMS is a linear polymer, while SiC is a three-dimensional lattice-structured crystalline material.

Fig. 2 shows the dependence of Si α on the O-content of the samples studied. The points pertaining to DLCSiO and DLCSiN samples scatter along the line connecting the points of SiC and PDMS. This trend offers a qualitative explanation for the relationship stated above between Si α and the degree of crosslinking: obviously, the increase of concentration of the (two-valent) oxygen atoms leads to the increase of linear chain-portions, in which Si ions have limited extra-atomic relaxation possibilities.

The dependence of Si α on the N-content is shown for the DLCSiN samples in Fig. 3. Clearly, Si α increases with the N-content significantly. This is in agreement with the expectations, since the three-valent nitrogen is a potential crosslinking atom in these systems, whose incorporation should increase the extent of the extra-atomic relaxation of the Si ion. This is also in agreement with other experimental findings, according to which Si α increases with the N-content in SiO_xN_y samples [18].

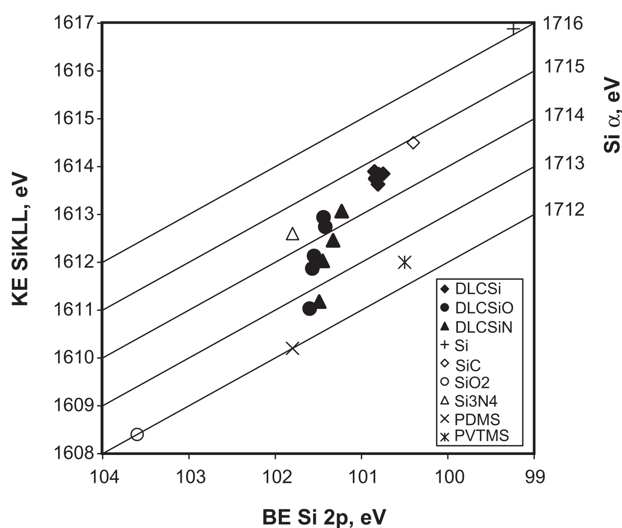


Fig. 1. Chemical state plot for Si for DLCSi, DLCSiO and DLCSiN films and reference substances.

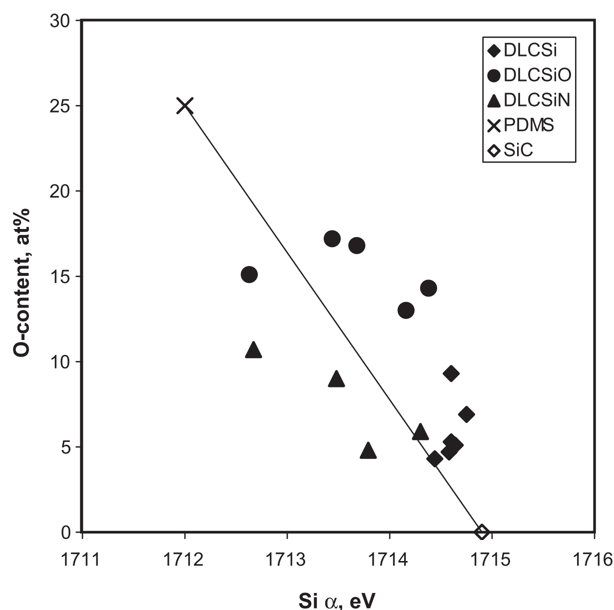


Fig. 2. Modified Auger parameter for Si vs. O-content of DLCSi, DLCSiO and DLCSiN films and reference substances.

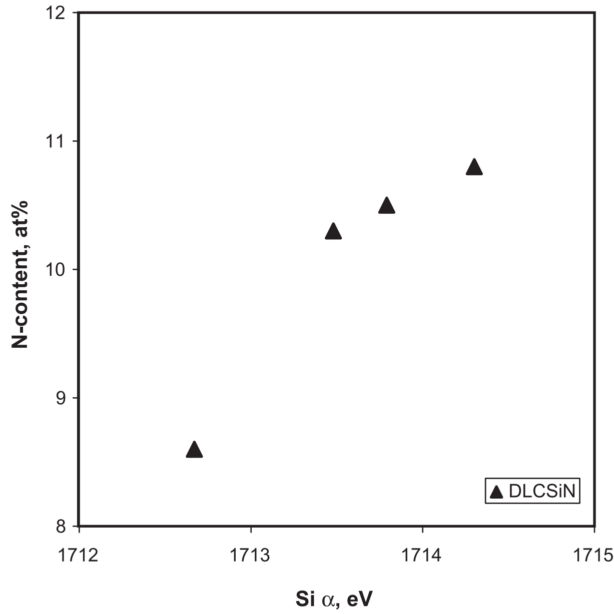


Fig. 3. Modified Auger parameter for Si vs. N-content of the DLCSiN films.

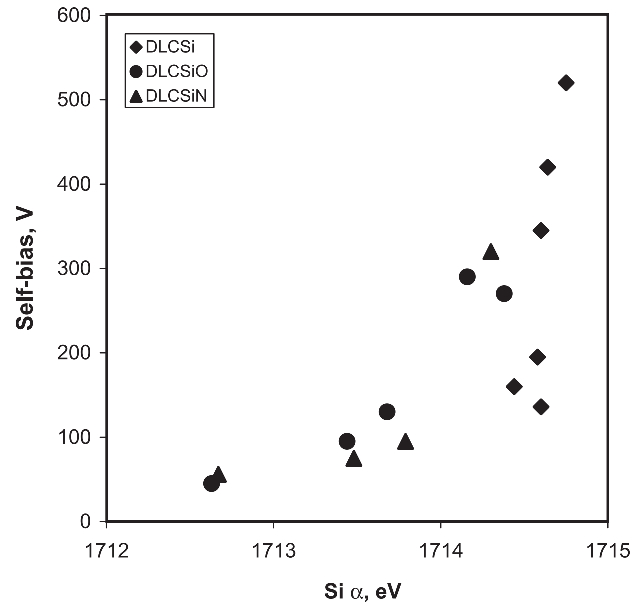


Fig. 5. Modified Auger parameter for Si vs. self-bias developed during sample deposition.

Fig. 4 shows the dependence of BE of the Si 2p peak on the O-content of the samples. Judging by this figure, the oxygen present in the DLCSiO and DLCSiN samples studied is mainly bound to Si, because the BE of the Si 2p electrons has an increasing trend with increasing O-content for these samples. On the contrary, for the DLCSi samples the BE of the Si 2p peaks does not depend on the O-content, proving that the majority of O is not bound to Si in these samples, but obviously to C.

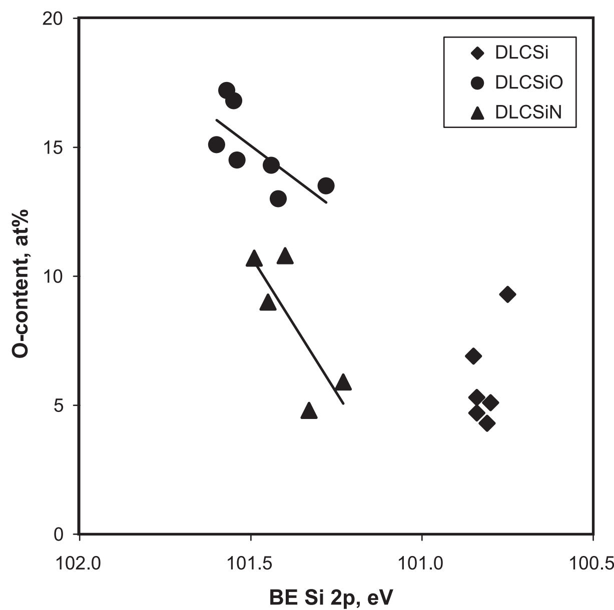


Fig. 4. Binding energy of the Si 2p peak vs. O-content of the DLCSi, DLCSiO and DLCSiN films.

Fig. 5 shows the dependence of Si α on the self-bias developed during sample deposition. For the DLCSiO and DLCSiN samples Si α increases clearly with the increase of self-bias. For the DLCSi samples there is little change in Si α with the change in bias. The dependence observed implies that the degree of crosslinking should be enhanced with the increase of the self-bias for the DLCSiO and DLCSiN samples.

Sample DLCSi5 has been treated with 2 keV Ar^+ ion beam in situ in the sample treatment chamber of the XP spectrometer. Although the O-content significantly decreased (from 5.1 to 2.2 at.%) as a result of ion beam

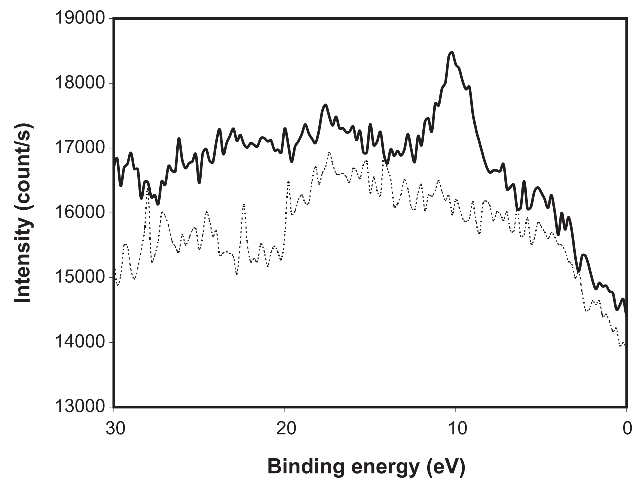


Fig. 6. Valence band of sample DLCSi-5 before (bottom spectrum) and after (top spectrum) Ar^+ ion beam treatment.

treatment, the BE value of the Si 2p peak slightly increased. Simultaneously, an intense peak appeared in the valence band at about BE ≈ 9 eV (Fig. 6). According to a previous ab initio calculation performed by the Hartree-Fock LCAO crystal orbital method for various polyorganosiloxanes [19], this peak can be attributed to the lone pair of oxygen present in Si–O type bonds. Consequently, Ar^+ ion bombardment of a DLCSi sample containing O-contamination leads not only to a preferential sputtering of O from such a sample, but also to a redistribution of the remaining oxygen atoms, resulting in the formation of Si–O type bonds. This is in line with our previous observation [20], according to which the ion beam-treated PVTMS takes up oxygen upon exposure to air, with the attack of O occurring predominantly on Si and to a smaller extent on C. In turn, this is in agreement with the known superior reactivity of organosilicon compounds in comparison with their organic analogues, due to the high atomic radius, lower electronegativity and relatively low-lying d levels of Si.

4. Conclusions

Significant loss of C-rich fragments occurred from the TMS, HMDSO and HMDSA precursors upon the ECWR plasma deposition of DLCSi, DLCSiO and DLCSiN layers. Similarly, a loss of N-rich fragments took place when depositing DLCSiN layers. The O/Si ratios remained practically unaltered upon deposition of DLCSiO layers. The modified Auger parameter of Si decreased with increasing oxygen content and increased with increasing N content for DLCSiO and DLCSiN layers. For these layers the Auger parameter reflected sensitively the degree of crosslinking, which could be altered by the deposition conditions, in particular by the self-bias. The oxygen present in the DLCSiO and the O-contaminated DLCSiN samples was predominantly bound to Si. In the O-contaminated DLCSi layers O was bound to C. Ar^+ ion bombardment of the latter layer led to the preferential sputtering of a part of O and to the redistribution of the remaining O, resulting in the formation of Si–O type bonds.

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