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# Effect of Substrate Temperature on the Properties of PECVD SiCN Films

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An influence of substrate temperature on the properties of SiCN films deposited on silicon substrates by plasma enhanced chemical vapor deposition (PECVD) technique using hexamethyldisilazane is analyzed. The films were studied using XRD, FTIR, XPS, AFM, Knoop hardness test and nanoindentation. It was established that all films were X-ray amorphous and had low surface roughness. Hydrogen effusion takes place above 400 °C, which leads to corresponding changes in chemical bonding and mechanical properties of the films.

**Keywords:** PECVD, Hexamethyldisilazane, SiCN films, FTIR, Nanoindentation

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## 1. INTRODUCTION

Si-C-N system is new kind of semiconductor materials that connect the best properties of silicon carbide and nitride. It shows specific physical and mechanical properties such as high hardness (up to 30 GPa), low thermal expansion and high thermal and mechanical stability [1, 2]. Moreover, it is possible to obtain Si-C-N films with the controlled energy gap in the region of 2.4-5.0 eV, since the energy gaps of SiC and $Si_3N_4$ are located in the ranges of 2.4-3.2 eV and of ~ 5.0 eV, respectively [3, 4]. Doe to these properties, Si-C-N films are used in microelectronic, photoelectronic and semiconductor technologies, as well as wear-resistant and protective coatings.

Today, Si-C-N films are obtained by many chemical and physical methods: CVD [5], PECVD [3, 6-8], vapor transport CVD [4], magnetron sputtering [9, 10], ion or plasma sputtering [11], ion implantation [12, 13] etc., which confirms the growing interest to these films.

The aim of this study is to investigate the effect of substrate temperature on the properties of Si-C-N thin films obtained by PECVD using hexamethyldisilazane as a main precursor.

## 2. EXPERIMENTAL DETALIES

SiCN thin films were deposited with using high-frequency plasma-chemical equipment on base "WUP-5". The main discharge was excited by high-frequency (HF) generator (40.68MHz). Hexamethyldisilazane (HMDS, $(CH_3)_6Si_2NHN$). was used as a main precursor. The HMDS vapor, produced in a thermostated bubbler heated to 40 °C, was transported into the reaction chamber by hydrogen. Substrate bias was produced by a HF generator (5.27 MHz). The films were deposited on polished Si(001) substrates.

The films were deposited at different substrate temperatures ($T_S$) 40, 120, 200, 300 and 400 °C and at fixed other deposition parameters: substrate bias -200 V, gas mixture pressure in the reactor 0.2 Torr, discharge power Pc=0.2 W/cm$^3$, flow rate of hydrogen through the thermostated bubbler with HMDS $F_{H+HMDS}$ = 12 sccm. Deposition time was 60 min.

X-ray diffraction (XRD) investigations of the films were carried out by using a diffractometer "DRON-UM1". The films surface was studied by an atomic-force microscope "NanoScope IIIa Dimension 3000TM". The chemical bonding pattern was studied by Fourier traform infrared spectroscopy (FTIR) with the help of a spectrometer "FSM 1202" LLC "Infraspek" and x-ray photoelectron spectroscopy (XPS) by using the UHV Analysis-System, SPECS (Germany), equipped with a hemispherical analyzer PHOIBOS–150. Nanoindentation was carried out with the help of a device G200 equipped with the Berkovich indenter. Nanohardness (H) and elastic modulus (E) were determined using the Oliver and Pharr procedure [14]. Knoop hardness (HK) was determined by a device "MICROMET 2103 Microhardness Tester" (BUEHLER, USA) at loading of 10 mN. The thickness of the films was estimated by an optical profilometer "Micron - alpha" (Ukraine). The film thicknesses approximate 0.8 μm, and slightly decrease with increasing $T_S$.

## 3. RESULTS AND DISCUSSION

X-ray pattern shown in Fig. 1. indicates the absence of any crystalline phases. It follows that the deposited films are x-ray amorphous (a-SiCN). The peaks at 2Θ ~ 33 °, 62 ° and 69 ° correspond to the Si substrate.

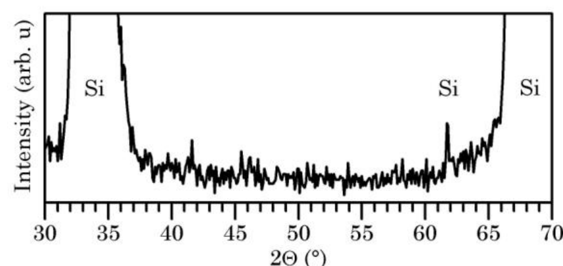


**Fig. 1** – X-ray pattern of Si-C-N films deposited at $T_S$ = 300 °C

FTIR spectra of the SiCN films deposited at $T_S$ = 40 °C, 300 °C and 400 °C are shown in Fig. 2. They are studied with using literature data [3, 7, 15-17]. The spectra have a broad absorption region at 600-1200 cm$^{-1}$ that can be presented by a superposition of several absorption bands: Si-C (650-850 cm$^{-1}$) [19-20], Si–N


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(850-990 cm-1) [21, 4, 7], Si-O (1000-1030 cm -1) [17], Si–H (870 cm-1) [7] and $C-H_n$ (990 cm-1) [4]. The intensity of the broad band decreases with increasing $T_S$, which is supposed to be due to gradually effusion hydrogen and oxygen from the films.

Other absorption bands are originated from C-C at 1550 cm-1 [17], Si-H [18], C-H [3] and N-H [7, 18] at 2130 cm-1, 2877 cm-1 and 3375 cm-1 vibrations.

The intensity of Si-H and N-H bands decreases, when $T_S$ increases (cf. Fig. 2). On the contrary, the intensity of the C-H band increases with substrate temperature. These findings point to that, as $T_S$ is raised up to 300 °C, the Si-H and N-H bonds are broken and the free hydrogen forms new C-H bonds. Above 300 °C, the C-H bonds begin to break. As a consequence, the intensity of the C-H vibrations lowers for $T_S$ > 300 °C.

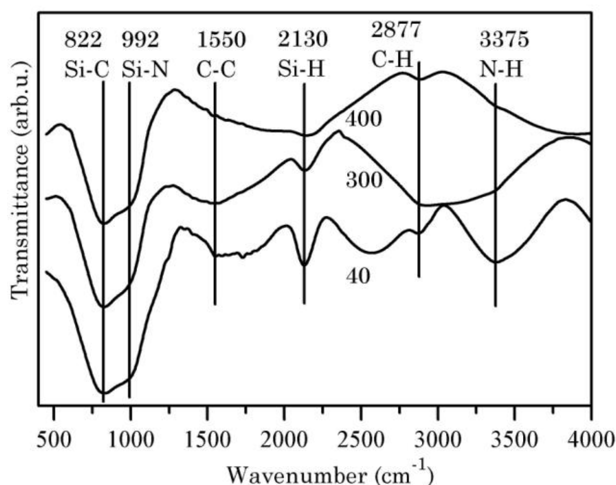


**Fig. 2** – FTIR spectrum of Si-C-N films deposited at different substrate temperatures

Further analyses of the chemical bonding state were done by using the X-ray photoelectron spectroscopy of the core levels Si 2p, C 1s, N 1s and O 1s. The XPS spectra of the films deposited at substrate temperature 40 °C and 300 °C are shown in Fig. 3. All the spectra shift towards lower binding energies, when substrate temperature increases. The intensity of the Si 2p, N 1s and O 1s photoelectron peaks decreases, and the intensity of C 1s photoelectron peak increases with increasing $T_S$. The XPS spectra clearly indicate the presence of Si-N [19], C-C [22], N-C [23] and O-Si [19] bonds.

In Fig. 4 we show the decomposition of the XPS spectra by the Gaussian curves. The Si 2p photoelectron spectrum was represented in the view of three Gaussian components centered at 103.0 eV, 101.7 eV and 100.5 eV that are assigned to the Si-C bonds (100.5 eV) in SiC [4, 24], Si-N bonds (101.7 eV) in $Si_3N_4$ [24, 25] and Si-O bonds (103 eV) [7]. An increase in temperature leads to an increase in the intensity of the deconvoluted Si-C peak, and to a decrease in the deconvoluted Si-N and Si-O peaks. The XPS C 1s spectra are decovoluted into three peaks centered at 283.2 eV, 284.8 eV and 286.8 eV that correspond to C-Si bonds [4], C-C bonds in SiC [15], and C-N bonds [23], respectively. We note that the hydrogen C-H bonds with the binding energies of 284.5 eV, 285.0 eV and 286.5 eV [26] can contribute to all the deconvoluted peaks. An increase in the intensity of the XPS C 1s spectrum with $T_S$ occurs mostly due to an increase in the number of C-C and C-H bonds.

The three Gaussian peaks of the XPS N1s spectra are centered at 397.8 eV, 398.6 eV and 400.1 eV, and can be assigned to N-Si bonds in $Si_3N_4$ (397.1-397.8 eV) [15,26], N-C sp$^3$ in $C_3N_4$ and N-C sp$^2$ bonds (398.3-400.3 eV) [23,27,28], respectively. One can see that the reduction of the intensity of the XPS N 1s spectrum with increasing $T_S$ (cf. Fig. 3) is mainly caused by a decrease of the N-C sp$^3$ Gaussian peak (cf. Fig. 4). Finally, the XPS O 1s spectra were fitted into two Gaussian components centered at 531.6 eV and 532.8 eV. These components correspond to O-C and O-Si bonds, respectively [29]. An increase of substrate temperature leads to the reduction of the O-Si Gaussian peak and, in turn, to the reduction of the intensity of the XPS O 1s spectrum. The presence of oxygen in the films may be due both to the oxidation of films during storage and presence the oxygen in films source component.

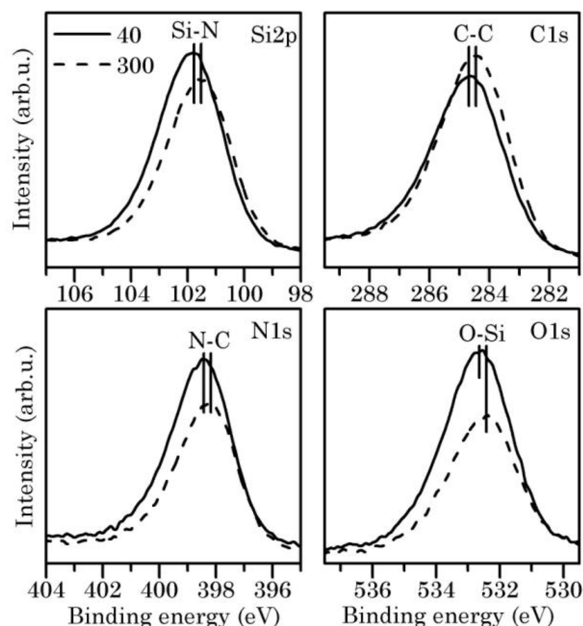


**Fig. 3** – XPS spectra of Si-C-N films deposited at different substrate temperatures

The picture of chemical bonding that follows from the XPS measurements is consistent with that obtained from the FTIR studies and points to that, in the deposited films, there are such main bonds as: Si-N, Si-C, C-N, C-C and Si-O. We see that an increase in substrate temperature leads to strengthening Si-C and C-C bonds and to weakening Si-N, C-N and O-Si interactions, as well hydrogen bonds.

The AFM images of the films deposited at 40 °C and 400 °C are sown on the Fig. 5. The RMS of the films deposited at 40 °C and 400 °C are 0.5 nm and 0.2 nm, respectiely. The RMS of silicon substrates was 0.4 nm. These data indicate that an increase in $T_S$ promotes a reduction of the roughness of the film surface. We suppose that the decrease of film roughness is due to hydrogen effusion and film densification.

The results of the nano- and micro-indentations of the films are shown in Figs. 6 and 7. Nanohardness

increases from 8 to 19 GPa, and elastic modulus increases from 75 to 150 GPa, when substrate temperature rises from 40 °C to 400 °C, respectively. It was found that the changes in nanohardness and Knoop hardness depending on substrate temperature were similar (cf. Fig. 7 (a)). The H/E ration for the film deposited at 400 °C is 0.13, which indicates that the film should demonstrate good tribological properties.

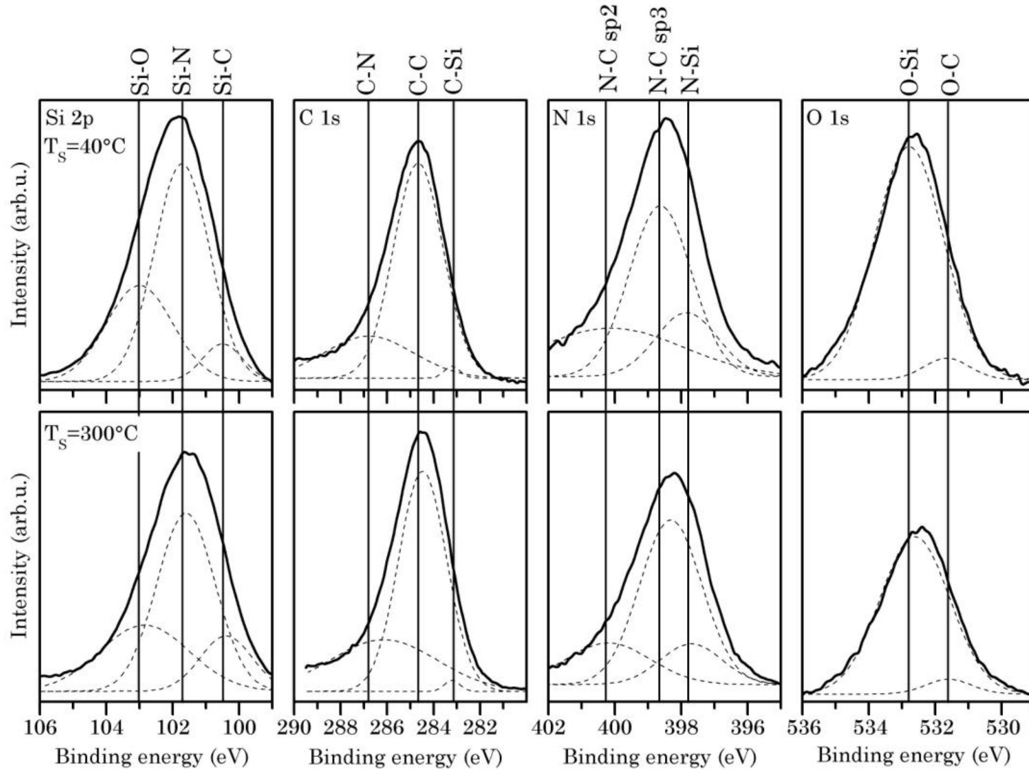


**Fig. 4** – Deconvolution of the XPS spectra of the deposited films

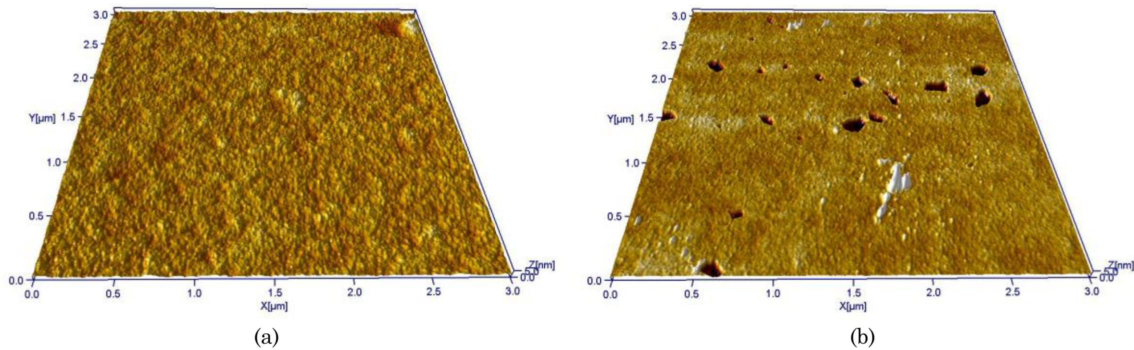


**Fig. 5** – AFM - images of the surface of SiCN films deposited at TS=40 °C (a) and TS=400 °C (b)

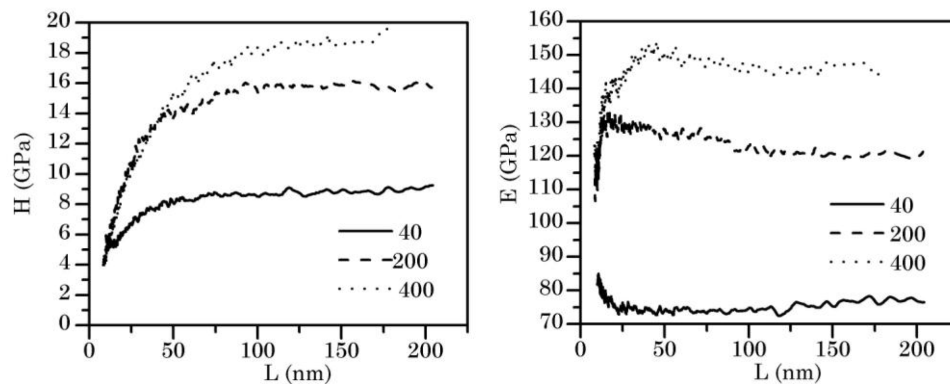


**Fig. 6** – Nanohardness (H) and elastic modulus (E) of the films deposited at $T_S$=40 °C, 200 °C and 400 °C as functions of indenter penetration

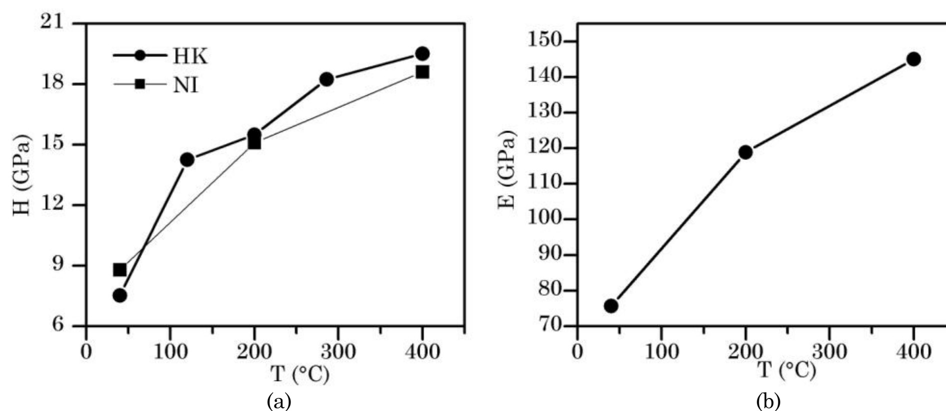


**Fig. 7** – Variation of the Knoop hardness (HK), nanohardness (NI) (a) and Young's modules (E) (b) as functions of substrate temperature

The theoretical and experimental results predict hydrogen and oxygen effusions, as well the strengthening of Si-C bonds with increasing substrate temperature. It is this change in chemical bonding that can be responsive for the observed increase in nanohardness and elastic modulus of the high temperature films compared to those of the low-temperature ones.

## 4. CONCLUSIONS

1. Amorphous SiCN films were deposited by PECVD using hexamethyldisilazane at substrate temperatures in the range of 40-400 °C.

2. An increase in substrate temperature leads to: a reduction of surface roughness; hydrogen and oxygen effusions, as well the strengthening of Si-C and C-C bonds; an increase in hardness and elastic modulus. e.

3. The main chemical bonds in the films are Si-N, Si-C, C-C and C-N ones. Besides, FTIR and XPS investigations indicate the presence of Si-O, C-O, C-H, Si-H and N-H bonds.

4. Effusion oh hydrogen and oxygen, as well the strengthening of Si-C bonds promotes the film densification, which, in turn, causes a increases of hardness and elastic modulus with increasing deposition temperature.

5. The results of this investigation allow us to suppose that the PECVD SiCN films deposited by using hexamethyldisilazane can be used for the production of microelectromechanical systems (MEMS).


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