Optical Properties of PECVD Si-C-N Films

A.O. Kozak, V.I. Ivashchenko, O.K. Porada, L.A. Ivashchenko, V.Ya. Malakhov, T.V. Tomila

Institute for Problems of Materials Sciences, NAS of Ukraine, 3, Krzhyzhanovsky Str., 03142 Kyiv, Ukraine

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The structural properties and the energy gap of Si-C-N films deposited by PECVD method from hexamethyldisilazane in the temperature range of 200-700 °C were studied. The films were deposited on silicon and glass substrates that made it possible to perform the XRD analysis and study the absorption infrared (FTIR) and optical spectra. The deconvolution of main band by Gaussians indicates that the main contributions come from the vibrations of Si-C, Si-N and Si-O bonds. It is shown that an intensive effusion of hydrogen from the films occurs with increasing temperature. The band gap decreases from 2.3 to 1.6 eV as substrate temperature is changed from 200 to 700 °C.

Keywords: PECVD, Hexamethyldisilazane, Si-C-N films, FTIR, Optical spectra.

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1. INTRODUCTION

A successful combination of the optical, mechanical, and electrical properties of hydrogenated semiconductor Si-C-N thin films [1-3] promotes their efficient use in microelectronic, photoelectric, semiconductor technologies and as wear-resistant and protective coatings. Due to inheritance of the electronic properties of such wide band gap materials as silicon carbide and silicon nitride with the energy gap within 2.4 and 5.0 eV for SiC and Si_3N_4 [1, 2], respectively, it is possible to obtain thin Si-C-N films with the energy gap technologically controllable in a wide range. This property favors their use in various optoelectronic devices – UV detectors [4] and white blue LEDs [5]. In turn, SiC is an intensively used material in high-temperature, high-frequency and power semiconductor devices, and Si_3N_4 is a superhard material and is widely used due to its dielectric properties as electric insulators and diffusion barriers [3].

A large number of chemical and physical methods allowing to obtain amorphous thin Si-C-N films is currently used. Although the short-range order is important for the determination of the optoelectronic characteristics of the material, the absence of the translational symmetry promotes the appearance of additional permitted levels in the density of electronic states, whose density decays deep into the energy gap forming "tails" of the density of states that leads to significant changes in the physicochemical properties [6]. The presence of hydrogen plays an important role for obtaining films with qualitative semiconductor properties. Hydrogen passivates uncompensated dangling bonds, whose states are exhibited in the energy gap [7] that stimulates the development of new mechanisms for producing hydrogenated amorphous semiconductors. It should be noted that the majority of high-temperature chemical methods with the use of the precursors, which contain hydrogen [8, 9], are unsuitable for the production of hydrogenated Si-C-N films.

It was earlier shown the influence of the amount of additionally introduced nitrogen [7] and the substrate temperature [10] in a low-temperature range on the mechanical and structural properties of the films. The aim of this work is the study of the influence of the substrate temperature on the energy gap of Si-C-N films deposited from hexamethyldisilazane (HMDS, $(CH_3)_6Si_2NH$)), the molecules of which contain all the necessary components for the formation of hydrogenated Si-C-N films.

2. EXPERIMENTAL

Si-C-N films are deposited by plasma-enhanced chemical vapor deposition (PECVD) method at the laboratory facility of the planar type with capacitive plasma excitation system [11]. HMDS vapors were transported from the thermostated bubbler heated to 40 °C into the reactor chamber using hydrogen. The films were deposited on silicon (SHB-10) and glass substrates of 0.5 mm and 1.4 mm thickness, respectively. Directly before deposition silicon substrates were etched in 10 % solution of hydrofluoric acid and additionally washed by etching in hydrogen plasma.

Deposition of two series of the films was carried out. The main variable parameters when producing the films were the substrate temperature T_S, bias voltage on the substrate-holder U_D, and nitrogen flow into the reactor chamber F_{N2}. These parameters are given in Table 1. The invariable parameters for both deposition series are the following: gas mixture pressure $P_C = 0.2$ torr, discharge power of the main RF generator $P_W = 0.2$ W/cm^3, hydrogen flow through the bubbler with HMDS $F_{H+HMDS} =$ $= 12$ cm^3/min. Deposition time is 60 min.

Structure investigation is carried out by diffractometer DRON-3M. Study of the picture of chemical bonds is performed using Fourier transform infrared spectroscopy (FTIR) in the wave number range of 400-4000 cm^{-1} on spectrometer FSM 1202 by Micron-alpha Comp. Thicknesses of the films deposited on silicon substrates were determined by interference profilometer Micron-alpha. Measurements of the optical transmission spectra are conducted on two-beam optical spectrometer SPECORD-M40.

Table 1 – The main deposition parameters

Series	No	T_S, °C	U_D, V	F_{N2}, cm^3/min
A	1	200	– 200	0
	2	300		
	3	400		
B	1	300	– 250	1
	2	500		
	3	700		

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3. RESULTS AND DISCUSSION

In Fig. 1 we illustrate the typical for two series diffraction patterns of the obtained Si-C-N films. The absence of any reflexes, which can be attributed to nano- or microcrystalline inclusions, indicates that thin films are X-ray amorphous. Peaks at 33°, 62°, 69° correspond to the material of the silicon substrate.

The optical transmission spectra of thin Si-C-N films deposited on glass substrates at different temperatures and nitrogen flows in 350-900 nm wavelength range are shown in Fig. 2. The samples obtained at Ts < 500 °C in the optical range of 600-900 nm exhibit relatively high optical transparency (75-95 %). An increase in the deposition temperature to 700 °C leads to a sharp decrease in the film transmission (35-37 %). A shift of the fundamental absorption edge towards shorter waves occurs for the films produced without adding nitrogen with increasing temperature from 200 to 400 °C, while for the films from the series B there is a shift towards longer waves with increasing temperature.

Interference of the transmission spectra in the region with a low absorption level is caused by multiple reflection of radiation between two interfaces, namely, film/air and film/substrate. This implies a high structural perfection of the interfaces. Taking into account the position of the interference minima and maxima of the optical transmission spectra, it is possible to determine thicknesses of the films deposited on glass substrates according to the method proposed by Swanepoel [12].

Based on the results of the thickness measurements given in Table 2, it is seen that increase in the substrate temperature leads to the thickness decrease: this is caused by prevalence of the film consolidation process on account of the hydrogen effusion [10] and increase in the number of desorbed fragments from the films surfaces with increasing Ts [13]. In Table 2 for comparison, we present the thicknesses of the films deposited on silicon and glass substrates determined by interference profilometer. An increase in the film thickness on glass substrates compared with the same on silicon substrates can be induced by both the influence of the substrate properties [14] and the substrate thickness, which results in the temperature change on its surface.

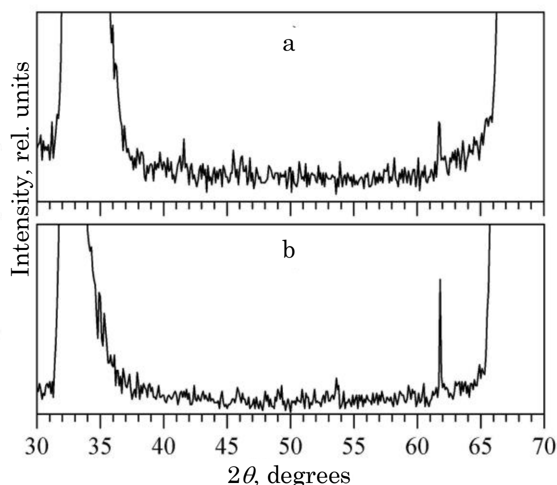

Fig. 1 – Diffraction patterns of Si-C-N films obtained at the substrate-holder temperature of (a) T_S = 300 °C (Series A, No2) and (b) T_S = 700 °C (Series B, No3)

Table 2 – Dependence of the film thickness on the deposition parameters and substrate material

Series A			Series B		
T, °C	D_g, μm	D_{Si}, μm	T, °C	D_g, μm	D_{Si}, μm
200	2.22	0.54	300	1.26	0.63
300	1.46	0.55	500	1.01	0.66
400	1.27	0.50	700	0.92	0.54

*D_g, D_{Si} are the thicknesses of the films obtained on glass and silicon substrates, respectively

Energy gap is one of the key parameters characterizing amorphous semiconductors. In these amorphous semiconductors it separates "tails" of the conduction band and the valence band. Estimation of the optical energy gap in this work is performed based on the study of the optical absorption spectra in the region near the fundamental absorption edge. To obtain the dependence of the absorption coefficient on the wavelength (λ) the following relation is used: $\alpha = \ln(1 / T)/d$ [15], where α is the absorption coefficient, T is the transmission (dependent on λ) and d is the film thickness. Taking into account the thickness of the samples determined from the interference extremes and dependence $T(\lambda)$ (Fig. 2), we have calculated the absorption spectra of thin Si-C-N films illustrated in Fig. 3. As seen from Fig. 3, for each series there is an increase in the absorption coefficient with increasing substrate temperature. At that, for the films obtained at 300 °C and with additional introduction of nitrogen into the reactor chamber the coefficient is the smallest. Relatively high values of the absorption coefficient ($\alpha = 10^3$-10^5 cm^{-1}), typical for amorphous films [16, 17], indicate a large number of structural defects in the studied films [18].

Estimation of the energy gap is carried out from the Tauc relation: $\alpha h\nu^{1/m} = A(h\nu - E_g)$ [19], where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical energy gap, A is the coefficient of proportionality. In this case, coefficient m in $\alpha h\nu^{1/m}$ was chosen to be 2 as for the majority of amorphous semiconductors that implies the case of indirect allowed transitions [20]. The Tauc curves for the deposited films are shown in Fig. 4. On the inset in Fig. 4 we present the obtained values of the energy gap estimated by extrapolation of the linear region of the dependence $\alpha h\nu^{1/2}$ to 0. It is immediately noticeable a gradual decrease in E_g at temperatures of 200-500 °C and a sharp decrease in E_g with further increase in the deposition temperature. For the films obtained at different nitrogen flows and substrate temperatures to 300 °C, energy gap is approximately equal to 2.3 eV. Decrease in the absorption value makes it possible to talk about some structural changes [7].

This behavior of the energy gap with increasing temperature can be explained based on the analysis of the picture of chemical bonds. In particular, FTIR spectrometry allows to study the change in the number of basic bonds formed in the films with changing temperature. FTIR spectra of thin Si-C-N films are shown in Fig. 5.

These spectra are characterized based on literature data [24-34]. A general view of the film spectra obtained at various substrate temperatures indicates the presence of a wide absorption region in 450-1300 cm^{-1} range and also several much lower absorption bands in the wavenumber range of 1500-3500 cm^{-1}. In the interval of 450-1300 cm^{-1}, there can appear vibrations of several ab-

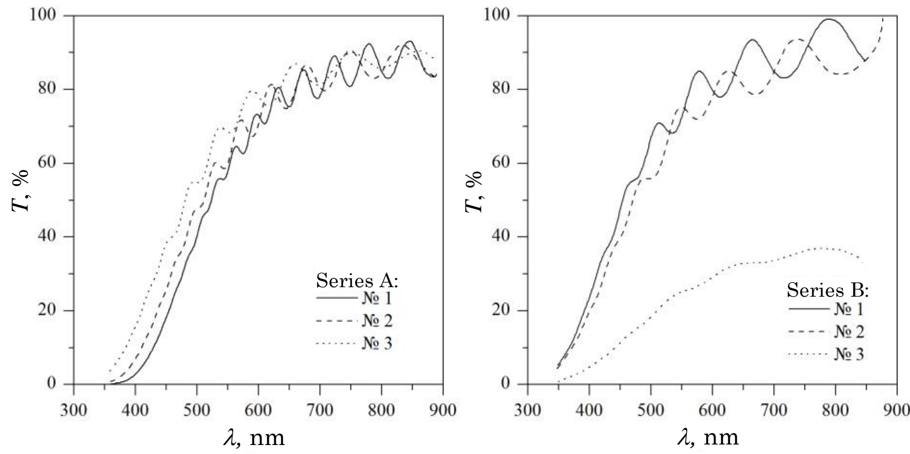

Fig. 2 – Optical transmission spectra of the films of the series A and B

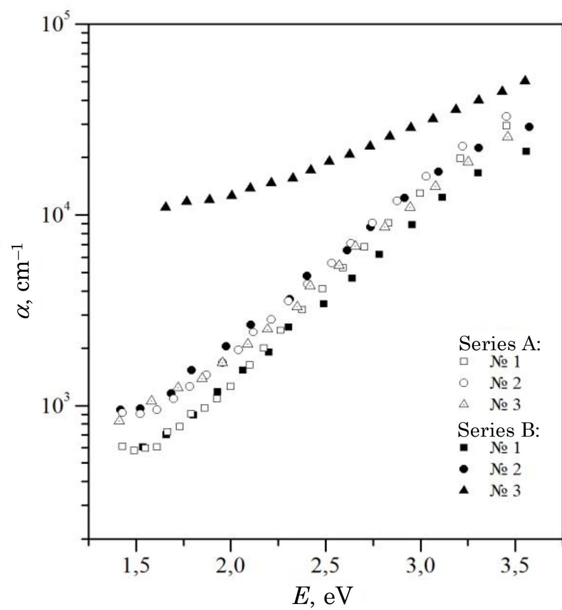

Fig. 3 – Dependence of the absorption coefficient of the obtained films on the deposition parameters

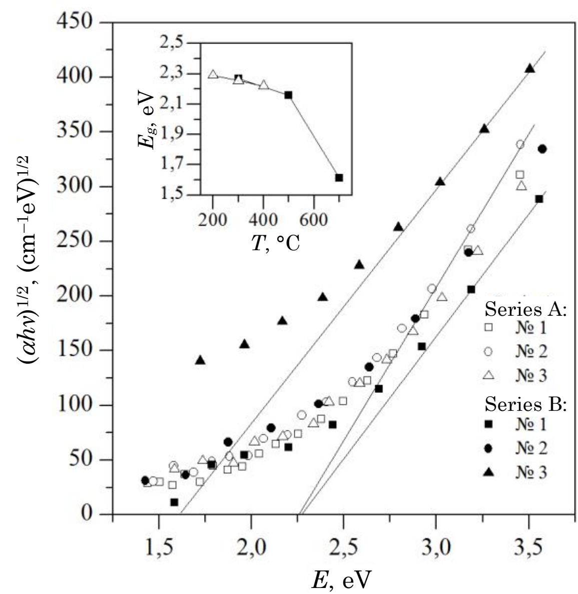

Fig. 4 – Tauc function $(\alpha h\nu)^{1/2}$ of the films obtained at different temperatures. On the inset: dependence of the energy gap on the deposition temperature

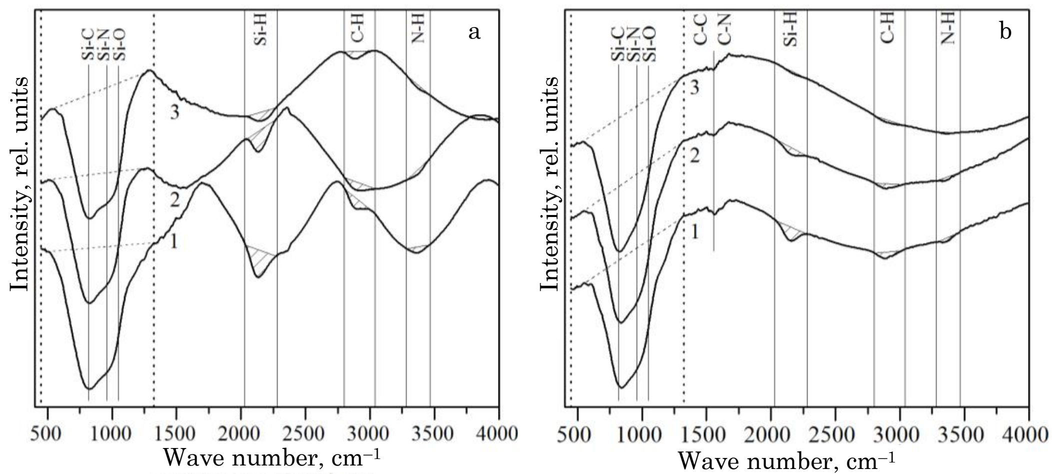

Fig. 5 – FTIR spectra of Si-C-N films: (a) series A, (b) series B. Numerals denote the deposition number. Dotted lines separate a wide absorption region which is general for all the spectra

sorption bands attributed to Si-N (450 cm^{-1} [24], 900-1000 cm^{-1} [26]), Si-C (650-810 cm^{-1} [16, 25, 27]) and Si-O (450 [24], 1000-1110 cm^{-1} [27]) bonds, which for these films usually prevail in the chosen spectral range [7].

In a wide band there are also the C-N bonds at 1055-1135 cm^{-1} [28, 29], C-C bonds at 1245 cm^{-1} [30] and hydrogen bonds Si-H, CH_3, SiH_2, CH_n and N-H with the peaks near 670-705 cm^{-1} [31], 1250 cm^{-1} [31], 860 cm^{-1}, 1000-1100 cm^{-1} [32] and 1150 cm^{-1} [29], respectively, which give a much smaller contribution. Since vibrations of many different types of bonds can be in the wave-number range corresponding to a wide transmission band, it is represented in the form of combination of several absorption bands by decomposition into components using the Gauss function. The results of decomposition are illustrated in Fig. 6. To take into account the error, the specified area was limited by the linear basic function, which connects two adjacent maxima in the FTIR spectrum (dotted lines in Fig. 5).

The presence of the component attributed to the Si-O bonds is probably caused by release of oxygen adsorbed on the inner walls of the reactor during deposition.

Spectra of the films, obtained with adding nitrogen at the same temperatures, are characterized by a larger area of the Gaussian components attributed to the Si-N and C-N bonds. As seen from Fig. 6, there is a decrease in the vibrational intensity of hydrogen bonds with increasing substrate temperature. We should note that the decrease in the area of the components of the Si-H, C-H and C-N bonds, peak positions of which are close to the edge of the selected transmission region, and also the increase in the number of Si-C and Si-N bonds promotes narrowing of a wide band with increasing temperature. In the case of the films obtained without adding nitrogen, edges of the wide band are shifted from 500-1350 cm^{-1} at 200 °C to 525-1285 cm^{-1} at 400 °C and for the films obtained with adding nitrogen – from 525-1330 cm^{-1} at 300 °C to 525-1300 cm^{-1} at 700 °C.

Significant changes in the FTIR spectra absorption behavior are observed in the range of 1500-3500 cm^{-1}, where vibrations of the hydrogen Si-H [25, 27], C-H [34] and N-H [27] bonds at 2130 cm^{-1}, 2875 cm^{-1}, 3380 cm^{-1}, respectively, are mainly localized. The peak, which is manifested in the FTIR spectra of the films obtained with adding nitrogen, near 1560 cm^{-1} is probably associated with the vibrations of the C-N bonds (1593 cm^{-1}) [17]; however, it can be also attributed to the vibrations of the C-C bonds (1515 cm^{-1}, 1580 cm^{-1}) [29]. It is seen from the FTIR spectra in the range of 2000-3500 cm^{-1} (Fig. 5a, b) and distribution of the Gaussian components of the wide absorption band that hydrogen bonds have a general tendency of decreasing the absorption intensity.

For a more detailed observation of the change in the number of bonds with increasing temperature, we have plotted the temperature dependences of the ratio of areas of the components attributed to each bond type. To determine the area of the components, the spectra should be limited by the basic line, which connects the adjacent maxima on both sides of the peak. At that, to obtain the stable results, it is important that the selected maxima were the same for all the samples. The regions attributed to the vibrations of hydrogen bonds in the wave number range of 2000-3500 cm^{-1}, which are chosen for the calculation, are shown by the shaded zones in Fig. 5.

Since thickness of the films obtained at different temperatures differs significantly (Table 2), then to decrease its influence on the pattern of distribution of chemical bonds, each component area is normalized [35] with respect to the film of 1 μm thick. In Fig. 7 we illustrate the vibrational intensities of separate bonds as functions of the substrate temperature. As seen, absorption intensity caused by the Si-H bonds reacts more sensitively to the temperature change than the absorption intensity caused by the C-H and N-H bonds. Comparing the areas of the Si-C and Si-N components, we note the decrease in the Si-N/Si-C ratio from 0.45 to 0.36 with increasing temperature from 500 °C to 700 °C. At that, Si-N/Si-C ratio remains almost constant in the range of 300-500 °C.

The obtained investigation results of the FTIR spectra imply that such main bonds as Si-C, Si-N, Si-O, C-C, C-H, N-H, C-N are formed in amorphous Si-C-N films. Thus, Si-C-N films are not just a combination of binary phases (SiC, SiN_x and CN_x), but also represent a complex network, which includes fragment of all three phases.

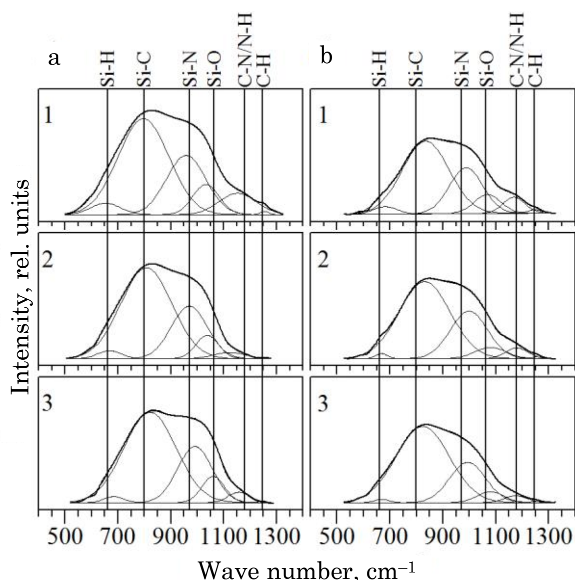

Fig. 6 – Decomposition into Gaussians of the FTIR spectra of Si-C-N films within 450-1300 cm^{-1}: (a) series A, (b) series B. Numerals denote the deposition number

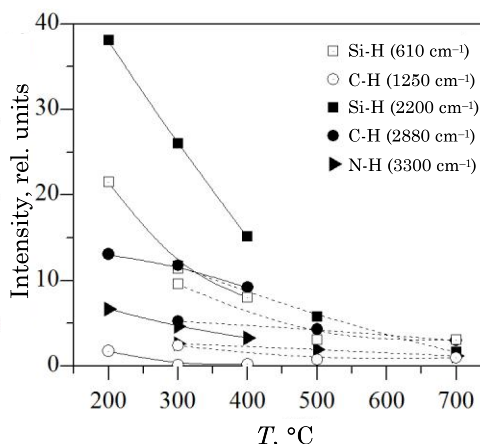

Fig. 7 – Influence of the substrate temperature on the area of the components attributed to the hydrogen bonds. Solid lines are the series A, dotted lines – series B

Taking into account the investigation results of the pattern of chemical bonds, the decrease in the energy gap of the films with increasing temperature is caused, most likely, by hydrogen effusion that is clearly seen in the FTIR spectra. In the films obtained at low temperatures, hydrogen passivates unsaturated dangling bonds. Destruction of hydrogen bonds occurs with increasing deposition temperature that leads to the appearance of other bonds as well as dangling bonds [36] and, thus, to the increase in the number of electronic states localized in the energy gap. This results in the energy gap narrowing. A significant energy gap narrowing of the films obtained at 700 °C is induced by the absence of hydrogen bonds and creation of additional electronic localized states due to the formation of new Si-C bonds [35].

4. CONCLUSIONS

In this work, thin Si-C-N films are obtained by the PECVD method from hexamethyldisilazane. The pattern of chemical bonds and the optical transmission spectra are studied. It is established that Si-C, Si-N, Si-O and C-N chemical bonds are main in the films. C-H, N-H and C-H hydrogen bonds are also revealed. Formation of new Si-C bonds and decrease in the number of hydrogen bonds occurs with increasing substrate temperature. It is assumed that decrease in the latter occurs due to hydrogen effusion from the films. As a result, energy gap narrowing is observed with increasing substrate temperature induced by the increase in the number of Si-C bonds and dangling bonds earlier passivated by hydrogen. A sharp decrease in the energy gap at temperatures higher than T_S = 500 °C implies that just this temperature is critical for hydrogen effusion from the amorphous hydrogenated Si-C-N films.

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