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Bis(trimethylsilyl)ethylamine: synthesis, properties and its use as CVD precursor

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Abstract

Bis(trimethylsilyl)ethylamine (BTMSEA) was synthesized and characterized as CVD precursor for silicon carbonitride SiC_xN_y films synthesis (vapor pressure, thermodynamic modeling). SiC_xN_y films were deposited by PECVD from BTMSEA in the temperature range of 100-700 °C using two additional gases (He or NH_3). FT-IR, Raman spectroscopy, ellipsometry, EDX, SEM, UV-Visible spectroscopy and nanoindentation tests were used for film characterization. FT-IR analysis showed that temperature increase lead to the transition from a low-temperature polymeric-like films to the high-temperature inorganic material. It was also shown that the high-temperature films content predominantly Si-C bonds independently on the additional gas type. As it was confirmed by Raman spectroscopy, high-temperature SiC_xN_y films content carbon phase. Ammonia addition into the reaction mixture resulted in the shift of the temperature boundary of carbon phase-free region. The transmittance of SiC_xN_y films obtained using BTMSEA + He mixture in the deposition temperature range of 100-500 °C was 85-95 % and decreased significantly in the case of carbon phase formation at T_{dep} more than 500 °C. Optical band gap estimated from UV-Vis spectra varied in the range of 1.9-4.4 eV depending on the deposition temperature. NH_3 addition to initial mixture led to the film transmittance decrease to 80-90 %, the optical band gap changed in the range of 2.0-5.1 eV. Nanoindentation tests showed that hardness of the films synthesized at high temperature was 18.5-21.5 GPa.

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Keywords: Silicon carbonitride films; PECVD; organosilicon precursor; vapor pressure; hardness; optical band gap

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1. Introduction

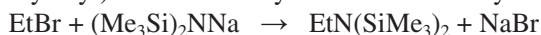
Silicon carbonitride is a nonstoichiometric compound that exhibits a combination of SiC and Si₃N₄ binary compounds unique properties. It makes them suitable for a wide range of applications. The wide bandgap changing from 5 eV for Si₃N₄ to 2.8 eV for SiC allows to use SiC_xN_y films in optoelectronic applications such as UV detection or low-voltage white-blue electroluminescence devices [1]. The refractive index can also be tuned in a wide range depending on the chemical composition. Due to their dielectric constant k below 3.5 SiC_xN_y films can be used as interlayer dielectric and dielectric barrier / etch stop material in microelectronic devices [2-3]. Silicon carbonitride also possesses such characteristics as high thermal stability and high chemical inertness, in addition to well-known high hardness [4-6]. Its mechanical properties are useful for modification of material surface. Such films may increase hardness significantly and reduce friction of metal surfaces, thus improving their wear resistance. Additionally SiC_xN_y films seem to be a suitable component for the formation of multi-layer coatings of superior mechanical strength.

Plasma enhanced chemical vapor deposition (PECVD) from different mixtures is the most attractive technique for SiC_xN_y film synthesis. Complex gas mixtures, such as SiCl₄ + C₃H₈ (C₂H₄) + N₂ [7], CH₄ + SiH₄ + NH₃ + H₂ [8], SiH₄ + CH₄ + H₂ + N₂ [9] are usually used for silicon carbonitride film synthesis. However, as silane is a dangerous substance, both toxic and explosive, a lot of studies have been done to find new precursors to fabricate silicon carbonitride films. In a view of the literature data, SiC_xN_y films can effectively be produced from a number of organosilicon compounds using various chemical vapor deposition CVD techniques, such as remote plasma CVD from (dimethylamino)dimethylsilane [4], PECVD from bis(dimethylamino)dimethylsilane [10-11], remote plasma CVD from bis(dimethylamino)methylsilane [12], PECVD from bis(trimethylsilyl)carbodiimide [13], low pressure CVD, PECVD and hot wire CVD from hexamethyldisilazane [14-17], atmospheric pressure CVD from tetramethyldisilazane [18], microwave and remote plasma CVD from tris(dimethylamino)silane [19-20], PECVD from trimethylsilane [21].

In the present work, a bis(trimethylsilyl)ethylamine BTMSEA EtN(SiMe₃)₂ was synthesized and used as a precursor to deposit silicon carbonitride films. Bis(trimethylsilyl)ethylamine contains the C-N and Si-N units with tertiary nitrogen atom, which may readily be incorporated into the film structure. The presence of tertiary N atom in the initial molecule is important for the formation of SiC_xN_y films with good mechanical properties as was confirmed by Blaszczyk-Lezak et al. [22]. Moreover, the presence of Si-C, Si-N and C-N fragments in bis(trimethylsilyl)ethylamine molecule makes the synthesis of the film with binding between all of the elements possible. Use of different additional gases allows varying both physical and chemical properties of the films significantly. So, helium and ammonia were used as additional gases for plasma generation. The film composition, optical and mechanical properties were analyzed by means of several techniques and correlated with the molecular structure of the precursor. The goal of this study was to find the relationships between the chemical structure and resulting properties of SiC_xN_y films. Since the properties of silicon carbonitride films are mostly related to the deposition parameters, the structure - property relationships presented in this paper seem to be an important aspect enhancing knowledge of this material.

2. Experimental

The single-source precursor BTMSEA was synthesized by modified reaction of sodium bis(trimethylsilyl)amide with ethyl bromide in tetrahydrofuran [23]:



Initial sodium bis(trimethylsilyl)amide was prepared by well-known procedure [24]. Yield of target compound is 45%, b.p. 163-164 °C, $n_{25} = 1,4105$ [25]. Element analysis for C₈H₂₅NSi₂: found, %: C 50.50; H

12.39; N 7.41; calculated, %: C 50.72; H 12.24; N 7.39. The details on precursor synthesis and characterization one can find in [26].

Silicon carbonitride films were synthesized by PECVD from BTMSEA. Helium or ammonia were used as additional gases. Deposition experiments were performed under total pressure of 3-4 Pa. The pressure of BTMSEA in the reactor was 1.6 Pa, additional gas - 0.8 Pa. Films were deposited on wafers of different types: Si (100) wafers were used for IR and Raman investigations, Ge (100) - to determine the element composition by EDX and fused SiO₂ - for UV-Vis studies. The syntheses were carried out at different deposition temperatures $T_d = 100-700$ °C. A radio frequency generator (40.68 MHz) supplied RF power to the reactant gas mixture with a constant power value of 20 W.

The thickness of the films deposited on Si (100) wafers was measured ellipsometrically at a wavelength of 632.8 nm using a laser ellipsometer LEF-3M. The average thickness values of the films deposited in the present study varied in the range of 200–300 nm. The samples prepared especially for nanoindentation tests had the thickness of ~1 micrometer. FT-IR absorption spectra of the films deposited on Si wafers were recorded in transmission mode on a FT-IR- spectrophotometer SCIMITAR FTS 2000 (Digilab) in the wavenumber range of 400-4000 cm⁻¹ with a resolution of 1 cm⁻¹. Raman spectra were recorded by a Raman spectrometer Triplemate (Spex, USA) in the range 400-1800 cm⁻¹. Surface morphology and element composition of the films were investigated using a scanning electron microscope JSM 6700F equipped by EX-23000 BU EDX system. UV-Vis spectra were recorded using a scanning spectrophotometer Shimadzu UV-3101PC in the range of 200-2000 nm. Nanoindentation tests were performed using NanoSCAN 3D nanoindenter (Russia).

3. Results and discussion

3.1. Film synthesis.

3.1.1. Deposition rate.

The growth rate was calculated as the ratio of ellipsometric film thickness to the synthesis time. No film was obtained in low pressure CVD at the temperature of 700 °C during 2 hours. So PECVD was used for silicon carbonitride films synthesis. Different deposition rates were obtained depending on the additional gas type. The change of the growth rate was nonmonotonic for the films obtained from BTMSEA + He mixture. One can find two regions corresponding to the different processes. At low temperatures, the decrease in the growth rate from 380 Å / min at $T_d = 100$ °C to 100 Å / min at 400 °C was observed, that is typical for plasma processes and is associated with changes in the chemical composition and structure of the resulting films. There is an information on such behavior in literature [27]. At temperatures above 400 °C and up to 700 °C the growth rate was almost unchanged. The absence of a significant contribution of thermal decomposition of the precursor is worth mentioning as was confirmed by LPCVD. Ammonia addition into the reaction mixture led to a significant drop of the growth rate in the range of 100-400 °C (100 Å / min) in comparison to that for the films obtained from BTMSEA + He mixture. This fact confirmed an important role of the reaction between the organosilicon fragments of the initial molecule and activated ammonia.

3.1.2. FT-IR analysis.

Fig. 1 shows the FT-IR spectra of the liquid BTMSEA precursor and SiC_xN_y films deposited at various temperatures. FT-IR absorbance spectra were normalized to the film thickness to give information on the bonding density in the volume of the film. The particular absorption bands were identified according to the literature data [1-2, 11-12, 14]. The absorption spectra exhibited a set of characteristic peaks summarized in Table I. The first absorption area was a broad band in the range of 650-1300 cm⁻¹ which was the overlapping of several peaks, that included CH₃ symmetric bending in Si-(CH₃)_x at 1260 cm⁻¹, CH₂ wagging in Si-CH₂-Si

bonds at around 1025 cm^{-1} , Si–O stretching in Si–O–Si bonds in the $1025\text{--}1110\text{ cm}^{-1}$ range, stretching of the Si–C bonds at around 830 cm^{-1} . The band at 1020 cm^{-1} could not be resolved into the Si–O and Si–CH₂–Si components due to their extremely strong overlap. The second absorption area lied between 2100 and 2300 cm^{-1} and referred to Si–H and C≡N bonds. The third band of absorption was found between 2700 and 3700 cm^{-1} and was mainly due to CH_x stretching vibrations ($2700\text{--}3100\text{ cm}^{-1}$) and N–H vibrations ($3100\text{--}3500\text{ cm}^{-1}$).

According to FT-IR analysis, three kinds of films could be identified depending on the deposition temperature. The spectra of the films grown at $100\text{--}300\text{ °C}$ from BTMSEA + He mixture contained N-H, C-H bands and a wide band in the range of $600\text{--}1300\text{ cm}^{-1}$. The $600\text{--}1300\text{ cm}^{-1}$ area was presented by the most of the peaks revealed by the organic source molecule. So it is possible to find the bands relevant to vibrations in Si-C, Si-N, Si-O / Si-CH₂-Si, Si-CH₃ bonds. The data denoted the polymeric-like structure of the films formed by large fragments of the precursor molecule integrated in the film. As can be noted from Fig. 1 the increase in substrate temperature involved substantial changes in the film spectra. A significant drop in the intensity of absorption bands from C–H ($2960\text{--}2790\text{ cm}^{-1}$) bounds was observed in the films spectra obtained in the range of $400\text{--}500\text{ °C}$. This appeared to be due to thermally induced rupture of the C–H bonds in the methyl and ethyl groups. The temperature increase led to the band of $600\text{--}1300\text{ cm}^{-1}$ narrowing. The peak was centered at $860\text{--}900\text{ cm}^{-1}$ that is an intermediate position between Si-C and Si-N bands. The further increase in deposition temperature led to the shift into the area ($820\text{--}850\text{ cm}^{-1}$) that corresponds to the SiC_x film formation.

The low-temperature films obtained from BTMSEA + NH₃ mixture also demonstrated polymeric-like structure. The absorption band corresponding to C–N bond was very intense in the spectrum of BTMSEA precursor. So, an interesting feature of the film spectra was the absence of this band in the films obtained from BTMSEA + He. Ammonia addition into the reactive mixture led to appearance of the C–N band (1185 cm^{-1}) and increase in the N–H peak intensity in the spectra of the films obtained even at 100 °C . These bands existed in the high-temperature films deposited up to $T_d = 500\text{ °C}$. The spectra of the films prepared at $600\text{--}700\text{ °C}$ contained only peak at 830 cm^{-1} , that corresponded to Si-C binding.

Table I. Positions and assignments of FT-IR features.

Wavenumbers, cm^{-1}	Assignments
830	Si–C stretching mode
940	Si–N stretching mode
1020	CH ₂ wagging mode in Si–CH ₂ –Si and/or Si–O stretching mode in Si–O–Si
1185	C–N stretching and/or N–H bending modes in Si–NH–C and/or Si–NH–Si
1250	CH ₃ symmetric bending mode in Si–(CH ₃) _x
2205	C≡N stretching mode in Si–CN
2700–3100	CH _x stretching mode
3100–3500	N–H stretching mode

To summarize information on the film composition and bonding density:

- (i) the films obtained in the temperature range of $100\text{--}300\text{ °C}$ possess polymer-like structure;
- (ii) films grown in the temperature range of $400\text{--}500\text{ °C}$ had the Si-N and Si-C bonds simultaneously. Ammonia addition allowed obtaining films with even C-N binding in this temperature region;
- (iii) the films synthesized in the temperature range of $600\text{--}700\text{ °C}$ were close to SiC_x both in the case of BTMSEA + He and BTMSEA + NH₃ reactive mixtures.

3.1.3. Raman spectroscopy.

Raman spectroscopy was used to investigate the carbon type included in the film structure. Raman spectra of the low-temperature films did not contain any features, while the high-temperature SiC_xN_y film spectra contained two peaks at the 1340 cm^{-1} and $1540\text{--}1580\text{ cm}^{-1}$ corresponding to the D- and G-modes of free disordered carbon. The G-peak corresponded to the stretching vibrations of any sp^2 -atoms pair in the line and in the ring, while the D-mode was associated to pulsating vibrations of sp^2 sites only in the rings [28]. The carbon phase appearance in high-temperature films is typically due to the high carbon content in the precursor molecule [29-30].

Carbon phase was observed for the films synthesized from BTMSEA + He mixture at $600\text{--}700\text{ }^\circ\text{C}$. The size of carbon nanocrystallites was estimated using the empiric rule described by Tuinstra et al. in [31]. The intensity ratio of D- to G-peaks was used for carbon particles calculations. The size of nanoparticles was estimated as about 2 nm. Ammonia addition moved the temperature boundary of graphite-free films formation to high temperature region, so the D- and G- modes were obtained only for the films obtained at $700\text{ }^\circ\text{C}$. In this case, the particle size estimated in the same way was 3-4 nm.

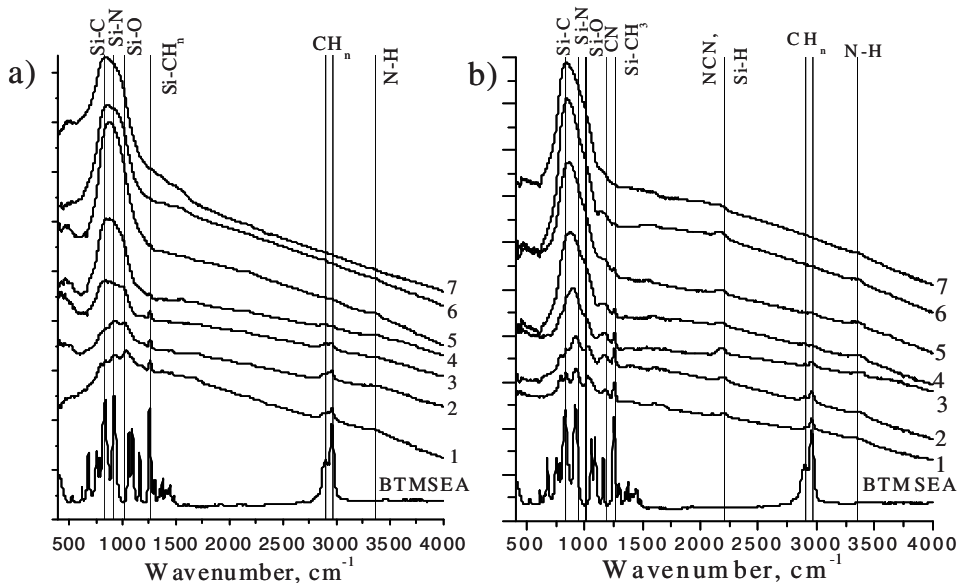


Fig. 1. FT-IR spectra of SiC_xN_y thin films deposited from different mixtures as a function of temperature (1-100, 2-200, 3-300, 4-400, 5-500, 6-600, 7-700 $^\circ\text{C}$): BTMSEA + He (a) and BTMSEA + NH_3 (b).

3.1.4. Element analysis.

The element composition of the films was estimated by EDX technique for $\text{SiC}_x\text{N}_y / \text{Ge}$ (100) structures (Fig. 2). As it was shown by FT-IR spectroscopy, the films obtained in low temperature region contained the hydrogen as Si-CH_3 and C-H fragments from the organosilicon precursor. However the EDX technique does not determine the hydrogen content, so these data were used only to approximate the change in other elements content. Depending on the synthesis conditions the deposited films contained Si, C and N in different proportions, and O as an impurity. The oxygen content did not exceed 10 at. %. Oxygen contamination, also revealed by FTIR analysis as the Si-O bands may originate from two potential sources. The first may be etching of the quartz walls of the CVD reactor by highly reactive atomic plasma species, resulting in incorporation of oxygen-containing etch products into the growing film [12]. The second source may arise from the reactions of long-lived dangling bonds in the deposit with atmospheric oxygen or moisture, which may occur after film is exposed to the ambient environment.

Carbon content detected in the films synthesized from BTMSEA + He mixture was much higher than other elements content. This value decreased with the temperature from 75 at. % (100 °C) to a minimum value of 30 at. % at $T_d = 500$ °C and then raised with increasing substrate temperature and reached 55 at. % at 700 °C. This dependence could be explained by presence of carbon of different types in the low-temperature and high-temperature films. While the low-temperature carbon corresponded to the organic fragments incorporated to the film from an organosilicon precursor and disappeared completely at the T_d higher than 500 °C, as indicated by the FT-IR spectra, the high-temperature carbon was due to the carbon phase formation as was revealed by Raman spectroscopy.

Ammonia addition led to increase in relative nitrogen content in comparison with the films produced from BTMSEA + He mixture. The minimum in carbon content was also found for the films synthesized from BTMSEA + NH_3 mixture but its value shifted to 600 °C. In fact, it should be noted that reasonable correlation existed between the EDX and Raman data. So, carbon inclusions were found only in the films obtained at 700 °C, as was shown above by Raman spectroscopy.

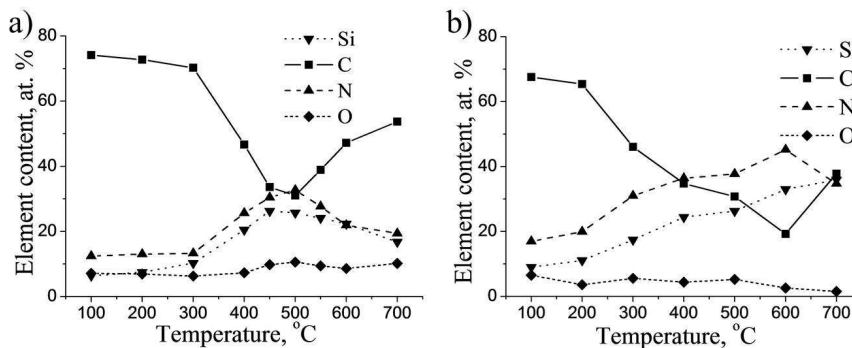


Fig. 2. Element analysis of the films obtained from BTMSEA + He (a) and BTMSEA + NH_3 (b) mixtures as a function of temperature.

3.1.5. SEM.

The results of the SEM study performed for SiC_xN_y films produced at different T_d values indicated that the substrate temperature did not influence the surface morphology of the films in the region of 100-400 °C. The film surface, being very smooth and defect-free, exhibited an excellent morphological homogeneity, irrespective of the deposition temperature in this region. However the increase in temperature led to the change of the surface morphology. The rough surface was found for the films obtained at 700 °C from BTMSEA + NH_3 mixture. The increase in roughness of the films may originate from formation of nanoparticles that may occur at the high temperature. This is demonstrated by SEM images in Fig. 3, which exemplify the surface of SiC_xN_y films deposited at two different deposition temperatures (400 and 700 °C) from BTMSEA + He and BTMSEA + NH_3 mixtures.

3.2. Films properties.

Fig. 4 presents some experimental UV-Visible transmission spectra. The low-temperature polymeric-like $SiC_xN_y:H$ films deposited on SiO_2 from BTMSEA + He mixture up to 500 °C revealed the transmittance of 85-95 % in the visible light range, while for SiO_2 substrate this value was just 93 %. The further increase in deposition temperature resulted in the significant drop of the transmittance values due to the carbon phase formation. The films obtained from the BTMSEA + NH_3 mixture possessed lower transmittance in the temperature region of 100-500 °C in comparison to those obtained from BTMSEA + He. However, ammonia addition into the reaction mixture allowed increasing the transmittance in the high-temperature region. These results showed the ability to use these films in optical devices where highly transparent coatings are required.

E_g Tauc band gap value decreased significantly from 4.4 to 1.9 eV with the temperature for the films obtained from BTMSEA + He mixture (Fig. 5). Ammonia addition allowed extending the E_g area to 5.1-2.0 eV, and the values also decreased with temperature. The decrease in organic-like carbon content and films conversion to the inorganic material with carbon inclusions resulted in an optical bandgap gradual reduction, thus providing the ability of band gap engineering.

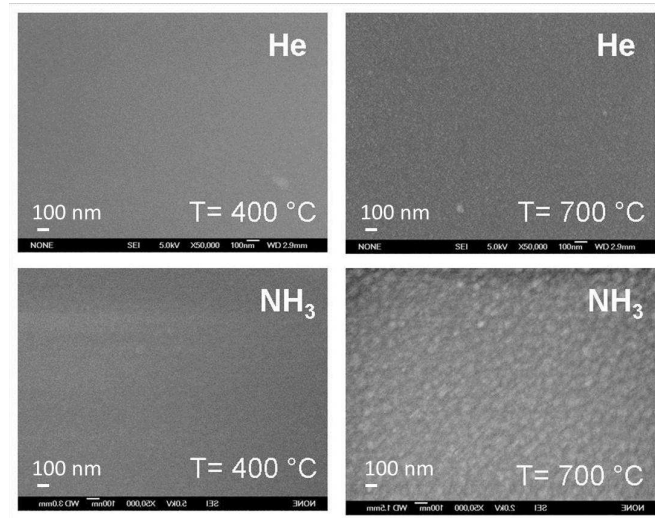


Fig. 3. SEM micrographs of thin films obtained from BTMSEA + He and BTMSEA + NH₃ mixtures.

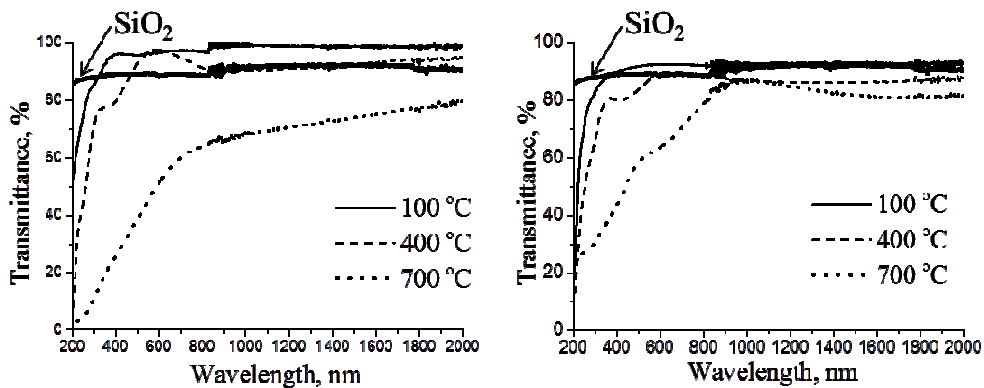


Fig. 4. UV-Visible experimental spectra of SiC_xN_y films obtained from BTMSEA + He (a) and BTMSEA + NH₃ (b) mixtures.

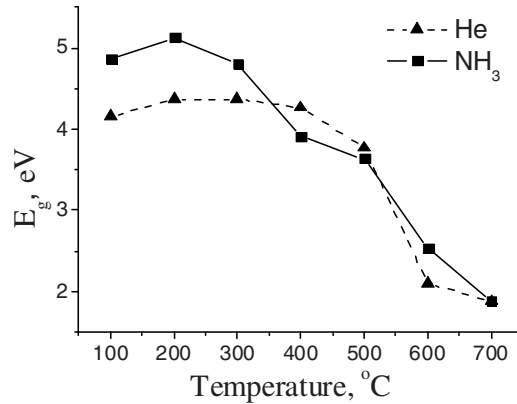


Fig. 5. E_g band gap from UV–Visible transmission spectra of thin films obtained from BTMSEA + He and BTMSEA + NH_3 mixtures as a function of deposition temperature.

The hardness values of several films is presented in Table II. Each experimental point was an average value of 10 measurements. The highest hardness, 21.5 GPa (sample 1), was observed for the sample obtained at 600 °C from BTMSEA + NH_3 mixture. The temperature increase up to 700 °C resulted in reduce in hardness to 20.8 GPa (sample 2). The films prepared from BTMSEA + He mixture appeared to be a more soft material: the hardness obtained for a film synthesized at 700 °C was 19.5 GPa (sample 3), at 600 °C – 18.5 GPa (sample 4). In fact, sample 1 was the only film that did not contain carbon phase. Indeed, the negative impact on the graphite hardness is well known. The increase in temperature (sample 2) led to reduce in the hardness due to start of the carbon formation. The films obtained from BTMSEA + He also contained carbon, as was confirmed by Raman spectroscopy. The difference in the hardness of the films obtained from the different mixture was probably explained by increase in the nitrogen-contained bond density that was shown by the element analysis.

Table II. Film hardness and PECVD conditions

Temperature, °C	Additional gas type	
	NH_3	He
600	21.5 GPa (Sample 1)	18.4 GPa (Sample 3)
700	20.8 GPa (Sample 2)	18.8 GPa (Sample 4)

4. Conclusion

Silicon carbonitride films were produced from a new organosilicon precursor - bis(trimethylsilyl)ethylamine $\text{EtN}(\text{SiMe}_3)_2$ – and characterized using a set of analytical techniques. Structural and optical properties of SiC_xN_y films, deposited by PECVD method using BTMSEA as an organosilicon precursor and He or NH_3 as additional gases, had been investigated for different deposition temperatures, in the range of 100–700 °C. FT-IR analysis showed that deposition temperature increase led to the transition from a low temperature polymeric-like films to the inorganic material. It was also shown that the high-temperature films contain predominantly Si-C bonds independently on the additional gas type (FTIR). As it was confirmed by Raman spectroscopy, high-temperature SiC_xN_y film appeared to be a mixture of at least two phases: silicon carbonitride and carbon phase. Ammonia addition into the reaction mixture resulted in the increase of the temperature boundary of carbon phase-free region from 500 to 700 °C.

The films with transmittance greater than 90% and hardness up to 21.5 GPa were obtained. SiC_xN_y films possessed the optical band gap of 1.9-5.1 eV. Functional properties of the films were shown to be sensitive to the presence of carbon phase and were changed at high deposition temperatures. However, the introduction of NH₃ into the reaction mixture led to increase in hardness and transmittance of the films compared to that obtained from BTMSEA + He.

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References

- [1] Vassallo E., Cremona A., Ghezzi F., Delleria F., Laguardia L., Ambrosone G., Coscia U., 2006. Structural and optical properties of amorphous hydrogenated silicon carbonitride films produced by PECVD. *Appl. Surf. Sci.* 252, p. 7993.
- [2] N.I. Fainer, M.L. Kosinova, Yu. M. Romyantsev, E.A. Maximovskii, F.A. Kuznetsov, 2008. Thin silicon carbonitride films are perspective low-*k* materials. *J. Phys. Chem. Solids.* 69, p. 661.
- [3] S.W. King, J.A. Gradner, 2009. Intrinsic stress fracture energy measurements for PECVD thin films in the SiO_xC_yN_z:H system. *Microel. Reliability.* 49, p. 721.
- [4] I. Blaszczyk-Lezak, A.M. Wrobel, D.M. Bielinski, 2006. Remote hydrogen microwave plasma chemical vapor deposition of silicon carbonitride films from a (dimethylamino)dimethylsilane precursor: Compositional and structural dependencies of film properties. *Diamond Relat. Mater.* 15, p. 1650.
- [5] S Boughaba, GI Sproule, J.P McCaffrey, M Islam, M.J Graham, 2002. Synthesis of amorphous silicon carbonitride films by pulsed laser deposition. *Thin Solid Films* 402, p. 99.
- [6] J. Vlček, M. Kormunda, J. Čížek, Z. Soukup, V. Peřina, J. Zemek, 2003. Reactive magnetron sputtering of Si–C–N films with controlled mechanical and optical properties. *Diamond Relat. Mater.* 12, p. 1287.
- [7] C.W. Chen, C.C. Huang, Y.Y. Lin, L.C. Chen, K.H. Chen, 2005. The affinity of Si–N and Si–C bonding in amorphous silicon carbon nitride (a-SiCN) thin film. *Diamond Relat. Mater.* 14, p. 1126.
- [8] W. Cheng, F. Lin, W. Shi, X. Ma, D. Shen, Y. Zhang, 2006. Synthesis and characterization of new mesoporous material with conducting polypyrrole confined in mesoporous silica. *Mater. Chem. Phys.* 98, p. 504.
- [9] Y. Fu, Ch. Sun, H. Du, B. Yan, 2001. From diamond to crystalline silicon carbonitride: effect of introduction of nitrogen in CH₄/H₂ gas mixture using MW-PECVD. *Surf. Coat. Technol.* 160, p. 165.
- [10] R. Di Mundo, F. Palumbo, F. Fracassi, R. Agostino, 2009. Thin Film Deposition in Capacitively Coupled Plasmas Fed with Bis(dimethylamino)dimethylsilane and Oxygen: An FTIR study. *Plasma Process. Polym.* 6, p. 506.
- [11] W. Kafrouni, V. Rouessac, A. Julbe, J. Durand, 2010. Synthesis and characterization of silicon carbonitride films by plasma enhanced chemical vapor deposition (PECVD) using bis(dimethylamino)dimethylsilane (BDMADMS), as membrane for a small molecule gas separation. *Appl. Surf. Sci.* 257, p. 1196.
- [12] I. Blaszczyk-Lezak, A.M. Wrobel, M.P.M. Kivitorma, I.J. Vayrynen, A. Tracz, 2007. Silicon carbonitride by remote microwave plasma CVD from organosilicon precursor: Growth mechanism and structure of resulting Si:C:N films. *Appl. Surf. Sci.* 253, p. 7211.
- [13] Y. Zhou, D. Probst, A. Thissen, E. Kroke, R. Riedel, R. Hauser, H. Hoche, E. Broszeit, P. Kroll, H. Stafast, 2006. Hard silicon carbonitride films obtained by RF-plasma-enhanced chemical vapour deposition using the single-source precursor bis(trimethylsilyl)carbodiimide. *J. Eur. Ceram. Soc.* 26, p. 1325.
- [14] S. Bulou, L. Le Brizoual, P. Miska, L. de Poucques, R. Hugon, M. Belmahi, J. Bougdira, 2011. Structural and optical properties of a-SiCN thin film synthesised in a microwave plasma at constant temperature and different flow of CH₄ added to HMDSN/N₂/Ar mixture. *Surf. Coat. Technol.* 205, p. S214.
- [15] W. Kafrouni, V. Rouessac, A. Julbe, J. Durand, 2009. Synthesis of PECVD a-SiC_xN_y:H membranes as molecular sieves for small gas separation. *J. Membr. Sci.* 329, p. 130.
- [16] M.L.P. da Silva, I.H. Tan, A.P. Nascimento Filho, E. Galeazzo, D.P. Jesus, 2003. Use of plasma polymerized highly hydrophobic hexamethyldisilazane (HMDS) films for sensor development. *Sens. Actuators, B.* 91, p. 362.
- [17] I. Ferreira, E. Fortunato, P. Vilarinho, A.S. Viana, A.R. Ramos, E. Alves, R. Martins, 2006. Hydrogenated silicon carbon nitride films obtained by HWCVD, PA-HWCVD and PECVD techniques. *J. Non-Cryst. Solids.* 352, p. 1361.

- [18] S. Guruvenket, .S. Andrie, M. Simon, K. W. Johnson, R. A. Sailer, 2012. Atmospheric-Pressure Plasma-Enhanced Chemical Vapor Deposition of a-SiCN:H Films: Role of Precursors on the Film Growth and Properties. *Appl. Mater. Interfaces* 4, p. 5293.
- [19] A. M. Wrobel, I. Blaszczyk-Lezak, P. Uznanski, B. Glebocki, 2010. Silicon Carbonitride (SiCN) Films by Remote Hydrogen Microwave Plasma CVD from Tris(dimethylamino)silane as Novel Single-Source Precursor. *Chem. Vap. Deposition*. 16, p. 211.
- [20] A. M. Wrobel, I. Blaszczyk-Lezak, P. Uznanski, B. Glebocki, 2011. Remote Hydrogen Microwave Plasma Chemical Vapor Deposition of Amorphous Silicon Carbonitride (a-SiCN) Coatings Derived From Tris(dimethylamino)Silane. *Plasma Process. Polym.* 8, p. 542.
- [21] S. Peter, M. Günther, S. Berg, A. Clausner, F. Richter, 2013. Mid-frequency PECVD of a-SiCN:H films and their structural, mechanical and electrical properties. *Vacuum* 90, p. 155.
- [22] I. Blaszczyk-Lezak, A.M. Wrobel, M.P.M. Kivitorma, I.J. Vayrynen, T. Aoki, 2006. Remote hydrogen microwave plasma chemical vapor deposition of silicon carbonitride films from a (dimethylamino)dimethylsilane precursor: Characterization of the process, chemical structure, and surface morphology of the films. *Diamond Relat. Mater.* 15, p. 1484.
- [23] Rühlmann K., 1961. Über die Si—N-Bindung, VII. Synthese und Hydrolyse der N.N-Bis-trialkylsilyl-alkylamine. *Chem. Ber.* 94, p. 2311.
- [24] R.E. Bailey, R. West, 1965. Physical and chemical properties of *N*-halohexamethyl-disilazanes. *J. Organomet. Chem.* 4, p. 430.
- [25] E.W. Abel, D.A. Armitage, 1964. Some New Alkylaminosilanes. *J. Chem. Soc.* p. 1528.
- [26] Sysoev, S. V., Kolontaeva, A. O., Nikulina, L. D., et al., 2007. Films based on the phases in the Si-C-N System: Part 1. Synthesis and characterization of bis(trimethylsilyl)ethylamine as a precursor. *Glass Phys. Chem.* 38, p. 8.
- [27] A.M. Wrobel, I.Blaszczyk-Lezak, A. Walkiewicz-Pietrzykowska, 2007. Silicon carbonitride thin-film coatings fabricated by remote hydrogen–nitrogen microwave plasma chemical vapor deposition from a single-source precursor: Growth process, structure, and properties of the coatings. *J. Appl. Polym. Sci.* 105, p. 122.
- [28] A.C. Ferrari, J. Robertson. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B.* 61 (1999) 14095.
- [29] Yu. M. Romyantsev, N. I. Fainer, B. M. Ayupov, V. I. Rakhlin, 2011. Plasma enhanced chemical deposition of nanocrystalline silicon carbonitride films from trimethyl(phenylamino)silane. *Glass Phys. Chem.* 37, p. 316.
- [30] N.I. Fainer, E.A. Maximovski, Yu.M. Romyantsev, M.L. Kosinova, F.A. Kuznetsov, 2001. Study of structure and phase composition of nanocrystal silicon carbonitride films. *Nucl. Instrum. Methods Phys. Res. A.* 470, p. 193.
- [31] Tuinstra F., Koenig J.L., 1970. Raman Spectrum of Graphite. *J. Chem. Phys.* 53, p. 1126.