PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **2** No 2, 02FNC11(4pp) (2013)

Effect of Added Nitrogen on Properties of SiCN Films Prepared by PECVD Using Hexamethyldisilazane

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

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

(Received 27 May 2013; published online 31 August 2013)

Silicon carbonitride thin films were obtained by plasma-enhanced chemical vapor deposition using native precursor hexamethyldisilazane with a nitrogen addition. Films were investigated by X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy and nanoindentation. It is established that all the films were X-ray amorphous. An increase in nitrogen flow rate leads to increasing the number of Si-N bonds, which, in turn, promotes the rise of nanohardness and elastic modulus up to 20 GPa and 160 GPa, respectively. The optimum deposition parameters were established. The films can be recommended as hard coatings for strengthening cutting tools.

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

PACS numbers: 81.15.Gh, 73.61.Jc, 62.20.Qp

1. INTRODUCTION

It is well known that the films of the Si-C-N system (SiCN) are used as wear resistant and protective coatings due to their unique physical and mechanical properties such as high hardness, low thermal expansion, high chemical and thermal stability [1, 2].

SiCN films can be obtained both by chemical vapor deposition (CVD) at high-temperature synthesis $T_S \sim 1200$ °C [3] and by physical vapor deposition (PVD), for en example, such as magnetron sputtering [4, 5]. CVD methods are used not only for high-temperature synthesis but traditionally are used to deposit SiCN films using explosive mixtures of reagents that complicates the technology. A certain alternative of the mentioned methods can be plasma-enhanced chemical vapor deposition (PECVD) by using liquid precursors containing silicon, carbon and nitrogen. This is mainly silazanes (hexamethyldisilazane ($C_6H_{19}NSi_2$) and hexamethylcyclotrisilazane [$(CH_3)_2SiNH]_3$) [6], with the ratios of nitrogen and silicon [N]/[Si] are 0.5 and 1.0, respectively, which is not sufficient for the synthesis of the films with the stoichiometric composition (the [C]/[Si] ratio ~ 1.0) without an additional introduction of nitrogen into the reaction mixture.

2. EXPERIMENTAL DETALIES

SiCN films were obtained by PECVD with the help of a laboratory installation "PLASMA-01N". The plasma was exited in the capacity-coupled system at 40.68 MHz. The substrate bias was generated with a RF generator of 5.27 MHz. Deposition parameters are summarized in Table 1.

The thickness of the obtained films were measured by optical interference profilometer "Micron-alpha" (Ukraine) and reached the value of 0,4-0,7 µm. Structural analysis of the films was determined by X-ray difractometer DRON-3M (Cu-K_α–radiation). The presence of chemical bonds were detected by Fourier transform infrared (FTIR) spectra, which were measured at room temperature in the range of 400-4000 cm^{-1} by a FTIR spectrometer "FSM 1202" LLC «Infraspek». For a research of hardness and Young's modulus, a device G200 equipped with Berkovich indenter was used. Nanohardness and Young's modulus were calculated by method of Oliver and Phar from nanoindentation results [7].

3. RESULTS AND DISCUSSION

In Fig. we show the X-ray diffraction (XRD) spectra of the deposited films. One can see that the XRD spectra do not contain any features that could be assigned to the nanocrystallites. The reflections peaks at 33° and 69° correspond to the substrate material.
FTIR spectra of SICN films obtained with different nitrogen flow (F_{N2}) rates are shown in Fig. 2a. They were characterized on the basis of literary data [8-11]. In the FTIR spectra of the obtained films, dominant wide band of absorption in the range 600-1300 cm^{-1} and four absorption bands in the range 1300-3500 cm^{-1} are observed. The dominant absorption band can be interpreted as vibrations of Si–C (800-850 cm^{-1}), Si–N (900-980 cm^{-1}) [8] and Si–O (1000-1030 cm^{-1}) [9] bonds. Absorption bands in the range 1300-3500 cm^{-1} can be attributed to vibrations of C–C [9] bond at 1555 cm^{-1} and C–N [9] and / or Si–H [10] bonds at 2142 cm^{-1}, as well as the vibrations of hydrogen bonds C–H [6] and N–H [10, 11] at 2890 cm^{-1} and 3400 cm^{-1}, respectively. It should be noted that all absorption bands that observed in the range of 1300 cm^{-1} to 3500 cm^{-1} retain their positions despite nitrogen flow rate change, while the positions of the peaks in the range 600-1300 cm^{-1} depend on the amount of added nitrogen.

To analyze the absorption band in this range, we made deconvolution of the wide absorption peak into lorentzian components. This enabled us to establish the contributions of different vibrations to this peak. The results of the deconvolution are shown in Fig. 2b. The selected area was presented by three components. For

---

[*] ivash@ipms.kiev.ua

© 2013 Sumy State University

Table 1 – Deposition parameters of SiCN films on laboratory PECVD installation „PLASMA-01N”. T_s – temperature of the substrate holder; p_w – introduced power density RF (40,68 МГц) of gas discharge; U_d – negative bias on the substrate holder; p_c – pressure of the gas mixture in the reactor chamber; F_{H+HDMS} – flow rate of a mixture of hydrogen and transported him vapor of hexamethyldisilazane from the bubbler; F_{N2} – nitrogen flow rate, further introduced into the reaction mixture

F_{N2}, sccm	T_s, °C	– U_d, V	p_c, Pa	t, min	p_w, W/cm^3	F_{H+HDMS}, sccm
0,0	450	200	26,66	60	0,2	12
1,0	450	200	26,66	60	0,2	12
2,0	450	200	26,66	60	0,2	12
4,0	450	200	26,66	60	0,2	12

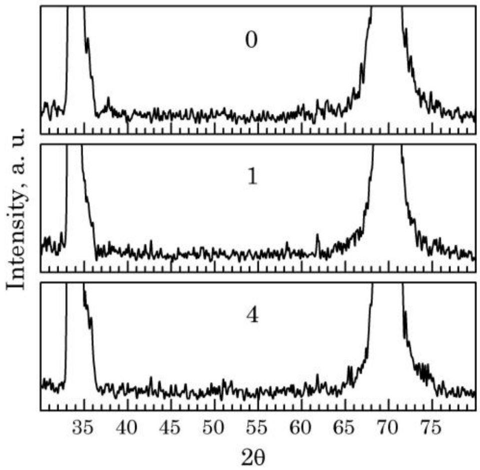

Fig. 1 – X-ray diffraction patterns of SiCN films obtained by PECVD using hexamethyldisilazane with different flow rate of added nitrogen. Reflexes at 33° and 69° associated with the silicon substrate. Numbers 0-4 indicated flow rate of added nitrogen in sccm

the films deposited without adding nitrogen, the positions of the deconvoluted peaks correspond to 795 cm^{-1}, 918 cm^{-1} and 1021 cm^{-1}, which can be attributed to vibrations of Si–C, Si–N and Si–O bonds, respectively. With an addition of nitrogen, the peaks centered at 918 cm^{-1} (Si–N) and 1021 cm^{-1} (Si–O) shifted to higher wavenumbers and reaches 970 cm^{-1} (Si–N), 975 cm^{-1} (Si–N), 1030 cm^{-1} (Si–O) at flow rate 1 sccm and 4 sccm, respectively. In this case, the area related to the Si–N bonds increased more than twice, and the area related to the Si–O bonds decreased substantially. The area and position of the lorentzian component related to the Si–C bonds are almost not changed.

It follows that an input of nitrogen leads to a significant increase of the number of Si–N bonds due to decreasing the number of Si–O bonds. The concentration of Si–C bonds remained practically unchanged.

We investigated some of the mechanical characteristics of the deposited films. Fig. 3 shows dependence of both the nanohardness (*H*) and the Young's (*E*) modulus of SiCN films deposited under various F_{N2} on nanoindenter penetration.

The films deposited with an addition of nitrogen have higher both the hardness and the Young's modulus (19-20 GPa and 130-150 GPa, respectively compared to those of the films deposited without addition of nitrogen (16 GPa and 100 GPa, respectively). This is confirmed by the results presented in Fig. 4, where the values of H and E are shown as functions of F_{N2}. The observed increase in both the nanohardness and Young's modulus can be explained by changing in bond configuration, particularly, by increasing number of Si–N bonds.

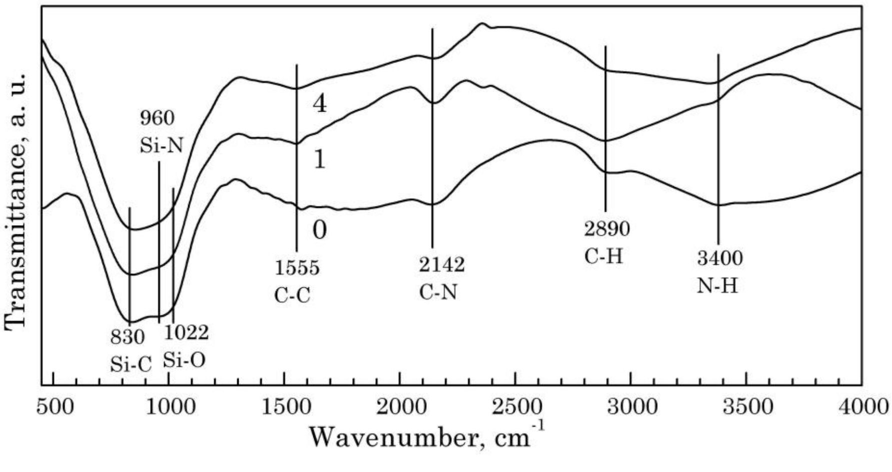

Fig. 2a – IR spectra of films deposited at different flow rate of added nitrogen. Numbers 0-4 indicated flow rate of added nitrogen in sccm.

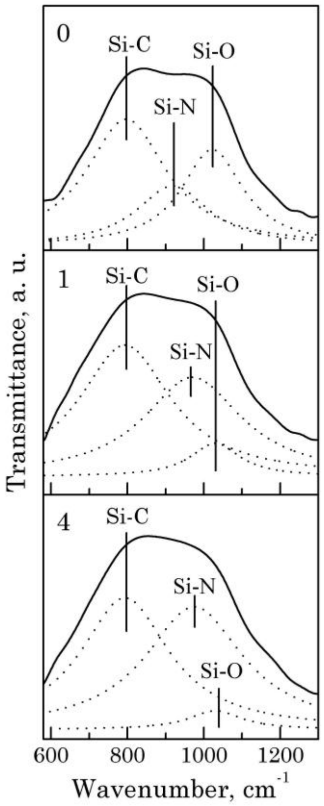

Fig. 2b – IR deconvoluted spectra in range 600-1300 cm^{-1}. Numbers 0-4 indicated flow rate of added nitrogen in sccm. The inversion bands were done

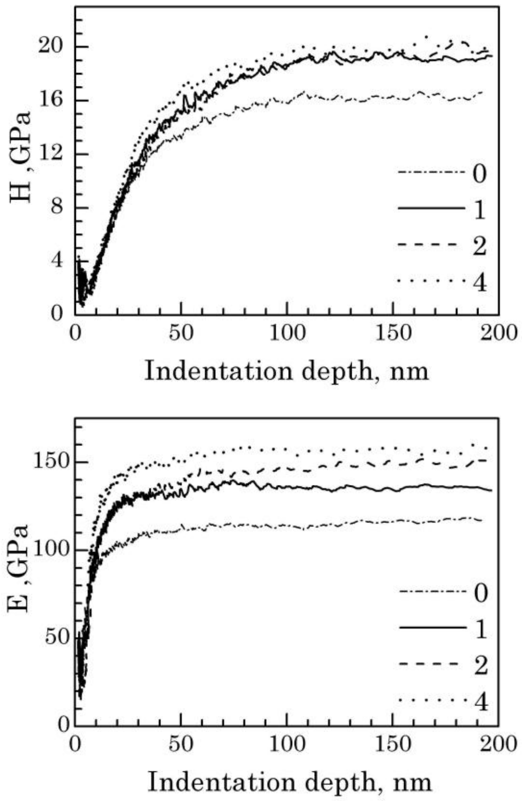

Fig. 3 – Variation of the hardness and Young's moduls of PECVD thin films as a function of the indentation depth to different flow rate of added nitrogen. Numbers 0-4 indicated flow rate of added nitrogen in sccm

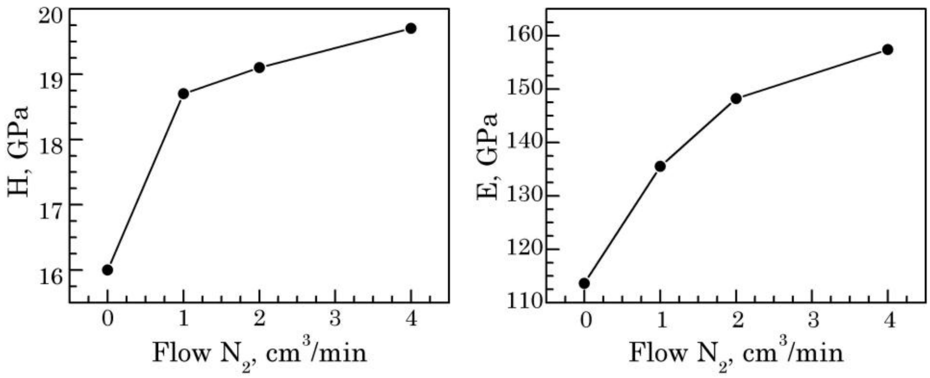

Fig. 4 – Variation of the hardness and Young's moduls as a function of flow rate of added nitrogen

4. CONCLUSIONS

1. It is found that the addition of nitrogen in reaction mixture does not effect on the structure of the films. All SiCN films were the X-ray amorphous.
2. An additional input of nitrogen into reaction mixture leads to an increase of the nanohardness and the elastic modulus mostly due to forming the additional Si–N bonds.
3. The results obtained in this investigation, indicate a perspective of PECVD SiCN films deposited by varying nitrogen flow rates as hard coatings for strengthening cutting tools.

This work was supported by STCU contract No 5539. The authors are grateful to Dr. S.N. Dub for nanoindentation of samples.

REFERENCES

1. B.P. Swain, N.M. Hwang, et al., *Appl. Surf. Sci.* **254**, 5319 (2008).
2. C. Pusch, H. Hoche, *Surf. Coat. Technol.* **205**, 119 (2011).
3. A. Bendeddouche, R. Berjoan, et al., *Surf. Coat. Technol.* **111**, 184 (1999).
4. Z. Shi, Y. Wang, et al., *Appl. Surf. Sci.* **258**, 1328 (2011).
5. V.N. Ng, M. Xu, et al., *Thin Solid Films* **506-507**, 283 (2006).

6. T.P. Smirnova, A.M. Badalina, et al., *Thin Solid Films* **429**, 144 (2003).
7. W.C. Oliver, G.M. Pharr, *J. Mater. Res.* **7**, 1564 (1992).
8. Y. Awad, M.A. El Khahani, et al., *J. Appl. Phys.* **107**, 033517 (2010).
9. I. Ferreira, E. Fortunato, et al., *J. Non-Cryst.* **352**, 1361 (2006).
10. D. Sarangi, R. Sanjinés, A. Karimi, *Thin Solid Films* **447-448**, 217 (2004).
11. P. Jedrzejowski, J. Cizek, et al., *Thin Solid Films* **447-448**, 201 (2004).