ISSN 0020-1685, Inorganic Materials, 2015, Vol. 51, No. 9, pp. 897–902. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © Yu.M. Rumyantsev, M.N. Chagin, M.L. Kosinova, F.A. Kuznetsov, 2015, published in Neorganicheskie Materialy, 2015, Vol. 51, No. 9, pp. 974–980.

Synthesis of Thin Silicon Carbonitride Films from Hexamethyldisilazane in an Inductively Coupled Plasma Reactor

Yu. M. Rumyantsev, M. N. Chagin, M. L. Kosinova, and F. A. Kuznetsov†

Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

e-mail: marina@niic.nsc.ru

Received September 28, 2014; in final form, March 19, 2015

Abstract—SiC_xN_y:H films have been grown by inductively coupled plasma chemical vapor deposition via hexamethyldisilazane decomposition at substrate temperatures from 50 to 450°C and rf powers from 100 to 500 W. The growth rate and physicochemical properties of the films (their elemental composition, refractive index, optical band gap, and optical transmittance) have been shown to be weak functions of process conditions. The process offers high stability, and the films are uniform in thickness over the entire substrate surface. The SiC_xN_y:H films have a polymer-like structure, high transmission, a refractive index near 2.0, and hardness of 8–9 GPa, which is typical of films produced from hexamethyldisilazane by low-temperature plasma deposition processes.

DOI: 10.1134/S0020168515090162

INTRODUCTION

Plasma synthesis of thin films for various applications using hexamethyldisilazane (HMDS), $[(CH_3)_3Si]_2NH$, as a precursor has long attracted researchers' attention because both the precursor and synthesis products possess unique properties. HMDS is a highly volatile organosilicon compound, sufficiently safe and stable during storage and available commercially. The high partial pressure of HMDS vapor (on the order of several millimeters Hg near room temperature) makes it rather convenient for use in chemical vapor deposition processes, and the presence of several elements in its molecule (silicon, nitrogen, and carbon) makes it possible to obtain complex substances using a single source. Depending on synthesis conditions, thin films grown using HMDS may offer high chemical stability, good mechanical strength, high optical transmission, good dielectric properties, etc. Owing to the high stability of HMDS molecules, in vapor phase growth of thin films these molecules are activated not only thermally but also using an rf plasma. Extensive studies have been concerned with the growth of thin silicon carbonitride layers of various compositions by plasma processes using HMDS in mixtures with helium, nitrogen, hydrogen, and ammonia [1–4]. In those studies, use was made of capacitively and inductively coupled plasmas at frequencies of 13.56, 27.12, and 40.28 MHz, but no marked distinction between results of similar processes was detected. Also, no distinction was observed between film growth processes using nitrogen and hydrogen as activator gases, and only the use of ammonia instead of these gases led to changes in the properties of the films. It is reasonable to assume that this is associated with the way these gases are excited by the rf field at the frequency and power used. In a number of studies [5, 6] where microwave radiation was used to excite gas mixtures of HMDS with nitrogen, hydrogen, and argon, other relationships between process parameters and properties of films were obtained. A microwave plasma has a higher frequency (2.45 GHz) and is excited at higher initial gas pressures, which leads to a different behavior of nitrogen and hydrogen in the silicon carbonitride film growth process. Varying the relative flow rate $r(N_2) = F_{N_2}/(F_{N_2} + F_{H_2})$ from zero to unity, one can obtain films ranging in composition from SiC_y:H to SiN_x:H.

It is of great interest to use an inductively coupled plasma in chemical vapor deposition processes (ICP CVD). Possessing an increased density and uniformity of the particle distribution over the cross section of the reactor, such plasma ensures better homogeneity of films throughout the substrate surface. First used in the plasma etching of semiconductor structures [7, 8], ICPs were subsequently used to grow dielectric layers through the decomposition of organosilicon compounds [9, 10]. At the same time, the ICP CVD processes underlying the growth of thin silicon carbonitride films have not yet been studied systematically.

The objectives of this work were to develop a process for the growth of silicon carbonitride layers

† Deceased.

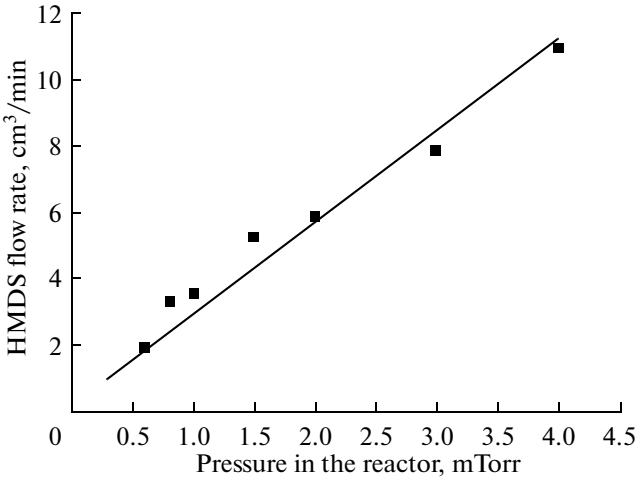

Fig. 1. HMDS flow rate as a function of HMDS vapor pressure in the reactor.

through the decomposition of vapor of an organosilicon compound (HMDS) in an inductively coupled plasma reactor and to study the key features of the process. In this paper, we present our findings on the growth kinetics and some physicochemical properties of silicon carbonitride layers.

EXPERIMENTAL

Silicon carbonitride films were grown in a plasma-enhanced chemical vapor deposition reactor using a low-pressure, high-density inductively coupled plasma. In our experiments, we used an apparatus designed at the Institute of Physics and Technology, Russian Academy of Sciences (Moscow) [11]. It includes all necessary systems: a reactor with an air-lock chamber, vacuum system, gas delivery system, rf generators with matching units, control unit, and computer. A 300-mm-diameter steel reactor is surrounded by permanent magnets and has an rf susceptor in its top part. The central part of the reactor contains a heated pedestal for 100-mm-diameter substrates, to which an rf bias is applied. Substrates are exchanged manually through an air lock, without breaking the vacuum in the reactor. The reactor is evacuated by a turbomolecular pump at a rate of 700 L/s to a residual pressure of 3×10^{-4} Torr. In the film growth process, a pressure on the order of 1×10^{-2} Torr is maintained. The gas delivery system comprises four controlled channels for delivering process gases to the reactor: He, Ar, N_2, and others. Two 1-kW rf generators operating at a frequency of 13.56 MHz make it possible to tune the plasma power in a wide range. The substrate temperature can be varied in the range from 20 to 450°C.

For the growth of dielectric films in this apparatus, we had to modify its design. Since the vapor pressure of organosilicon precursors is rather low, their flow rates in existing gas channels of the apparatus can be neither controlled nor measured. We produced an additional channel which included a thermostated liquid precursor source, a metering valve for controlling the flow rate, and stop valves in the delivery lines. Gas flow rates were calibrated against the pressure in the system; for this purpose, appropriate calibrations were performed. For research purposes, the heated pedestal was adjusted to the use of substrates of various dimensions and shapes. Typically, substrates 10×10 mm^2 in dimensions were sufficient. In our film growth runs, the reactor had to be cleaned at regular intervals to remove the decomposition products of the organosilicon compounds. To this end, it was depressurized and mechanically processed.

This apparatus was used to grow silicon carbonitride films on various substrates: Si(100), Ge(111), and fused silica. The precursor used was HMDS, and argon was employed as the plasma gas. We carried out several series of experiments, varying one parameter while maintaining the others constant: deposition time, plasma power, substrate temperature, and HMDS flow rate. We measured the thickness and refractive index of the films; took their IR, Raman, and optical transmission spectra and surface micrographs; and determined the percentages of major elements. The properties of the SiC_xN_y:H films were studied by a variety of modern physicochemical characterization techniques. The thickness and refractive index of the films were determined by monochromatic null ellipsometry with an LEF-3M instrument (λ = 632.8 nm). The growth rate of the films was evaluated as the ratio of the film thickness to the growth time. The composition of the films was studied using IR spectroscopy on a SCIMITAR FTS2000 Fourier transform spectrometer at wavenumbers from 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. Raman spectra were measured on a Triplemate Raman spectrometer (Spex, USA) in the range 400–1800 cm^{-1}. The surface microstructure and elemental composition of the films were analyzed by scanning electron microscopy on a JEOL JSM-6700F equipped with an EDS EX-23000 BU energy dispersive spectrometer system. To study the optical properties of the films (their band gap and their transmission in the IR and visible spectral regions), we measured their transmission and reflection spectra on a Shimadzu UV-3101 PC scanning spectrophotometer in the range 200–2000 nm. The mechanical properties of the films were studied by nanoindentation using a Nano Test instrument (Micro Materials Ltd., UK).

RESULTS AND DISCUSSION

In preliminary experiments, we determined some technologically important characteristics of the CVD apparatus. Because of the low HMDS vapor pressure in the source, its output flow rate cannot be measured by the conventional flow meter mounted in the appa-

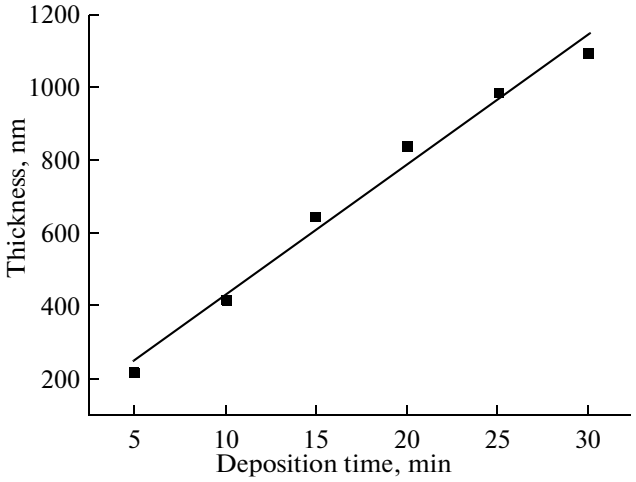

Fig. 2. Thickness of SiC_xN_y:H films as a function of growth time.

ratus. At the same time, it can be calculated from the pressure change in the reactor when the flow is turned on or changed. Quantitative data were obtained by examining the loss of the substance in the source under various operation conditions. The loss rate was determined by weighing the source before and after operation for a certain length of time. In addition, we measured the pressure in the reactor. The plot of the HMDS flow rate vs. pressure in the reactor is linear (Fig. 1) and can be used in other experiments to monitor the flow rate of the substance in the system without weighing the source. In a series of experiments under fixed conditions, we assessed the stability of the process and the film growth rate as a function of growth time. At deposition times from 5 to 30 min, the thickness of the films was proportional to the growth time (Fig. 2), which indicates that the growth rate was constant and that the process was reproducible.

Taking into account the results thus obtained, we carried out two series of experiments to grow SiC_xN_y:H films at rf plasma powers from 100 to 500 W (series 1) and substrate temperatures from 200 to 450°C (series 2). The other process parameters were maintained constant and no rf bias was applied to the substrate.

In series 1, the substrate temperature was 200°C, the argon flow rate was 43 cm^3/min, and the growth time was 10 min. Increasing the rf plasma power from 100 to 500 W slightly reduces the growth rate (from 50 to 35 nm/min), whereas the refractive index remains essentially unchanged (≃2.0). The latter can be interpreted as evidence that the composition and structure of the films produced under these conditions do not vary. As shown earlier [1–3], the refractive index of silicon carbonitride films is significantly influenced by changes in the chemical and phase compositions of the films, and, as a rule, n increases with increasing growth temperature. That the chemical composition of the films is constant is evidenced by their IR spectra (Fig. 3). It is seen that all of the spectra are similar to each other and contain peaks corresponding to the Si–C, Si–N, Si–CH_3, Si–H, C–N, N–H, and C=C

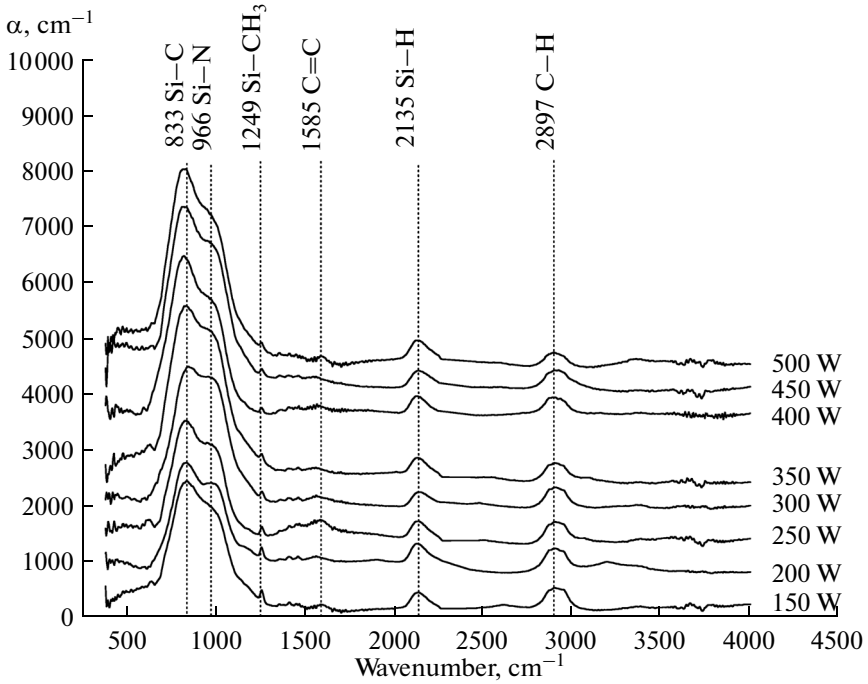

Fig. 3. IR spectra of SiC_xN_y:H films produced at a deposition temperature of 200°C and various rf plasma powers.

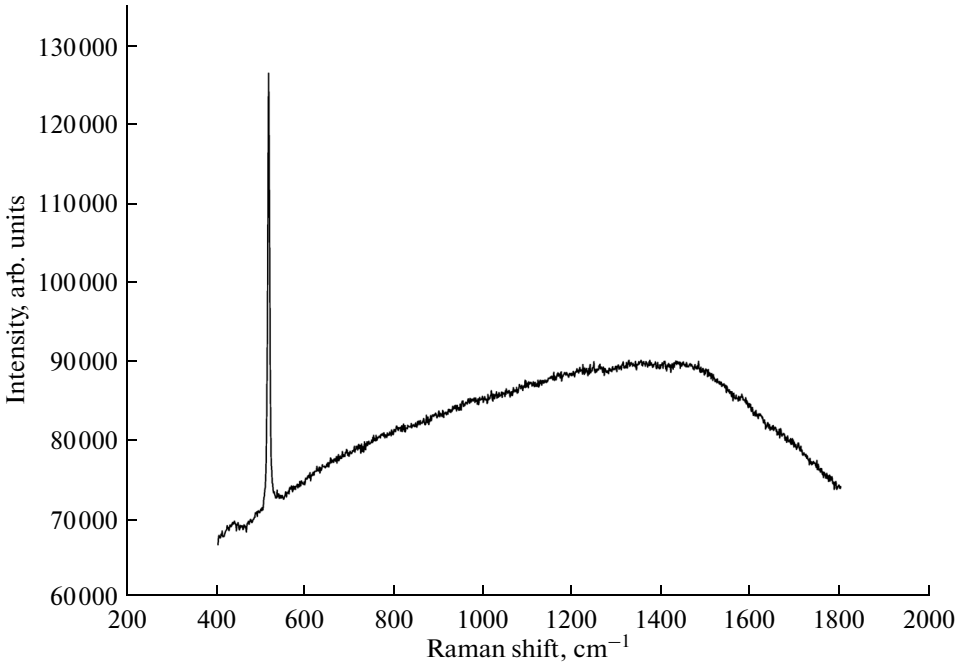

Fig. 4. Typical Raman spectrum of films grown in an inductively coupled plasma reactor at the process parameters used in this study.

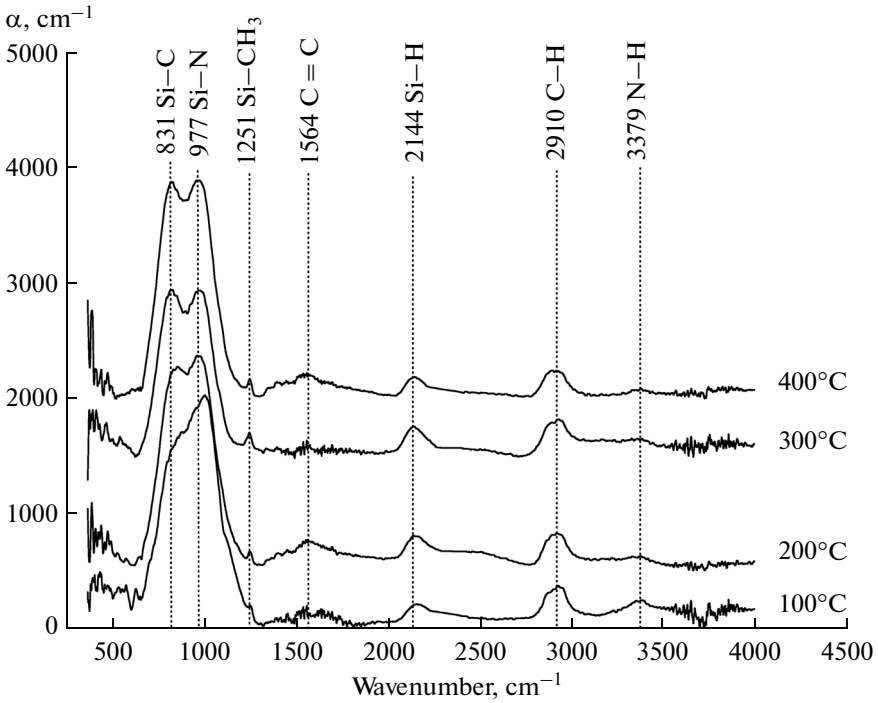

Fig. 5. IR spectra of SiC_xN_y:H films produced at an rf plasma power of 200 W and various deposition temperatures.

bonds. This combination of chemical bonds is characteristic of polymer-like films produced by low-temperature plasma deposition processes using HMDS [1–3]. The films contain no carbon clusters, as follows from their Raman spectra (Fig. 4). At the same time, according to energy dispersive spectroscopy data the films have high carbon content: for example, C, 65.0; N, 13.0; Si, 14.5; and O, 7.5 at % at a plasma power of 200 W and a substrate temperature of 400°C. In this composition, hydrogen is left out of consideration, because it cannot be determined by the method in question, so the results are only tentative. The consid-

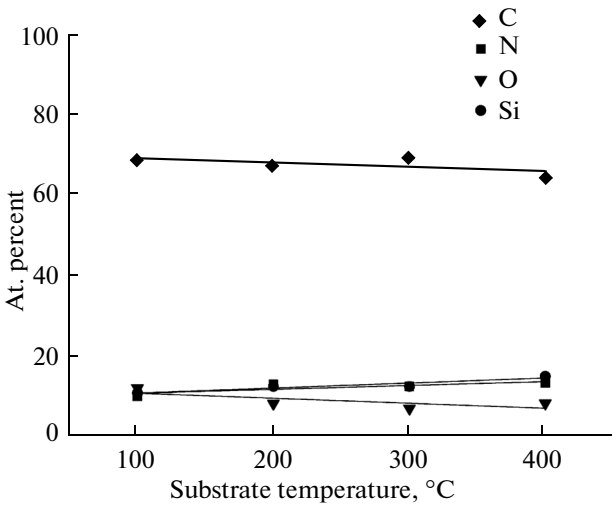

Fig. 6. Effect of substrate temperature on the composition of the films.

erable percentage of oxygen seems to result from the reaction of the low-temperature film with air during storage.

In series 2, we varied the growth temperature in the range ensured by the CVD apparatus: from room temperature to 450°C. The other process parameters were maintained constant: rf plasma power, 200 W; argon flow rate, 43 cm^3/min; growth time, 10 min. In the temperature range studied, the growth rate decreases from 30 to 22 nm/min and the refractive index increases from 1.65 to 1.84 with increasing temperature. This is due to the slight changes in the chemical composition of the films with increasing growth temperature. Analysis of the IR spectra of the films obtained in this series (Fig. 5) indicates a slight decrease in the concentration of hydrogen-containing bonds with increasing temperature and a change in the relationship between the Si–C and Si–N bonds in the main band of the spectrum. The elemental compositions of the films determined by energy dispersive spectroscopy also demonstrate slight changes in the percentages of Si, C, and N with increasing growth temperature (Fig. 6). Nevertheless, the films remain polymer-like and amorphous even at the highest growth temperature of 450°C.

The SiC_xN_y:H films grown in this study have high optical transmission. Their transmittance was determined by spectrophotometry in a wide spectral range: from 200 to 2000 nm. The transmission spectra of the films differ little from each other, independent of film growth conditions (Fig. 7). Their transmittance exceeds 90% in the range from 500 to 2000 nm. Their optical band gap evaluated from the spectra is E_g = 2.4–2.7 eV and is a weak function of plasma power and deposition temperature. In this respect, the SiC_xN_y:H ICP CVD process differs from other similar plasma deposition processes. The hardness of the films reaches 8–9 GPa at an indent depth of 10% of the film thickness.

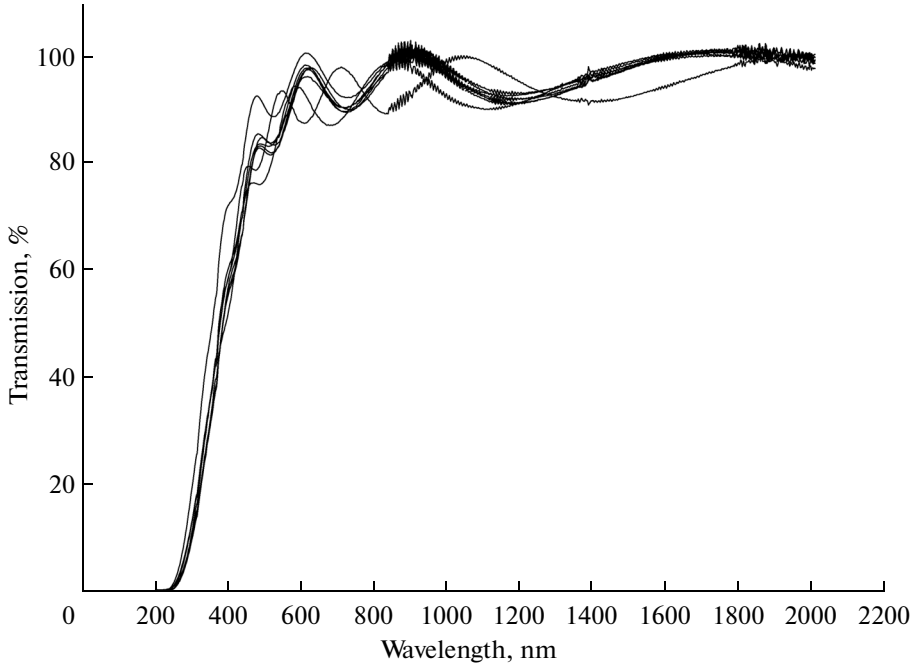

Fig. 7. Optical transmission spectra of SiC_xN_y:H films produced in an ICP reactor at various plasma powers (samples of series 1).

CONCLUSIONS

The growth of thin SiC_xN_y:H films via plasma deposition from HMDS vapor in an inductively coupled plasma reactor has a number of distinctive features in comparison with other similar processes. First, it ensures that films grown on substrates up to 100 mm in diameter are uniform in thickness. The growth rate and some characteristics of the films (their elemental composition, refractive index, optical band gap, and optical transmittance) are essentially independent of process parameters in the range of deposition conditions studied, which helps to obtain reproducible results. We have identified growth conditions that enable highly transparent SiC_xN_y:H films to be produced.

ACKNOWLEDGMENTS

This work was supported in part by the RF Ministry of Education and Science (state research target for the Nikolaev Institute of Inorganic Chemistry, Siberian Branch (SB), Russian Academy of Sciences (RAS): SiC_xN_y:H film growth process development) and the SB RAS Presidium (SB RAS–National Science Council, Taiwan joint project: characterization of the films).

REFERENCES

1. Fainer, N.I., Rumyantsev, Yu.M., and Kosinova, M.L., Functional nanocrystalline silicon carbonitride films, *Khim. Interesakh Ustoich. Razvit.*, 2001, vol. 9, pp. 685–870.
2. Fainer, N.I., Kosinova, M.L., and Rumyantsev, Yu.M., Silicon and boron carbonitride thin films: growth, composition, and structure, *Ross. Khim. Zh.*, 2001, vol. 45, no. 3, pp. 101–108.
3. Hoffmann, P., Fainer, N., Kosinova, M., Baake, O., and Ensinger, W., Compilation on synthesis, characterization and properties of silicon and boron carbonitride films, *Silicon Carbide—Materials, Processing and Applications in Electronic Devices*, Mukherjee, M., Ed., InTech, 2011, ch. 21, pp. 487–546.
4. Limmanee, A., Otsubo, M., Sugiura, T., Sato, T., Miyajima, S., Yamada, A., and Konagai, M., Effect of thermal annealing on the properties of a-SiCN:H films by hot wire chemical vapor deposition using hexamethyldisilazane, *Thin Solid Films*, 2008, vol. 516, pp. 652–655.
5. Ray, S.K., Maiti, C.K., and Chakrabarti, N.B., Low-temperature deposition of dielectric films by microwave plasma enhanced decomposition of hexamethyldisilazane, *J. Electron. Mater.*, 1991, vol. 20, no. 11, pp. 907–913.
6. Bulou, S., Le Brizoual, L., Miska, P., de Poucques, L., Hugon, R., Belmahi, M., and Bougdira, J., Structural and optical properties of a-SiCN thin film synthesised in a microwave plasma at constant temperature and different flow of CH_4 added to $HMDSN/N_2/Ar$ mixture, *Surf. Coat. Technol.*, 2011, vol. 205, pp. 214–217.
7. Sukhanov, Ya.N., Ershov, A.P., Rudenko, K.V., and Orlikovsky, A.A., Comparative study of inductively coupled and microwave BF_3 plasmas for microelectronic technology applications, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2004, vol. 5401, pp. 55–63.
8. Rudenko, K.V., Diagnostics of plasma processing steps in micro- and nanoelectronics, *Extended Abstract of Doctoral (Phys.–Math.) Dissertation*, Moscow: Inst. of Physics and Technology, 2007.
9. Kshirsagar, A., Nyaupane, P., Bodasc, D., Duttagupta, S.P., and Gangal, S.A., Deposition and characterization of low temperature silicon nitride films deposited by inductively coupled plasma CVD, *Appl. Surf. Sci.,* 2011, vol. 257, pp. 5052–5058.
10. Fainer, N.I., Kosinova, M.L., Maximovsky, E.A., Rumyantsev, Yu.M., Kuznetsov, F.A., Kesler, V.G., and Kirienko, V.V., Study of the structure and phase composition of nanocrystalline silicon oxynitride films synthesized by ICP-CVD, *Nucl. Instrum. Methods Phys. Res.*, 2005, vol. 543, pp. 134–138.
11. Orlikovsky, A.A., Rudenko, K.V., and Averkin, S.N., Fine-line plasma-enhanced processes on the basis of a set of pilot units with a scalable inductively coupled plasma source for use in microelectronics, *High Energy Chem.*, 2006, vol. 40, no. 3, pp. 182–193.

Translated by O. Tsarev