I. A. Romanov¹, I. N. Parkhomenko¹, L. A. Vlasukova¹, F. F. Komarov², 
N. S. Kovalchuk³, O. V. Milchanin³, M. A. Makhavikou², A. V. Mudryi¹,
V. D. Zhivulko⁴, Hong-Liang Lu⁵

¹Belarusian State University, Minsk, Belarus
²A. N. Sevchenko Institute of Applied Physical Problems of the Belarusian State University, Minsk, Belarus
³Joint Stock Company “Integral” Minsk, Belarus
⁴Scientific and Practical Materials Research Center of the National Academy of Sciences of Belarus, Minsk, Belarus
⁵State Key Laboratory of ASIC and System, School of Microelectronics, Fudan University, Shanghai, China

BLUE AND RED LIGHT-EMITTING NON-STOICHIOMETRIC SILICON NITRIDE-BASED STRUCTURES

Abstract. The two triple-layered SiO₂/SiNₓ/SiO₂ structures with Si-rich and N-rich silicon nitride active layer were fabricated on p-type Si-substrates by chemical vapour deposition. The SiNₓ layer of different composition (x = 0.9 and x = 1.4) was obtained by changing the ratio of the SiH₂Cl₂/NH₃ flow rates during deposition of a silicon nitride active layer (8/1 and 1/8, respectively). The spectroscopic ellipsometry and photoluminescence (PL) measurements showed that the refractive index, the absorbance and luminescence properties depend on a chemical composition of silicon nitride layers. The structures with Si-rich and N-rich SiNₓ active layers emit in the red (1.9 eV) and blue (2.6 eV) spectral ranges, respectively. The PL intensities of different structures are comparable. The rapid thermal annealing results in the intensity decrease and in the PL spectra narrowing in the case of SiNₓ active layer, whereas the increase in the emission intensity and the PL spectra broadening are observed in the case of the annealed sample with a SiNₓ active layer. The PL origin and the effect of annealing treatment have been discussed, taking into account the band tail mechanism of radiative recombination. Multilayered (SiO₂/SiNₓ)ₙ/Si structures are of practical interest for creation of effective light sources on the basis of current Si technology.

Keywords: non-stoichiometric silicon nitride, photoluminescence, spectral ellipsometry, absorption edge, rapid thermal annealing


И. А. Романов, И. Н. Пархоменко, Л. А. Власукова, Ф. Ф. Комаров, Н. С. Ковалчук, О. В. Мильчанин, М. А. Махавиков, А. В. Мудрый, В. Д. Живулько, Хонг-Лианг Лу

1Белорусский государственный университет, Минск, Беларусь
2Институт прикладных физических проблем АН Белорусской государственной академии наук, Минск, Беларусь
3ОАО «Интеграл», Минск, Беларусь
4Научно-практический центр Национальной академии наук Беларуси по материаловедению, Минск, Беларусь
5Школа микроэлектроники Фуданского университета, Шанхай, China

СВЕТОИЗЛУЧАЮЩИЕ СТРУКТУРЫ НА ОСНОВЕ НЕСТЕХИОМЕТРИЧЕСКОГО НИТРИДА КРЕМНИЯ

Аннотация. Методом химического газофазного осаждения на кремниевых подложках ρ-типа изготовлены две трехслойные структуры SiO₂/SiNₓ/SiO₂ с нестехиометрическими пленками нитрида кремния, обогащенными кремнием (x = 0.9) или азотом (x = 1.4), в качестве активных слоев. Активные слои SiNₓ нестехиометрического состава (x = 0.9 и x = 1.4) получены при различном соотношении реагирующих газов (SiH₂Cl₂/NH₃) в процессе осаждения (8/1 и 1/8 соответственно). Методами спектральной эллипсометрии и фотолюминесценции показано, что показатель преломления, поглощение и люминесцентные свойства зависят от стехиометрического состава нитрида кремния. Структуры с активными слоями нитрида с избытком кремния и азота излучают в красной (1.9 eV) и синей (2.6 eV) областях спектра соответственно, причем интенсивность свечения сравнима для двух образцов. Быстрая термическая обработка приводит к уменьшению интенсивности и сужению спектра фотолюминесценции образца с активным
samples were cut out from the structures and undergone rapid thermal annealing (RTA) at 1200°C for 3 min using the setup ‘JetFirst-100’. The thicknesses of layers in the fabricated structures...
were investigated by scanning electron microscopy (SEM) using the Hitachi S-4800 microscope. Spectroscopic ellipsometry measurements of the refraction index ($n$) and the extinction coefficient ($k$) in the range of 200–1000 nm were performed using the spectroscopic ellipsometer HORIBA UVISEL 2. Photoluminescence (PL) spectra were recorded at room temperature in the spectral range of 350–800 nm with a He-Cd laser (325 nm) as excitation source using a home-made setup.

**Results and discussion.** Fig. 2 shows the SEM images of deposited films. Unfortunately, the interface between SiN$_x$ and SiO$_2$ layers were not revealed due to low contrast. As a result, SEM gave information only on a total thickness of the fabricated structures. The total thickness of triple-layered structure was equal to 126 nm and 212 nm for the SRN and NRN samples, respectively. However, the features of used deposition techniques (PECVD and LPCVD) could help to determine the depth of SiN$_x$ layer. Namely, during PECVD process the film is deposited only on one side of the wafer while during the LPCVD process film is deposited on both sides of wafer due to vertical design of the used furnace.

**Fig. 1.** Steps of CVD deposition of triple-layered SiO$_2$/SiN$_x$/SiO$_2$ on Si wafer

**Fig. 2.** SEM images of the SRN and NRN samples. The triple-layered SiO$_2$/SiN$_x$/SiO$_2$ structure was deposited on the face side of the Si substrate. Simultaneously, the SiN$_x$ layer of appropriate thickness was deposited on the back side of the Si substrate.
So, the single silicon nitride film of the same thickness as in the triple structure was deposited in the back side of Si wafer. Thus, the SEM images of wafer back side shows that the thickness of active SiN\(_x\) layer is equal to 76 nm and 149 nm for the SRN and NRN samples, respectively.

Fig. 3 shows the variation of optical constants such as the real part of the refraction index \(n(\lambda)\) and the extinction coefficient \(k(\lambda)\) of the as-deposited SRN and NRN structures. As can be seen from Fig. 3, the optical properties of deposited structures depend on active layer composition. For the SRN structure, the refractive index has higher values in the visible spectral range. A similar trend of \(n\) increase with the increasing N/Si atomic ratio of SiN\(_x\) films has been shown in literature [13, 22–24]. It should be noted the anomalous behavior of \(n\) for the SRN structure in the range of (200–300 nm). It is typical for silicon nitride films with large excess of Si [22, 24]. The both obtained structures show the extinction coefficient amplitude increase to become nearby lower wavelengths (UV spectral range). The extinction coefficient \(k\) is quasi null for the wavelength higher than 610 nm and 250 nm for the SRN and NRN, respectively.

Fig. 4 shows the corresponding absorption coefficient \(\alpha\) calculated from the extinction coefficient \((\alpha = 4\pi k/\lambda)\).

It is evident the absorption edge blue shift with increasing \(x\) parameter. It indicates an optical band gap widening with increase of N/Si ratio. Assuming parabolic bands, the absorption edge could be determined using the well-known Tauc’s equation:
\[(\alpha E)^{1/2} = B(E - E_g),\]

where \(E\), \(E_g\), and \(B\) are the photon energy, indirect optical gap and the Tauc constant (slope), respectively. \(E_g\) calculated by the straight line extrapolation in the linear region of Tauc’s plots with the energy axis are equal to 3.2 eV and 5.5 eV for SRN and NRN structures, respectively. These values are differed with the \(E_g = 5\) eV of stoichiometric Si\(_3\)N\(_4\) deposited by LPCVD [25].

\(E_g\) reduction with the decreasing N/Si ratio was reported for Si-rich films elsewhere [12, 15, 26] and explained via the progressive replacement of Si–N bonds by Si–Si bonds. The nonstoichiometric silicon nitride film is composed of a random network of Si–N and Si–Si bonds. In the case of Si-rich alloys, the band edges are formed by the Si–Si states. In the N-rich alloys, the replacement of Si–Si bonds by stronger Si–N bonds causes the band gap increase with the increasing stoichiometric parameter \(x\).

Tauc slope \(B\) could provide information about the degree of spreading tails of valence and conduction bands [23]. The value of \(B\) determined from the Tauc’s plots is equal to 540 (eV·cm\(^{-1/2}\)) and 245 (eV·cm\(^{-1/2}\)) for SRN and NRN structures, respectively. It is known that the width of band tail states can depend on static disorder due to structural randomness. In some papers [20, 27–28], band-tail states in the non-stoichiometric Si\(_3\)N\(_x\) films are attributed to a long-range disorder due to spatial fluctuations of the elemental composition. The dependence of \(B\) on stoichiometric parameter is not linear. In Ref [23], Si-rich and stoichiometric nitride films (\(x = 0.34–1.34\)) were studied. According to [23] the minimal value of \(B\) is equal to 130 (eV·cm\(^{-1/2}\)) for \(x = 1.34\). The change of \(B\) for a wider range of \(x\) (\(x = 0–1.6\)) was discussed in [26, 29]. In this case, a minimum in the Tauc slope (250 (eV·cm\(^{-1/2}\))) is at around \(x = 1.0\). According to [14] the \(B\) decreases linearly with the increasing \(x\) from 0 to 1.5 and increases abruptly for the \(x > 1.5\). The magnitude of \(B\) is inversely proportional to energy ranges occupied by tail states. In the case of investigated SRN and NRN structures, it can be concluded that both ones exhibit band tail states. However, NRN structure exhibits a more significant tailing.

Fig. 5 shows the room-temperature PL spectra of the as-deposited SRN and NRN samples. The position and full width at half maximum (FWHM) of the PL bands depend on the composition of active layer. The PL bands maxima are located in red range at \(\sim 1.9\) eV (650 nm) for the SRN sample and in blue range \(\sim 2.6\) eV (470 nm) for the NRN sample. PL bands are broader for the NRN films (FWHM is equal
to ~0.7 eV) than for the SRN (FWHM is equal to ~0.6 eV). It should be noted that an additional weak emission in blue spectral range is registered for the SRN structure.

Fig. 6 shows the effect of RTA on light-emitting properties of the structures. In the case of the structure with Si-rich silicon nitride as active layer (SRN sample), the annealing results in increase of PL intensity with the broadening to short wavelength range. On the contrary, the annealing of the structure with N-rich silicon nitride as active layer (NRN sample) leads to a negative effect on PL intensity. Besides, the PL spectra of NRN sample become narrower after annealing. It should be noted that blue shift of PL maximum after annealing is observed for both SRN and NRN samples.

The energy positions of the PL bands (1.9 and 2.8 eV) are quite far away from the band edges \( E_g \) calculated from the ellipsometry data (3.2 and 5.5 eV for SRN and NRN structures, respectively). This suggests that PL arises from radiative recombination via band tail and/or defect states. The blue shift of PL maximum as well as PL spectrum broadening with \( x \) increasing for SiN\(_x\) alloys are typical features of the emission via radiative recombination of within localized states at the band tail [20, 30]. Indeed, the shift of PL band to blue spectral range for the NRN sample in comparison with SRN one is caused by larger \( E_g \). It was shown that the NRN structure possesses band tails broader than those observed for the SRN structure. It results in fact that PL spectra of NRN structures is broader in comparison with SRN ones.

Surprisingly, the intensity of PL spectra of the as-deposited SRN and NRN structures are comparable. Taking into account the band-tail origin of PL, there are two factors which influence negatively PL intensity of the samples. For NRN structures, the sub-gap excitation \( (E_{\text{exc}} = 3.8 \text{ eV} < E_g = 5.5 \text{ eV}) \) is realized (Fig. 5, b). In this case, the absorption occurs only into the band tail-states, and weak absorption results in weak emission [3]. For SRN structures, the above-gap excitation \( (E_{\text{exc}} = 3.8 \text{ eV} > E_g = 3.2 \text{ eV}) \) is realized (Fig. 5, b). In this case, all photons are absorbed, but photoexcited carriers thermalize toward the demarcation energy that result in increasing probability of non-radiative recombination [3]. It should be noted that an additional blue weak band in PL spectrum of SRN samples can be originated from the band-to band recombination without thermalization process involving band tail states. Thus, despite the same mechanism of luminescence for both structures the measured emission intensities are caused by different reasons. Besides, in the case of triple-layered structures SiO\(_2\)/SiN\(_x\)/SiO\(_2\), the interference effects can also influence their emission intensities [31]. But, discussion of this effect is beyond the scope of our study.
The blue shifts of PL maxima observed for both structures after annealing can be explained by the widening band gap due to the band tail shrinking. In turn, elimination of band tail states is caused by “smoothing” out structural inhomogeneity after annealing. Indeed, band-tail states in the non-stoichiometric SiN films as well as in amorphous SiO films should be related to short-range disorder due to a spatial fluctuation of the elemental composition [32–33]. In the case of PECVD silicon nitride films characterized with high concentration of Si–H bonds, annealing at some regimes can cause an increase of Si dangling bonds via hydrogen effusion which results in increase of localized tail states. However, in the case of LPCVD silicon nitride films (the ones deposited at high temperature), additional annealing can result only in reduction of native defect and dangling bond density as well as degree of structural disorder. Therefore, decrease of band tail spread and band gap increase are expected after annealing in our experiment. It could explain a blue shift of PL maxima. Besides, in the case of SRN, it should increase the absorption of excited photons ($E_{\text{exc}}$ approaches to $E_g$) and, as a result, the PL intensity should increase, too. In the case of NRN structure, the opening band gap should result in reduction of absorption and constriction of band tail energy range involved in the recombination process. As a consequence, the emission and PL spectra should become weaker and narrower, respectively. It is in agreement with the annealing effect on luminescence observed for the SRN and NRN samples.

**Conclusions.** Two triple-layered structures SiO$_2$/SiN$_{1/4}$/SiO$_2$ and SiO$_2$/SiN$_{1/4}$/SiO$_2$ prepared by CVD method emit under the excitation by laser light (3.8 eV) in blue (2.8 eV) and red (1.9 eV) spectral ranges, respectively. The spectral ellipsometry investigation reveals the larger band edge of active nitride layer in the case of SiO$_2$/SiN$_{1/4}$/SiO$_2$ (5.5 eV) in comparison with SiO$_2$/SiN$_{1/4}$/SiO$_2$ (3.2 eV). Based on the calculated Tauc slope, it can be concluded that an energy range occupied by band tail states for the N-rich active nitride layer is larger in comparison with that for the Si-rich active layer. The correlation between features of energy-band structure and light-emitting properties suggests that the origin of luminescence can be mainly attributed to the band-tail recombination. Annealing has different effects on emission of the structures with Si-rich and N-rich active layers. The PL spectra become more intensive and wider for the SiO$_2$/SiN$_{1/4}$/SiO$_2$ structure after annealing. On the other side, annealing results in the degradation of emission intensity and contraction of PL spectra of the SiO$_2$/SiN$_{1/4}$/SiO$_2$ structure. This effect is also explained by the band tail mechanism of radiative recombination.

**Acknowledgments.** This research was partially sponsored by the Belarusian Republican Foundation for Fundamental Research (Grants No. F17KIG-007) and by the National Key R&D Program of China (No. 2016YFE0110700).

**References**


Information about the authors

Ivan A. Romanov – Postgraduate Student of the Department of Physical Electronics and Nanotechnology, Junior Researcher in the Materials and Device Structures at the Micro- and Nanoelectronics Laboratory, Belarusian State University (1, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: romivan@bsu.by

Irina N. Parkhomenko – Ph. D. (Physics and Mathematics), Senior Researcher in the Materials and Device Structures at the Micro- and Nanoelectronics Laboratory, Belarusian State University (5, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: parhomir@yandex.by

Liudmila A. Vlasukova – Ph. D. (Physics and Mathematics), Head of the Materials and Device Structures at the Micro- and Nanoelectronics Laboratory, Belarusian State University (5, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: vlasukova@bsu.by

Natalia S. Kovalchuk – Ph. D. (Engineering), Deputy Chief Engineer, Joint Stock Company “Integral” (121 A, Kazinets Str., 220108, Minsk, Republic of Belarus). E-mail: kovalchuk@yandex.by

Faddei F. Komarov – Corresponding Member, Dr. Sc. (Physics and Mathematics), Professor, Head of the Elionics Laboratory, A. N. Sevchenko Institute of Applied Physical Problems of the Belarusian State University (7, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: komarovf@tut.by

Oleg V. Milchanin – Senior Researcher of the Elionics Laboratory, A. N. Sevchenko Institute of Applied Physical Problems of the Belarusian State University (7, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: milchanin@tut.by

Maxim A. Makhavikou – Junior Researcher of the Elionics Laboratory, A. N. Sevchenko Institute of Applied Physical Problems of the Belarusian State University (7, Kurchatov Str., 220108, Minsk, Republic of Belarus). E-mail: m.mohovikov@gmail.com

Alexander V. Mudryi – Ph. D. (Physics and Mathematics), Chief Researcher, Scientific and Practical Materials Research Center of the National Academy of Sciences of Belarus (19, Brovka Str., 220072, Minsk, Republic of Belarus). E-mail: mudryi@ifttp.bas-net.by

Vadim D. Zhivulkov – Junior Researcher, Scientific and Practical Materials Research Center of the National Academy of Sciences of Belarus (19, Brovka Str., 220072, Minsk, Republic of Belarus). E-mail: vad.zhv@gmail.com

Hong-Liang Lu – Ph. D. (Physics), Associate Professor, Department of Microelectronics at the Fudan University (220, Handan Rd., 200433, Shanghai, China). E-mail: honglianglu@fudan.edu.cn

Information об авторах

Романов Иван Александрович – аспирант факультета радиофизики и компьютерных технологий Белорусского государственного университета, младший научный сотрудник НИЛ «Материалов и приборных структур микро- и наноэлектроники», Белорусский государственный университет (ул. Курчатова, 1, 220108, г. Минск, Республика Беларусь). E-mail: romivan@bsu.by

Пархоменко Ирина Николаевна – кандидат физико-математических наук, старший научный сотрудник НИЛ «Материалов и приборных структур микро- и наноэлектроники», Белорусский государственный университет (ул. Курчатова, 5, 220108, г. Минск, Республика Беларусь). E-mail: parhomir@yandex.by

Власукова Людмила Александровна – кандидат физико-математических наук, заведующий НИЛ «Материалов и приборных структур микро- и наноэлектроники», Белорусский государственный университет (ул. Курчатова, 5, 220108, г. Минск, Республика Беларусь). E-mail: vlasukova@bsu.by

Комаров Фадей Фадеевич – член-корреспондент, доктор физико-математических наук, заведующий лабораторией элионики, Институт прикладных физических проблем им. А. Н. Севченко Белорусского государственного университета (ул. Курчатова, 7, 220108, г. Минск, Республика Беларусь). E-mail: komarovf@bsu.by

Мильчанин Олег Владимирович – старший научный сотрудник лаборатории элионики, Институт прикладных физических проблем им. А. Н. Севченко Белорусского государственного университета (ул. Курчатова, 7, 220108, г. Минск, Республика Беларусь). E-mail: milchanin@tut.by

Моховиков Максим Александрович – младший научный сотрудник лаборатории элионики, Институт прикладных физических проблем им. А. Н. Севченко Белорусского государственного университета (ул. Курчатова, 7, 220108, г. Минск, Республика Беларусь). E-mail: m.mohovikov@gmail.com

Мудрый Александр Викторович – кандидат физико-математических наук, главный научный сотрудник, Научно-практический центр Национальной академии наук Беларуси по материаловедению (ул. П. Бровки, 19, 220072, г. Минск, Республика Беларусь). E-mail: mudryi@ifttp.bas-net.by

Живулько Вадим Дмитриевич – младший научный сотрудник, Научно-практический центр Национальной академии наук Беларуси по материаловедению (ул. П. Бровки, 19, 220072, г. Минск, Республика Беларусь). E-mail: vad.zhv@gmail.com

Хоанг-Ланг Лу – доктор философии (физика), доцент, Школа микроэлектроники Фуданского университета (220, Handan Rd., 200433, Shanghai, China). E-mail: honglianglu@fudan.edu.cn