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Ion-beam formation of light-emitting structures based on silicon nitride layers on silicon

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The paper shows the advantage of silicon nitride for use as a light-emitting element in integrated circuits. Along with this, the chosen methods for obtaining the studied samples enable us to determine all possible causes responsible for radiative recombination. The effect of irradiation with Xe^+ ions of 200 MeV in the dose range $10^9 – 10^{14}$ ions/cm^2 on the optical properties and the structure of silicon enriched silicon nitride (SRN) films deposited on the Si substrate by chemical vapor deposition under low pressure was studied. Based on the Raman scattering (RS) data, it was concluded that the irradiation by 200 MeV Xe ions with a dose of 1×10^{14} ions/cm^2 leads to the dissolution of the amorphous Si phase in the nitride matrix. According to the results of transmission electron microscopy, preliminary irradiation with swift heavy ions (SHI) enhances the phase separation process in the nitride layer with a 22% excess of Si during the subsequent annealing at 1100°C for 60 minutes. The SHI irradiation, followed by the heat treatment, leads to a further increase in the intensity of the photoluminescence (PL) in the spectral range 600–750 nm compared with that in case of annealed films without preliminary irradiation. It is known that radiation in this spectral range is due to Si nanocrystals (Si NCs).

Key words: Si-rich SiN_x/Si, nanoclusters, swift heavy ions, photoluminescence, K-centers.
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1 Introduction

The physical fundamentals of the development of new materials and technologies are currently in the center of attention for many researchers. By controlling the size of the structural components of a material, it becomes possible to produce qualitatively new electronic devices.

The radiative properties of silicon nanoparticles in the visible range are of the considerable interest.

Despite the advances in the study of the light-emitting system "Si nanocrystals in a SiO_2 matrix" [1-3], many authors believe that silicon dioxide is not the best matrix to obtain luminescence. The Si_3N_4 matrix is more preferable for the formation of silicon nanocrystals arrays.

Silicon nitride is one of the main dielectrics in integrated circuits with a band gap of ~ 5.3 eV. This material is more suitable for the development of electroluminescent devices compared to SiO_2 (E_g=8.2eV).

Initially, the interest to the light-emitting properties of silicon nitride arose during the formation of the system "Si nanoclusters in a dielectric matrix" on its basis. Indeed, such a system exhibits intensive luminescence. However, the silicon nitride matrix luminesces itself, and the nature of this radiation is being widely discussed in the literature.

In connection with the foregoing, in this work, it seems appropriate to expand research in the field of creating a light-emitting structure based on silicon nitride enriched with silicon.

2 The structure of crystalline and amorphous Si_3N_4

Silicon nitride is a refractory compound with a predominantly covalent type of bonds. Si_3N_4 is a polymorphic compound that exists in three modifications. In the crystalline state, there are two hexagonal phases: α- and β-Si_3N_4 (Figure 1), with the structure

of phenacite [4]. At temperatures below 1150°C, the β-phase is stable; at higher temperatures, the α-phase is stable. The density of these phases is almost the same 3.1-3.2 g·cm^{-3}.

The cubic γ-modification was obtained at a pressure of 15 GPa and a temperature above 1700°C by the method of laser heating in a diamond cell. In the literature, this modification is referred to as the c-modification. It has a spinel-type structure in which two silicon atoms have an octahedral coordination with six nitrogen atoms, one silicon atom is coordinated tetrahedrally with four nitrogen atoms (Figure 2). It is theoretically shown that this structure should have a high hardness, similar to that of a diamond and c-BN [4-8].

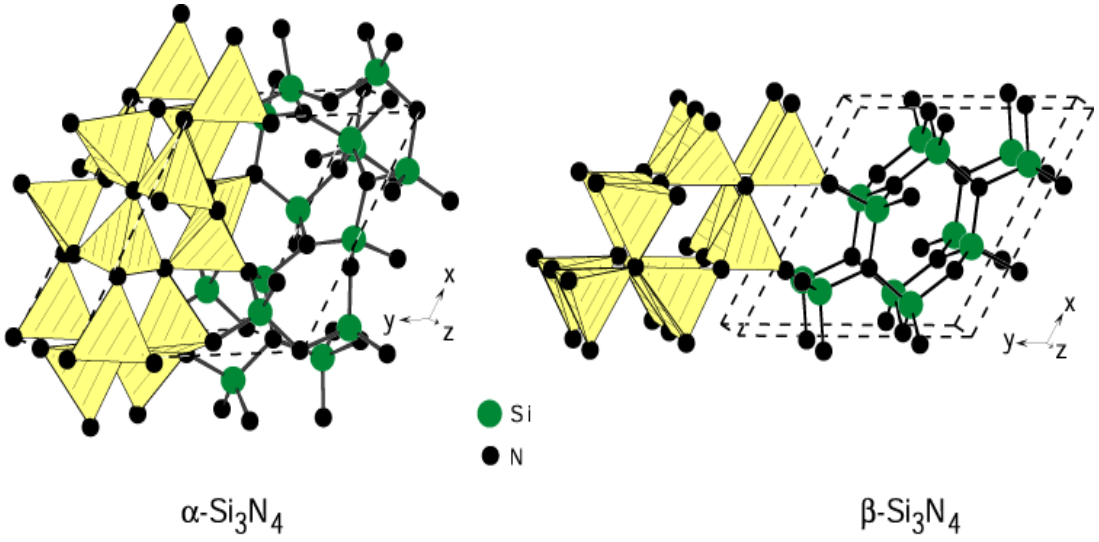


Figure 1 – α-Si_3N_4 and β-Si_3N_4 unit cells

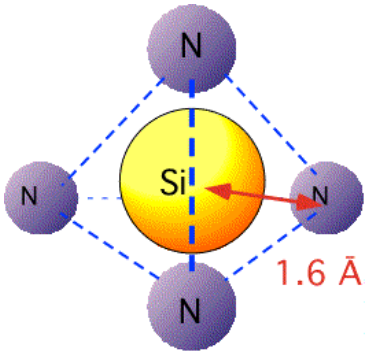


Figure 2 – The main structural unit of Si_3N_4

In the work [ref.] Gritsenko V.A. reports the parameters of elementary cells of α- and β-modifications. The unit cell of α-Si_3N_4 contains 28 atoms (12 Si and 16N) and has lattice constants a = 7.75 Å and c = 5.62 Å. The β-Si_3N_4 cell contains 14 atoms (6 Si and 8 N), the lattice constants, a = 7.71 Å, c = 2.91 Å. By the symmetry, α-Si_3N_4 is referred to P31c space group, β-Si3N4 – P63/m. Both phases have a tetrahedral structure.

Non-stoichiometric silicon nitride (SiN_x) differs from stoichiometric nitride (Si_3N_4) by the amount of excess silicon in the composition (Si_{exc}) [9].

$$Si_{exc.} = \frac{Si_{at.\%}}{Si_{at.\%}+N_{at.\%}} - \frac{3}{7} \qquad (1)$$

3 Luminescence of defects. Edge luminescence

In recent years, a number of studies have appeared in which PL of silicon nitride is associated with radiative transitions between the energy levels of defects [10–15].

In this case, the K- and N- centers act as the main centers of radiative recombination. The K-center is an intrinsic defect in the silicon nitride matrix, which is a silicon atom bound to three nitrogen atoms (N3≡Si •). The presence of K-centers in the silicon nitride matrix can lead to luminescence in the range of 2.5±0.1 eV (478–517 nm). The N-center is a two-coordinated nitrogen atom (Si2 = N •).

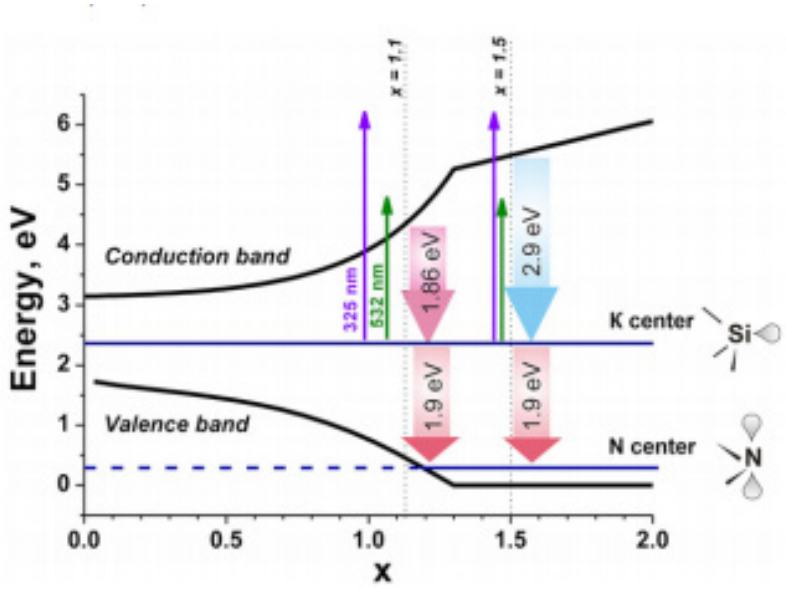
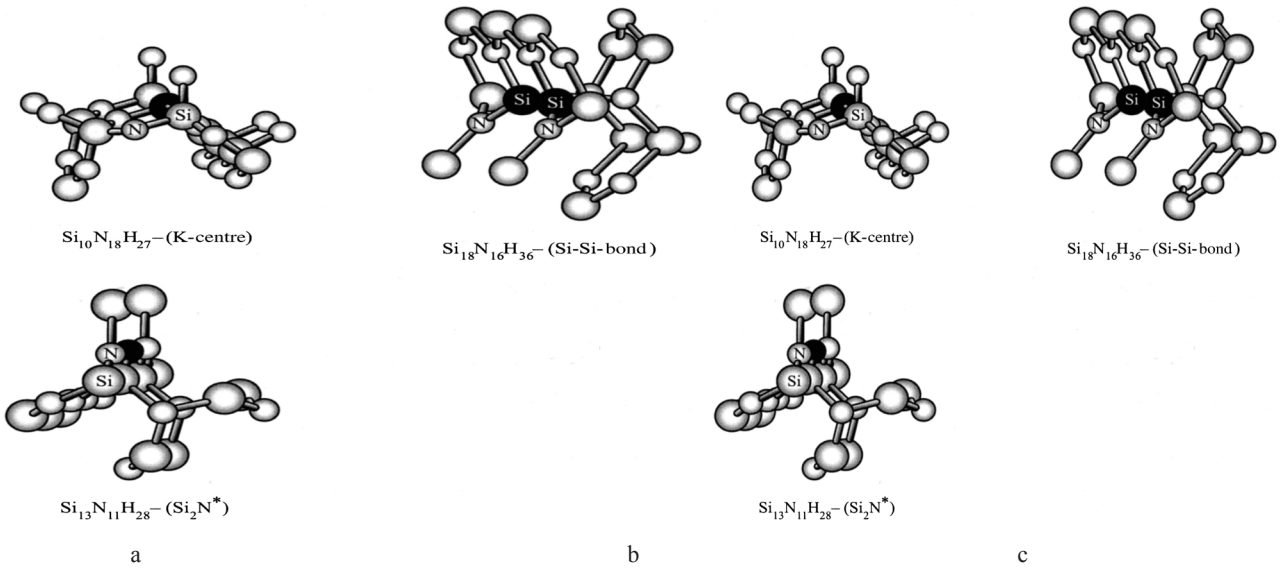


Figure 3 – Model of possible optical transitions based on the Robertson's band diagram for amorphous SiN_x



a – $Si_{10}N_{18}H_{27}$-(K-center); b – $Si_{18}N_{16}H_{36}$-(Si-Si-bond); c – $Si_{13}N_{11}H_{28}$-(Si_2N*)

Figure 4 – Models of defects in silicon nitride.

Models of the centers are shown in Figure 4.

These centers are already present in the initial silicon nitride films, but their number increases noticeably after high-temperature annealing as a result of the dissociation of the N-H bonds [16, 17].

The energy of electronic transitions with the participation of K-centers is 2.1–2.6 eV; therefore, the luminescence in the green region (470–590 nm) is often attributed to the K-centers [18, 19].

In the model of edge luminescence, there is a process of transition of excited carriers to neighboring localized states with lower energy, followed by the light emission. In amorphous materials, there is only a short-range order. Therefore, in these materials, one can observe new phenomena, which are explained by the presence of localized electronic states. The energy levels of these localized states lie near the bands' edges, expanding them into the region of

the bandgap. The formation of localized states in amorphous silicon nitride, in contrast to crystalline states, leads to a higher photosensitivity and the appearance of PL due to radiative recombination of charges localized at the band edges [20-23].

This model was quite successfully applied to explain PL and its shift with increasing concentration of Si in SRN films, in which Si nanoclusters were not detected by high-resolution transmission electron microscopy (TEM). Using this model, researchers managed to explain the position of the PL band and the change in the PL intensity depending on the composition of the nitride film [24-28].

The intensity and the spectral range of PL in silicon nitride films strongly depend on the regimes and conditions of deposition, as well as on subsequent heat treatments.

4 Experiment

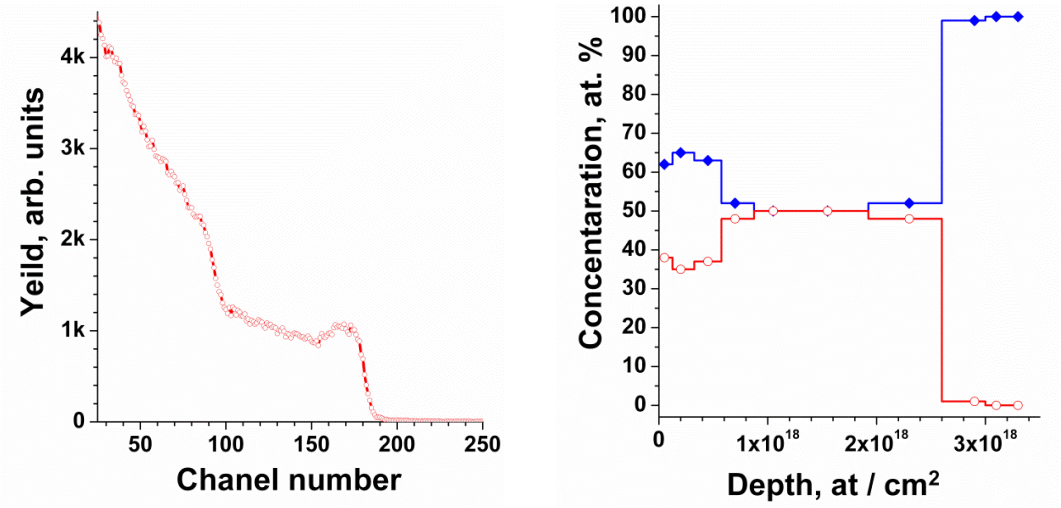
The silicon nitride film was deposited on a Si (100) n-type substrate by chemical vapor deposition at low pressure from a gas mixture of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3). The temperature of the substrate during the deposition was 800°C. The SiH_2Cl_2/NH_3 ratio was changed during the deposition process to form a nitride film consisting of two layers with a different stoichiometric parameter "x". The composition of as-deposited SiNx films was determined by Rutherford backscattering spectrometry using 1.3 MeV He+ ions from the HVE AN-2500 accelerator. It was done to compare the effects of thermal annealing and swift heavy ion irradiation on SiN_x matrix. The refractive index of the nitride film, measured by laser ellipsometry, is 2.22. Samples of SiN_x/Si structure with size of 1×1 cm^2 were cut out and irradiated on a DC-60 cyclotron (Astana, Kazakhstan) with 200 MeV Xe ions in the dose range 10^9-10^{14} ions/cm^2. The structural characteristics of the as-deposited and annealed silicon nitride films were investigated by transmission electron microscopy in the "cross-section" geometry (XTEM) using a Hitachi H-800 microscope operated at 200 keV. Some samples were annealed in a nitrogen atmosphere at 1100°C for 60 min in a furnace with resistive heating.

5 Results and Discussion:

To determine the composition of the initial films, the Rutherford backscattering method was used.

In Figure 5, which represents the dependence of the concentrations of Si and N atoms on the layer depth, one can see the two regions with different Si/N ratio. The surface layer of the nitride is characterized by "x" =0.54 ($SiN_{0.54}$). This corresponds to the silicon excess (Si_{exc}) ≈22%. Beneath this region, there is a layer with "x"=1.0 ($SiN_{1.0}$), where the level of silicon excess is ≈7%.

The existence of the two layers in the studied nitride film is proved by the data of transmission electron microscopy. Figures 6-8 show TEM images of (vertical) cross section of the "deposited sample", as well as samples after heat treatment and after Xe^+ ion irradiation with subsequent annealing.



a b

a – RBS spectrum of SiNx film, b – calculated distribution profiles of Si (blue) and N (red).

Figure 5 – Rutherford backscattering spectrum of the SiN_x film

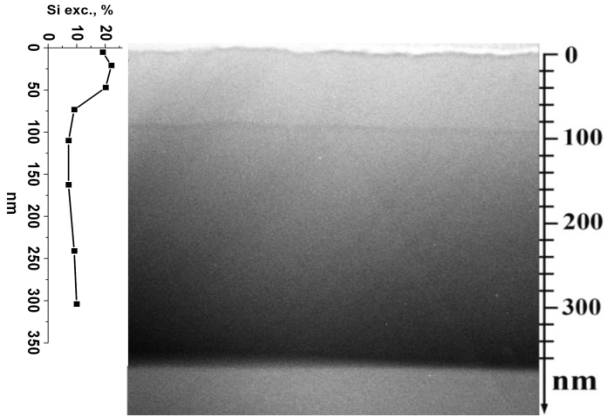


Figure 6 – TEM image of the silicon nitride film. Left part of the TEM image shows the distribution of Si excess (given in %) by depth from RBR data

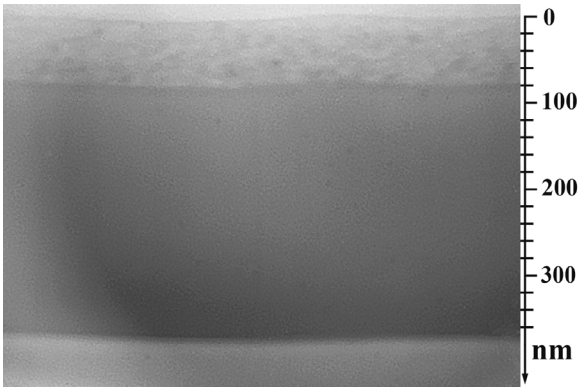


Figure 7 – TEM image of cross section of the silicon nitride film after annealing at 1100°C, 60 min

On TEM image, the two layers are clearly seen: the surface layer with thickness ~80 nm and a layer beneath it – the second one with thickness ~290 nm (Figure 6).

Annealing leads to the formation of inclusions with dark contrast within the surface layer of the nitride (Figure 7).

Taking into consideration the high level of Si excess in this region (≈22%), it can be concluded that these inclusions are crystalline precipitates of Si. It is known that high-temperature annealing of Si-reach SiN_x films leads to the formation of silicon nanocrystals embedded in a nitride matrix [29, 30].

It should be noted the absence of any inclusions in the deeply-lying second nitride layer with excessive Si ≈7%.

Figure 8 shows the effects of heat treatment and the combined processing of SHI irradiation with subsequent annealing on the structure of the nitride film.

It can be seen that in case of the sample irradiated with swift heavy ions before the heat treatment, the inclusions become darker and clearly visible comparing to that in the sample after annealing.

In order to determine the phase state of the studied samples before and after irradiation with swift heavy ions the method of Raman spectroscopy (RS) was used. Figure 9 shows the RS spectra of the sample immediately after the nitride deposition and the samples after irradiation with Xe^+ ions.

The RS spectra of the nitride films contain a few bands with maxima at ~180 and ~ 480 cm^{-1}, as well as weak lines in the frequency region of 300-400 cm^{-1}. These bands are due to the scattering on amorphous phase of Si.

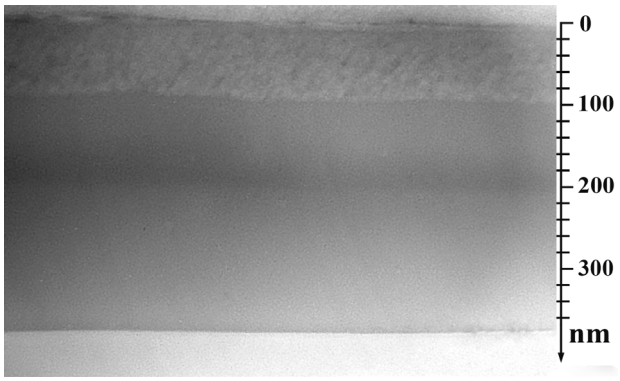
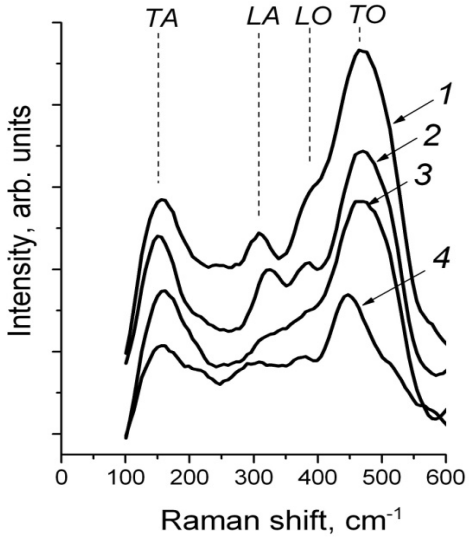


Figure 8 – TEM image of the nitride film after irradiation with Xe^+ (200 MeV, 10^{14}) with subsequent annealing



1 – initial; 2 – 10^9 ions/cm^2; 3 – 10^{12} ions/cm^2; 4 – 10^{14} ions/ cm^2

Figure 9 – RS spectra (λ_{exc}=355 nm) of initial sample and samples irradiated with Xe^+ ions

According to data in works [31, 32], spectra of amorphous Si demonstrate intensive bands of transverse acoustic (TA), longitudinal acoustic (LA) and transverse optical (TO) phonons with maxima at 150, 310 and 480 cm^{-1}, respectively.

The spectra also contain weak signal from the longitudinal optical phonon (LO) in form of a shoulder at 370 cm^{-1}. Thus, it can be concluded that there are amorphous silicon clusters in the samples.

The increase of irradiation dose from 10^9 to 10^{12} ions/cm^2 leads to the decrease of intensity of the bands referred to amorphous phase of silicon. The increase of the ion dose up to 10^{14} ions/cm^2 leads to extinction of the signal from amorphous phase of Si in RS spectrum. It can be explained by the dissolution of amorphous Si clusters within the nitride matrix as a result of SHI irradiation.

Characters of luminescence of amorphous and crystalline silicon nitride differ sufficiently. To study the radiation properties of these samples we analyse photoluminescence spectra (PL), excited by UV-laser with the wavelength of 325 nm (3.8 eV).

For the sample after deposition of nitride film, the photoluminescence spectrum was not registered. Figure 10 shows PL spectra of initial and irradiated samples after annealing, which were registered under UV-laser excitation.

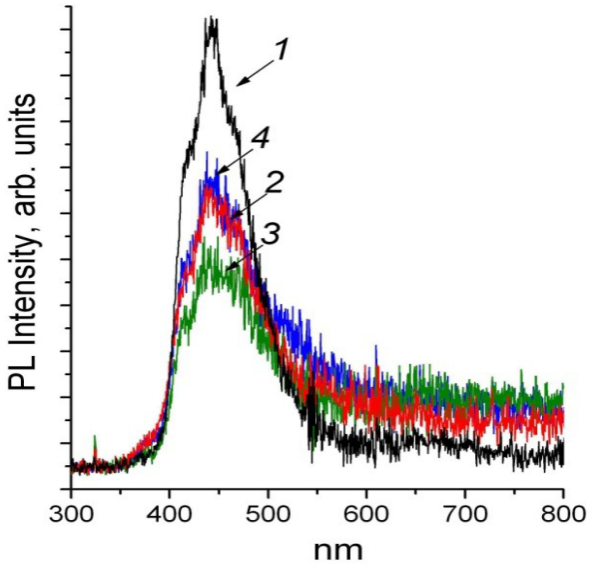
As it is seen in Figure 10, a wide band of a complex form in the green-blue spectral region with the maximum at 440 nm dominates in the spectrum. This band can be connected with radiative recombination of carriers on K- and N- radiative centers. The existence of such defects leads to the emission of photons with energy of 3±0.1 eV (400-427 nm). Thus, the complex form of the green-blue band is explained by the contribution of intrinsic defects of silicon nitride into radiative recombination.

Irradiation with swift heavy ions with doses 10^{12} ions/cm^2 and higher leads to the PL quenching. However, blue radiation can partly be recovered by the heat treatment after irradiation.

For deeper understanding of the light-emitting mechanism of "complex" samples, it is required to study photoluminescence excited with lasers of the different wavelength.

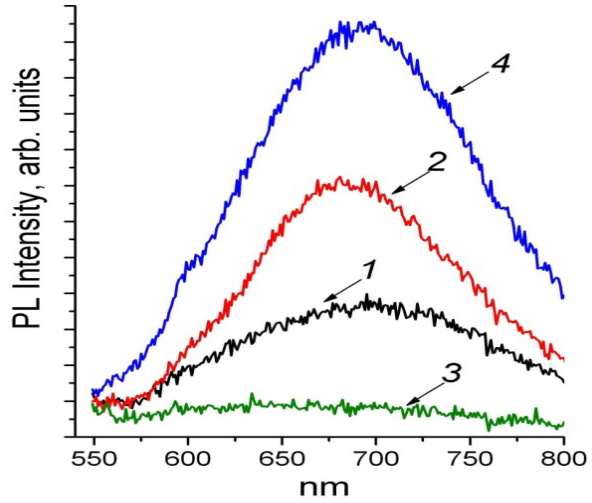
With this purpose, the PL was excited with green laser (λ = 532 nm). Under this excitation energy (2.33 eV) the contribution from Si nanocrystals becomes dominant in the luminescence (Figure 11).

It is seen that in the PL spectrum of the Si-reach silicon nitride films there is a domination of a wide "red" band with the maximum at ~700 nm, which can be referred to the recombination of excitons in Si nanoclusters.



initial; 2 – 10^9 ions/cm^3; 3 – 10^{12} ions/cm^2; 4 – 10^{14} ions/cm^2. PL spectra were obtained under UV-laser excitation (λ = 325 nm)

Figure 10 – PL spectra of initial samples and samples irradiated with SHI Xe^+ and annealed (1000°C, 60 min).



1 – initial sample; 2 – initial sample after annealing (1100°C, 60 min); 3 – sample after irradiation with swift Xe^+ ions with dose 10^{14} ions/cm^2; 4 – sample after irradiation with swift Xe^+ ions with dose 10^{14} ions/cm^2 and subsequent annealing (1100°C, 60 min)

Figure 11 – PL spectra of the Si-reach SiN_x/Si samples, obtained at green excitation (532 nm).

The annealing leads to the increase of PL intensity. This can be explained by the crystallization of Si clusters. As it is seen from Figure 11, SHI

irradiation leads to luminescence quenching. It agrees with the RS data about the dissolution of amorphous Si clusters in the nitride matrix as a result of SHI irradiation.

However, SHI irradiation with subsequent heat treatment leads to the stronger effect of the PL intensity increase, compared to that in case of annealed films without preliminary irradiation. This additionally proves the assumption that preliminary irradiation with heavy ions enhances the process of phase separation in the surface layer of the nitride with high Si excess during the heat treatment.

6 Conclusion

Using Raman spectroscopy it was shown that irradiation with swift heavy Xe ions with energy 200 MeV and dose 1×10^{14} ions/cm^2 leads to the dissolution of amorphous phase of Si in the silicon nitride matrix. By TEM analysis it was revealed that preliminary irradiation with swift heavy ions enhances the process of phase separation in the nitride layer with Si excess of 22% during the annealing at 1100°C for 60 min. It was also shown that SHI irradiation causes the PL quenching in the visible range in the nitride film.

Irradiation with swift heavy ions with subsequent heat treatment leads to the stronger effect of the increase of PL intensity in the spectral range 600-750 nm comparing to that in case of annealed films without preliminary irradiation. It is known that radiation in this spectral range is caused by Si nanocrystals. Therefore, preliminary irradiation enhances the process of crystallization of amorphous Si clusters within the nitride layer with high Si excess during the heat treatment.

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