Increasing the photoluminescence intensity of silicon nitride by forming K and N radioactive centres

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Abstract. Creating a light emitter to transfer an electrical signal by optical way has a great importance in development of optoelectronics. The silicon nitride films studied by photoluminescence techniques, and determined luminescence is associated with presence of an extended zone of tail states. Defects play the main role in radiative recombination for structures annealed at 600 °C and 1100 °C. Photoluminescence (Pl) intensity of obtained films by plasma enhanced chemical vapor deposition is increased after annealing at 600 °C which are related to increased concentration of defects as a result of broken Si–H and N–H bonds. Due to the formation of N-centers through the breaking of N–H bonds, annealing at 1100 °C led to sharp decrease in the luminescence intensity 5 and 3 times for SiN$_{1.1}$ and SiN$_{1.5}$ samples respectively. Replacement of Si-Si bonds by Si-N enhance $E_g$ with increasing stoichiometric parameter, which leads to blue shift edge of photoluminescence maximum. Carbon implantation of silicon nitride films with extra Si obtained by Plasma Enhanced Chemical Vapor deposition at 1x10$^{14}$ cm$^{-2}$, 2x10$^{15}$ cm$^{-2}$, and 1x10$^{16}$ cm$^{-2}$ fluencies, in combination with prolonged annealing at 1100 °C temperature leads to the formation of additional K-centers.

1. Introduction
Silicon nitride and oxide are the key dielectrics in planar silicon technology. To create light-emitting structures “dielectric based on silicon + Si nanoparticles” silicon nitride is preferable to oxide due to lower tunneling barriers and, accordingly, the best conditions for carrier transfer into Si nanoclusters [1-3]. Along with silicon nanocrystals, a contribution to luminescence is made by intrinsic defects of silicon nitride (called K-center, which is a Si atom with a dangling bond an N-center, respectively, an N atom with a dangling bond), as well as recombination between tail states in the band gap.

The main attention focused on silicon enrichment of the silicon nitride films. It should be noted that SiN$_x$> 1.3 films that do not contain silicon nanocrystals (enriched with nitrogen) are also characterized by intense luminescence in the blue region [4-7].

An effective way to increase the luminescent properties of silicon nitride is the method of ion implantation and subsequent heat treatment. The main feature of this method is the impurity concentration may introduce above the solubility limit of the target substance. A number of studies have investigated the photoluminescence of silicon nitride implanted with Ge and Ar and Si ions, as well as rare earth elements [8,9].
Chemically active nitrogen ions can form chemical bonds in the irradiated film and create defective complexes with a silicon deficiency of the N-center type. The energy level of the particles is close to the valence band and so they effectively capture holes, while serving as memory cells. The difficulty is that they become active during high-temperature annealing (more than 1000 °C).

The implantation of silicon nitride with carbon ions stimulates the formation of additional emitting centers, which are appearing growth points for silicon nanoclusters. Moreover, this method makes it possible to set the sizes of nanocrystals, change their concentration, as well as the properties of the "nanocluster - matrix" interface. All of the above makes photoluminescence controllable and increases its intensity.

A feature of this work is the different approaches to the formation of K and N emitting centers and increasing their concentration using the method of ion implantation and subsequent heat treatment.

Thus, new data on the modification of the luminescent properties of silicon nitride by implanting nitrogen ions will be useful from the point of view of the possibility of increasing the luminescent properties of SiN$_x$, and they will provide additional information for interpreting the nature of the luminescence of silicon nitride.

2. Experimental procedure

Synthesis of silicon nitride thin film was carried out by PECVD method. Monocrystalline (100) oriented silicon wafers with diameter 100 mm were used as a substrates. The substrate temperature during deposition was 350 °C, the chamber pressure was - 70 Pa.

It is known, that the «x» parameter for stoichiometric Si$_3$N$_4$ is ~ 1.3. To obtain nonstoichiometric films composition, the ratio of the reacting gases was varied in the experiment. To analyze the distribution of Si and N over the depth of the nitride layers, the Rutherford backscattering (RBS) technique of helium ions with energy 1.3 MeV was used. The ratio of the reacting gases SiH$_4$/N$_2$ was 1/3 and 1/6 for the SiN$_{1.1}$ and SiN$_{1.5}$ samples, respectively. The thickness of the samples measured by Ellipsometry technique was ~ 300 nm.

After the deposition of a nitride film, obtained SiN$_x$/Si structures were cut into 1×1 cm$^2$ size samples. Part of them was annealed in a resistive heating furnace at temperatures of 600 and 1100 °C for 60 minutes in an inert argon atmosphere.

3. Results and discussion

Figure 1 shows PL spectra of initial SiN$_{1.1}$ and SiN$_{1.5}$ samples, which are similar in thickness but differ in stoichiometric composition. The spectra were excited by UV radiation from a He-Cd laser (325 nm). It is clear seen from Figure 1, that the shape of the initial samples PL spectra depends on stoichiometric composition of film. Luminescence spectrum for an excess silicon sample is shifted to longer wavelengths compared to an excess nitrogen sample. The luminescence intensity of initial sample with excess nitrogen SiN$_{1.5}$ significantly exceeds then for SiN$_{1.1}$ sample. In addition, the PL spectrum of sample with an excess nitrogen is wider than for the sample with excess silicon. These differences in PL spectra of two samples can be explained by taking into account the presence of "tail" states at the valence band edges and the conduction band. According to Robertson J., it is quite obvious that the band gap for SiN$_{1.1}$ much less than for SiN$_{1.5}$ sample. The SiN$_x$ band gap can be adjusted by varying the silicon content. Nonstoichiometric SiN$_x$ films consist of random network of Si–N and Si–Si bonds., The replacement of Si – Si bonds by stronger Si – N bonds in SiN$_{x}> 1.3$ layers causes band gap enhancement with an increasing in stoichiometric parameter “x”. Therefore, the elemental composition of the SiN$_x$ film affects its optical properties [10-12].
Thus, expansion of the band gap with an increase in the N/Si ratio leads to blue shift of absorption edge and PL maximum position. In addition, the energy of the exciting laser in our experiment (3.8 eV) significantly exceeds the band gap of SiN$_{1.1}$. When excited electron reached conduction band the "long" process of thermalization occurs, in which an extended zone of tail states is involved. This process increases the probability of no radiative transitions, which negatively effect on the PL intensity. In the case of the SiN$_{1.5}$ sample, the excitation energy is less than the band gap. Absorption occurs only through "tail" states at the edge of the zone. Moreover, the energy range of "tail" states involved in thermalization process and subsequent recombination is much narrower than for the SiN$_{1.1}$ sample. This explains the high probability of radiative transitions and, therefore, more intense photoluminescence signal. The described mechanism of radiative recombination schematically shown in Figure 2.
Figure 2 shows the PL spectra of initial and annealed samples during an hour at 600 °C and 1100 °C. After equilibrium thermal annealing in a quartz tube at 600 °C, a blue shift of the PL maximum and an increase in the luminescence intensity are observed for all samples. The effect of an increase in the photoluminescence (PL) intensity pronounced especially for sample with an excess silicon. Thus, for the SiN$_{1.1}$ sample the luminescence intensity increased by 3.9 times, while for the SiN$_{1.5}$ sample only by 1.22 times. Such an increase in the PL intensity after annealing at 600 °C of the films obtained by the PECVD method can be associated with an increase in the concentration of defects as a result of the breaking of Si–H and N–H bonds. It is known that PECVD films contain a large amount of hydrogen due to the low deposition temperature [13]. These bonds are thermally unstable and their concentration decreases during annealing. Once the bonds are broken, hydrogen atoms can escape from the matrix, leaving the broken bonds. Thus, the dissociation of Si-H bonds leads to the creation of K-centers. It is obvious that the concentration of Si – H bonds is higher for SRN films than for NRN films. This explains the sharp increase in the PL intensity of the SiN$_{1.1}$ sample after annealing at 600 °C, in contrast to SiN$_{1.5}$ sample. Annealing at 1100 °C leads to quenching of luminescence of the initial films, which is most likely associated with decrease in K centers concentration due to nitridization processes (formation of Si-N) at high temperatures. It should also be noted that the high temperature annealing at 1100 °C results in a sharp decrease in luminescence intensity SiN$_{1.1}$ (5 times) than SiN$_{1.5}$ sample (3 times). This can be explained by the fact that sample with an excess nitrogen at high temperature treatment with annealing K centers may occur forming N-centers by breaking N-H bonds. In the case of the SiN$_{1.1}$ sample, N-center level falls below the edge of the valence band and, as a consequence, this center is inactive during the recombination process. For sample with an excess nitrogen the level of N-center is located inside the band gap, which allowing to participate in the emission process.

![Figure 3](image_url)

**Figure 3.** PL spectra of a - SiN$_{1.1}$; b - SiN$_{1.5}$; 1 - initial sample; 2 - annealed at 600 °C; 3 - annealed at 1100 °C

It is worth noting the similar shape and position of the maxima of the PL spectra after annealing at 1100 °C for the samples enriched with silicon and nitrogen. Taking into account the above features of nitride structure, can be explained as follows. After high-temperature treatment, the density and participation in recombination processes of tail states is insignificant. In this case, defects are responsible for emission of annealed films: residual K centers for the SiN$_{1.1}$ sample, as well as K centers and additionally formed N centers for the SiN$_{1.5}$ sample. The levels of the K centers are located in the middle of the band gap of the nitride, while the levels of the N centers are closer to the bottom.
of the band gap. Taking into account the difference in the band gap and the optical transitions for SiN$_{1.1}$ and SiN$_{1.5}$ (for example, the transition "conduction band - K-center" for SiN$_{1.1}$ and the transition "K-center - N-center" for SiN$_{1.5}$) will have the same energy. This is shown more clearly in Figure 3.

Figure 4. Annealed sample at 1100 °C: a) decomposition of the PL spectrum into two Gaussian bands for the SiN$_{1.5}$ sample; b) diagram of the radiative transitions for the SiN$_{1.1}$ sample; c) diagram of radiative transitions for the SiN$_{1.5}$ sample

After annealing at 600 °C for an hour, the PL signal restored. Also, the effect of carbon implantation for the SiN$_{1.1}$ sample with an excess silicon was investigated. It is known that carbon implantation can stimulate the additional formation of radiation centers [14]. The implantation fluences were $1 \times 10^{14}$ cm$^{-2}$, $2 \times 10^{15}$ cm$^{-2}$ and $1 \times 10^{16}$ cm$^{-2}$ in experiment. Figures 4 and 5 show the PL spectra for samples after implantation and subsequent heat treatments. As in the case of samples of implanted nitrogen, implantation of carbon resulted in complete quenching of the photoluminescence signal. Moreover, there are no visible differences in the spectra in samples annealed in the same mode, “pure” and those have additional implantation. In addition, depending on the implantation fluence not revealed. Thus, it clear seen that carbon implantation in combination with subsequent heat treatment at 600 °C does not lead to additional centers, either radiative or without radiative recombination.

Figure 5. PL spectra: 1 - initial sample SiN$_{1.1}$; 2 – SiN$_{1.1}$ sample annealed at 600 °C; 3 - sample after carbon implantation fluence of $1 \times 10^{14}$ cm$^{-2}$; 4 - sample after carbon implantation fluence of $2 \times 10^{15}$ cm$^{-2}$; 5 - sample after carbon implantation fluence of $1 \times 10^{16}$ cm$^{-2}$
Figure 6. PL spectra: a) PL spectra of samples annealed at 1100 °C for one hour; b) PL spectra of samples annealed at 1100 °C for four hours: 1 - samples without implantation; 2 - samples with carbon implantation fluence of $1 \times 10^{14}$ cm$^{-2}$; 3 - samples with carbon implantation fluence of $2 \times 10^{15}$ cm$^{-2}$; 4 - samples with carbon implantation fluence of $1 \times 10^{16}$ cm$^{-2}$.

As seen in Figure 6, the spectrum detected in the minimum fluence ($1 \times 10^{14}$ cm$^{-2}$) and subsequent annealing at 1100 °C for one-hour samples. It noted that at this annealing temperature an additional band appears with a maximum at 450 nm. This indicates that at a given annealing temperature, the presence of carbon leads to additional centers of radiative recombination. To confirm this effect, the duration of annealing at 1100 °C extended to four hours. At a given duration of annealing, a luminescence signal already appears for samples implanted with increased fluencies ($2 \times 10^{15}$ cm$^{-2}$ and $1 \times 10^{16}$ cm$^{-2}$). For sample implanted fluence of $1 \times 10^{14}$ cm$^{-2}$ and annealed for four hours at 1100 °C, the luminescence spectrum is more intense and shifted to the short-wavelength region compare to sample with a similar annealing without pre-implantation. This confirms the participation of carbon atoms in the formation of radiative recombination centers at high annealing temperatures.

4. Conclusions
Firstly, prolonged annealing of SiN$_{1.5}$ and SiN$_{1.1}$ samples obtained by the PECVD method at 600 °C for an hour leads to an increase in the luminescence intensity, on the contrary annealing at 1100 °C for similar duration leads to a luminescence quenching. However, it should be noted that the effect of heat treatments is more pronounced for silicon nitride films with silicon excess than for nitrogen excess. Secondly, it has been demonstrated that for the initial SiN$_{1.5}$ and SiN$_{1.1}$ films, recombination occurs due to an extended zone of tail states, while for annealed films is largely due to the presence of defects (K and N centers). Finally, it shown that high fluence carbon implantation can lead to the formation of additional centers of radiative recombination only in combination with prolonged heat treatments at high temperatures (~ 1100 °C). At a lower annealing temperature (600 °C), carbon pre-implantation does not affect to the emission properties of silicon nitride.

It opens the possibility of designing materials with adjustable band gap by forming a Si quantum dots in dielectric matrix, which absorbs photons within certain energy ranges. It can be used in photovoltaics for solar cells of the third generation. Another possible application is an optical data transmission system in an integrated circuit.

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