Fadei KOMAROV[1], Ludmila VLASUKOVA[1], Iulia PARKHOMENKO[1], Paweł ŻUKOWSKI[2],
Oleg MILCHANIN[1], Alexander MUDRYI[3], Vadim ŻHYVULKA[3], Jerzy ZUK[4], Przemysław KOPYCIŃSKI[4],
Danatbek MURZALINOV[5]

Belarusian State University; Belarus (1), Lublin University of Technology, Poland (2), Scientific and Practical Materials Research Center, National Academy of Sciences of Belarus, Belarus (3), Maria Curie-Sklodowska University, Poland (4), L.N. Gumilyov Eurasian National University, Astana, Kazakhstan (5)

Origin of visible photoluminescence of Si-rich and N-rich silicon nitride films

Abstract. Amorphous Si-rich and N-rich silicon nitride films were deposited by plasma-enhanced chemical vapour deposition (PECVD) and, subsequently, annealed at 600, 800 and 1100°C in Ar ambient. The different dependences of photoluminescence (PL) spectra on annealing temperatures were revealed for Si-rich and N-rich SiN_x films. The origin of PL is discussed on the basis of band diagram depending on the x value and taking into account radiative defects in amorphous SiN_x films. The PL spectra transformation after thermal treatment is explained by structural modification via competing process of creation and annealing defects.

*Streszczenie. Amorficznie wzbogacony Si i N warstwy azotku krzemu zostały utworzony przez wspomagane plazmą osadzanie chemiczne z fazy gazowej (PECVD), a następnie wygrzany w temperaturze 600, 800 i 1100°C w atmosferze Ar. Różne zależności widm fotoluminescencji (PL) w temperaturze wygrzewania zostały ujawnione dla wzbogaconych Si i N warstw SiN_x. Pochodzenie PL omówiono w oparciu o schemat pasma w zależności od wartości x, z uwzględnieniem defektów radiacyjnych amorficznej warstwy SiNx. Transformacji widma PL po obróbce cieplnej jest wyjaśniona przez strukturalną modyfikację spowodowaną konkurencyjnymi procesami tworzenia się i wygrzewania defektów. (**Pochodzenie widocznych fotoluminescencyjnych warstw azotku krzemu wzbogaconych Si i N**).*

Keywords: visible photoluminescence, spectra transformation, amorphous films, silicon, light-emission.
Słowa kluczowe: widma fotoluminescencyjne, widma transformacji, amorficzne warstwy, emisja światła.

Introduction

Amorphous silicon nitride films have been long used for a wide variety of applications in microelectronics as the gate dielectric in thin film transistors, charge storage medium in non-volatile memories. Recently, the interest in SiN_x as an appropriate material for future generation of optoelectronic devices has risen again. This application requires an understanding of the nature of light-emission properties in view of fundamental interest and practical application. There are a lot of publications devoted to explanation of visible luminescence of silicon nitride films. The most of them are focusing on the PL of Si-rich SiN_x to fabricate light-emitting structure «Si nanoclusters in wide-gap matrix». In this case, a visible luminescence is explained by quantum confinement effect of crystalline or amorphous Si nanoclusters [1-4]. In other cases, the luminescence has been attributed to defect states [5-7] or radiative recombination between localized band-tail states [8-11]. Thus the origin of photoluminescence (PL) of SiN_x films is still an object of controversy.

In this study we present an investigation of PL for both Si-rich and N-rich silicon nitride films. The comparison of PL dependence on annealing temperature for SiN_x films with different composition will be useful for understanding nature of PL.

Experimental

The Si-rich and N-rich silicon nitride films were deposited on n-type (100)-oriented Si substrates by plasma-enhanced chemical vapor deposition (PECVD) at 350°C using the gaseous mixture of silane (SiH_4) and nitrogen (N_2) as precursors. The thickness of nitride films measured by laser ellipsometry was ~300 nm. The ratio of reagent gases SiH_4/N_2 was 1/3 for Si-rich and 1/6 for N-rich silicon nitride films. The composition of as-deposited SiN_x films was determined by Rutherford backscattering spectrometry using 1.3 MeV He^+ ions from HVE accelerator. The samples with the size of 1×1 cm^2 were cut out of wafers and annealed in argon ambient at 600, 800 and 1100°C for 60 min in a resistance furnace. PL spectra were recorded at room temperature in the spectral range of 350–800 nm using a UV He–Cd laser source with λ = 325 nm and in the range of 600 – 900 nm using a Nd laser source with λ = 532 nm.

Results and discussion

The stoichiometric parameter "*x*" for SiN_x films was calculated from Rutherford backscattering data. It is known, the parameter "*x*" for stoichiometric silicon nitride Si_3N_4 is equal to 1.3. In our experiment this parameter is equal 1.1 and 1.5 for Si-rich and N-rich silicon nitride films, correspondingly. Further, these samples are labeled $SiN_{1.1}$ and $SiN_{1.5}$.

Fig. 1 shows the PL spectra of $SiN_{1.1}$ and $SiN_{1.5}$ as-deposited and annealed samples. The inset in Fig.1 shows PL spectra excited with 532 nm laser line. As can be seen from Fig. 1 a, there is a clear difference between the PL spectra of Si-rich and N-rich as-deposited samples. The PL maxima lie in red region for Si-rich sample and blue region for N-rich sample. The photoluminescence excited by UV-laser intensity is higher for as-deposited $SiN_{1.5}$ sample (Fig.2a). The red PL excited by green laser is recorded only for $SiN_{1.1}$ sample.

Some structural features of amorphous silicon nitride should be discussed to interpret PL spectra. Firstly, silicon nitride, as other amorphous material, is characterized by absence of long-range order and localized electron states. The nonstoichiometric SiN_x films consist of a random network of Si-N and Si-Si bonds. For $SiN_{x<1.3}$, band edges are formed by the Si-Si states. For $SiN_{x>1.3}$, the replacement of Si-Si bonds by stronger Si-N bonds causes the band gap to increase with increasing "*x*" [12]. Thus, the band gap of the SiN_x can be adjusted by changing the silicon content. Optical properties are very sensitive to the chemical composition of the film. It is known, that absorption edge and PL maximum shift toward higher energy with the increase of N/Si ratio [8-10]. Therefore, a visible emission via radiative recombination between localized band-tail states can be controlled by varying the film composition.
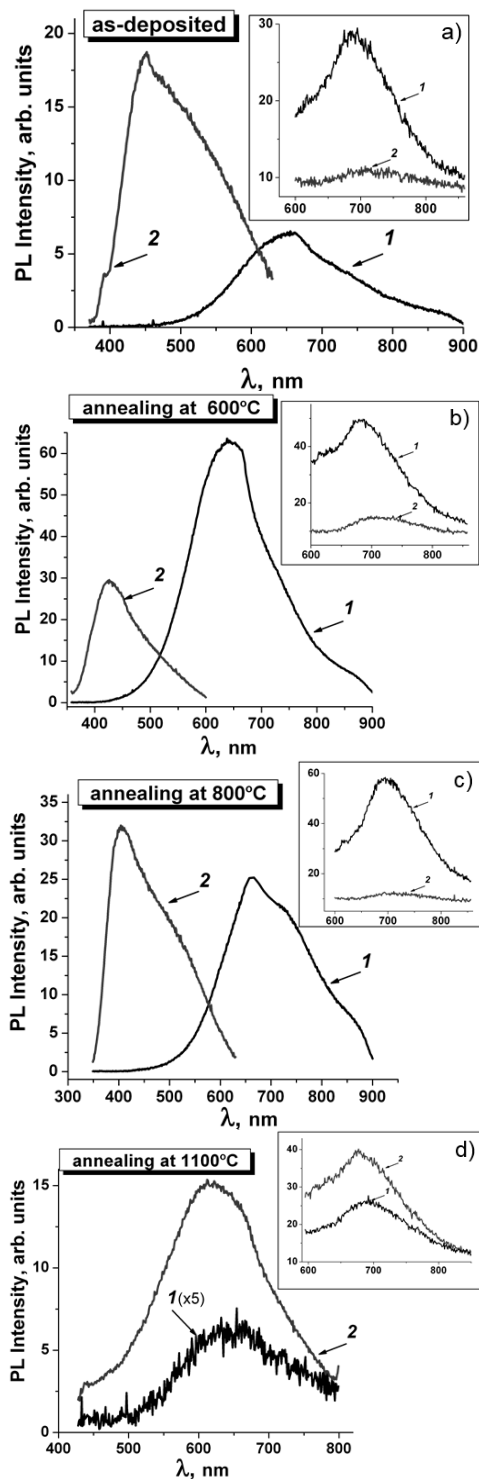
Fig.1. PL spectra of as-deposited (a) and annealed at 600°C (b), 800°C (c) and 1100°C (d) Si-rich $SiN_{1.1}$ (curve 1) and N-rich $SiN_{1.5}$ (curve 2) silicon nitride films.

Secondly, there are many charge trapping centers in silicon nitride film identified as different types of defects. The dominant trap for holes and electrons in amorphous silicon nitride is the Si-dangling bond back bonded to three N atoms, $\equiv Si^0$ [13] termed the K-center. The presence of K-centers with unpaired electron in as-deposited Si-rich as well as N-rich silicon nitride films has been proved by electron paramagnetic resonance [14-15]. The energy level of K-center is located in the middle of the silicon nitride band gap [12]. The amphoteric nature of K-center (capture electrons as well as holes) causes the electronic transitions

between K-centre and conduction band $E_c \rightarrow \equiv Si^0$ and K-centre and valence band $\equiv Si^0 \rightarrow E_v$.
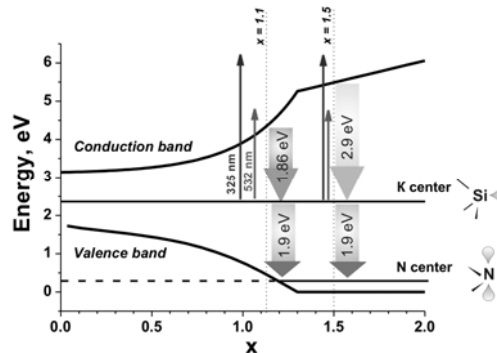

Fig.2. Model of possible optical transitions based on Robertson's band diagram for amorphous SiN_x showing the K center at mid-gap and the N center just above valence band.

Fig. 2 demonstrates a model for PL mechanism based on the Robertson's band diagram for amorphous SiN_x [12]. This band diagram shows band gap widening with increasing N fraction (or parameter "x") and the location of K-center energy level at mid-gap, and N-center energy level just above valence band. As can be seen, an energy level difference between K-center and conduction band amounts to 2.9 eV (430 nm) at x=1.5 (N-rich film) and 1.85 eV (670 nm) at x=1.1 (Si-rich sample). It correlates with positions of PL maxima for Si-rich and N-rich films observed in our experiment. Therefore, we suppose that the PL bands for both as-deposited samples (Fig.1a) are closely related to the electronic transitions between the K-center level and the conduction band tail states.

The laser energy 325 nm (3.82 eV) is high enough to excite the electrons from K-center to conduction band tail for both samples. However, the excitation laser energy 3.82 eV is significantly exceeds transition energy between K-center and conduction band for Si-rich sample. In this case of above-gap excitation, photoexcited carriers thermalize toward the demarcation energy, diffuse and recombine via nonradiative process [8, 10]. It explains that PL intensity of $SiN_{1.1}$ sample is less than one of $SiN_{1.5}$ sample at UV excitation.

On the other hand, the green laser energy 2.3 eV is not high enough to excite electron transition between K-center and conduction band for N-rich $SiN_{1.5}$ film. In the case of Si-rich $SiN_{1.1}$ sample, the excitation energy of green laser exceeds gap between K-center and conduction band. That's why noticeable light emission excited by green laser is recorded only for the $SiN_{1.1}$ sample.

It should be noted that asymmetrical shape of PL spectra is also can be related to recombination via band tail states [10]. It additionally proved our assumption that observed PL can be attributed to electron transitions between K-center and band tail states.

The annealing at 600°C (Fig.1b) and 800°C (Fig.1c) results in increase of PL intensity without any significant changes in spectral shape. It should be noted that the effect of increasing PL intensity via annealing is more significant for Si-rich sample. Besides, the PL intensity of the Si-rich sample annealed at 600°C is higher than for the sample annealed at 800°C.

The effect of increasing PL intensity can be caused by increase of defect concentration via film dehydrogenization during the annealing at 600 – 800°C. It is known, PECVD films contain large amounts of hydrogen bonded to silicon as Si-H and to nitrogen as N–H due to low deposition temperature. These bonds are thermal unstable, and their

density decreases during the high-temperature post-deposition annealing [16]. The dissociating of Si–H bonds can be resulted in formation of K-centers. It is obvious that concentration of Si–H bonds is higher for Si-rich films, than for N-rich. It explains expansive increase of PL intensity for $SiN_{1.1}$ sample which is not observed for $SiN_{1.5}$ sample. Despite weaker PL for as-deposited Si-rich films, PL intensity of Si-rich sample exceeds one of N-rich sample after annealing at 600°C.

It is known that density of Si–H bonds decreases with increasing annealing temperature [16]. However, dissociating of Si–H bonds not always results in creation of K-centers. If Si-H and N-H are spatially correlated, Si-H bonds will react with N-H bonds to form Si-N bonds, which are not precursors to the K-centers [16]:

(1) $Si - H + H - N + heat \rightarrow Si - N + H_2$
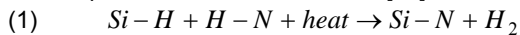
Also, K-centers created via Si-H bond breaking can react with N-H bonds to form Si–N bonds [16]:

(2) $K - center + H - N + heat \rightarrow Si - N + H$
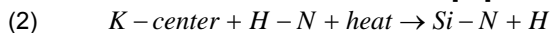
It is obvious that these processes not result in increase of PL intensity. The probability of these reactions increases with increase of annealing temperatures. It explains the weakened PL intensity of the $SiN_{1.1}$ sample annealed at 800°C in comparison with the PL intensity of $SiN_{1.1}$ sample annealed at 600°C.

Annealing at 1100ºC for 1 hour results in decrease of PL signal for both samples. The PL excited by UV as well as green laser is stronger for N-rich sample. PL maxima for annealed samples don't depend on composition of the films and lie in red spectral range for both Si-rich and for N-rich samples.

The PL quenching after annealing at 1100ºC can be assigned to decrease in K-center concentration due to the reaction (1) and (2) and decreasing density of band tail states due to reduction of structural disorder during annealing. It is known, the thermal energy to dissociate the Si-H bonds is lower than to dissociate N-H bonds. Therefore, it is expected that concentration of N-center will increase with annealing temperature via breaking N-H bonds [16]. Considering the band diagram (Fig.3), the level of N-center is located above the valence band for $SiN_{1.5}$ and can participate in radiation recombination. In the case of $SiN_{1.1}$ sample, N-center level falls below the valence band edge and N-center is hence inactivated as recombination center. It can be supposed that weak PL can be attributed to capture a hole from valence band (for $SiN_{1.1}$) or N-center (for $SiN_{1.5}$) to K-center. It explains similar position of PL maxima in red range for both Si-rich and N-rich films as shown in Fig.2.

Conclusion
PL of Si-rich and N-rich silicon nitride films has been investigated. PL spectra of as-deposited samples depend on composition of the films. The PL maxima of Si-rich and N-rich films are located in red and blue spectral range, correspondingly. The PL intensity can be significantly increased after annealing. The most preferable annealing temperatures are 600ºC for $SiN_{1.1}$ film and 800ºC for $SiN_{1.5}$ film. The annealing at 1100ºC results in PL quenching, and PL maxima lie in red region for both Si-rich and N-rich sample.

Our results are in agreement with the Robertson's widening diagram for SiN_x alloys. Positions of emission bands correspond to the transitions between K-center level and band tail states. The behaviour of PL spectra after thermal treatment is explained by competing process of creation and annealing defects. Thus, the PL can be attributed to optical transitions between band tail states and the native defects in amorphous silicon nitride films.

Authors: *Fadei Komarov, Ludmila Vlasukova, Iulia Parkhomenko, Oleg Milchanin, Belarusian State University; Minsk, Belarus; e-mail: komarovF@bsu.by, Paweł Żukowski, Lublin University of Technology, Lublin, Poland, Alexander Mudryi, Vadim Żhyvulka Scientific and Practical Materials Research Center, National Academy of Sciences of Belarus, Minsk, Belarus, Jerzy Żuk, Przemysław Kopyciński, Maria Curie-Sklodowska University, Lublin, Poland, Danatbek Murzalinov, L.N. Gumilyov Eurasian National University, Astana, Kazakhstan*

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