Emission Dependent on composition of Si-rich-SiNₓ Films obtained by PECVD

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Abstract

Silicon-rich silicon nitride films with different stoichiometry were grown on silicon substrate using the plasma-enhanced chemical vapor deposition. The excess silicon content in the films was monitored via a variation of the NH₃/SiH₄ gas flow ratio from 0.45 up to 1.0. Morphology and luminescence properties of the films were studied by means of atomic force microscopy (AFM) and photoluminescence (PL) methods. High-temperature annealing was employed to produce the silicon nanocrystals in the films and to enhance the photoluminescence in the range of 1.6-3.0 eV. The PL spectrum was found to be complex due to the contribution of several radiative channels in emission process. It was determined that their competition leads to the non-monotonous variation of total PL peak position with the increase of the Si excess content. It was observed that the shape of PL spectra depends on an excitation wavelength. The ways to control the PL emission is proposed based on the discussion of the PL mechanism.

Keywords Silicon nanocrystals, silicon nitride, plasma-enhanced chemical vapour deposition, photoluminescence.

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1. Introduction

Silicon nano photonics is attracting the significant attention in the field of development of silicon-based photonic devices that allows efficient data transfer at low cost as compared to conventional optoelectronics devices. Bandgap engineering of Si-based materials through the control of the distribution of Si nanocrystals (Si-NCs) offers future applications of these materials in optoelectronics and photovoltaics.

Si₃N₄-based materials have been extensively investigated because of their inherent advantages in the chemical, mechanical and optical properties [1]. The creation of the Si-NCs in a silicon nitride host offers the several key advantages over silicon oxide [2]. Silicon nitride is a more promising matrix for Si-NCs due to its structural stability upon microelectronic fabrication processing. Favorable electrical properties resulting from the lower tunneling barriers allow the better transport of electrons and holes into Si-NCs formed in silicon nitride [3]. In addition, Si-NCs coordinated with oxygen atoms are subject to charge trapping at the interface, which effectively limits the emission quanta from such Si-NCs to less than 2 eV.
Since Si- NCs coordinated with nitrogen atoms do not exhibit the same limitation, the emission has been demonstrated to occur at energies across the entire visible spectrum [3,5,6]. The process of a Si- NCs formation in silicon nitride is also more favorable due to the much lower annealing temperature required for an achievement of bright luminescence compared to silicon oxide [7, 8]. However, the Si- NCs formation in the films has been found to occur in a more complex process, with the appearance of both amorphous and crystalline clusters and a strong dependence on both deposition and processing conditions [3,9,10].

In this work, the morphology and luminescent properties of Si-rich-silicon nitride films grown by plasma-enhanced chemical vapor deposition (PECVD) were investigated versus excess silicon content. The detailed analysis of the results allows getting insight in the nature of emission and excitation processes in the films.

2. Experimental details
Si-rich silicon nitride films were grown by the PECVD technique on the p-type silicon (100) substrates. To achieve different stoichiometry in the films, the NH3/SiH4 (99.9999%) gas flow ratio (R) was varied in the range of R=0.45–1.0 keeping SiH4 flow constant at 14 sccm. The working pressure, the plasma power and the growth temperature were 0.5 Torr, 20 W, and 350 °C, respectively. Thermal annealing at 1100 °C for 30 min in flowing nitrogen was applied to produce the Si-NCs in the films [11].

Morphology and luminescence properties of the films were studied by means of atomic force microscopy (AFM) and photoluminescence (PL) methods. A Nano-Scope IIIa was applied for AFM measurements at room temperature in tapping and covered modes. The PL spectra were excited by either a 325-nm (3.82eV) line of a He-Cd laser or by a 488-nm (2.54eV) line of an Ar+ laser. The power of laser beam was about 80 mW. More details about the PL experiment can be found elsewhere [12, 13]. To investigate the evolution of PL spectra with temperature of measurement in the range of 20-300 K, the samples were mounted in a closed-cycle He cryostat.

3. Experimental results and discussion
AFM images of studied films with different R parameters have been presented in figure 1. The film morphology varies versus R: the film roughness decreases from 13.8-14.8 nm (at R=0.71-1.0) down to 7.8 nm (at R=0.50). It was shown early [14] using the X-ray diffraction study that the SiNx matrix is characterized by the hexagonal Si3N4 phase in annealed films obtained at R=0.7-1.0 with the NC size of 26-30 nm. The NC size in SiNx matrix falls down to 2.8-3.0 nm (at R=0.63) and, finally, the films became amorphous at R=0.45-0.50 [14]. Thus, the change of roughness detected at AFM study is related, apparently, to the change of crystallinity of the SiNx matrix versus R parameters.

Room-temperature PL spectra of annealed samples demonstrate the variation of their shape with excitation light energy (Fig.2 and Fig. 3). The comparison of Fig.2 with Fig.3 shows that at the higher excitation energy, the broader PL spectrum was observed demonstrating the appearance of asymmetry in the higher energy side (Fig.2). The total PL peak position has shifted also towards the higher energies.

When the films are excited by the 2.54-eV light, only broad PL band was detected and with R increasing its peak position shows the tendency to shift gradually from 1.6 eV (R=0.45) to 2.2 eV (R=0.83) (Fig.3). The PL intensity varied non-monotonously with R, demonstrating the highest intensity for the films grown with R=0.59-0.67. This behavior of PL spectra indicates the presence of multiple luminescence centers in the films. The spectra
can be considered as a superposition of three components peaked at 1.6-1.7 eV (B1) 1.9-2.0 (B2) and at 2.2-2.3 eV (B3) (Fig.4a).

![Figure 1](image1.png)

**Figure 1** AFM images obtained in the films prepared at different R parameters.

![Figure 2](image2.png)

**Figure 2** PL spectra of annealed films versus R measured at 3.82-eV excitation light energy. The spectra were normalized on the intensity of their maximum.

The detection of PL spectra under 3.82-eV excitation light supports this assumption. The PL spectra became more complex at higher excitation energy demonstrating also the highest intensity for the films grown with $R=0.59-0.67$. The total PL peak position does not demonstrate a systematic shift with R varying (Fig.2). The analysis of PL spectra has revealed that all spectra excited by 3.82-eV light can be decomposed on four PL bands with the maxima situated at 1.7-1.8 eV (B1), 2.0-2.2 eV (B2), 2.4-2.5 eV (B3) and 2.9-3.0 eV (B4) (Fig.2 and Fig.4b). It is obvious that three former components are the same as those observed
under 2.54-eV excitation light described above that demonstrate as well the slight high energy shift of the PL peak position with excitation energy increasing.

![Normalized PL Intensity (ar. un.) vs. Energy (eV)](image)

**Figure 3** PL spectra of annealed films versus R measured at 2.54-eV excitation light energy. The spectra were normalized on the intensity of their maximum.

The investigation of PL temperature dependences (Fig.5) has showed that only the PL band B1 demonstrates the shift of the PL peak position with cooling similar to the shrinkage of the Si band gap (Fig.5). The B1 peak position at 20K was found to be at about 1.96 eV and its shift to 1.91eV at 300K. Simultaneously, the other PL peaks B2, B3 and B4 do not change their peak position with cooling. Taking into account the spectral position of the PL component B1 and its behavior with temperature variation, one can assume that this PL emission is due to the exciton recombination in the Si-NCs [15].

However, one cannot rule out that with cooling the intensity of the B2 component increases synchronously with the intensity of B1 component. This fact can be explained by the close location of corresponding emitting centers to the Si-NCs interface that allows an efficient energy transfer between them to be realized. At the same time, based on the model proposed in [16, 17], the B3 (2.4-2.6eV) and B4 (2.9-3.0 eV) PL components can be ascribed to the Si dangling bonds (so called K^0-centered, ~2.40 eV) and the nitrogen dangling bond levels (N^+ and N_2^0, ~3.0 eV). These latter can be excited only by the high-energy excitation light (3.82 eV) as demonstrated in Fig.2. Thus the variation of excitation energy and the temperature of measurements allowed us to detect the different radiative centers in the films. It is seen that for the films fabricated with $R \leq 0.56$ and $R \geq 0.63$ the main contribution into PL spectra is given by the host defects, whereas for $R = 0.56-0.63$ the Si-NCs form the main radiative channel.
Figure 4 Deconvolution of PL spectrum excited by energy 2.54eV(a) and 3.82eV(b) measured at 300 K for the film grown with R=0.59.

Figure 5 The evolution of the PL spectrum of the same film with temperature of measurement in the range 20-300K. Excitation energy is 3.82 eV.

Conclusions
Silicon-rich-silicon nitride films with different stoichiometry were fabricated by the PECVD method on the Si substrates. The investigation of PL spectra using different excitation energies and temperatures gives the possibility to extract the information about the contribution of different radiative channels in the PL process. The optimal fabrication conditions for the bright emission were determined.

Acknowledgements The authors would like to thank the SIP-IPN, Mexico (projects 20160285), as well as the National Academy of Sciences of Ukraine and Center of National Scientific Research (CNRS) of France for the financial support.
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