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Strong Room-Temperature Photoluminescence of Si-rich and N-rich Silicon-Nitride Films

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Si-rich and N-rich silicon nitride films were deposited at low temperature 300 °C by using plasma-enhanced chemical vapor deposition (PECVD). The optical and structural properties of these films have been investigated by ellipsometry, Rutherford backscattering (RBS), transmission electron microscopy (TEM), Raman spectroscopy (RS) and photoluminescence (PL). The formation of silicon clusters in both Si-rich and N-rich silicon nitride films after annealing at 900 °C and 1000 °C for hour in N_2 ambient has been shown by TEM. Dependency of PL spectra on stoichiometry and post-annealing temperature was analyzed. The contribution of Si and N-related defects in emitting properties of Si-rich and N-rich SiNx has been discussed.

Keywords: Non-Stoichiometric Silicon Nitride, PECVD, Thermal Annealing, Si Clusters, Photoluminescence, N-related Defects.

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1. INTRODUCTION

The creation of light emitter based on silicon technology is still actual problem. Well-known as insulating layer silicon nitride is promising candidate for Si-based full-color light-emitting devices. In spite of numerous works devoted to investigation of light-emission properties of silicon nitride, nature of PL is still not unambiguously understood. Some authors assign PL to the quantum confinement effect of Si nanoclusters in silicon nitride [1, 2], while others attribute it to radiative defects [3, 4] or band tail recombination [5, 6]. The most of these works are devoted to investigation of Si-rich SiN_x (x<4/3), because it is an initial material for formation of system "Si nanocrystals in dielectric matrix". The aim of this paper is an investigation of structural and optical properties of both Si-rich and N-rich silicon nitride films. The comparison of properties of such types of SiN_x will be useful for understanding nature of PL.

2. EXPERIMENTAL

In this study, SiN_x films were deposited on n-type Si(100) substrates by PECVD using the gases of monosilane (SiH_4) and ammonia (NH_3) as the precursors. The deposition temperature was 300 °C. The stoichiometric composition depended on the ratio NH_3/SiH_4 in the gaseous mixture. The thickness and refractive index were measured by ellipsometry. Then the samples were annealed in N_2 at 900 - 1100 °C for 1 hour using resistance furnace. The depth distribution of N and Si atoms and stoichiometric composition SiN_x were analyzed with RBS spectrometry using 1.3 MeV He^+ ions. Raman spectra in a back-scattering geometry were measured using micro-Raman setup Integra Spectra with excitation wavelength of 473 nm at room temperature. Structural properties of as-deposited and annealed SiN_x films were investigated with plan-view (PV) technique using a 200 keV-Hitachi H-800 electron microscope. The PL spectra were measured at room temperature using the 325 line of a He-Cd laser as the excitation source.

3. RESULTS AND DISCUSSION

3.1 Structural properties of SiN_x films

Figure 1 shows the profiles of Si and N conce?tration obtained from measured RBS spectra for as-deposited samples. It is known that ratio of Si/N atoms is equals to 0.75 for stoichiometric silicon nitride. It corresponds to 42.86 at.% Si and 57.14 at.% N. In our experiment calculated concentrations of Si atoms are about 50 at.% and 40 at.% for the Si-rich and N-rich silicon nitride respectively. The stoichiometry parameter "x" and the excess of Si in silicon nitride were calculated from RBS data using formula from [7]:

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

The parameter "x", the excess of Si and data obtained from ellipsometry (the refractive index and the thickness) are shown in Table 1.

Fig. 2 shows the PV TEM micrographs of the as-deposited and annealed samples SiN_x. As can be seen the furnace annealing at 900 °C and 1000 °C results in the formation of precipitates in both samples. It should be noted that the density of precipitates in Si-rich sili-

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con nitride is higher in comparison with the N-rich silicon nitride.

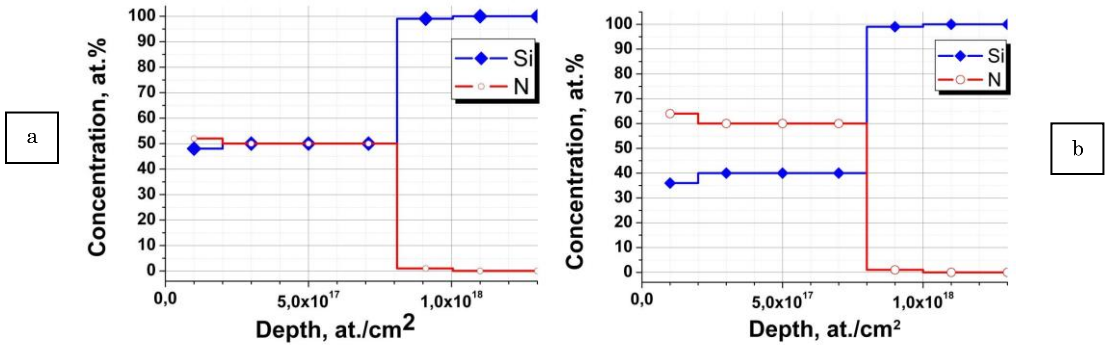

Fig. 1 – Depth distributions of Si and N atoms calculated from RBS spectra for the as-deposited Si-rich (a) and N-rich (b) silicon nitride films.

Table 1 – Parameters of as-deposited SiN_x/Si samples obtained from RBS and ellipsometer data

Samples	Refractive index *n*	Thickness, nm	Stoichiometric parameter "x"	Silicon excess, %
Si-rich	1,97	98,6	1,0	7,1
N-rich	1,92	93,2	1,5	-2,9

In order to analyze a structural-phase transformation in SiN_x during the annealing RS was used. We failed to register a signal from amorphous or crystalline Si clusters due to small thickness of SiN_x layer and strong scattering from Si substrate. However we observed the band proved presence of hydrogen in layers. Raman spectra of as-deposited and annealed at 900 °C films are shown in Fig. 3 in the range from 1800 to 3000 cm^{-1}. Raman spectra of as-deposited samples contain broad peak approximately at 2270 cm^{-1} corresponding to absorption on stretching vibrations of $Si\text{-}H_2$ bonds [8]. The Raman spectra of annealed samples don't exhibit this band (Fig. 3 b).

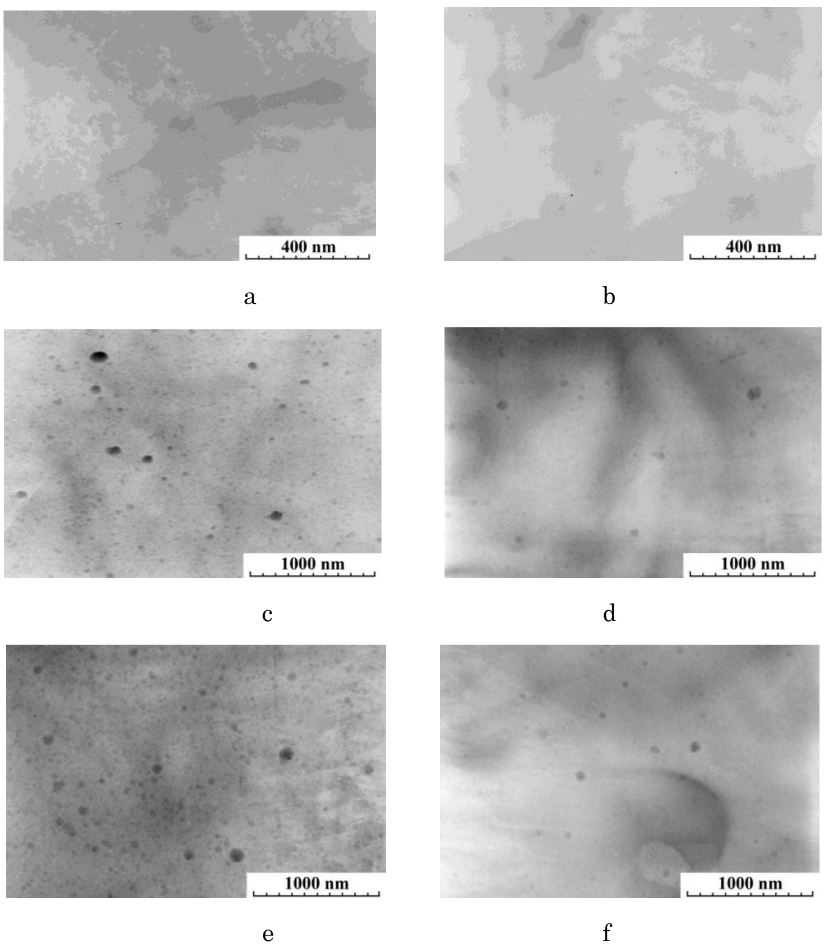

Fig. 2 – Bright-field PV TEM images of the as-deposited (a, b) and annealed at 900 °C (c, d) and 1000 °C (e, f) Si-rich (a, c, e,) and N-rich (b, d, f) silicon nitride films.

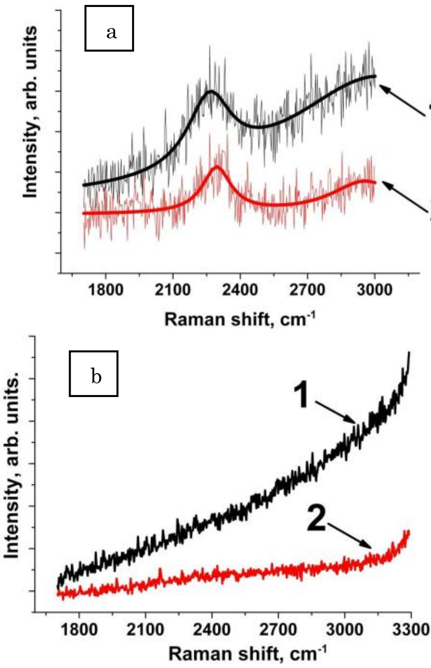

Fig. 3 – Raman spectra of Si-rich (curve 1) and N-rich (curve 2) silicon nitride films: as-deposited (a) and annealed at 900 °C in N_2 ambient for 60 min. (b).

Thus, both as-deposited films of Si-rich and N-rich silicon nitride contain hydrogen which disappeared after annealing. It is obvious because we used hydrogen-bearing gases (SiH_4 and NH_3) and deposition temperature was 300 °C. It is known that dehydrogenization starts at temperature >350 °C. Also TEM data confirmed the existence of Si clusters in both samples after annealing. Si clusters in the N-rich SiN_x can be originated from Si atoms remained after weak-link scission of Si-H during annealing.

3.2 Photoluminescence of SiN_x films

As can be seen from TEM data as-deposited samples do not contain any Si clusters. It is known that spectrum of silicon nitride films without Si clusters should be represented one band, the position and half width of which depend on SiN_x stoichiometric composition [5, 6]. We could not observe PL from as-deposited samples.

The RS spectra of our samples demonstrate that the annealing at 900 ° and 1000 °C for one hour leads to dehydrogenization of the films. The dissociation of Si-H and N-H bonds can result in formation of Si clusters (Fig. 2) and defects creation in matrix or at cluster/matrix interface. All this process may initiate emergency of luminescence. The annealing of our samples results in light emission of both samples. The PL spectra of Si-rich and N-rich silicon nitride films annealed at 900 ° and 1000 °C are shown in Fig. 4. The PL spectra have complicated waveform in wide range from UV to IR. Six possible main emission peaks are marked in the PL spectra with arrows at 3.2 eV, 3 eV, 2.8 eV, 2.5 eV, 2.2-2.1 eV and 1.5 eV.

The spectra of samples annealed at 900 °C differ from ones at 1000 °C. The most significant differences are observed in blue-violet range (2.7-3.3 eV). So, the intensity of the PL peaks at 2.8 - 3 eV is reduced with increasing temperature for both Si-rich and N-rich silicon nitride films. In particular, blue-violet PL is more than five times greater for N-rich silicon nitride film annealed at 900 ° then for the same annealed at 1000 °C. Ref. [3, 4] demonstrated that the PL in blue-violet range originated from defect-related states and attributed to the recombination from the conduction band to the N_2^0 level or from the valence band to the N_4^+ level. It is known that high annealing temperature is required to generate these nitrogen defects [9]. In our case annealing at 900 ° can be produced nitrogen defects, especially in N-rich film. The blue-violet Pl decay after increasing annealing temperature to 1000 °C can be explained by decreasing of amount of N-related defects at this temperature. It is possible due to involvement of N atoms in nitridation process (the additional Si-N bonds formation). Also it is known that release of hydrogen from the films in the form of molecular NH_3 is possible after annealing [10]. Such type of dehydrogenization also may reduce N-related defects.

The general features of the spectra of Si- and N-rich samples annealed at 1000 °C that maximum of PL lies at 2.5 eV. The PL peak 2.5 eV arises from the radiative recombination between the electron and holes in the tails states of the conduction and valance bands and the metastable silicon dangling bond (K^0) center [3, 4].

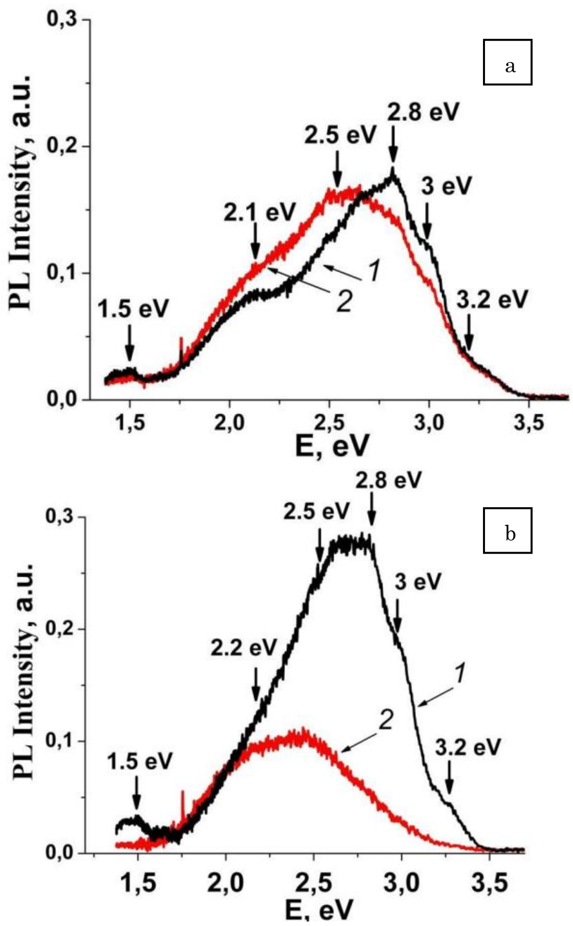

Fig. 4 – PL spectra of Si-rich (a) and N-rich (b) silicon nitride films annealed at 900 °C (curve 1) and 1000 °C (curve 2) in N_2 ambient for 1 hour

The band at 2.1-2.2 eV may be originated from silicon clusters which size does not exceed 5 nm [2]. Unfortunately, we could not observe such small clusters.

Accordingly to the Ref. [4] the IR band at 1.5 eV can be attributed to the following recombination processes: between conduction edge of the intrinsic band and N_4^+ level, and between the N_4^+ and N_2^0 states. It is interesting to note that intensity of this band correlates with PL intensity in blue-violet range. So, blue-violet and IR PL are maximal for N-rich sample annealed at 900 °C and are minimal for N-rich sample annealed at 1000 °C. It is an additional evidence that PL in blue-violet and IR range originates from the same radiative center – N-related defects.

4. CONCLUSIONS

Structural and optical properties of thin films of SiN_x deposited on the silicon wafers by PECVD at 300 °C have been investigated. We have compared Si-rich and N-rich silicon nitride. According to the RS data the as-deposited films contain hydrogen. The annealing results in dehydrogenization of the SiN_x films. We have observed formation of silicon clusters in both Si-rich and N-rich silicon nitride films after annealing at 900 °C and 1000 °C for hour in N_2 ambient. Strong PL is observed at room temperature after annealing and has wide distribution from 1.5 to 3.4 eV. We attributed this PL to preferential excitation of defect-related states and probably to emission from silicon clusters.

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