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Structural and light emitting properties of silicon-rich silicon nitride films grown by plasma enhanced-chemical vapor deposition

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ABSTRACT

Si-rich Silicon nitride films fabricated by plasma enhanced chemical vapor deposition (PECVD) on p-type silicon substrates were investigated by means of photoluminescence (PL) and X-ray diffraction (XRD) methods. The film stoichiometry was controlled via varying the NH_3/SiH_4 ratio (R) in the range $R=0.56$–1.0. Thermal annealing at 1100 °C for 30 min in the nitrogen flow was applied to form the Si nanocrystals (NCs) embedded in the films. XRD experiment has revealed also the formation of hexagonal silicon nitride NCs with the sizes of 26–30 nm in the films grown with $R=1$. When R decreasing, the sizes of silicon nitride NCs decreases down to 2.8–3.0 nm ($R=0.63$). In the films grown with $R=0.56$ the amorphous silicon nitride, amorphous Si and crystallized Si phases have been detected. PL study showed the non-monotonic behavior of PL intensity with the R decreasing. The highest PL intensity was detected for the films grown with $R=0.63$. PL spectra of all films were found to be complex containing a set of PL bands peaked at about 2.8–3.0, 2.5–2.7, 2.1–2.2 and 1.8–2.0 eV. Temperature behavior of PL spectra was investigated in the range 20–300 K that allowed analyzing the nature of each PL component. It was shown that the peak position of all PL bands varies with the SiN_x stoichiometry and Si NC sizes, demonstrating a "red" shift with R decreasing. It was revealed that the former three PL bands did not change their peak positions versus temperature of measurement that permits to assign them to the carrier recombination via radiative defects in the silicon nitride matrix. The PL band at 1.8–2.0 eV has demonstrated a "blue" spectral shift with cooling similar to the Si band gap shrinkage. Based on this behavior, the 1.8–2.0 eV PL band has been attributed to exciton emission inside of Si NCs. The role of silicon nitride NCs in photoluminescence and its excitation is discussed.

1. Introduction

Light emission from the bulk silicon, owing to its indirect band-gap nature and phonon-assisted recombination transitions, is not efficient in comparison with the fast non-radiative transitions and not suitable for active optical applications [1].

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The low-dimensional silicon structures, such as Si nanocrystals (NCs) embedded in silicon oxide, were investigated earlier for the optical needs. Although this material demonstrates the efficient photoluminescence (PL), it suffers from the low efficiency of its electroluminescence [2–7].

During the past decades, many strategies have been employed to overcome the low probability of electron injection in Si NCs embedded in silicon oxide. However, in spite of significant research efforts, the absence of efficient silicon-based light sources still prevents the realization of silicon photonic chips.

One approach to achieve the more prominent conductivity is using the Si-NCs embedded in silicon nitride. Earlier, silicon nitride was considered as an oxidation mask, a dopant diffusion barrier, the gate or inter-level dielectric in the thin film transistors, as well as a charge storage layer in nonvolatile memories or as a final passivation layer for device packaging. Along with this, the silicon nitride films demonstrate efficient emission [5–16] that opens some perspectives for its application in optoelectronic devices with CMOS techniques.

Stoichiometric Si_3N_4 and Si-rich Si_3N_4 (SiN_x) materials can be produced by the different techniques. Among them the plasma-enhanced or hot filament-assisted chemical vapor depositions are most addressed [8–11,16]. In last cases the different SiN_x stoichiometry can be achieved via varying the working gas ratio (R), either for $[N_2]/[SiH_4]$ [6,7,16] or $[NH_3]/[SiH_4]$ [8,9].

The quantum confinement effect was considered to be responsible for the emission process in the amorphous Si clusters [6] or Si-NCs [7]. It was shown that monitoring the Si-NC size allows tuning the PL peak position from the near infrared range (1.38 eV) to ultraviolet one (3.02 eV). However, in some cases the PL spectrum was found to be complex and the mechanism of optical transitions was unclear [7–13]. To investigate the different radiative channels, the study of recombination dynamics was applied [12,13]. It was shown that the quantum confinement effect itself cannot explain unambiguously the PL properties of SiN_x films because the host defects play an important role in the radiative recombination as well. To discriminate the contribution of different radiative channels, the study of PL temperature dependences can be applied also. In this paper we present a comparative study of structural and light emitting properties for the Si-rich silicon nitride films aiming to distinguish the PL components related to emissions via the Si-NCs and/or silicon nitride defects.

2. Experimental details

Si-rich silicon nitride films were grown by the PECVD technique on the silicon substrates (B-doped, (100) orientation, a resistivity of 0.02 Ω cm). The film stoichiometry was monitored via varying of the NH_3/SiH_4 (99.9999%) gas flow ratio (R) in the range of 0.56–1.0. 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 the nitrogen flow was applied to produce the Si nanocrystals in the films. The samples were investigated by means of the photoluminescence and X-ray diffraction (XRD) methods. The chemical composition was controlled by the Rutherford Back Scattering (RBS) and Elastic Recoil Detection Analysis (ERDA) methods. More details can be found in Ref. [15].

The samples were mounted in a closed-cycle He cryostat, where the temperature was varied in the range 20–300 K. PL spectra were excited by a He–Cd laser with a wavelength of 325 nm and a beam power of 80 mW. More details about PL set up used can be found elsewhere [17,18]. XRD experiments (at low grazing angle (0.5°) configuration) were done using the equipment of Model XPERT MRD with the Pixel detector, three axis goniometry and parallel collimator with the resolution of 0.0001°. X-ray beam was achieved from the Cu source, $K_{\alpha 1}$ line ($\lambda = 1.5406$ Å).

3. Experimental results and discussion

3.1. XRD results

The X-ray diffraction technique has been used to control the phase variation in the silicon nitride films versus the R values and the structure quality after thermal annealing. Low grazing angle XRD patterns were recorded at the first for the film obtained with $R = 1.0$ after thermal annealing (Fig. 1, Table 1). The XRD analysis has shown that all observed peaks, based on the comparison with the JCPDS-00-33-1160 data sheet (Table 1), can be assigned to the hexagonal silicon nitride structure with corresponding (hkl) indices and d-spacing data [19]. It is clear seen from Table 1 that the experimental XRD peaks match well with tabled data (with uncertainty within $\Delta 2\Theta = \pm 1°$), and testifying on the formation of a hexagonal phase Si_3N_4 NCs in this film after thermal annealing. Note that the wide XRD band with the maximum at $2\theta = 22.82°$ indicates on the presence of amorphous SiN_x phase in the film as well. Similar to the approach described in [20], XRD data has been used to calculate the NC size from the full-width at half-maximum (FWHM) of highest intensity XRD peaks applying Debye–Scherrer's formula

$$d = \frac{K\lambda}{\Delta(2\theta)\,\mathrm{Cos}\ \theta} \quad (1)$$

where $\lambda = 1.5406$ Å is a wavelength of the X-rays source, θ is the Bragg diffraction angle at a peak position, Δ(2θ)

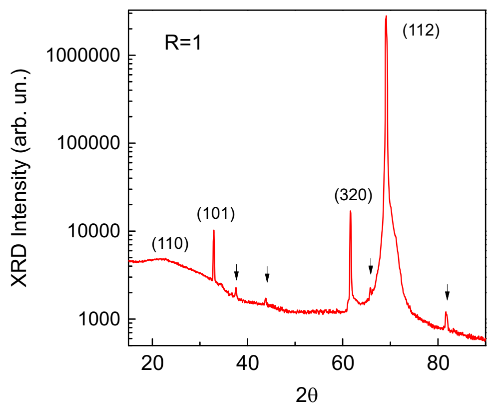

Fig. 1. XRD diagram for the film obtained at $R = 1.0$.