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Effect of the stoichiometry of Si-rich silicon nitride thin films on their photoluminescence and structural properties

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ABSTRACT

Si-rich Silicon nitride films were grown on silicon substrates by plasma enhanced chemical vapor deposition. The film stoichiometry was controlled via the variation of NH_3/SiH_4 ratio from 0.45 up to 1.0. Thermal annealing at 1100 °C for 30 min in the nitrogen flow was applied to form the Si nanocrystals in the films that have been investigated by means of photoluminescence and Raman scattering methods, as well as transmission electron microscopy. Several emission bands have been detected with the peak positions at: 2.8–3.0 eV, 2.5–2.7 eV, 2.10–2.25 eV, and 1.75–1.98 eV. The temperature dependences of photoluminescence spectra were studied with the aim to confirm the types of optical transitions and the nature of light emitting defects in silicon nitride. The former three bands were assigned to the defects in silicon nitride, whereas the last one (1.75–1.98 eV) was attributed to the exciton recombination inside of Si nanocrystals. The photoluminescence mechanism is discussed.

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1. Introduction

Silicon-rich silicon nitride (SiN_x) materials attract considerable attention due to their utility in a wide variety of micro- and optoelectronic applications and because of their compatibility with the existing mainstream of complementary metal–oxide–semiconductor technology [1,2]. Wide bandgap SiN_x materials demonstrating a high density of deep level traps [3,4], allowed strong trapping of electrons and holes, achieving intense luminescence in the blue–green spectral range to be realized [5,6]. This offers the possibility for the development of multicolor Si-based light-emitting devices. This material requires a weaker electrical field for the injection of carriers into SiN_x (2–4 MV/cm) than that needed for SiO_2 (6–10 MV/cm [7]). Besides, SiN_x demonstrates a breakdown strength lower than that observed for stoichiometric Si_3N_4 (9 MV/cm) [8]. Although the band gap of Si_3N_4 is about 5.3 eV (contrary to 9 eV for SiO_2) it should be sufficient to confine the charge carriers in the host [9,10]. Moreover, silicon nitride has higher dielectric constant ($\varepsilon_{Si3N4} = 7$) than silicon oxide ($\varepsilon_{SiO2} = 3.9$) [3] that is the advantage for its future microelectronic application.

From the optical point of view, silicon nitride shows better parameters than those of silicon oxide. In fact, its higher refractive index (for instance, $n_{Si3N4} = 2.03$ [11] vs. $n_{SiO2} = 1.46$ at 1.95 eV [12]) allows the stronger light confinement, whereas a good solubility of rare-earth ions offers an achievement of specific light emitting parameters [10,13].

Previous photoluminescence (PL) investigations have revealed that the PL efficiency of silicon nitride films can be enhanced significantly owing to the formation of Si nanocrystals (Si-NCs) upon high-temperature annealing in nitrogen ambient [14,15]. Besides, the PL efficiency of such materials was found to exceed the PL intensity of Si-NCs embedded in SiO_2 matrix [16,17]. For the films fabricated by plasma enhanced chemical vapor deposition (PECVD) method using either SiH_4 and N_2 [18,19] or SiH_4, N_2 and H_2 [20] such enhancement was ascribed to the passivation of Si-NCs' surface by hydrogen.

The quantum confinement effect in Si-rich-Si_3N_4 materials was demonstrated for both amorphous Si clusters and crystallized Si-NCs [18–21]. It was shown that the variation of nitrogen-to-silane flow ratio at the constant hydrogen flow allows tuning of the sizes of amorphous Si clusters in the range of 1.4–2.4 nm which favors the shift of PL peak position from 2.0 eV to 2.76 eV [18]. The similar phenomenon was described in [19] where the variation of PL color from the near infrared (1.38 eV) to the ultraviolet (3.02 eV) was achieved via monitoring of nitrogen-to-silane flow ratio. Similar approach was realized in [20] to control the sizes of crystallized Si-NCs and to turn the PL peak position from 2 eV nm to 2.96 eV. Later, the PL emission in the range 1.77–2.75 eV was achieved from Si-rich-Si_3N_4 films fabricated using the SiH_4 and NH_3 gases as precursors [21]. Similar PL properties were demonstrated by the films containing either amorphous Si clusters or crystallized Si-NCs [18–21]. In spite of observed correlation between the variation of PL peak position and Si-NCs' sizes, different authors

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reported different energetic PL peak positions for Si-NCs with the same sizes [14–21]. This fact indicates that the PL bands connected with the recombination of either exciton inside the Si-NCs or the carriers via host defects were not discriminated clearly yet. At the same time, such consideration could allow defining the ways to control and to monitor the luminescent parameters of SiN_x materials. The present work directs on investigating the effect of deposition conditions on the structural and luminescent properties of Si-rich-Si_3N_4 films grown by the PECVD approach in order to optimize their parameters for microelectronic and photonic applications.

2. Experimental details

Non-stoichiometric Si-rich silicon nitride films were deposited by remote controlled PECVD method at 300 °C on (100) p-type silicon substrates for 30 min. The flow of SiH_4 was kept at 14 sccm. The NH_3 flow was varied from 6.3 to 14 sccm to achieve output gas ratio R = $[NH_3]/[SiH_4]$ in the range of R = 0.45–1.0. The latter allows controlling the excess Si content (C_{Si}) in the films in the range 40–70 at.% (Table 1). The stoichiometry of the samples was controlled by Rutherford Back Scattering and Elastic Recoil Detection Analysis methods. More details can be found in Ref. [22].

An annealing treatment of the samples was performed in a conventional furnace in nitrogen flow at 700–1100 °C for 30–60 min. However, hereafter only the samples annealed at 1100 °C for 30 min will be considered aiming to demonstrate the effect of excess Si content on Si-NCs formation. An effect of other annealing conditions was discussed in [14].

The samples were investigated by means of photoluminescence (PL), Raman scattering and high-resolution transmission electronic microscopy (HR-TEM) methods. PL emission was excited by a He–Cd laser with a wavelength of 325 nm and a beam power of 80 mW. The spectra were measured at 20–300 K using He closed circle cryostat and recorded with a PL setup equipped with a spectrometer SPEX500 described in [23,24]. Raman scattering spectra were investigated by means of Jobin-Yvon LabRAM HR 800 UV micro-Raman system using 532-nm excitation light of Ar ion laser [25,26]. To confirm the formation of Si-NCs in the samples, the cross-sectional specimens were prepared for HR-TEM observations by the standard procedure involving grinding, dimpling and Ar^+ ion beam thinning until electron transparency. The samples were examined on a JEOL 2100F operating at 200 keV equipped with a corrector for spherical aberration and the last generation of the Gatan imaging filters [15].

3. Result and discussion

3.1. Raman scattering and HR-TEM study

Raman scattering method, being a non-destructive approach and high-sensitive to the structural disorder in solids, allows insights on crystalline structure and its evolution with annealing treatment. However, it should be noted that for thin films grown on Si substrates, the analysis of Raman scattering spectra of the films themselves can suffer from an essential contribution of the signal from the underlined substrate, namely for the measurement in the back-scattering geometry used in our study.

Table 1
Deposition conditions and excess Si content of the films investigated.

Parameter	No. of samples					
	#1	#2	#3	#4	#5	#6
Deposition time (min)	30					
Temperature of substrate (°C)	300					
Applied bias (V)	70					
Microwave power (W)	500					
SiH_4 flow (sccm)	14					
NH_3 flow (sccm)	14	11.6	10	8.8	7.4	6.3
Gas ratio, R = $[NH_3]$ / $[SiH_4]$	1.00	0.83	0.71	0.63	0.53	0.45
Excess Si content, C_{Si} (at.%)	40	44	54	59	65	69

Fig. 1 represents the evolution of Raman scattering spectra of the films investigated versus the R values. All spectra consist of several vibration modes in the range 100–1100 cm^{-1}. To discriminate the signals from the films themselves and that from the Si substrate, the signal from Si substrate is also shown in Fig. 1. It is known that the diamond structure of monocrystalline silicon allows only one first-order Raman active phonon of symmetry Γ_{25} located at the Brillouin zone (BZ) center corresponding to $\omega_{bulk\text{-}Si\text{-}TO(\Gamma)} = 520.0 \pm 1.0$ cm^{-1} with the full width at half maximum (FWHM) of 3.5 cm^{-1} [27,28].

Besides this most intense phonon, the longitudinal acoustic (LA(X), $\omega_{bulk\text{-}Si\text{-}LA} = 300$ cm^{-1}) and the longitudinal optical (LO(X), $\omega_{bulk\text{-}Si\text{-}LO} = 410$ cm^{-1}) phonons in the X direction of BZ were also observed. The presence of LA(X) and LO(X) phonons is caused by the coordination defects in the films [29]. The peaks at about ω_{2LA} = 610 cm^{-1} and ω_{2TO} = 960 cm^{-1} are overtones of the main LA(X) and TO(L) phonons, respectively [28]. Although all mentioned bands were detected for the Si substrate as well (Fig. 1), they were found to be dominant in Raman scattering spectra of the films grown with R = 0.71–1.0 (Fig. 1).

At the same time, the Raman scattering spectra of the films fabricated with R = 0.45–0.63 show the broadening of the TO phonon line ($\omega_{bulk\text{-}Si\text{-}TO}$) towards 420 cm^{-1} that becomes more pronounced with the R decrease (Fig. 1). Besides an appearance and an increase in intensity of the transverse-acoustic (TA) vibrational mode ($\omega_{bulk\text{-}Si\text{-}TA}$ = 150 cm^{-1}) occur that give an evidence about the medium-range order of amorphous network [30]. The shift of the TO(Γ) phonon towards the lower frequency side and its broadening are considered usually as the evidence of the formation of nanostructured Si [31,32].

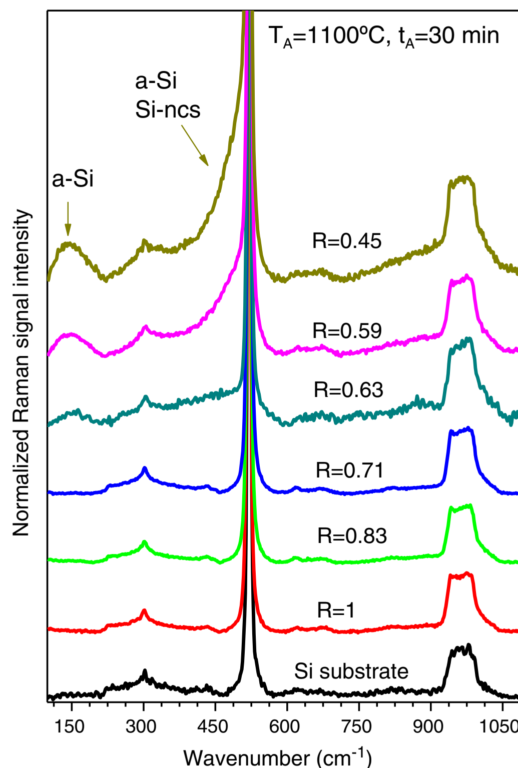

Fig. 1. Raman scattering spectra of the samples fabricated with R = 0.45–1.0. The spectra were normalized on the intensity of TO-phonon of Si substrate (521 cm^{-1}) and shifted in vertical direction for clarity. The spectrum of Si substrate is also present to demonstrate the presence of amorphous Si phase in the films after high temperature annealing.

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