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# Structure and light emission of Si-rich Al<sub>2</sub>O<sub>3</sub> and Si-rich-SiO<sub>2</sub> nanocomposites

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## ABSTRACT

This work presents the comparative investigation of  $Si_x(Al_2O_3)_{1-x}$  and  $Si_x(SiO_2)_{1-x}$  films with different excess Si content, *x*, grown by RF magnetron sputtering. Their properties were investigated by means of Raman scattering, X-ray diffraction, Electron paramagnetic resonance and photoluminescence methods. As-deposited films with the  $x \ge 0.3$  were found to be two-phase systems that contained an amorphous Si phase. Contrary to  $Si_x(SiO_2)_{1-x}$  films, tensile stresses were observed for  $Si_x(Al_2O_3)_{1-x}$  samples due to lattice mismatch between the film and quartz substrate. The Si nanocrystals (Si-ncs) were formed upon annealing at 1150 °C for 30 min in nitrogen flow in both types of samples. Along with this, for the films with the  $x \ge 0.3$ , amorphous Si phase was also detected, but its contribution was smaller in the  $Si_x(Al_2O_3)_{1-x}$  films. Besides, the Si-ncs embedded in  $Al_2O_3$  host remained under tensile stresses after annealing. For the films with the same *x* values, the Si-ncs in  $Al_2O_3$  were found to be larger than those embedded in SiO<sub>2</sub>. Photoluminescence spectra showed that the main radiative channel in  $Si_x(SiO_2)_{1-x}$  films is exciton recombination in Si-ncs, while in  $Si_x(Al_2O_3)_{1-x}$  films the defect related emission prevails due to higher amount of interface defects in the  $Si_x(Al_2O_3)_{1-x}$ . The nature of these defects is discussed. © 2013 Elsevier B.V. All rights reserved.

#### 1. Introduction

One of the important tasks of photonics and microelectronics is the realization of low-cost integrated optoelectronic devices fully based on well-developed Si-based CMOS technology (i.e. all-in-one Si chip). In this regard, silicon nanocrystallites (Si-ncs) attract considerable interest due to significant transformation of their optical and electrical properties caused by quantumconfinement effect [1–3].

Light-emitting Si-ncs embedded in dielectric hosts offer potential applications in optoelectronic devices because of their compatibility with the existing manufacturing infrastructure for silicon integrated circuits. Among different dielectric materials, silicon oxide is the most addressed as a host for Si-ncs [4–7]. The properties of Si-ncs–SiO<sub>2</sub> systems have been widely investigated during the last decades [2–9].

However, the downscaling of microelectronic devices requires the elaboration of novel materials to overcome the bottleneck of silicon oxide as a gate material. In this regard, other dielectrics such as  $ZrO_2$ ,  $HfO_2$  and  $Al_2O_3$  are considered as promising gate dielectrics [10]. It was also demonstrated that Si-ncs embedded in such high-k host offer a wider application for non-volatile memories due to the higher performance of the corresponding devices [11,12].

Among different dielectrics,  $Al_2O_3$  is not well addressed as photonic material. Meanwhile, it has relatively higher refractive index (1.73 at 1.95 eV) in comparison with that of SiO<sub>2</sub> (1.46 at 1.95 eV) at similar band gap energies offering better light confinement which makes compact device structures possible. Recently, alumina-based waveguides have been developed by sol-gel techniques for optical communication [13,14].

It is worth to note that the reports on the properties of Si-rich Al<sub>2</sub>O<sub>3</sub> materials are not numerous. Only few groups reported on Si-ncs–Al<sub>2</sub>O<sub>3</sub> materials fabricated by ion implantation or electron beam evaporation [15–17]. At the same time, magnetron sputtering was not often considered for fabrication of Al<sub>2</sub>O<sub>3</sub> materials with embedded Si-ncs [18–20] in spite of the relative simplicity of this approach and its wide application for the fabrication of Si-ncs–SiO<sub>2</sub> films [7,9]. Moreover, the films grown on silica substrates were not practically investigated whereas such structures have an importance for optical communication.

The present paper deals with the comparative investigation of Si-rich-Al<sub>2</sub>O<sub>3</sub> and Si-rich-SiO<sub>2</sub> films with different Si content. It demonstrates the application of magnetron sputtering for the







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fabrication of such films. The study of the effect of post-deposition processing on the evolution of microstructure of the films and their optical and luminescent properties allowed to get information about the Si-ncs formation and the nature of the emitting centers in the films with different Si content as well as to find a way to control luminescent properties of these materials.

## 2. Materials and methods

The Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> and Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> films were deposited by radio frequency magnetron co-sputtering of two separated targets (pure Si and pure oxide (Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>)) in pure argon plasma on an elongated non-rotated silicon oxide substrate kept at 20 °C. Our approach permitted to vary excess Si content along the film length (0.15  $\leq x \leq 0.70$ ) during one deposition run at fixed powers applied to the targets [6,19,20]. The length and the width of the film were about 3 and 140 mm due to template use. An anneal treatment of such long film gives the possibility to investigate simultaneous formation of the Si-ncs in the films with different Si excess.

The background vacuum in the chamber was about  $1 \times 10^{-5}$  Pa prior to the deposition. The RF powers applied on the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> targets were 60 and 80 W, respectively, whereas the power applied to the Si cathode was 40 W in both cases. The deposition time was chosen to grow the films with the thickness of about 1  $\mu$ m. The as-deposited original films were annealed at 1150 °C during 30 min in nitrogen flow to form the Si-ncs in oxide hosts and then they were cut to smaller (1 cm in length) segments (called hereafter as samples) to simplify the investigation of their properties.

To investigate the microstructure and luminescent properties of the films, a Horiba Jobin-Yvon T-64000 Raman spectrometer equipped with confocal microscope and automated piezo-driven XYZ stage was used. The measurements were performed at the center of each segment. The micro-Raman scattering (µ-RS) and micro-photoluminescence (µ-PL) spectra were detected in the 100-900 cm<sup>-1</sup> and the 500-900 nm spectral ranges, respectively. A 488.0 nm line of Ar-Kr ion laser was used as the excitation source. The laser power on the sample surface was always kept below 5 mW to obtain the best signal-to-noise ratio, preventing a laser heating of the investigated sample. The spectral resolution of the spectrometer was less than 0.15 cm<sup>-1</sup>. X-ray diffraction (XRD) study was carried out using a Philips X'Pert-MRD diffractometer with Cu K<sub> $\alpha$ </sub>-radiation ( $\lambda$  = 0.15418 nm) in a grazing geometry (with the angle  $\omega \sim 0.5^{\circ}$ ). Electron paramagnetic resonance (EPR) spectra were measured by means Varian-12 X-band spectrometer to obtain the information about the defect structure of

As-deposited

Si-rich-Al<sub>2</sub>O

Si-rich-SiO

300

400

500

200

(a)

400

Raman scattering intensity (cps)

100

the samples. The accuracy of the determination of *g*-factor values was  $\Delta g = \pm 0.0005$ . All our investigations were performed at 300 K.

# 3. Results

## 3.1. Raman scattering spectra

Our Raman scattering study showed that as-deposited  $Si_x(Al_2O_3)_{1-x}$  and  $Si_x(SiO_2)_{1-x}$  films with the  $x \ge 0.5$  contained an amorphous silicon (a-Si) phase (Fig. 1a). The shift of the peak position of the transverse optic (TO) band to  $\omega_{TO-a-Si} = 460 \text{ cm}^{-1}$  was observed for  $Si_x(Al_2O_3)_{1-x}$  films contrary to that detected for  $Si_x(SiO_2)_{1-x}$  counterparts ( $\omega_{TO-a-Si} = 480 \text{ cm}^{-1}$ ). This latter corresponds to the TO phonon peak position of relaxed amorphous silicon. The low-frequency shift observed for  $Si_x(Al_2O_3)_{1-x}$  samples can be ascribed to tensile stresses between the film and fused quartz substrate due to the lattice mismatch between silica fused substrate and the Si-rich- $Al_2O_3$  film. It is obvious that this effect is negligible for the  $Si_x(SiO_2)_{1-x}$  films.

Annealing treatment at  $T_A = 1150$  °C results in the increase of TO phonon band intensity and its narrowing that is evidence for Si-ncs formation in both types of the samples (Fig. 1b). When the *x* decreases, the shift of the  $\omega_{\text{TO-nc-Si}}$  to the lower wavenumbers occurs for Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> (Fig. 1b, inset) that can be ascribed to the decrease of Si-ncs sizes.

In all  $Si_x(Al_2O_3)_{1-x}$  samples, the  $\omega_{TO-nc-Si}$  is shifted to lower wavenumbers (517.3–518.7 cm<sup>-1</sup>) in comparison with the peak position of TO phonon band of bulk Si ( $\omega_{TO-bulk-Si} = 521$  cm<sup>-1</sup>). But contrary to  $Si_x(SiO_2)_{1-x}$  films, for the  $Si_x(Al_2O_3)_{1-x}$  samples with x = 0.55-0.7 only, a slight shift of the  $\omega_{TO}$  band towards the higher wavenumbers is detected with the decrease of x (Fig. 1b, inset).

It is worth to note that along with Si crystalline phase, the amorphous Si phase was also detected in annealed samples (Fig. 1b,  $(\omega_{TO-a-Si} = 160 \text{ and } 480 \text{ cm}^{-1})$ ). However, for the samples with the same *x* values its contribution is lower for the Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> samples than for the Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> counterparts.

#### 3.2. XRD patterns

(b)

. 515

1000

100

520

510

505

200

Raman scattering intensity (cps)

XRD signal was detected for  $Si_x(SiO_2)_{1-x}$  with x > 0.3 and for  $Si_x(Al_2O_3)_{1-x}$  with x > 0.5. The estimation of Si-ncs embedded in  $Al_2O_3$  host, based on the Scherrer equation, was found to be about 14 nm for x > 0.5 and did not vary with x [17,18]. The Si-ncs formed in the SiO<sub>2</sub> matrix were found to be smaller for the same x values [5,7]. For x > 0.5 their mean size was about 5–6 nm and did not

Si-rich-Al\_O

Si-rich-SiO

0,7 0,8

400

500

0,5 0,6

Si-rich-Al\_O

Si-rich-SiO

300

Si excess (x)

0,4

~517,3cm

T\_=1150°C

t\_=30 min

~515,7cm

600

x=0.68

=0.68

700



700

=0.68

x = 0.68

<u>ω<sub>το</sub>~460cm</u>ີ

\_\_\_\_<mark>∞\_~480cm</mark>

600

change with *x*, whereas for 0.3 < x < 0.5 the decrease of Si-ncs from 5 to 2.5 nm was observed with the *x* decrease [7].

## 3.3. EPR study

The presence of amorphous Si phase in as-deposited samples was also revealed by EPR measurements. As one can see from Fig. 2, the EPR spectra of the both types' samples with  $x \ge 0.3$  are dominated by the signal with  $g_1 = 2.0055$  (Fig. 2) that corresponds to the silicon dangling bonds (Si DB) and testifies to the presence of amorphous Si phase. Its intensity reflects the total number of these centers and decreases with decreasing *x*. The dangling bond concentration estimated from the EPR spectra with x = 0.7 is higher for Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> samples (~10<sup>19</sup> centers/cm<sup>3</sup>) than for Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> ones (~10<sup>18</sup> centers/cm<sup>3</sup>).

For the Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> with  $x \le 0.3$  the appearance of an anisotropic signal with  $g_2 = 2.0018$  was observed (Fig. 2, curve 2). The *g*-factor of this signal was determined as the intersection of the EPR signal with the zero-line. With decreasing *x* the intensity of this anisotropic signal increases at first and then decreases. The maximum intensity being at x = 0.22 (not shown here). Such dependence could mean that the corresponding EPR center is connected both, silicon oxide and excess silicon. In this case the increase of the intensity is due to the increase of the silicon oxide phase while the decrease is caused by the decrease of excess Si content. This conclusion is in agreement with the absence of this anisotropic signal in films deposited from the silicon oxide target only. This signal is similar to that observed for milled quartz, but its nature needs additional study.

Annealing treatment results in the transformation of EPR spectra of both types of samples. In  $Si_x(SiO_2)_{1-x}$  films with x > 0.3, an asymmetric signal with  $g_3 = 2.0062$ , whose intensity was found to be slightly lower than that of the signal from Si DB related centers, is observed. Its intensity increases also with x (Fig. 2a). The asymmetric shape of this signal and the shift of g-factor to higher values as well as the decrease of its intensity, in comparison with that of as-deposited samples, allow assigning it to superposition of signals from Si DB and P<sub>b</sub>-like centers that appeared when Sincs are formed [6]. When x < 0.45, an additional isotropic signal with  $g_4 = 2.0028$  and a peak-to-peak width  $\Delta H \sim 3.5$  G appeared instead of the anisotropic one with  $g_2 = 2.0018$ . Its intensity, at first, increases and then it decreases with the decrease of x. The highest amplitude of this signal is observed for samples with x = 0.22 (Fig. 2c). The signal with  $g_4 = 2.0028$  was also observed for oxidized silicon annealed additionally in oxygen-free ambient at 960-1130 °C and can be ascribed to S-centers, previously assigned to E'-like defects of type O<sub>2</sub>Si=Si· and/or OSi<sub>2</sub>=Si· [21], i.e. this is an excess-Si defect in SiO<sub>2</sub> matrix (that can be considered as a signal of non-stoichiometric silicon oxide). It is obvious that such defects in  $Si_x(SiO_2)_{1-x}$  films can be built by excess Si atoms which cannot form Si-ncs due to their low amount. Similar behavior of the intensities of signals with  $g_4 = 2.0028$  (annealed samples) and  $g_2 = 2.0018$  (as-deposited ones) versus x allows to assume that the former signal appears due to the transformation of the latter one.

Instead of single signal with  $g_1 = 2.0055$  detected for as-deposited films, annealed Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> samples showed two signals with  $g_5 = 2.0068$  and  $g_6 = 2.0027$  (Fig. 2d and e). The first of them dominates for the samples with x > 0.45, while the other is observed at x < 0.45. The signal with the  $g_5 = 2.0068$  can be attributed to the superposition of Si dangling bonds and P<sub>b</sub>-like centers that can be the feature of both Si/SiO<sub>2</sub> and Si/Al<sub>2</sub>O<sub>3</sub> interfaces [22].The higher value of  $g_5$ -factor in comparison with  $g_3$ -one (2.0068 vs. 2.0062) and the more pronounced decrease of EPR signal intensity, after annealing in comparison with corresponding Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> samples,

allow us to conclude that in the case of  $Si_x(Al_2O_3)_{1-x}$  films the contribution of DB in the signal is lower.

As was mentioned above, the  $g_6 = 2.0027$  of the signal observed for annealed Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> is close to the  $g_4 = 2.0028$  of the signal in corresponding Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> samples. Also, both signals have similar peak-to-peak widths (~4.0 G vs. ~3.5 G). Therefore, it can be concluded that the center with  $g_6 = 2.0027$  in Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> is obviously an S-center, being a characteristic feature of non-stoichiometric silicon oxide. The dependence of its intensity on x (Fig. 2f) is also similar to that obtained for the Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> films (Fig. 2c).

## 3.4. Photoluminescence

No PL emission was observed for the as-deposited  $Si_x(SiO_2)_{1-x}$  films, whereas weak PL band in the orange spectral range was detected from the  $Si_x(Al_2O_3)_{1-x}$  films with x < 0.5. Similar PL emission was also observed in pure  $Al_2O_3$  film (Fig. 3) and can be assigned to  $F_2^{2+}$  centers [23].

Annealing of  $Si_x(SiO_2)_{1-x}$  films results in the appearance of one broad PL band in red-near-infrared spectral range (Fig. 3). Its peak position shifts from 1.4 to 1.8 eV when the *x* decreases from 0.45 to 0.3 and changes slightly for x > 0.5 [9].

Annealed  $Si_x(Al_2O_3)_{1-x}$  films demonstrate a PL spectrum in a wider spectral range (Fig. 3). These spectra contain two broad PL bands with maxima in "green–orange"<sup>1</sup> (2.06–2.18 eV) and "red" (1.65–1.77 eV) spectral ranges. The second one is accompanied by near-infrared tail or a weak band (at 1.55–1.60 eV). All mentioned bands can be well-separated (for x = 0.3-0.5) unless when they strongly overlapped.

The "green–orange" band consists of two overlapped components with maxima positions at ~2.06 and ~2.18 eV (Fig. 3). The emission at ~2.18 eV is similar to PL emission from  $F_2^{2+}$  centers in Al<sub>2</sub>O<sub>3</sub> and it is clearly seen in the sample with *x* = 0.3. This PL band presents also in other spectra, testify that the Si-ncs are incorporated into Al<sub>2</sub>O<sub>3</sub> matrix.

## 4. Discussion

The investigation of structural properties of as-deposited  $Si_x(SiO_2)_{1-x}$  and  $Si_x(Al_2O_3)_{1-x}$  films showed that one of their specific features is the presence of an amorphous Si phase. This phase is detected by Raman scattering for the samples with x > 0.45, whereas EPR data confirms its presence for the samples with x > 0.3 that is due to the higher sensitivity of the EPR method.

The Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> films were found to be tensile stressed contrary to the relaxed Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> ones. This can be a reason of higher concentration of Si DB in the Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> films.

Comparison of XRD and Raman scattering data shows that after annealing treatment the Si-ncs in  $Si_x(Al_2O_3)_{1-x}$  samples are stressed. In fact, the peak position of the TO phonon band of the Si-ncs for the samples with x > 0.5 is shifted to the lower frequency side ( $\omega_{TO-nc-Si} = 517-518 \text{ cm}^{-1}$ ) in comparison with that of bulk Si ( $\omega_{TO-bulk-Si} = 521 \text{ cm}^{-1}$ ). At the same time, the mean size of the Sincs, estimated from XRD data, is about 14 nm. It is obvious that the contribution of phonon quantum confinement effect is negligible in this case. This means that the Si-ncs in the  $Si_x(Al_2O_3)_{1-x}$  samples are under tensile stress contrary to the Si-ncs in the  $Si_x(SiO_2)_{1-x}$ films. This is in agreement with Raman scattering data obtained for the as-deposited samples.

As mentioned above the peak position of Raman band of the Sincs in  $Si_x(Al_2O_3)_{1-x}$  for the samples with x = 0.6-0.8 shifts slightly to higher frequencies with the decrease of x that cannot be caused

 $<sup>^{1}\,</sup>$  For interpretation of color in Fig. 3, the reader is referred to the web version of this article.



**Fig. 2.** EPR data for  $Si_x(SiO_2)_{1-x}$  (a-c) and  $Si_x(Al_2O_3)_{1-x}$  (d-f) samples with x = 0.70 (a and d), 0.32 (e) and 0.22 (b). EPR spectra for  $Si_x(SiO_2)_{1-x}$  (a and b) and  $Si_x(Al_2O_3)_{1-x}$  (d and e) measured for as-deposited (AD) and annealed samples; (c and f) the dependence of the integrated intensities of the two main EPR signals versus x for  $Si_x(SiO_2)_{1-x}$  (c) and  $Si_x(Al_2O_3)_{1-x}$  (f). The star in (d) and (e) marks the signal of the superfine component of the MgO:Cr<sup>3+</sup> reference.

by the change of crystallite sizes because the decrease of Si content should result in the decrease of Si crystallites and lead to opposite shift of Raman line. The observed shift is obviously caused by the decrease of amorphous Si phase content that is in agreement with the decrease of intensity of TA phonon of amorphous Si ( $\omega_{TA-a-Si} = 150 \text{ cm}^{-1}$ ). Thus, the size of the Si-ncs in the Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> films cannot be estimated from Raman data.

Another situation occurs in the  $Si_x(SiO_2)_{1-x}$  films. With the decrease of x a shift of the  $\omega_{TO-nc-Si}$  to the lower wavenumbers takes place (Fig. 1b, inset). Also, an increase of the full-width at half maximum of this phonon band is observed (not shown). The sizes of Si-ncs embedded in SiO<sub>2</sub> host can be estimated from the fitting of Raman scattering spectra. Based on such analysis the increase of Si-ncs mean size from ~2.7 to 6.0 nm was found for  $Si_x(SiO_2)_{1-x}$ 

samples when x increases from 0.3 to 0.5, whereas for x > 0.5, the size of the ncs does not change. These results are in a good agreement with XRD data.

Raman scattering spectra of annealed films showed also a higher relative contribution of amorphous Si phase in  $Si_x(SiO_2)_{1-x}$  in comparison with that of  $Si_x(Al_2O_3)_{1-x}$ . This is in agreement of EPR data. In fact, higher contribution of the Si DB signal in the EPR spectra of  $Si_x(SiO_2)_{1-x}$  samples is obviously caused by higher contribution of the amorphous Si phase. This can be due to a faster crystallization of the amorphous Si clusters in  $Al_2O_3$  host in comparison with that in SiO\_2. This is in the agreement with the data of Ref. [15]. These clusters can be present in the films after deposition as well as to be formed upon annealing due to phase separation. It is interesting that in  $Si_x(Al_2O_3)_{1-x}$  samples with low



**Fig. 3.** Room-temperature PL spectra of annealed  $Si_x(SiO_2)_{1-x}$  (1) and  $Si_x(Al_2O_3)_{1-x}$  (2,3) samples with x = 0.30 (1.2) and x = 0.50 (3). The excitation wavelength was 488 nm. The spectra for SiO<sub>2</sub> (4) and Al<sub>2</sub>O<sub>3</sub> (5) are given for comparison.

*x* values the EPR signal that is characteristic of non-stoichiometric silicon oxide is observed. Since this signal appears under thermal treatment, we can conclude that silicon suboxide phase is formed under phase separation process.

The results obtained showed also that the mean size of Si-ncs in  $Al_2O_3$ , estimated from XRD measurements for x > 0.5, exceeds that of the Si-ncs in  $SiO_2$  for the films with the same x values. This can be also caused by a faster crystallization of amorphous Si clusters in Al<sub>2</sub>O<sub>3</sub> host compared with that in SiO<sub>2</sub>. In spite of the difference in Si-ncs sizes these films have one thing in common. For the samples with x > 0.5 the mean Si-ncs size does not change with x. This can be connected with the presence of amorphous Si inclusions in as-deposited films. In this case their crystallization can contribute to the appearance of Si-nc in addition to the phase separation process. For x > 0.5 this contribution can be crucial. If these inclusions are big enough (that can be expected for high Si excess) they will form as amorphous Si films and the crystallite sizes will be determined by the temperature and duration of annealing. Indeed, rapid thermal annealing of  $Si_x(Al_2O_3)_{1-x}$  samples results in the formation of smaller the Si-ncs, but their mean size was also found to be independent of x for x > 0.5 [20].

Obtained data show significant difference in PL properties of  $Si_x(SiO_2)_{1-x}$  and  $Si_x(Al_2O_3)_{1-x}$  films. For  $Si_x(SiO_2)_{1-x}$  films, evolution of PL peak position versus *x* correlates with the variation of Si-ncs mean size. This allows ascribing it to exciton recombination in Si-ncs. Thus, in these films exciton recombination in Si-ncs is dominant radiative channel.

At the same time several radiative channels are observed in  $Si_x(Al_2O_3)_{1-x}$  films. The investigation of temperature dependence of the PL spectra showed that the peaks positions and the intensities of PL, peaked at 2.06–2.18 and 1.65–1.77 eV do not change with cooling [20]. This allowed ascribing them to radiative recombination of carriers through defects in the matrix (probably, F-like centers) and/or Si-ncs/host interface states. It is worth to note that PL components at ~1.65–1.77 and ~2.06 eV were observed only when Si-ncs are present in the film. This can be explained by their location near Si-ncs or at Si-ncs/host interface.

At the same time the contribution of the near-infrared tail or the band peaked at about 1.55-1.60 eV increases with cooling [20] which is a typical feature of the Si-ncs excitons. However, its PL intensity is much smaller than the emission of oxide-related defects contrary to that observed in Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub> films. This can be due to high number of non-radiative defects at Si-ncs/Al<sub>2</sub>O<sub>3</sub> interface. These non-radiative centers can be P<sub>b</sub>-like centers. The obtained EPR data allow then to concluding that the concentration of these defects is higher in  $Si_x(Al_2O_3)_{1-x}$  samples than in  $Si_x(SiO_2)_{1-x}$  samples with the same *x* values. In fact, the pronounced shift of *g*-factor in annealed  $Si_x(Al_2O_3)_{1-x}$  samples is the evidence that the contributions of both P<sub>b</sub>-like centers and Si DB in EPR spectra are comparable. In addition, the concentration of EPR centers responsible for the signal from Si DB and P<sub>b</sub>-like centers in  $Si_x(Al_2O_3)_{1-x}$  is higher than that in  $Si_x(SiO_2)_{1-x}$  films with the same *x* values.

It is worth to point that obtained results showed some advantages of Si<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub> in comparison with Si<sub>x</sub>(SiO<sub>2</sub>)<sub>1-x</sub>. In particular, in the former materials Si nanoclusters can be created and crystallized at lower temperature and shorter duration of anneal treatment. Such materials can be used, for instance, for the creation of p-MOS or n-MOS nanomemory structures. In the case of activation of n- or p-regions, the doping with P or B ions is required. Usually, dopant's activation is carried out at 950 °C that is much lower than the temperature of Si-ncs crystallization in  $Si_x(SiO_2)_{1-x}$ films. Earlier we've shown that rapid thermal annealing at 1000-1050 °C for 1 min allowed to create 5 nm Si-ncs in Al<sub>2</sub>O<sub>3</sub> host contrary to 1100-1150 °C used for formation of similar crystallites in  $Si_x(SiO_2)_{1-x}$  with the same x values [19,20]. It is clear that such high annealing temperature can stimulate the redistribution of dopants and spreading of n- or p-regions, as well as the modification of the interface between gate dielectric and silicon channel (see, for example, [24]).

# 5. Summary

In this work structural and luminescence properties of  $Si_x(SiO_2)_{1-x}$  and  $Si_x(Al_2O_3)_{1-x}$  films with different Si content prepared by magnetron sputtering on quartz substrate were compared. The formation of amorphous Si clusters upon deposition process was observed in both types of the films for the samples with x > 0.3. The annealing treatment at 1150 °C during 30 min results in formation of Si nanocrystallites (Si-ncs). Because of the presence of amorphous Si inclusions in the as-deposited films, two processes can contribute to their formation: the crystallization of existing inclusions and the phase separation at high temperatures. The first process can be responsible for independence of mean sizes of crystallites for x > 0.5 that was observed in the both types of annealed films. At the same time a number of differences were found in the structural and photoluminescent properties of the investigated films. Raman scattering and EPR spectra of the annealed films showed the higher relative contribution of amorphous Si phase in  $Si_x(SiO_2)_{1-x}$  in comparison with  $Si_x(Al_2O_3)_{1-x}$  as well as the presence of tensile stress in Si-nc embedded in  $Si_x(Al_2O_3)_{1-x}$ films. The first can be caused by the lower temperature for the crystallization of amorphous Si clusters in Al<sub>2</sub>O<sub>3</sub> host compared with that in SiO<sub>2</sub>, while the second is due to mismatching between the lattice parameters of fused quartz and the film. In addition, Sincs mean sizes were found to be larger in  $Si_x(Al_2O_3)_{1-x}$  films than that in  $Si_x(SiO_2)_{1-x}$  counterparts with the same x values. This can be also caused by the faster formation and crystallization of the amorphous Si clusters in Al<sub>2</sub>O<sub>3</sub> host compared with that in SiO<sub>2</sub>. It is shown that exciton recombination in Si-ncs is the dominant radiative channel in  $Si_x(SiO_2)_{1-x}$  films, while the emission of oxide or Si/matrix interface-related defects dominates in  $Si_x(Al_2O_3)_{1-x}$ films. This can be due to high number of non-radiative defects at  $Si-ncs/Al_2O_3$  interface.

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## References

- [1] L.T. Canham, Appl. Phys. Lett. 57 (1990) 1046–1048.
- [2] V. Lehman, U. Gosele, Appl. Phys. Lett. 58 (1991) 856-858.
- [3] T. Shimizu-Iwayama, S. Nakao, K. Saitoh, Appl. Phys. Lett. 65 (1994) 1814–1816.
  [4] X.Y. Chen, Y.F. Lu, L.J. Tang, Y.H. Wu, B.J. Cho, X.J. Xu, J.R. Dong, W.D. Song, J.
- [4] A.T. Chen, F.F. Lu, L.J. Tang, T.H. Wu, B.J. Cho, A.J. Au, J.K. Dong, W.D. Song, J. Appl. Phys. 97 (2005) 014913.
- [5] L. Khomenkova, N. Korsunska, V. Yukhimchuk, B. Jumaev, T. Torchinska, A. Vivas, J. Lumin. 102 (103) (2003) 705–711.
- [6] N. Baran, B. Bulakh, Thin Solid Films 517 (2009) 5468-5473.
- [7] L. Khomenkova, N. Korsunska, M. Baran, B. Bulakh, T. Stara, T. Kryshtab, G. Gomez, Physica E 41 (2009) 1015–1018.
- [8] G.G. Qin, X.S. Liu, S.Y. Ma, J. Lin, G.Q. Yao, X.Y. Lin, K.X. Lin, Phys. Rev. B 55 (1997) 12876–12879.
- [9] L. Khomenkova, N. Korsunska, T. Torchynska, V. Yukhymchuk, B. Jumaev, A. Many, Y. Goldstein, E. Savir, J. Jedrzejewski, J. Phys.: Condens. Matter 14 (2002) 13217–13221.
- [10] L. Khomenkova, X. Portier, J. Cardin, F. Gourbilleau, Nanotechnology 21 (2010) 285707.
- [11] R.F. Steimle, R. Muralidhar, R. Rao, M. Sadd, C.T. Swift, J. Yater, B. Hradsky, S. Straub, H. Gasquet, L. Vishnubhotla, E.J. Prinz, T. Merchant, B. Acred, K. Chang, B.E. White Jr., Microelectron. Reliability 47 (2007) 585–592.

- [12] T. Baron, A. Fernandes, J.F. Damlencourt, B. De Salvo, F. Martin, F. Mazen, S. Haukka, Appl. Phys. Lett. 82 (2003) 4151–4153.
- [13] G.N. van den Hoven, E. Snoeks, A. Polman, J.W.M. van Uffelen, Y.S. Oei, M.K. Smit, Appl. Phys. Lett. 62 (1993) 3065–3067.
- [14] M.K. Smit, G.A. Acket, C.J. van der Laan, Thin Solid Films 138 (1986) 171–181.
   [15] A.N. Mikhaylov, A.I. Belov, A.B. Kostyuk, I.Yu. Zhavoronkov, D.S. Korolev, A.V.
- [15] A.Y. Mikhaylov, A.J. Belov, A.D. Rostyuk, Fru Zhavornikov, D.S. Kolev, A.V. Nezhdanov, A.V. Ershov, D.V. Guseinov, T.A. Gracheva, N.D. Malygin, E.S. Demidov, D.I. Tetelbaum (St. Petersburg, Russia), Phys. Solid State 54 (2012) 368–382.
- [16] S. Yerci, U. Serincan, I. Dogan, S. Tokay, M. Genisel, A. Aydinli, R. Turan, J. Appl. Phys. 100 (2006) 074301 (5 pages).
- [17] S. Núñez-Sánchez, R. Serna, J. García López, A.K. Petford-Long, M. Tanase, B. Kabius, J. Appl. Phys. 105 (2009) 013118 (5 pages).
- [18] L. Bi, J.Y. Feng, J. Lumin. 121 (2006) 95-101.
- [19] N. Korsunska, T. Stara, V. Strelchuk, O. Kolomys, V. Kladko, A. Kuchuk, L. Khomenkova, J. Jedrzejewski, I. Balberg, Physica E 51 (2013) 115–119.
- [20] N. Korsunska, T. Stara, V. Strelchuk, O. Kolomys, V. Kladko, A. Kuchuk, B. Romanyuk, O. Oberemok, J. Jedrzejewski, L. Khomenkova, I. Balberg, Nanoscale Res. Lett. 8 (2013) 273.
- [21] A. Steasman, V.V. Afanas'ev, Microelectron. Eng. 36 (1997) 201-204.
- [22] B.J. Jones, R.C. Barklie, J. Phys. D.: Appl. Phys. 38 (2005) 1178–1181.
- [23] S. Yin, E. Xie, C. Zhang, Z. Wang, L. Zhou, I.Z. Ma, C.F. Yao, H. Zang, C.B. Liu, Y.B. Sheng, J. Gou, Nucl. Instr. Methods B 12–13 (2008) 2998–3001.
- [24] S. Yamazaki, J. Kawaga, Jpn. J. Appl. Phys. 10 (1971) 1028-1036.