SiO\(_x\)/SiN\(_y\) multilayers for photovoltaic and photonic applications

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Abstract
Microstructural, electrical, and optical properties of undoped and Nd\(^{3+}\)-doped SiO\(_x\)/SiN\(_y\) multilayers fabricated by reactive radio frequency magnetron co-sputtering have been investigated with regard to thermal treatment. This letter demonstrates the advantages of using SiN\(_y\) as the alternating sublayer instead of SiO\(_2\). A high density of silicon nanoclusters of the order 10\(^{19}\) nc/cm\(^3\) is achieved in the SiO\(_x\) sublayers. Enhanced conductivity, emission, and absorption are attained at low thermal budget, which are promising for photovoltaic applications. Furthermore, the enhancement of Nd\(^{3+}\) emission in these multilayers in comparison with the SiO\(_x\)/SiO\(_2\) counterparts offers promising future photonic applications.

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Introduction
Silicon nanoclusters [Si-ncs] with engineered band gap [1] have attracted the photonic and the photovoltaic industries as potential light sources, optical interconnectors, and efficient light absorbers [2-5]. Multilayers [MLs] of silicon-rich silicon oxide [SiO\(_x\)] alternated with SiO\(_2\) became increasingly popular due to the precise control on the density and size distribution of Si-ncs [6,7]. Moreover, the efficiency of light emission from SiO\(_x\)-based MLs exceeds that of the single SiO\(_x\) layers with equivalent thickness due to the narrower Si-nc size distribution. The ML approach is also a powerful tool to investigate and control the emission of rare-earth [RE] dopants, for example, Er-doped SiO\(_x\)/SiO\(_2\) MLs [8]. It also allows us to control the excitation mechanism of the RE ions by adjusting the optimal interaction distance between the Si-ncs and the RE ions. However, achieving electroluminescence and hence extending its usage for photovoltaic applications are problematic due to the high resistivity caused by SiO\(_2\) barrier layers [9]. Hence, replacement of the SiO\(_2\) sublayer by alternative dielectrics becomes interesting. Due to the lower potential barrier and better electrical transport properties of silicon nitride [Si\(_3\)N\(_4\)] in comparison to SiO\(_2\), multilayers like SiO\(_x\)/Si\(_3\)N\(_4\) [10], Si-rich Si\(_3\)N\(_4\) (SiN\(_y\))/Si\(_3\)N\(_4\) [11], and Si-rich Si\(_3\)N\(_4\)/SiO\(_2\) [12] were proposed and investigated [13] for their optical and electrical properties.

In this letter, we investigate SiO\(_x\)/SiN\(_y\) MLs and compare them with the SiO\(_x\)/SiO\(_2\) counterparts reported earlier [9,14]. We demonstrate that an enhancement in the conductive and light-emitting properties of SiO\(_x\)/SiN\(_y\) MLs can be achieved with a reduced thermal budget. We also report a pioneering study on Nd-doped SiO\(_x\)/SiN\(_y\) MLs. A comparison between the properties of Nd\(^{3+}\)-doped SiO\(_x\)/SiO\(_2\) and SiO\(_x\)/SiN\(_y\) MLs are presented, and we show the benefits of using SiN\(_y\) sublayers to achieve enhanced emission from Nd\(^{3+}\) ions.

Experimental details
Undoped and Nd-doped 3.5-nm SiO\(_x\)/5-nm SiN\(_y\) (50 periods) MLs were deposited at 500°C on a 2-inch p-Si substrate by radio frequency [RF] magnetron co-sputtering of Si and SiO\(_2\) targets in hydrogen-rich plasma for the SiO\(_x\) sublayers and a pure Si target in nitrogen-rich plasma for the SiN\(_y\) sublayers. An additional Nd\(_2\)O\(_3\) target was used to dope the SiO\(_x\) and SiN\(_y\) sublayers by

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Nd³⁺ ions. More details on the growth process can be found elsewhere [15]. The excess Si content in the corresponding SiOₓ and SiNᵧ single layers obtained from RBS studies are calculated to be 25 and 11 at.%, respectively (i.e., SiOₓ₋₁ and SiNᵧ₋₁.₀₃). Conventional furnace annealing under nitrogen atmosphere at different temperatures, \( T_\text{A} \) = 400 to 1,100°C, and times, \( t_\text{A} \) = 1 to 60 min, was performed on the MLs. X-ray diffraction analysis was performed using a Phillips XPert HPD Pro device (PANalytical, Almelo, The Netherlands) with CuKα radiation (\( \lambda = 0.1514 \) nm) at a fixed grazing angle incidence of 0.5°. Asymmetric grazing geometry was chosen to increase the volume of material interacting with the X-ray beam and to eliminate the contribution of the Si substrate. Photoluminescence [PL] spectra were recorded in the 550- to 1,150-nm spectral range using the Triax 180 Jobin Yvon monochromator (HORIBA Jobin Yvon SAS, Longjumeau, Paris, France) with an RS108 Hamamatsu PM tube (Hamamatsu, Shizuoka, Japan). The 488-nm Ar⁺ laser line served as the excitation source. All the PL spectra were corrected by the spectral response of the experimental setup. Top and rear-side gold contacts were deposited on the MLs by sputtering for electrical characterization. Current-voltage measurements were carried out using a SUSS Microtec EP4 two-probe apparatus (SUSS Microtec, Germany) equipped with Keithley devices (Keithly, Cleveland, OH, USA). Energy-filtered transmission electron microscopy [EFTEM] was carried out on a cross-sectional specimen using a TEM-FEG microscope Tecnai F20ST (FEI, Eindhoven, The Netherlands) equipped with an energy filter TRIDIEM from Gatan (Gatan, München, Germany). The EFTEM images were obtained by inserting an energy-selecting slit in the energy-dispersive plane of the filter at the Si (17 eV) and at the SiO₂ (23 eV) plasmon energy, with a width of ± 2 eV.

Results and discussions

Effect of annealing on the PL

Since an annealing at \( T_\text{A} = 1,100°C \) and \( t_\text{A} = 60 \) min is the most suitable to achieve an efficient PL from Si-ncs either in sputtered SiOₓ single layers [7] or in SiOₓ/SiNᵧ MLs [16], such treatment was first employed on SiOₓ/SiNᵧ MLs. The X-ray diffraction [XRD] broad peak centered around 20 = 28° is the signature of the Si nanoclusters’ formation in the SiOₓ/SiO₂ (Figure 1, curve 1) and SiOₓ/SiNᵧ MLs (Figure 1, curve 2) as already observed by means of atomic scale studies on similar multilayers [17]. However, contrary to the PL emission obtained from the SiOₓ/SiO₂ MLs, no PL emission was observed in the SiOₓ/SiNᵧ MLs after such annealing (Figure 2a). This stimulated a deeper investigation of the post-fabrication processing to achieve efficient light emission from the SiOₓ/SiNᵧ MLs.

It was observed that the PL signals from the MLs annealed during \( t_\text{A} = 60 \) min are significant only at lower temperatures (\( T_\text{A} = 400°C \) to 700°C), and high intensities are obtained when the samples are annealed at high temperatures for a short time (\( T_\text{A} = 900°C \) to 1,000°C, \( t_\text{A} = 1 \) min). It is interesting to note that an interplay between \( T_\text{A} \) and \( t_\text{A} \) can yield similar PL efficiencies, as can be seen for \( T_\text{A} = 900°C \) and \( t_\text{A} = 1 \) min, and \( T_\text{A} = 700°C \) and \( t_\text{A} = 15 \) min (Figure 2a).

The highest PL intensity in SiOₓ/SiNᵧ MLs was obtained with \( T_\text{A} = 1,000°C \) and \( t_\text{A} = 1 \) min (Figure 2b, c), whereas the SiOₓ/SiO₂ MLs showed no emission after such short-time annealing treatment (Figure 2a). Corresponding XRD pattern of this short-time annealed [STA] (STA = 1 min, 1,000°C) SiOₓ/SiNᵧ showed a broad peak in the range 20 = 20° to 30° which is absent.
in STA SiO$_x$/SiO$_2$ MLs (Figure 1, curves 3 and 4). This suggests the presence of small Si clusters in the SiO$_x$/SiN$_y$ MLs, with lower sizes (broader peak) by comparison with higher annealing temperature (1,100°C; Figure 1, curves 1 and 2). However, we cannot distinguish which of the sublayer is at the origin of the PL emission. Consequently, the recorded PL may be a combined contribution of the Si-ncs in the SiO$_x$ sublayers and the localized bandtail defect states in the SiN$_y$ sublayers.

Absorption and electrical studies
The absorption studies show similar absorption coefficients for as-grown and STA MLs, whereas annealing at $T_A = 1,100°C$ and $t_A = 60$ min results in an absorption enhancement (Figure 3a). One can say that, at such temperature, an increase in density and size of the Si-ncs occurs due to phase separation of the SiO$_x$ sublayers into Si and SiO$_2$ phases. The formation of Si nanocrystals is complete at $T_A = 1,100°C$ and $t_A = 60$ min and leads to this enhancement. This reasoning is supported by the results obtained from the PL and XRD analysis of the samples annealed at such temperature. The PL in the SiO$_x$/SiN$_y$ MLs is quenched after an increase in the time and temperatures of annealing (Figure 2a), and this can be attributed to the increase in the size leading to the loss of quantum confinement effect. The formation of Si nanoclusters can be witnessed from the appearance of the XRD peak at $2\theta = 28°$ (Figure 1, curve 2), which is not seen in the short-time annealed sample (Figure 1, curve 3).

Considering a balance between light emission and absorption for photovoltaic applications, we chose to study STA SiO$_x$/SiN$_y$ MLs with a total thickness of 850 nm for electrical measurements. Figure 3b compares the dark current curves of 3.5-nm SiO$_x$/5-nm SiN$_y$ with our earlier reported 3.5-nm SiO$_x$/3.5-nm SiO$_2$ (140 nm) MLs [14]. The resistivity was calculated at 7.5 V to be 2.15 and 214 MΩ·cm in the SiO$_x$/SiN$_y$ and SiO$_x$/SiO$_2$ MLs, respectively. Since the thickness of the SiO$_x$ sublayer is the same in both cases (3.5 nm), this decrease in the resistivity of the SiO$_x$/SiN$_y$ MLs can be ascribed to the substitution of 3.5-nm SiO$_2$ by 5-nm SiN$_y$ sublayers. This hundred-times enhanced conductivity at low voltage paves way for further improvement of the SiO$_x$/SiN$_y$ MLs’ conductivity, for example, by decreasing the thickness of this SiN$_y$ sublayer.

Microstructural studies
The high-resolution transmission electron microscope (HRTEM) and EFTEM observations on STA SiO$_x$/SiN$_y$ show Si-ncs in the SiO$_x$ sublayers with an average diameter of 3.4 nm. Only a couple of Si nanocrystals were...
observed in the HRTEM (Figure 4a), whereas a high density of Si-nanoclusters of about $10^{19} \text{ nc/cm}^3$ can be witnessed from the EFTEM images taken at the Si plasmon energy (Figure 4c) implying that they are predominantly amorphous. Interestingly, this density of the Si-nanoclusters (Si-ncs) in the SiO$_x$/SiN$_y$ MLs is an order of magnitude higher than the Si-ncs formed in the SiO$_x$/SiO$_2$ MLs fabricated under similar conditions. The brighter SiO$_x$ sublayers are distinguished from the darker SiN$_y$ sublayers by filtering the Si$_2$O$_4$ plasmon energy (Figure 4b). No evidence of Si-ncs within the SiN$_x$ sublayers was obtained. The STA could favor the formation of Si-ncs only in SiO$_x$ and not in SiN$_y$ sublayers. This could be attributed to the different mechanism of Si-ncs formation in SiO$_x$ and SiN$_y$ in MLs as opposed to that in single layers [18] and/or the low Si-excess content in SiN$_y$.

**Effect of Nd$^{3+}$-doping**

Understanding the microstructure of MLs and considering the enhancement of absorption and emission properties in SiO$_x$/SiN$_y$ MLs compared to the SiO$_x$/SiO$_2$ MLs, we investigate the effect of using SiN$_y$ sublayer on...
the PL emission from Nd$^{3+}$ ions. For this purpose, the SiO$_x$-Nd/SiN$_y$-Nd and SiO$_x$-Nd/SiO$_2$-Nd MLs were fabricated, and their PL properties were compared. No PL emission was detected from the Nd$^{3+}$-doped SiN$_y$ single layers at the different annealing treatments investigated here. Figure 5 shows the PL spectra of the Nd$^{3+}$-doped as-grown MLs under non-resonant excitation with peaks corresponding to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions at 1.37 and 1.17 eV, respectively. The comparison between the PL properties of undoped (Figure 2c) and Nd$^{3+}$-doped MLs (Figure 5, inset) clearly shows the quenching of visible PL emission and the appearance of two Nd$^{3+}$-related PL peaks in the Nd-doped MLs. Moreover, the intensity of Nd$^{3+}$ PL from the doped SiO$_x$/SiN$_y$ MLs exceeds that of the SiO$_x$/SiO$_2$ MLs (Figure 5, inset). Thus, we deal with the efficient energy transfer towards Nd$^{3+}$ ions not only in SiO$_x$ but also in SiN$_y$ sublayers. Since this emission is observed for as-grown MLs, when no Si-ncs were formed in these MLS, it is obvious that the emission from the Nd$^{3+}$ ions in the SiN$_y$-Nd sublayers is due to an efficient energy transfer from SiN$_y$-localized defect states towards the Nd$^{3+}$ ions [19,20]. PL observed from the doped MLs after STA was not intense, and it was quenched with increasing annealing time. The same behavior was observed for the 900°C annealing. This could be due to the decrease in the number of defect-related sensitizers in SiN$_y$ and the formation of Nd$_2$O$_3$ clusters in the SiO$_x$ sublayers [21].

On the other hand, annealing at $T_A = 400^\circ$C to 700°C,

Figure 4 HRTEM (a) and EFTEM (b, c) images. SiO$_x$/SiN$_y$ ML annealed at $T_A = 1,000^\circ$C, $t_A = 1$ min by filtering the energy at SiO$_2$ plasmon (b) and Si plasmon (c) energies, respectively.

Figure 5 PL intensity with annealing time and temperature. Evolution of the Nd$^{3+}$ PL intensity at 1.37 eV for doped SiO$_x$/SiN$_y$ MLs with annealing temperature and time. (Inset) PL spectra of as-grown Nd$^{3+}$-doped SiO$_x$/SiN$_y$ and SiO$_x$/SiO$_2$ MLs with equal number of periods. The thicknesses of the SiO$_x$, SiO$_2$, and SiN$_y$ sublayers are 3.5, 5.0, and 5.0 nm, respectively.
discussed above for the undoped SiO$_x$/SiN$_y$ MLs, enhance Nd$^{3+}$ PL emission when applied to the doped counterparts (Figure 3). Thus, we attain intense PL at a low thermal budget with $T_A$ (400°C to 700°C) and $t_A$ (1 min). To optimize Nd$^{3+}$ emission, the effect of the thickness of each sublayer in SiO$_x$/SiN$_y$ MLs is under consideration now.

Conclusion
In conclusion, we show that SiO$_x$/SiN$_y$ MLs fabricated by RF magnetron sputtering can be engineered as structures for photovoltaic and photonic applications. The as-grown and STA SiO$_x$/SiN$_y$ MLs show enhanced optical and electrical properties than the SiO$_x$/SiO$_2$ counterparts. Besides achieving a high density of Si-ncs at a reduced thermal budget, we show that high emission and absorption efficiencies can be achieved even from amorphous Si-ncs. The Nd-doped MLs, as-grown and those annealed at lower thermal budgets, demonstrate efficient emission from rare-earth ions. We also show that our STA SiO$_x$/SiN$_y$ MLs have about a hundred times higher conductivity compared to the SiO$_x$/SiO$_2$ MLs. These results show the advantages of SiO$_x$/SiN$_y$ MLs as materials for photovoltaic and photonic applications and open up perspectives for a detailed study.

Abbreviations
MLs: multilayers; PL: photoluminescence; Si-nc: silicon nanoclusters; SiN$_x$: silicon-rich silicon nitride; SiO$_x$: silicon-rich silicon oxide; STA: short time annealing at 1,000°C for 1 min.

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Authors’ contributions
RPN fabricated the undoped multilayers under investigation and carried out the characterization studies. UK and OD fabricated the Nd-doped layers and studied the effect of Nd doping on the MLs. JC and CD made contributions to the optical studies. MC performed the EFTEM measurements. FG conceived of the study and participated in the coordination of the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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