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Frequency Conversion Layers for Si Solar Cell Efficiency Improvement

Fabrice Gourbilleau, Lucile Dumont, Julien Cardin, Anaïs Gouesmel, Ing-Song Yu, Christophe Labbé and Hocine Merabet

Abstract SiN_x and SiN_x: Tb³⁺ thin layers deposited by reactive magnetron co-sputtering have been studied with the aim of optimizing the light management in Si solar cells. Those Si-based layers are developed to be compatible with the Si-PV technology. An efficient energy transfer between matrix and terbium ions has been demonstrated and optimized. The layer composition and microstructure as well as its optical properties have been analyzed to favor the required optical properties for achieving a good solar cell, i.e., good anti-reflective properties and high luminescence emission intensity. Finally a Tb-doped SiN_x thin film has been deposited on the top of a Si solar cells and solar cell characteristics studied.

Keywords Si solar cell • Frequency conversion • Down conversion • Down shifting • Silicon nitride • Alumina

Managing the energy harvesting is one of the key issues for this century. Many efforts have been devoted these last years to develop innovative solutions for (i) decreasing the CO₂ production (ii) limiting the energy consumption, (iii) increasing the renewable energy use. Among these solutions proposed, such as energy storage, energy conversion, fuel cells, cooling systems, the development of luminescent materials with high efficiency keeping a low cost process is one of the challenges to face. Luminescent materials are well known to be widely used in light

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emitting diodes, sensors, scintillators, as well as in photovoltaic applications. In most cases, the photon emission is obtained taking benefit of rare earth ion excitation mechanism that offers a wide range of emission wavelengths ranging from the UV to the infrared.

For the case of Silicon solar cell, increasing its efficiency while keeping a low cost process is one of the goals of the Si-PV industry to continuously decrease the cost of the power generation. This is the industrial condition to remain a major player in the provision of power generation solutions in the forthcoming years. The different loss paths in a Si solar cell are well identified and many developments have been performed to solve them. Among them, the thermalization mechanism that is the consequence of the mismatch between the solar spectrum energy (UV region) and the solar cell band gap energy (1.1 eV of the Si solar cell) can be overcome. Such an objective can be achieved by using frequency conversion layers so-called Down Conversion (DC) [1–4] or Down Shifting (DS) [1, 5] layers. Such layers have been developed in order to convert one UV incident photon into two IR ones (DC case) or one UV incident photon into one visible one (DS case) that can be absorbed by the Si cell. To reach this objective many systems using a couple of trivalent ions such as $\text{Pr}^{3+}\text{-Yb}^{3+}$, $\text{Tb}^{3+}\text{-Yb}^{3+}$, $\text{Ce}^{3+}\text{-Yb}^{3+}$ for DC process or one trivalent ions such Pr^{3+} , Tb^{3+} for the DS conversion have been studied. Unfortunately, the major drawbacks of these layers are the use of a non Si-compatible process due to the nature of the host matrix as well as the low absorption cross section of the rare earth ions that limits their excitability in the solar spectrum range [5–9]. To overcome this problem, a Si-PV compatible host matrix containing sensitizers has been developed. The presence of sensitizers allows to efficiently excite rare earth ions. Moreover, to keep a low cost process for a future development in the SI-PV industry, the host matrix developed should have good anti-reflective properties.

This paper details the development a Si-PV compatible host matrix that efficiently absorbs the solar spectrum and allows an efficient excitation of rare earth ions. Moreover, such a host matrix should favor the incorporation of a high content of rare earth ions without the detrimental clustering effect [10, 11]. The purpose of this paper is to describe the fabrication and study of Tb:Yb and Tb-doped Si-based thin films or Al-based thin films deposited by reactive co-sputtering or ALD techniques, respectively.

The layers have been deposited on p-type 250 μm -thick [001] 2'' silicon (Si) substrates by either reactive magnetron co-sputtering in a nitrogen-rich plasma or Atomic Layer Deposition using an oxygen plasma. For the former, the matrix composition (Si/N ratio) was tuned by varying the Ar/N_2 ratio of the gas flux injected or the plasma pressure while for the later, the Al_2O_3 -based layer characteristics have been monitored through the Oxygen Plasma time and the substrate temperature. For the sputtering approach, the rare earth ions incorporation was controlled by the RF power density applied on the Tb^{3+} target (RFP_{Tb}). RFP_{Tb} was varied between 0.3 and 1.8 W/cm^2 . After optimization, Yb ions have been incorporated to produce the DC layers. For all the undoped- and Tb^{3+} - and $\text{Tb}^{3+}\text{-Yb}^{3+}$ doped -SiN_x deposited layers, the target power density applied on the silicon target

was fixed at 4.5 W/cm^2 in agreement with previous studies [12]. The deposition temperature was set at $200 \text{ }^\circ\text{C}$ while the deposition time was adjusted to obtain 90 nm-thick films whatever the deposition conditions. After deposition, the samples were annealed during 1 h by classical thermal annealing (CTA) at $850 \text{ }^\circ\text{C}$. Concerning the ALD deposition techniques, only DS layers have been fabricated using precursors containing Tb. The fabricated layers have been annealed after deposition at lower temperature ($<650 \text{ }^\circ\text{C}$) using either classical thermal annealing or rapid thermal annealing approaches. The composition of the fabricated layers has been investigated by means of Fourier Transform Infrared measurements (FTIR). They were performed at room temperature thanks to a Thermo Nicolet Nexus 750 II spectrometer working in the $4000\text{--}400 \text{ cm}^{-1}$ range, with a resolution of 5 cm^{-1} . The emission and excitation properties, photoluminescence (PL) and photoluminescence in excitation (PLE) experiments were performed at room temperature on the films. PL experiments have been carried out using a Lot-Oriel 1 kW-Xenon lamp connected to an OMNI300 monochromator. The PL spectra were recorded with a Hamamatsu (R5108) photomultiplier tube after the dispersion of the PL signal by a MSH 300 OMNI monochromator. The detection system was locked in with a SR830 amplifier referenced at the excitation light beam chopped frequency. The same system has been used for the PLE experiment. PL and PLE spectra obtained corrected by the set-up and by the lamp emission intensity in the PLE case.

First Tb-doped systems have been optimized to get the maximum photoluminescence emission under UV range excitation for DS process or prior to incorporating the Yb^{3+} ions. An example of the achieved Tb emission in a Tb-doped SiN_x host matrix fabricated by reactive co-sputtering is shown on Fig. 1a. The same feature is achieved for the Tb-doped Al_2O_3 layers obtained by ALD. Four emission peaks can be observed corresponding to the transitions from the $^5\text{D}_4$ to the $^7\text{F}_i$ levels as presented on Fig. 1b. Note that the emission spectrum has been achieved under a low photon flux ($1.9 \times 10^{15} \text{ photons/cm}^2$) excitation at 300 nm for the Tb^{3+} ions which has a low absorption cross section below $2 \times 10^{-21} \text{ cm}^2$ as reported in [13]. Such a result evidences an efficient indirect excitation of Tb^{3+} ions which may witness a sensitization of the Tb^{3+} ions by defect states of the matrix as already evidenced in Tb^{3+} -doped SiO_xN_y and $\text{Tb-Si}_x\text{O}_y$ matrices [10].

With the incorporation of Yb^{3+} ions to the system, we observed a decrease of the Tb emission while the one corresponding to the $^2\text{F}_{5/2}\text{--}^2\text{F}_{7/2}$ transition (980 nm) of the Yb^{3+} ions rises. This is the signature of an efficient energy transfer from the Tb^{3+} ions to the Yb^{3+} ones. For this system, a quantum efficiency as high as 200% has been achieved in a composite or a multilayer structure. To improve the coupling rate between the rare earth ions, fabrication parameters have been optimized. The goal is to get the maximum of emitted photon at 980 nm. After optimization, these frequency conversion layers have been deposited on top of industrial crystalline Si solar cells. For this purpose, their deposition steps have been integrated in the industrial cells fabrication process.

Reflectance measurements have been carried out on the different frequency conversion layers before depositing the metallic contact for the achievement of the Solar Cell. A typical reflectance measurement result is displayed on Fig. 2. The

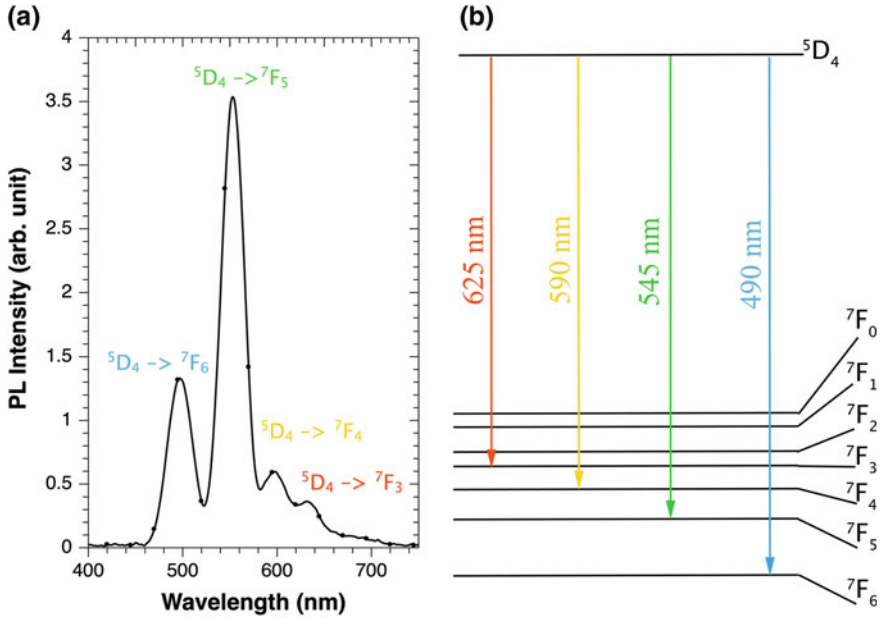


Fig. 1 **a** PL spectrum of a Tb-doped SiN_x under 300 nm excitation wavelength. **b** Energy level scheme of the Tb³⁺ ions

reflectance values for a nitride layer used as a reference and the Tb-doped layers are below the value of 5% in wide domain of wavelength ranging from 350 to 750 nm and a bump is observed after 1020 nm. The reflection efficiency in the 300–1200 nm range is of 6.04% for the device coated with the SiN_x layer and reaches 6.20% by adding the rare earth ion. Such value demonstrates the high anti-reflective properties of the SiN_x host matrix whatever it is doped or not.

External and Internal Quantum Efficiency measurements have been carried out on Si Solar Cell for these Down Shifting- and the Down Conversion- layers. A typical Internal Quantum Efficiency (IQE) of the solar cell on the top of which the SiN_x-based layers described in Fig. 2 have been deposited is displayed on Fig. 3.

The IQE spectra reveals that the Tb-doped layer has a higher IQE than the undoped one from 300 to 900 nm with a particular increase of 15% in the UV range (300–400 nm). Above 900 nm one can note a slight decrease of the doped layer with respect to the undoped one. This result shows that the IQE is larger for UV photons thanks to the Tb-doped layer.

Thus this latter acts as a down-shifting layer that may improve the solar cell efficiency. Such down-shifting layer can be a promising solution for improving the Si Solar Cell considering that the process developed is fully compatible with the industrial process. More details will be given on the electrical and optical

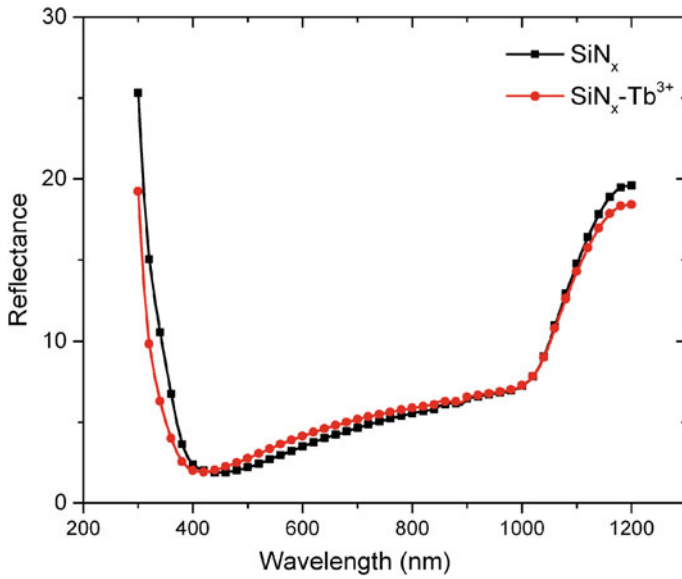


Fig. 2 Reflectance characteristics of the SiN_x (black) and SiN_x:Tb³⁺ (red) anti-reflective layers deposited on a textured Si surface

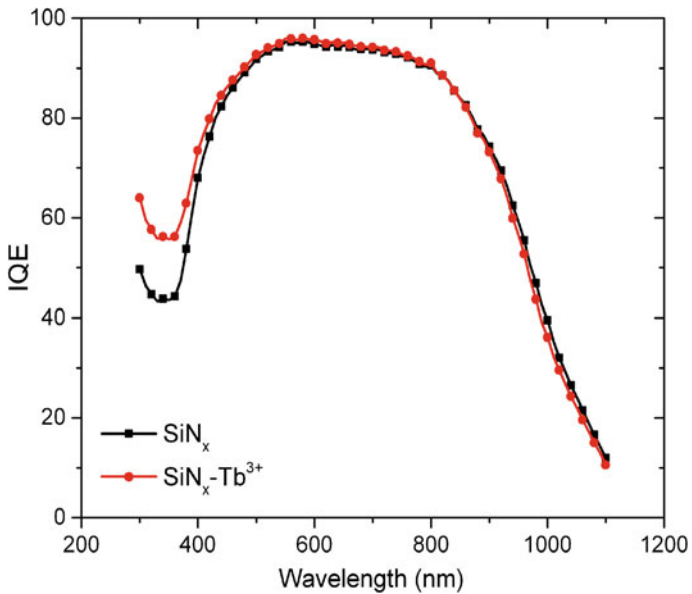


Fig. 3 IQE curves of a solar device with either the optimized SiN_x (black) or the optimized SiN_x:Tb³⁺ (red) layers on top

characteristics of these different frequency conversion layers and the increased efficiency achieved.

To conclude, in this paper, undoped, Tb^{3+} - and Tb^{3+} - Yb^{3+} doped SiN_x layers deposited by reactive magnetron co-sputtering have been studied in order to obtain a thin DS or DC layer that have good anti-reflective properties and favor the emission of NIR photon that can be absorbed by the solar cell. For the ALD deposited layer, only DS layer (Tb^{3+} - Al_2O_3) layers have investigated. Studies of the composition, the microstructure, and the optical properties have been carried out to get the maximum emission efficiency of the rare earth ions. The IQE of the optimized layers deposited by means of co-sputtering approach were compared. Thus it was found that the DS layer improve by 15% the IQE in the UV part of the solar spectrum and by 25% the global efficiency of the Si solar cell. Concerning the DC layer, a relative increase of 1.5% has been evidenced demonstrating the promising potential of these Si-PV compatible layer for enhancing the efficiency of Si Solar Cell.

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References

1. C. Strümpel, M. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Švrček, C. del Cañizo, I. Tobias, Modifying the solar spectrum to enhance silicon solar cell efficiency—an overview of available materials. *Solar Energy Mater. Solar Cells* **91**, 238–249 (2007). doi:[10.1016/j.solmat.2006.09.003](https://doi.org/10.1016/j.solmat.2006.09.003)
2. B.S. Richards, Enhancing the performance of silicon solar cells via the application of passive luminescence conversion layers. *Solar Energy Mater. Solar Cells* **90**, 2329–2337 (2006). doi:[10.1016/j.solmat.2006.03.035](https://doi.org/10.1016/j.solmat.2006.03.035)
3. K.D. Oskam, R.T. Wegh, H. Donker, E.V.D. van Loef, A. Meijerink, Downconversion: a new route to visible quantum cutting. *J. Alloys Comp.* **300–301**, 421–425 (2000). doi:[10.1016/S0925-8388\(99\)00755-0](https://doi.org/10.1016/S0925-8388(99)00755-0)
4. B.S. Richards, Luminescent layers for enhanced silicon solar cell performance: down-conversion. *Solar Energy Mater. Solar Cells* **90**, 1189–1207 (2006). doi:[10.1016/j.solmat.2005.07.001](https://doi.org/10.1016/j.solmat.2005.07.001)
5. E. Klampaftis, D. Ross, K.R. McIntosh, B.S. Richards, Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: a review. *Solar Energy Mater. Solar Cells* **93**, 1182–1194 (2009). doi:[10.1016/j.solmat.2009.02.020](https://doi.org/10.1016/j.solmat.2009.02.020)
6. K.R. McIntosh, G. Lau, J.N. Cotsell, K. Hanton, D.L. Bätzner, F. Bettiol, B.S. Richards, Increase in external quantum efficiency of encapsulated silicon solar cells from a luminescent down-shifting layer. *Prog. Photovolt. Res. Appl.* **17**, 191–197 (2009). doi:[10.1002/pip.867](https://doi.org/10.1002/pip.867)
7. D. Chen, Y. Wang, Y. Yu, P. Huang, F. Weng, Quantum cutting downconversion by cooperative energy transfer from Ce^{3+} to Yb^{3+} in borate glasses. *J. Appl. Phys.* **104**, 116105 (2008). doi:[10.1063/1.3040005](https://doi.org/10.1063/1.3040005)

8. Q. Duan, F. Qin, D. Wang, W. Xu, J. Cheng, Z. Zhang, W. Cao, Quantum cutting mechanism in Tb³⁺-Yb³⁺+co-doped oxyfluoride glass. *J. Appl. Phys.* **110**, 113503 (2011). doi:[10.1063/1.3662916](https://doi.org/10.1063/1.3662916)
9. X. Liu, S. Ye, Y. Qiao, G. Dong, B. Zhu, D. Chen, G. Lakshminarayana, J. Qiu, Cooperative downconversion and near-infrared luminescence of Tb³⁺-Yb³⁺+codoped lanthanum borogermanate glasses. *Appl. Phys. B.* **96**, 51–55 (2009). doi:[10.1007/s00340-009-3478-z](https://doi.org/10.1007/s00340-009-3478-z)
10. Y.-T. An, C. Labbé, M. Morales, P. Marie, F. Gourbilleau, Fabrication and photoluminescence properties of Tb-doped nitrogen-rich silicon nitride films. *Phys. Status Solidi C* **9**, 2207–2210 (2012)
11. L. Dumont, J. Cardin, P. Benzo, M. Carrada, C. Labbé, A.L. Richard, D.C. Ingram, W.M. Jadwisienczak, F. Gourbilleau, SiN_x:Tb³⁺-Yb³⁺, an efficient down-conversion layer compatible with a silicon solar cell process. *Solar Energy Mater. Solar Cells* **145**, 84–92 (2016). doi:[10.1016/j.solmat.2015.09.031](https://doi.org/10.1016/j.solmat.2015.09.031)
12. O. Debieu, R.P. Nalini, J. Cardin, X. Portier, J. Perrière, and F. Gourbilleau, Structural and optical characterization of pure Si-rich nitride thin films. *Nanoscale Res. Lett.* **8**(1), 31 (2013).
13. D.K. Sardar, K.L. Nash, R.M. Yow, J.B. Gruber, U.V. Valiev, E.P. Kokanyan, Absorption intensities and emission cross sections of Tb³⁺ (4f⁸) in TbAlO₃. *J. Appl. Phys.* **100**, 083108 (2006). doi:[10.1063/1.2358401](https://doi.org/10.1063/1.2358401)