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Down-shifting Si-based layer for Si solar applications

L. Dumont[a], P. Benzo[a,1], J. Cardin[a], I.-S. Yu[b], C. Labbé[a], P. Marie[a], C. Dufour[a], G. Zatryb[c], A. Podhorodecki[c], F. Gourbilleau[a,*]

[a] CIMAP, Normandie Univ, ENSICAEN, UNICAEN, CEA, CNRS, 6 Bd Maréchal Juin, 14050 Caen Cedex 4, France
[b] Department of Materials Science and Engineering, National Dong Hwa University, Hualien 97401, Taiwan
[c] Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland

ARTICLE INFO

ABSTRACT

SiN_x and $SiN_x:Tb^{3+}$ thin layers were deposited by reactive magnetron co-sputtering with the objective 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 SiN_x matrix and terbium ions (Tb^{3+}), enhancing this system absorption, has been demonstrated and optimized. The layer composition and microstructure as well as its optical properties have been analyzed with the aim of improving both its anti-reflective properties and its luminescence emission intensity. An optimized layer was obtained by co-sputtering of Si and Tb targets in a nitrogen rich atmosphere. The emission efficiency of the $SiN_x:Tb^{3+}$ layer is compared to the one of previously optimized $SiO_xN_y:Tb^{3+}$ layer. Finally we show how $SiN_x:Tb^{3+}$ thin films may be integrated on top of Si solar cells and act simultaneously as a down-shifting layer and antireflective coating.

1. Introduction

Solar energy is one of the sustainable energies considered for the progressive replacement of fossil fuels in our society. However, to continuously reduce the cost per Watt, improving Solar Cell (*SC*) efficiency is essential. Despite *Si-SC* technology being currently the most used, it suffers from a low efficiency ranging from 12% to 20% depending on the quality level of the system. This low efficiency is mainly due to the energy mismatch between the solar spectrum and the Si bandgap. Indeed, only the photons with energy higher than the Si bandgap are absorbed by the *SC*. Moreover, the energy excess of those photons with respect to the bandgap energy is released into the matrix via transfer to phonons in a thermalization process. Consequently, an increase of 1 °C above 25 °C leads to a decrease of the cell efficiency by around 0.65% [1–3]. The rising temperature also leads to a faster aging of the cell. Another cause of the low efficiency limit is the fact that all the light received by the cell is not absorbed due to reflection of the incident light at the surface of the *SC*. Even while using light-trapping devices, Yablonovitch [4] demonstrated that a maximum achievable light path length enhancement of $4 n^2$ may be attained (with n the refractive index of the bare *SC*).

As laboratory *Si-SC* efficiency is close its theoretical limit [5], one of the next steps for improving the single junction *Si-SC* efficiency consists in studying the management of the light within the *SC*. Some solutions are already implemented on *SC* such as texturation or anti-reflective layers [5–7]. New solutions consisting in a frequency conversion of the light to adapt the solar spectrum to the cell bandgap are down-shifting [8,9] and down/up-conversion layers [8,10–14]. Those frequency conversions are usually achieved by using rare earth-doped matrices. The up-conversion layer concerns the photons transparent for the *Si-SC* and thus is placed at the bottom of the cell. The down-conversion or down-shifting layers are deposited on top of the solar cells to improve the use of the incoming photons with an energy higher than the Si bandgap. In a down-conversion (*DC*) layer, one *UV* photon is transformed in two *IR* photons having an energy just above the *SC* bandgap. Thus the number of photons used by the cell increases while the thermalization decreases. Whereas a down-shifting (*DS*) layer will absorb one *UV* photon and reemit a single photon with an energy above the *SC* bandgap. Thus the down-shifted photons wavelengths better match the spectral photo-absorptivity response of the *Si-SC*. In addition the thermalization process will take place in the *DS* layer instead of the *SC*. Thus by thermally isolating the *DS* layer from the *SC*, with transparent materials, the thermalization could be partially decoupled from the cell which reduces the entropy flow and may increase the cell efficiency as described by Landsberg efficiency [15]. A *DS* layer is composed of a matrix containing one rare earth ion whereas in a down-conversion layer, two or more rare earth ions are incorporated in the matrix. Many matrices and rare earth ions have been

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studied in both cases [9,16–19].

The goal of our study consists in developing Si-based frequency conversion layers compatible with the *Si-SC* industry process in order to lower the production cost and increase the *SC* efficiency. Moreover, such *DS*- or *DC*-layer should be stable, which was not the case with most of the matrices studied. Indeed, they were either degraded during the *SC* processing or damaged by high energy photons during sun exposure [14]. In addition, some of those used materials were toxic because of the presence of fluorine [20] or of heavy metals such as cadmium [21], or lead [22]. Following this reasoning, various studies using a silicon oxynitride matrix, SiO_xN_y, doped with terbium ions (Tb^{3+}) have been carried out [23–25]. However, the presence of oxygen favors the rare earth clusters formation that is detrimental to an intense emission. Our study then focuses on the terbium-doped silicon nitride matrix, $SiN_x:Tb^{3+}$, such a system being free of oxygen to promote rare earth ions incorporation [26]. SiN_x has been chosen as host matrix since it is already used as anti-reflective layer on industrial *Si-SC* which is a way to develop new approach keeping a low production cost of the *SC*. Besides, such a host matrix should be an efficient sensitizer to the rare earth ions that have a weak absorption cross-section (below 2×10^{-21} cm^2 [27]) in silicon based matrices. Consequently, such a host matrix should have a high absorption in the *UV* range as well as efficient sensitizing properties toward Tb^{3+} ions while keeping its anti-reflective properties.

In this paper we will describe the optimizations of the undoped SiN_x and $SiN_x:Tb^{3+}$ layers. The goal is to develop a layer that presents at the same time an efficient *DS* frequency conversion process, and anti-reflective property. Thus the composition and microstructure, as well as the optical properties of these systems will be studied.

2. Material and methods

The layers studied were deposited on p-type 250 µm-thick [001] 2″ silicon (Si) substrates by radio-frequency reactive magnetron co-sputtering in a nitrogen-rich plasma. The matrix composition (Si/N ratio) was tuned by varying the Ar/N_2 ratio (rN_2) of the gas flux injected or the plasma pressure (*P*). In the case of the Tb^{3+}-doped system, the rare earth ions incorporation was controlled by the power density applied on the Tb target (RFP_{Tb}). This later was varied between 0.3 and 1.8 W/cm^2. For all the undoped- and Tb^{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 [28]. For all the samples, the deposition temperature was fixed at 200 °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 °C, under N_2 flow.

The composition of the studied layers has been investigated by means of Fourier Transform Infrared (*FTIR*) measurements. They were performed at room temperature using a Thermo Nicolet Nexus 750 II spectrometer working in the 4000–400 cm^{-1} range, with a resolution of 5 cm^{-1}. By fitting the obtained spectra with Gaussian functions, the vibration band positions were obtained.

Both the thickness and the complex refractive index of the studied layers were determined from ellipsometry measurements employing a UVISEL Jobin-Yvon ellipsometer with an incident angle of 66.2°. The experimental I_c and I_s ellipsometry spectra were recorded on a 1.5–5 eV range with 0.01 eV resolution. The parameters (thickness and n) are determined by fitting the experimental data by a dispersion law derived from the Forouhi-Bloomer model [29] of amorphous semiconductors using the DeltaPsi2 software.

In order to study the emission and excitation properties, photoluminescence (*PL*) and photoluminescence excitation (*PLE*) experiments were performed at room temperature on the films. Specifically, the *PL* setup included a Lot-Oriel 1 kW-Xenon lamp connected to an OMNI300 monochromator used as a tunable light source. 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 *PL* and *PLE* spectra obtained were normalized by the sample thickness and the PLE spectra are also corrected by the excitation intensity.

The PL decays were measured using modified Quanta Master system from Photon Technology International (PTI). A pulsed 266 nm line of an actively Q-switched diode-pumped solid state YAG:Nd laser (Elforlight Ltd.) was used in this experiment as the excitation source. The PL decay traces were measured at the emission wavelength of 545 nm, corresponding to the main $^5D_4$-$^7F_5$ transition of Tb^{3+} ions. The time resolution about 1 µs is small enough to resolve correctly the Tb^{3+} PL lifetimes.

A simulation program based on the transfer matrix method (*TMM*) [30] was run based on the deduced ellipsometric parameters (complex refractive index of a layer, substrate, superstrate and stack of layers, and thicknesses) to calculate the absorbance *A*, reflectance *R*, and transmittance *T* of the fabricated *DS* films deposited on top of a silicon *SC*. In addition, values representing the layer and its interaction with the AM1.5 solar spectrum [31] are defined. The absorbance efficiency (A_{eff}) is defined by the integration of the absorbance *A* convoluted by the solar irradiance spectrum ($I_{AM1.5}$) and normalized by the integrated solar irradiance spectrum ($I_{AM1.5}$):

$$A_{eff} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} A(\lambda) I_{AM1.5}(\lambda) d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_{AM1.5}(\lambda) d\lambda} \tag{1}$$

The reflectance (R_{eff}), and transmittance (T_{eff}) efficiencies are defined similarly using the reflectance *R*, and the transmittance *T* respectively A_{eff}, R_{eff} and T_{eff} represent the fraction of the sunlight that is absorbed, reflected and transmitted respectively by the layer over a given spectral range. Those values may be compared over different wavelength ranges and allow an easy comparison between samples.

The light emission and propagation in our samples were studied thanks to an 3*3 extended transfer matrix method (*ETMM*) coupled with electric dipole emitters [32–34]. This method uses the ellipsometric parameters (refractive indexes and thicknesses) of the sample and the surrounding media. With this method we can deduce the emission distribution as a function of the wavelength and the emission angle in each considered medium. The Tb^{3+} spectral line shape was assumed to be described by Gaussian functions representing the $^5D_4$ to $^7F_6$ and $^5D_4$ to $^7F_5$ energy transitions of the Tb^{3+} ions (Fig. 1). *PL* spectra were obtained by the integration over emission angles in the conversion layer, air, and silicon material substrate (wafer or *SC*). A supplementary integration over the bandwidth led to the luminescence integrated over the spectral range I^{PL}_i in each of the three media i
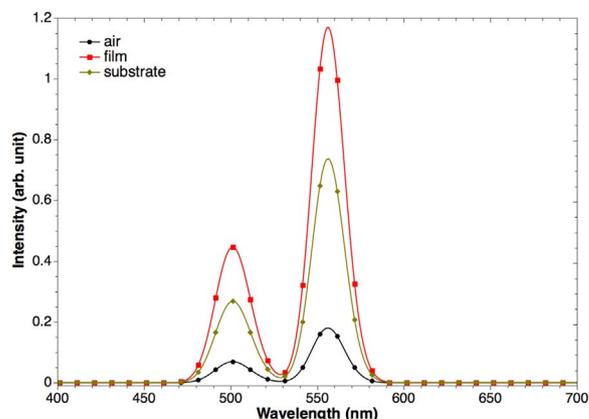

Fig. 1. Modeled Tb^{3+} *PL* spectra recorded in the three media, only the two more intense peaks/bands representing the $^5D_4$ to $^7F_6$ and $^5D_4$ to $^7F_5$ energy transitions are considered.