

Proceeding of ICNM - 2009

1st International Conference on Nanostructured Materials and Nanocomposites (6 – 8 April 2009, Kottayam, India)

Published by : Applied Science Innovations Private Limited,
India.

<http://www.applied-science-innovations.com>

Si-nanostructures for photovoltaic and photonic applications

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I. Introduction

Since the discovery of the quantum confinement effect (QCE) of carriers in nanometer scaled Si grains¹, numerous studies dealing with nanostructured Si-based thin films have been carried out. The main goal consists in taking benefit of the QCE for developing new low cost structures, CMOS compatible and presenting a wide range of industrial interest in several fields. Among all the possible applications either in microelectronic, photonic or photovoltaic domain, one can cite (i) the nanomemories²⁻⁴ and non linear properties⁵⁻⁶, (ii) the sensitizing effect of Si nanoclusters (Si-nc) towards rare earth ions (RE)⁷⁻¹¹ and (iii) more recently, the use of Si-nc as a promising material for the future generation of solar cells¹²⁻¹³. Among these potential applications, the efficient transfer from the Si-nc towards RE has attracted number of researches since it opened the ways of light emitting device based on nanostructured Si. In the same way, the widening of the Si band gap due to QCE offers new possibilities for providing thin films with a high solar conversion yield and a low fabrication cost for the third generation of solar cells.

In this paper, we will describe shortly some of the results obtained by our team on the fabrication and studies of nanostructured Si-based thin films for photovoltaic (PV) or photonic applications.

II. Experimental

Si-rich silicon oxide (SRSO) layers have been fabricated by a reactive process that we developed in 2001 and called reactive magnetron sputtering¹⁴. This process consists in sputtering a pure SiO₂ target with a hydrogen-rich plasma for incorporating a Si excess in the growing layer. By varying the deposition parameters such as hydrogen partial pressure and substrate temperature, we are able to control the Si incorporation in the samples¹⁵. For the rare

earth-doped materials, Nd-SRSO composite layers have been fabricated by the reactive co-sputtering of a SiO₂ target topped with Nd₂O₃ chips. The Nd content incorporated in the film is varied according to the number of Nd₂O₃ chips. After an appropriate annealing treatment, room temperature properties of the Nd³⁺ emission have been analyzed by photoluminescence (PL) measurements. For evidencing the sensitizing role of the Si-nc towards the RE, PL experiments have been carried out with the non resonant 488nm-excitation Ar laser line towards the Nd³⁺ ions. Concerning the PV applications, SRSO/SiO₂ multilayers have been fabricated varying the Si-ng size through the control of SRSO sublayer thickness. The effect of Si-ng size has been investigated on the optical properties of the MLs which have been previously annealed at 1100°C during 1 hour.

III. Results and discussion

III.1 Photonic applications

For the system Nd-doped Si-SiO₂ fabricated by reactive magnetron co-sputtering, Figure 1 reports the room temperature PL spectra recorded with the 488 nm Ar line excitation for layers prepared with different hydrogen partial pressure in the plasma (P_{H_2}). The inset displays the absorption spectrum obtained on a thick Nd-SiO₂ sputtered layer. It shows that

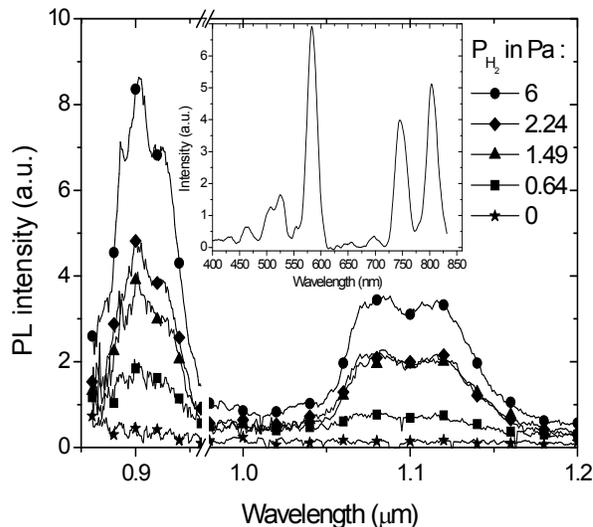


Figure 1 : Room temperature PL spectra of Nd-doped layers deposited using different hydrogen partial pressures P_{H_2} . The inset shows the absorption spectrum of Nd³⁺ ions in a Nd-doped-SiO₂ sputtered thick film.

the 488 nm excitation used for PL excitation is almost non-resonant for the Nd³⁺ ions since absorption is weak in this region. The different PL spectra of the figure 1 indicate that the PL emission of Nd³⁺ ions is almost undetectable for the sample free from Si excess, i.e. deposited with pure Ar plasma ($P_{H_2} = 0$ Pa). A slight increase of P_{H_2} leads to the appearance of two emission bands detected at 0.92 μm ($^4F_{3/2} \rightarrow ^4I_{9/2}$) and around 1.08 μm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) which represent the signature of Nd³⁺ intra 4f-transitions. The peak at 1.12 μm is attributed to the luminescence of the P type silicon substrate. Such a signature of the Nd³⁺ intra 4f-transitions is a clear evidence of the sensitizing role played by the Si-nc towards the RE ions. The evolution of the Nd³⁺ emission intensity with P_{H_2} can be attributed to an increase of

the Si-nc density due to the multiplication of the Si seeds favoured by a concomitant deposition-etching process occurring with the hydrogen species present in the plasma. This increase of the Si-nc density keeping constant the Si excess, means a growth of more numerous and smaller Si-nc, that allow an increase of the numbers of excited Nd³⁺ ions by reducing the average distance between the sensitizer and the RE. This increase of the number of excited RE can therefore explain the observed increase of the PL intensity. The benefit of exciting Nd³⁺ through Si-ng lies in the fact that the absorption cross section of Si-ng is four

orders of magnitude higher than that of Nd^{3+} which thus offers a higher efficiency for future photonic devices.

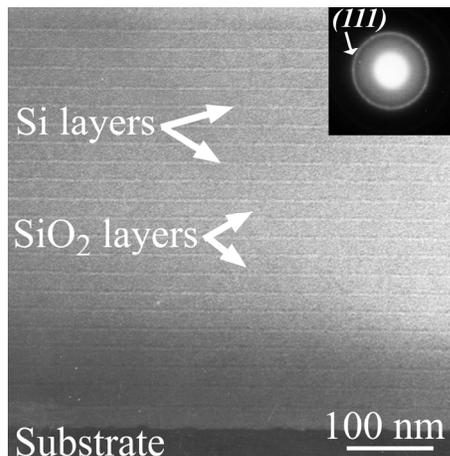


Figure 2 : Typical micrograph of a SRSO/SiO₂ multilayer with a 3 nm thick SRSO and 19 nm thick SiO₂ sublayers.

III.2 Photovoltaic applications :

A typical MLs micrograph of a sample consisting of a regular stacking of 3 nm thick SRSO and 19 nm thick SiO₂ is presented on figure 2. The corresponding electron diffraction pattern evidences the presence of Si nanocrystallites in the SRSO layers as revealed by the (111) ring.

Four different MLs deposited on fused quartz substrate are constituted of alternation of 1.5 nm thick SiO₂ sublayers and sublayers containing Si-ng which size varies from 1.5 nm to 8 nm. The total film thickness is fixed to about 1.4 μm for all the layers. After an annealing treatment at 1100°C during one hour, these films have been studied by transmission experiments and the resulting linear absorption α_{grain} of the Si-ng is plotted versus energy on figure 3. The curves show that the smallest Si grains offer the highest absorption coefficient while for grain diameters in the 3nm-8nm

range, α_{grain} is lower by a factor 4 and the absorption curves almost similar. Taking into account previous results in which we have observed that Si-ng are amorphous below 3 nm, one can thus conclude that the use of amorphous Si-ng as structure for absorbing the solar light should allow to optimize the yield of the cell.

Conclusion

Taking benefit of the quantum confinement effect in nanostructured Si-based thin films offers new possibilities of high performance structures in a wide range of applications. Such structures could open a way on new CMOS compatible devices which interests microelectronic, photovoltaic as well as photonic field.

Acknowledgements

This work is supported by French National Agency (ANR) through Nanoscience and Nanotechnology Program (Project DAPHNES n°ANR-08-NANO-005) and through ANR Solaire Photovoltaïque (Project DUOSIL).

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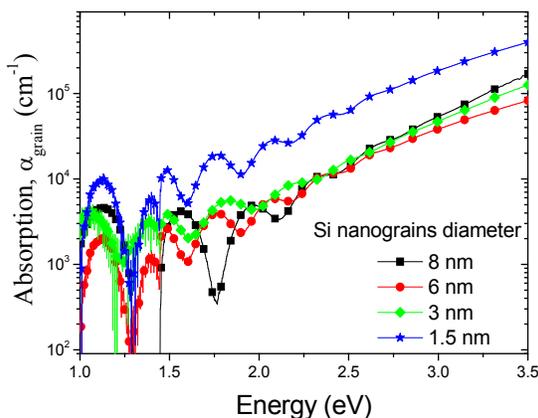


Figure 3 : Absorption spectra of Si-ng for different Si-ng diameters

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