HAL
open science

Enhancing The Optical And Electrical Properties of Si-based Nanostructured Materials

Ramesh Pratibha Nalini, Philippe Marie, Julien Cardin, Christian Dufour, Panagiotis Dimitrakis, Pascal Normand, Marzia Carrada, Fabrice Gourbilleau

To cite this version:

Ramesh Pratibha Nalini, Philippe Marie, Julien Cardin, Christian Dufour, Panagiotis Dimitrakis, et al.. Enhancing The Optical And Electrical Properties of Si-based Nanostructured Materials. Energy Procedia, 2011, European Materials Research Society ConferenceSymp. Advanced Inorganic Materials and Concepts for Photovoltaics, 10, pp.161-166. 10.1016/j.egypro.2011.10.170 . hal-01139866

HAL Id: hal-01139866

https://hal.science/hal-01139866v1

Submitted on 11 Apr 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

European Materials Research Society Conference
Symp. Advanced Inorganic Materials and Concepts for Photovoltaics

Enhancing The Optical And Electrical Properties of Si-based Nanostructured Materials

R. Pratibha Nalini[a *], P. Marie[a], J. Cardin[a], C. Dufour[a], P. Dimitrakis[b], P. Normand[b], M. Carrada[c], F. Gourbilleau[a]

[a] *CIMAP, UMR CNRS/CEA/ENSICAEN/UCBN, 6 boulevard du Maréchal Juin, 14050 Caen Cedex 4, France*
[b] *Institute of Microelectronics, NCSR « Demokritos », P.O. Box 60228, 15310 Aghia Paraskevi, Greece.*
[c] *CEMES/CNRS, 29 rue Jeanne Marvig, BP 94347, 31055 Toulouse Cedex 4, France.*

Abstract

Multilayer structures of Si rich silicon oxide (SiO_x) alternated with two types of dielectric sublayers viz. SiO_2 or SiN_x have been studied. An enhancement in the density of nanoclusters within the SiO_x sublayer is achieved by using the reactive magnetron co-sputtering method. The effect of SiN_x sublayer thickness on the photoluminescence properties is investigated. We succeed in enhancing the absorption and the pholuminescence properties of the multilayers by replacing SiO_2 by SiN_x sublayers. We also achieve a higher conductivity in SiO_x/SiN_x with an improved thermal budget. This preliminary study gives a deep insight to optimize materials for future solar cell device applications with enhanced properties at reduced thermal budget.

Keywords: Si nanoclusters; SiO_x; SiN_x; multilayers; absorption; photoluminescence; resistivity.

1. Introduction

Nanostructures of silicon have attracted the photovoltaic field due to their promising optoelectronic properties and their compatibility with the already existing Si technologies. The visible emission from Si based structures is attributed to the quantum confinement of the photogenerated carriers [1,2]. Hence it becomes important to precisely control the size of the nanostructured silicon. A multilayered (ML) configuration of Si nanoclusters (Si-ncs <5nm) alternated with dielectric sublayers such as SiO_2 is proved to exhibit quantum confinement effects [3-6]. An efficient absorption of light by the solar cell can be

E-mail address: pratibha-nalini.sundar@ensicaen.fr

attained by optimizing the density and size of Si-nc in such a ML configuration. The fabrication and optimization of Silicon Rich Silicon Oxide (SiO_x)/SiO_2 MLs using reactive magnetron sputtering approach have been demonstrated in our earlier reports [7,8]. Though an efficient photoluminescence is obtained by the aforesaid MLs the higher bandgap of SiO_2 serves as a barrier for electric transport and in turn the conductivity. Hence the replacement by SiN_x with smaller bandgap becomes a possible solution for more efficient solar cells. Visible luminescence from Si-nc embedded in SiN_x matrix has been recently demonstrated [9,10]. However there is no comprehensive study of electrical properties from SiO_x/SiN_x MLs. In this paper we propose reactive magnetron co-sputtering growth approach to increase the Si-ncs concentration within the SiO_x sublayers of MLs. We also compare two types of MLs (I) SiO_x/SiO_2 and (II) SiO_x/SiN_x grown by this approach and analyze their optical and electrical behaviors. This paper reports an enhancement in the optoelectronic properties of SiO_x/SiN_x in comparison to SiO_x/SiO_2 MLs.

2. Experimental

The SiO_x/SiO_2 (SiOx=SiO2=3.5) and SiO_x/SiN_x (SiOx=3.5 and SiNx=5.5) multilayers (referred herein to as type (I) and (II) MLs) were deposited on (100) Si substrate at 500°C, by a reactive magnetron cosputtering method. The SiO_x sublayers were fabricated by simultaneously sputtering the Si and the SiO_2 targets with power densities 7.4 W/cm^2 and 2.2 W/cm^2 respectively by adding hydrogen into the Ar plasma. The term "reactive" is used since the process takes advantage of the capability of hydrogen to reduce the oxygen in the plasma from the sputtered target as detailed elsewhere [8]. The SiN_x sublayers were fabricated by sputtering the Si target while adding nitrogen into the Ar plasma. The SiO_2 thickness and the SiO_x thickness in both types (I) and (II) of MLs were fixed at 3.5nm. In order to understand the influence of the SiN_x sublayers, different thicknesses ranging from 1.5 nm to 5.5 nm were investigated for the PL behavior. The SiO_x/SiO_2 and SiO_x/SiN_x MLs were annealed at 1100 °C for 1 hour and 1000 °C for 1 minute respectively under N_2 atmosphere. These annealing treatments were chosen because they were the best for the aforesaid layers in terms of PL properties as reported elsewhere [11]. The spectroscopic ellipsometry analysis was carried out between 1.5 and 4.5 eV by using a Jobin Yvon ellipsometer (UVISEL) at an incidence angle of 66.3° and different parameters such as the thickness, the refractive index n and the extinction coefficient k (imaginary part of the complex index) of the film was obtained. The fitting of the experimental data was performed with DeltaPsi2 software [12] using a dispersion law based on the Forouhi–Bloomer model (FBM) [13] modified for amorphous semiconductor and insulating materials using an improved parameterization [14]. The absorption coefficient α was calculated as follows: $\alpha = 4\pi k/\lambda$, where λ is the wavelength of the incident beam. The PL spectra of the annealed samples were obtained using TRIAX 180 Jobin Yvon monochromator in the wavelength range of 550-1100 nm with a R5108 Hamamatsu PM tube and using the 488 nm argon line from an Innova 90C coherent laser as excitation wavelength. EF-TEM was performed on cross-sectional specimen using a TEM-FEG microscope Tecnai F20ST equipped with an energy filter TRIDIEM from Gatan. The energy-filtered images were obtained by inserting an energy-selecting slit in the energy-dispersive plane of the filter at the Si and at the SiO_2 plasmon energy (16 eV and 23 eV respectively) and with a width of approximately 2 eV. Electrical measurements were made by using two probes apparatus (SUSSMicrotec EP4 equipped with Keithley devices) to obtain the I-V characteristics.

3. Results and Discussions

3.1. Structural studies

Fig.1 compares the EF-TEM image of our earlier MLs obtained by sputtering only SiO_2 in hydrogen rich plasma (Method 1) and the MLs discussed in this paper, grown by simultaneous sputtering of SiO_2

and Si in hydrogen rich plasma (Method 2). In addition to the structural analysis with regard to the growth techniques, to better understand the two types of MLs at their best annealing treatments,we have presented here SiO_x/SiO_2 grown using Method 1(Fig.1a) and SiO_x/SiN_x grown using Method 2 (Fig.1b). An enhancement in the concentration of the Si-ncs (10^{13} nc/cm^2) is achieved by using method 2, compared to the one obtained by method 1 (10^{12} nc/cm^2). It can also be seen that the Si-ncs in SiO_x obtained by Method 2 have lesser inter-distances in comparison to the SiO_x/SiO_2 MLs grown using Method 1. The Si-ncs are well distributed throughout the SiO_x layers and there is no formation of Si-ncs in both kinds of dielectric sublayers.

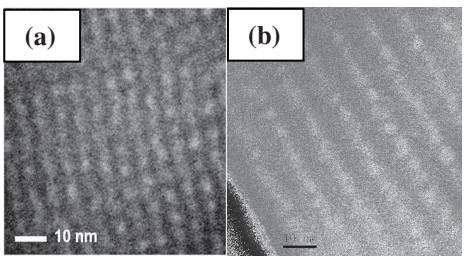

Fig.1.EF-TEM image obtained at Si plasmon peak (16eV): (a) Method 1 grown SiO_x/SiO_2 (1100°C,1h Annealed) [7] and (b) Method 2 grown SiO_x/SiN_x (1000°C,1min Annealed)

3.2. Absorption and photoluminescence studies

The extinction coefficient k of refractive index of the MLs, is obtained by fitting experimental ellipsometry data. The absorption coefficient α is then calculated using the following equation:

$$\alpha = (2\omega k)/c \quad (1)$$

where, ω is the angular frequency of the photon and c is the velocity of light.

The effect of annealing treatments on the absorption coefficient was investigated and Fig.2a shows the absorption coefficient spectra of ML types (I) and (II) annealed during 1h at 1100°C and 1 min at 1000°C respectively. The newly employed reactive magnetron co-sputtering technique has allowed us to enhance the absorption coefficient from the MLs owing to the high density of Si-ncs achieved and/or the replacement of the SiO_2 sublayer by the SiN_x one (Fig.2a). It can be seen from this figure SiN_x based ML has higher absorption coefficient than SiO_2 based ML in the 2.5-5.5eV range. Fig. 2b corresponds to the PL spectra obtained from the MLs in the visible range. The luminescence intensity from the short time annealed SiO_x/SiN_x ML is around 1.4 times higher compared to the luminescence obtained from long time annealed SiO_X/SiO_2 based ML. Also, the modeling [15] of emission in the multilayer structures performed considering the interference effects did not show any inversion of the intensity trends. There is also a shift in the peak position towards the higher energy in the SiO_x/SiN_x ML and this is one of the advantageous aspects in terms of solar cell applications. Though the SiN_x sublayer thickness plays a significant role in increasing the emission intensity as can be seen from the inset in Fig. 2b, it is still advantageous as it yields enhanced optical properties. However, the change in the SiN_x sublayer thickness showed only a negligible variation in the PL peak position (around 800 nm) and hence we infer that the Si-nc sizes remain the same. Though the origin of PL from SiO_x/SiN_x and its intensity trends are still under investigations, we infer from our earlier studies that there is a large contribution of Si-ncs in the

light emission, for the following reasons: a) Even if SiN_x shows a defect related PL, when alternated with SiO_x sublayers we have shown that the peak position shifts towards lower energies thereby making the luminescence of Si-nc more pronounced [11], b) The EF-TEM image in Fig.1b confirms the formation of Si-nc within the SiO_x sublayer even after a short time annealing treatment thereby indicating the Si-ncs formed within the ML plays a dominant role in the optical properties even after a short time annealing treatment.

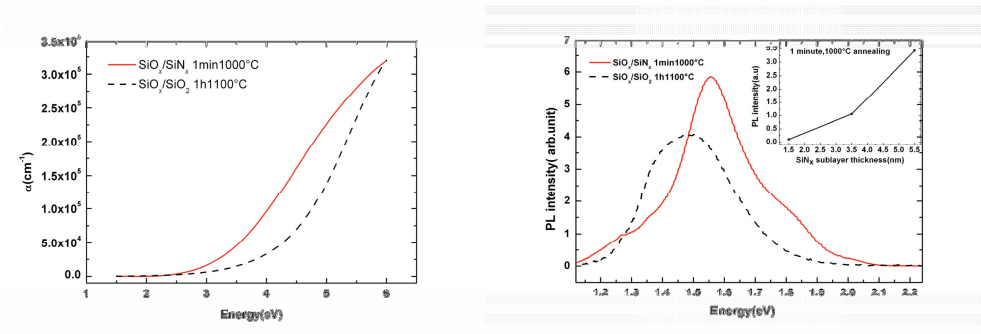

Fig.2. (a) Absorption coefficients and (b) PL spectra of the MLs, after suitable annealing treatments.

3.3 Electrical studies

I-V characteristic curves of the (I) and (II) MLs with and without annealing are presented in Fig.3a and Fig.3b. In the case of SiO_x/SiO_2 though an annealing treatment of 1h at 1100°C was successful in producing a significant density of Si-ncs, supported by an increase in the emission properties, this structure offers high resistivity and in turn offers limitations for device applications. The annealed MLs had a lesser conductivity compared to non annealed ones. The MLs resistance and resistivity after annealing were deduced from Fig.3a to be 14500 Ω and 0.73 x 10^8 Ω.cm respectively.

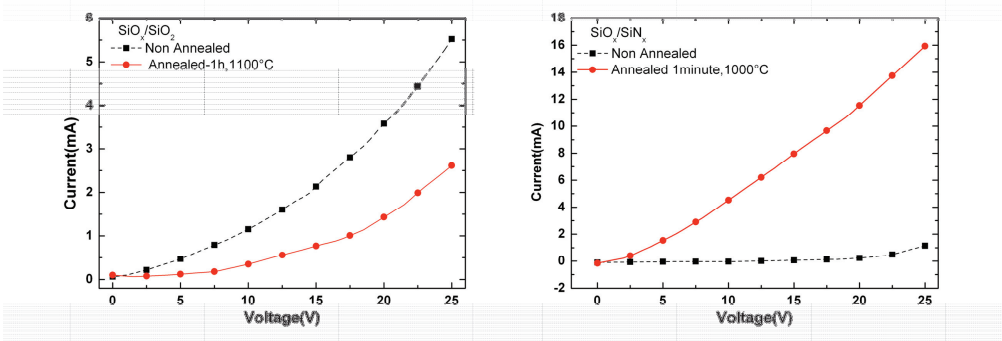

Fig.3. I-V characteristic curves of non annealed and annealed samples (a)SiO_x/SiO_2 (b) SiO_x/SiN_x

In the case of SiO_x/SiN_x a strong increase in the conductivity is noted after the annealing treatment. The values of resistance and resistivity as calculated from the I-V curves shown in Fig.3b are 1753 Ω and 0.14 x 10^7 Ω.cm respectively. The conductivity in SiN_x based ML is enhanced by more than one order of

magnitude compared to the oxide based ML owing to the reduced band gap of the former. Besides, even in the case of electrical studies, a short time annealing treatment in SiN_x based ML has proved to be successful in enhancing the conductive properties.

4. Conclusion

Structural and optoelectronic investigations on two types of SiO_x based MLs have been made. An incorporation of 'co-sputtering' in addition to our earlier used reactive magnetron sputtering methods for the fabrication of SiO_x layers has favoured an increase in the Si-nc density and a uniform distribution throughout the SiO_x sublayers.. The annealing treatment of 1100°C for 1 hour was found to be the best in SiO_x/SiO_2 MLs and 1000°C for 1 minute in the case of SiO_x/SiN_x MLs. The formation of Si-ncs in SiO_x/SiN_x MLs after a short time annealing treatment is promising for device applications with a control over the thermal budget .Replacement of SiO_2 by SiN_x in the ML structures, showed an enhancement in absorption and also in PL emission arising from Si-ncs. In addition to this improvement in optical properties, enhancement in conductivity is also observed in SiO_x/SiN_x MLs after a short time thermal annealing in contrast with the poor conductive SiO_x/SiO_2 MLs which become more resistive with annealing.

Acknowledgements

This study is supported by the DGA (Defense Procurement Agency) through the research program No. 2008.34.0031. We thank D. Maestre and O. Palais, IMN2P, Marseille, France for EF-TEM measurements on SiO_x/SiO_2 MLs.

References

[1] Cullis AG, Canham LT, Calcott PDJ. The structural and luminescence properties of porous silicon. Journal of Applied.Physics 1997;**82**:909-965.

[2] Charvet S, Madelon R, Gourbilleau F, Rizk R. Spectroscopic ellipsometry analysis of sputtered Si/SiO_2 nanostructures. Journal of Applied Physics 1999,**85**:4032-4039.

[3] Zacharias M, Blasing J, Veit P, Tsybeskov L, Hirschman K, Fauchet PM. Thermal crystallization of Si/SiO_2 superlattices. Applied Physics Letters 1999;**74**:2614-2616.

[4] Tsybeskov L, Hirshman KD, Dutlagupta SP, Zacharias M, Fauchet PM, McCaffrey JP, Lockwood DJ. Nanocrystalline silicon superlattice produced by controlled recrystallization. Applied Physics Letters 1998;**72**:43-45.

[5] Vinciguerra V, Franzo G, Priolo F, Iacona F, Spinella C. Quantum confinement and recombination dynamics in silicon nanocrystals embedded in Si/SiO_2 superlattices. Journal of Applied Physics 2000;**87**:8165-8173.

[6] Gourbilleau F, Portier X, Ternon C, Voivenel P, Madelon R, Rizk R. Si-rich/SiO nanostructured multilayers by reactive magnetron sputtering. Applied Physics Letters 2001;**78**:3058-3060.

[7] Gourbilleau F, Ternon C, Maestre D; Palais O, Dufour C. Silicon-rich SiO2/SiO2 multilayers: A promising material for the third generation of solar cells. Journal of Applied Physics 2009;**106**:013501-013501-7.

[8] Ternon C, Gourbilleau F, Portier X, Voivenel P, Dufour C. An original approach for the fabrication of Si/SiO_2 multilayers using reactive magnetron sputtering. Thin Solid films2002;**419**:5-10.

[9] Dal Negro L, Yi JH, Nguyen V, Yi Y, Michel J, Kimerling LC. Spectrally enhanced light emission from aperiodic photonic structures. Applied Physics Letters 2005;**86**:261905-261907.

[10] Kim BH, Cho CH, Kim TW, Park NM, Sung GY, Park SJ. Photoluminescence of silicon quantum dots in silicon nitride grown by NH_3 and SiH_4. Applied Physics Letters 2005;**86**:091908-091910.

[11] Pratibha Nalini R, Dufour C, Cardin J, Gourbilleau F. New silicon based multilayers for solar cell applications. Nanoscale Research Letters2011;**6**:156-161.

[12] http://www.horiba.com/scientific/products/ellipsometers/software/

[13] Forouhi AR, Bloomer I,Optical properties of crystalline semiconductors and dielectrics. Physical Review B 1986;**34**:1865-1874.

[14] Jellison GE Jr, Modine FA. Parameterization of the optical functions of amorphous materials in the interband region. Applied Physics Letters 1996;**69**:371-373.

[15] Yann G. Boucher. Theoretical investigation of amplified spontaneous emission in an active structure by extended (3x3) transfer matrix formalism: the case of a non uniform longitudinal distribution of emitters J. European Optical Society – Rapid publications 2006; **1**:06027-06027-6.