Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 10 (2011) 28 – 32

Energy Procedia

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

Assessment of the composition of Silicon-Rich Oxide films for photovoltaic applications by optical techniques

M. Morgano[a*], T. Zhang[b], I. Perez-Wurfl[b], S. Binetti[a], M. Acciarri[a], G. Conibeer[b]

[a]Milano-Bicocca Solar Energy Research Center (MIB-SOLAR), Dept. of Material Science, University of Milano – Bicocca, via Cozzi 53, 20125 Milano, Italy
[b]ARC Photovoltaic Centre of Excellence, UNSW, Sydney, 2052, Australia

---

Abstract

The deposition of sub-stoichiometric silicon rich oxide (SRO) is the first step to obtain well ordered silicon Quantum Dots (QDs) in a dielectric matrix. This structure is used also for third generation photovoltaic devices operating in a tandem architecture. A precise control and assessment of the stoichiometry of these films is crucial to tune the electrical and optical properties of the device. In this paper we discuss two optical techniques to assess the composition of such films and we compare their results.

Keywords: Quantum Dots; Photovoltaics; Silicon; Oxide; Tandem Cell; SRO.

---

1. Introduction

Tandem solar cells are a proposed design to overcome the 31% Schokley-Queisser limit of efficiency for single junction Si solar cells [1]. Using materials with decreasing band gap it is possible to convert more efficiently a larger portion of the solar spectrum, achieving efficiencies up to 68% in the limit of an infinite number of junctions (see i.e. [2]). To keep costs low and be competitive on the market, it has been proposed to use nanostructuration of silicon-based material to engineer the band gap at will. One way to do so is by depositing alternate layers of thin silicon-rich oxide (SRO) and stoichiometric silicon dioxide inter-layers. Upon annealing, the excess silicon in the SRO layers precipitates to form Si quantum dots

---

* Corresponding author. Tel.: +39-02-6448-5168 ; fax: +39-02-6448-5400 .
E-mail address: manuel.morgano@mater.unimib.it .

doi:10.1016/j.egypro.2011.10.147

(QDs) which remain confined between the silicon dioxide inter-layers [3]. Using this method it is possible to have a good control of the QDs size by varying the SRO layers thickness. The spacing of the QDs is mainly accounted for by the stoichiometry of the film, with more silicon-rich layers forming more closely spaced QDs [4]. It is clear, then, that a fine control of the stoichiometry is crucial for the performances of the devices based upon this material. A non-destructive, simple to use and readily available technique that can be used to assess the composition (i.e. the silicon excess) of such films could be useful to quickly measure the stoichiometry of the film before the material undergoes any process. In this paper we describe two of such potentially useful optical techniques. One is based on Fourier-Transform Infra-Red (FTIR) spectroscopy and the other is based on reflectivity and transmittance measurements on such films.

2. Samples description

The deposition was performed using a computer-controlled AJA ATC-2200 sputtering system. The stoichiometry of the film was varied from sample to sample by increasing the power applied to the silicon target, while keeping constant the one of the silicon dioxide target. The assumption is that the silicon excess in the film is directly proportional to the power on the silicon target above the deposition activation threshold in the range considered.

Four SRO films with different silicon composition have been deposited, on both, 1 mm thick quartz substrates and, on (100), 525 µm thick, p-type (1-10 Ω·cm resistivity) silicon substrates. The samples deposited on quartz have been annealed by rapid thermal annealing and used for UV-VIS transmittance measurements while those on silicon were left as deposited and used for FTIR spectra acquisition.

The samples have been measured with a NICOLET 5700 FT-IR from Thermo under dry N_2 purging. The absorbance spectrum is obtained from the sample by measuring the spectrum of the substrate suitably kept from any process and comparing it to the spectrum of the sample with the film deposited on the front surface. The final spectrum is the result of 100 averages of a single spectrum.

PANanalytical X'Pert MRD was configured for X-Ray Reflectivity (XRR) to examine the SRO layer thickness. The primary X-Ray source is CuKα (λ=0.154 nm), which is defined by divergence slit of 1/4° (divergence of 0.27°). Soller slits with 2.3° divergence were installed for incident and reflected beams. A 1/32° anti-scatter slit was used to improve resolution. A PIXcel3D detector was used and configured in 'receiving slit' mode to give better signal counts. For better statistical data, slow scanning speed and low scanning step were used to scan over the 20x15 mm^2 sample area. The software X'Pert reflectivity was applied to calculate the thickness of the SRO. The Fourier method involving automatic Fourier volume calculation was used to show clear peak values to identify the thickness, which eliminated errors from manually reading neighboring fringe peaks.

The transmission of Silicon Rich Oxide thin films on quartz substrate was measured using a UV/VIS Lambda1050 PerkinElmer spectrophotometer. A wavelength range from 200 to 2500 nm in 2 nm increments was used at an incident angle of 0°. Two detectors were used for the transmittance measurement, a Photomultiplier Tube (PMT) was utilized for 200 nm to 860 nm and an InGaAs photodiode detector for 860 nm to 2500 nm. To qualitatively evaluate optical and compositional properties of SRO, the WVASE simulation software tool from J. A. Woollam Co. was used to simulate the transmittance results using a Bruggeman EMA model.

3. Results and discussion

We gathered all the FT-IR absorbance spectra of the films, taken with respect to the substrate. The area under the Si-O asymmetric stretching vibration mode around 1080 cm^{-1} has been calculated from each spectrum, using a suitable baseline and spanning the same range from 800 cm^{-1} to 1300 cm^{-1} (Fig. 1) and normalized for the film thickness. If the effective medium approximation was strictly valid, the area under the band for a given film thickness should decrease linearly with the silicon richness, since less Si-O bonds are present, replaced with Si-Si bonds. The XRR measurements fixed independently the thickness values.

It is possible to see a trend where the normalized areas decrease as the silicon content increases. The linearity is followed also if we add to the graph the point corresponding to the normalized absorption area of a stoichiometric silicon dioxide sample (obtained setting to 0% the power applied to the silicon target), as can be seen in Fig. 1.

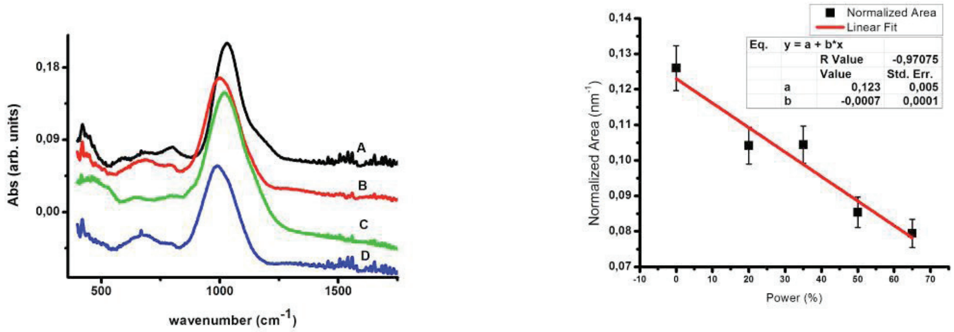

Fig. 1: IR spectra of the samples (A, B, C, D) in the region of interest (left). Correlation of the normalized area with the silicon sputter target power (right). The spectra have been acquired at room temperature with a resolution of 2 cm^{-1}.

The uncertainties inherent to this method are to be ascribed to the difficulty in setting the correct baseline and range of integration for each spectra, in particular with single side polished wafers. Also the error in the thickness plays a minor role in the determination of the precision of this method. Our estimate for the total error is roughly 5% of the value, which is accounted for in the error bars shown in Fig. 1.

We simulated the transmittance of Silicon Rich Oxide thin films using Bruggemann effective medium approximation (EMA) [5]. Although the Tauc-Lorentz model [6] is widely used for modelling amorphous dielectric materials with absorption and, by selecting the proper oscillators [7] to closely reproduce the measured transmittance of these films, it does not address the composition of mixed constituent films. We used an EMA model to represent the mix of SiO_2 and c-Si and utilized this method to evaluate the concentrations of Si corresponding to increasing Si sputtering power when depositing these films. The use of c-Si rather than amorphous Si as the more appropriate choice is due to the rapid thermal annealing process at 1100° after deposition, which should induce silicon crystallization. The superior fitting results also support the use of c-Si as a more acceptable choice. The thickness was fixed according to XRR results to reduce fitting parameters, so only the SiO_2 and c-Si volume fractions need to be fitted. Since an increased Si concentration enhances the absorption of SRO film in a manner not yet understood, the absorption wavelength region from 220 nm to 1000 nm was not fitted. Instead, the non-absorbing region of the spectrum extending from 1000 to 2500 nm was the spectrum used for the data fitting (see Fig. 2). In this region of the spectrum, Si and SiO_2 are transparent materials. As a result, only the real part of the refractive index 'n' needs to be taken into consideration and the extinction coefficient 'k' can be ignored. The structure used in our model contained an EMA SRO layer of variable thickness and a 1mm thick SiO_2 substrate. No intermix layer or surface roughness was added for these were not required to obtain good fittings. The fitting results are listed in Table 1 including thickness, composition and the Mean Squared Error (MSE). Refractive index is also included in the table, which increases with increasing silicon richness. It can be seen from the table that the simulated increasing silicon richness result is consistent with the increasing sputtering power on the silicon target. MSE values less than one indicate good fitting results that arise also because we reduced the number of free parameters by measuring the thickness independently. The uncertainties in the thickness and the fitting procedure combined introduce roughly a 3% error in the calculation of the Silicon content which is reflected in the error bars in Fig. 2..

Table 1. Summary of the measurements.

Sample	Si sputter target power (100% = 300 W)	Thickness (nm)	SiO2 (%)	Si (%)	n (@600 nm)	MSE	Normalized Area (nm^{-1})
A	20%	221.3	86.11	14.3	1.70	0.39	0.1042
B	35%	274.9	65.01	35.1	2.20	0.65	0.1044
C	50%	257.7	51.82	49.1	2.56	0.89	0.0854
D	65%	244.2	41.02	59.7	2.87	0.54	0.0794

As can be seen, the fit depicted in Fig. 2 is consistent and can be used as a first guess to give a semi-quantitative estimate of the SRO Si composition by plotting the results from the fit of the absorbance in the UV-VIS range versus the normalized area derived from the IR measurements (Fig. 3).

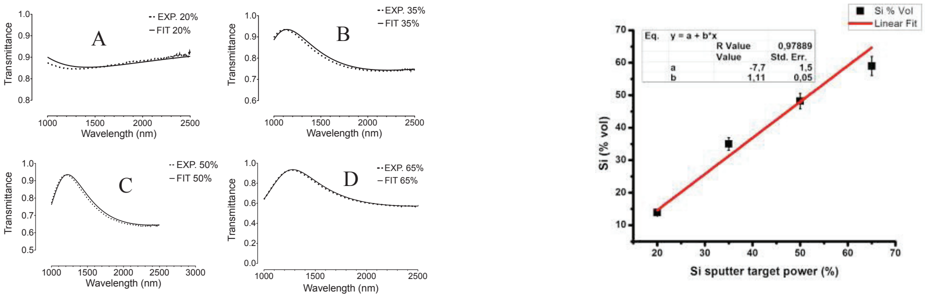

Figure 2. UV-VIS transmittance spectra and fits in the region of interest (left).Correlation of the fit results for Si volumetric content with the silicon sputter target power (right).

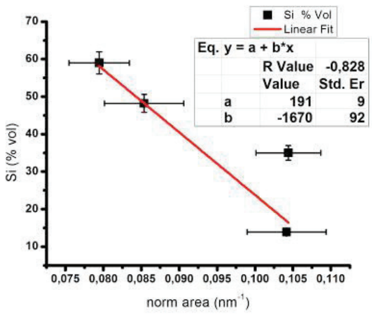

Fig. 3: Correlation between UV-VIS calculation of Si volumetric contents through transmittance fits and IR estimates.

This graph provides us with the link between integral area of the absorption peak of the Si-O asymmetric stretching mode and the silicon excess in a film of SRO. Using it we can assess the SRO composition by a quick, non destructive IR measurement of the absorbance of the film.

We can observe, however, that sample B is off the calibration curve. It should be noted that this sample also show the least agreement with each method, suggesting incorrect handling during the deposition or during the thickness measurement. Investigations on this sample are being carried out.

Finally, a sample with known composition (via, i.e., Rutherford Back Scattering technique) is under preparation and will eventually provide a calibration for this method [8], allowing its use for the assessment of the absolute stoichiometry of such films.

4. Conclusions

We have deposited various SRO films with different stoichiometry using a co-sputtering technique, measured their thickness with XRR and acquired both FT-IR absorbance and UV-VIS transmittance spectra to assess the film composition.

Both the characterization methods gave results consistent with the expected trends and the parameters used to assess the composition of the films scale linearly with the silicon excess, also (in the case of FT-IR) correctly predicting the value for the limiting case of stoichiometric silicon dioxide. We compared the two methods and found the linear relationship correlating the silicon volumetric content in the Buggerman effective medium to the normalized area of the Si-O absorption peak using the FT-IR, thus allowing us to assess the silicon excess by a single IR measurements.

The final validation of this method will be the comparison with an independent technique such as RBS. After this step it will be possible to routinely use this method as a quick stoichiometry assessment technique.

References

[1] W. Shockley, H. Queisser. Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells. *J. Appl. Phys.* 1961; **32:**510-9.

[2] M. A. Green. Energy, Entropy and Efficiency. In T. Kamiya, H. Venghaus, B. Monemar, Y. Yamamoto editors. *Third Generation Photovoltaics: Advanced Solar Energy Conversion*, Berlin Heidelberg: Springer-Verlag; 2003, pp. 27-8.

[3] Lu, Lockwood, Baribeau: Quantum confinement and light emission in SiO_2/Si superlattices; *Nature*, 1995, **378**, 258

[4] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, J. Blasing. Size-controlled highly luminescent silicon nanocrystals: A SiO/SiO_2 superlattice approach. *Appl. Phys. Lett.* 2002; **80**:661-3.

[5] D. E. Aspnes. Optical properties of thin films. *Thin Solid Films* 1982; **89**:249-262.

[6] J. G. E. Jellison, F. A. Modine. Parameterization of the optical functions of amorphous materials in the interband region.*Appl. Phys. Lett.* 1996; **69**:371-3.

[7] H. Song, A. B. Sproul, A. G. Aberle. Doping dependence of optical properties of solid-phase crystallized evaporated poly-Si thin films on glass. Conference on Optoelectronic and Microelectronic Materials and Devices. *COMMAD* 2008; 293-6.

[8] S. K. Shrestha, P. Aliberti, G. Conibeer. Energy selective contacs for hot carriers solar cells. *Sol. En. Mat. & Sol. Cells* 2010; **94**:1546-50