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Multi-characterization study of interface passivation quality of amorphous sub-stoichiometric silicon oxide and silicon oxynitride layers for photovoltaic applications

Jonathan Steffens[a], Maria Antonietta Fazio[b], Daniela Cavalcoli[b,*], Barbara Terheiden[a]

[a] Department of Physics, University of Konstanz, Germany
[b] Department of Physics and Astronomy, University of Bologna, Italy

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ABSTRACT

Si solar cells have achieved a world record efficiency of 26.7% as a result of both improvement of Si ingot growth and optimal passivation of surfaces and interfaces. In this framework, a clear understanding of the electronic, optical, structural and passivation properties of innovative Si based layers is mandatory. The present study reports on the characterization of amorphous sub-stoichiometric silicon oxide (a-SiO_x) and silicon oxynitride (a-SiO_xN_y) layers and their surface passivation properties. The layers have been deposited on float zone Si wafers (2 Ω cm, (100)-oriented, 250 µm thick) by plasma enhanced chemical vapour deposition (PECVD) adding increasing fractions of N_2O and CO_2 to the SiH_4 flux during deposition to increase the energy band gap of the layers. Composition, optical properties, light induced electronic transitions and minority carrier lifetimes of Si wafers passivated with these layers have been investigated by Fourier-transform infrared spectroscopy (FTIR), spectral ellipsometry, surface photovoltage (SPV) spectroscopy and photo conductance decay (PCD). The overall characterization of the layers has allowed us to understand the effect of increasing N_2O and CO_2 flux ratios during deposition on the interface properties. The present study establishes the importance of the approach of using multiple characterization methods in the evaluation of the passivation capability of layers that combine large optical band gap and surface passivation.

1. Introduction

The energy conversion efficiency of single-crystalline silicon solar cells has improved steadily over the last decades and has recently reached a world record efficiency of 26.7% [1]. In parallel, the increased production volumes and associated maturity of the technology have reduced the cost of photovoltaic modules so far that solar photovoltaic electricity has already reached grid parity in many countries and locations [2]. Such a strong enhancement of this technology is a consequence of the improvement of silicon ingot growth processes and the control of defects and contamination during solar cell fabrication. The bulk electronic quality of crystalline silicon wafers has improved to such a point that further device advances now rely on innovative surface passivation schemes. To achieve a high efficiency in silicon based solar cells an excellent control of interfaces must be adopted.

Intrinsic a-Si:H films have been known for some decades as effective passivation layers via chemical surface states passivation. Doping of these films as typically applied in Si heterojunction (SHJ) cells causes an additional field effect passivation, but it diminishes the surface state passivation at the interface. In order to improve the interface passivation, a few nm thick buffer layer of intrinsic a-Si:H is inserted between the c-Si substrate and the doped film. This strategy has led Sanyo, now Panasonic, to achieve high efficiency SHJ cells [3].

Recently, the role of surface passivation on the final efficiency of SHJ solar cells has been shown by Yoshikawa et al. [4]. These authors produced an inter-digitated contact (IBC) SHJ cell with a certified efficiency larger than 26% through careful optimization of optical and passivation properties and efficient carrier collection on the front side of the cell. Notwithstanding these high efficiencies achieved by SHJ cells, a-Si:H films present high parasitic absorption of light, causing a loss in short circuit current, and high series resistance, causing a reduction in fill factor. The absorption within the a-Si:H films can be minimized by widening the optical band gap, for example through the incorporation of carbon, nitrogen or oxygen in the amorphous matrix

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* Correspondence to: Physics and Astronomy, Dept University of Bologna, viale C Berti Pichat 6/II, 40127 Bologna, Italy.
E-mail addresses: jonathan.steffens@uni-konstanz.de (J. Steffens), maria.fazio2@unibo.it (M.A. Fazio), daniela.cavalcoli@unibo.it, cavalcoli@bo.infn.it (D. Cavalcoli), Barbara.Terheiden@uni-konstanz.de (B. Terheiden).

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[5,6 and references therein], while the resistivity can be reduced through the incorporation of crystalline phases [7,8].

While the a-Si:H /c-Si interface passivation mechanisms have been investigated for at least one decade [9,10], this is not the case for a-Si:H with incorporation of small amounts of O and N, which we refer to as amorphous sub-stoichiometric silicon oxide (a-SiO_x) and silicon oxynitride (a-SiO_xN_y) layers. Even if these materials are already applied in fields different from photovoltaics, e.g. as buffer layers for organic based photodetectors [11] or as matrix layer for superlattices with Si nanocrystals [12,13], their fundamental properties have not yet been investigated in detail. These innovative passivating layers consist of complex non-stoichiometric compounds containing amorphous and crystalline phases and their properties vary substantially as a function of the deposition method and subsequent annealing processes. Beside the fundamental properties, the influence of the structure of the amorphous network on electron-hole recombination processes at surfaces and interfaces is also not clear yet. However, a detailed understanding of this interrelation is in turn a mandatory requirement for the optimization of the layers for the application as means of surface passivation of Si wafers.

The aim of the present work is the discussion of a multi-characterization approach focused on the study of structural and passivation properties of sub-stoichiometric a-SiO_x and a-SiO_xN_y layers on c-Si surfaces. The knowledge and optimization of these properties are mandatory in order to further improve SHJ solar cell efficiency.

Therefore, we deposited these layers from silane gas (SiH_4) and added varying fluxes of N_2O or CO_2 gas to the PECVD reactor to obtain a-SiO_xN_y and a-SiO_x layers, respectively. These layers have on one hand a beneficial effect as their optical gap is improved with respect to a-Si:H, but on the other hand a detrimental effect as high flux ratios of N_2O or CO_2 during deposition lead to an increase in surface recombination.

Several properties of these layers have been evaluated with multiple techniques to investigate the implication of the structure of the amorphous network at the interface on electron-hole recombination processes in dependence of the N_2O and CO_2 flux compositions. In detail, optical properties, light induced electronic transitions and minority carrier lifetimes of these layers have been examined by Fourier-transform infrared spectroscopy (FTIR), spectral ellipsometry, surface photovoltage (SPV) spectroscopy and photoconductance decay (PCD). The present study establishes the importance of this approach based on the use of multiple characterization methods in the evaluation of the passivation capability of layers that combine large optical band gap and surface passivation.

2. Materials and methods

The a-SiO_xN_y (N sample set) and a-SiO_x (C sample set) layers were deposited by PECVD on 250 μm thick boron-doped silicon float-zone material of an area of $5 \times 5\,cm^2$ ($2\,\Omega\,cm$, (100)-oriented) using a commercial tool (PlasmaLab 100 from Oxford Instruments) with a radiofrequency of 13.56 MHz. All the parameters were kept constant for all depositions ($P = 100$ W, $p = 450$ mTorr, $T = 175$ °C, electrode distance $d = 20$ mm, deposition duration $t = 150$ s) except for the gas fluxes. Additional to pure SiH_4 gas, either N_2O or CO_2 gas was added to the plasma. The dilution ratios of N_2O and CO_2 in silane are defined by $R_x = [X]/([X] + [SiH_4])$ with $X = N_2O$ or CO_2 and the square brackets representing the gas fluxes. The ratios were varied in the range of 4.8–16.6% for N_2O and in the smaller range of 4.8–9.1% for CO_2, because each CO_2 molecule carries twice as many oxygen atoms as each N_2O molecule. A reference a-Si:H sample was deposited using pure SiH_4 gas only. The corresponding labelling of the samples and their flux ratios are listed in Table 1.

Immediately before each deposition, the samples were dipped in hydrofluoric acid solution (2%) to remove silicon oxide from the surfaces. The layers were deposited on both sides of each sample in separate depositions and immediately before the next sample was deposited, the deposition chamber was cleaned. Since the deposition duration was kept constant while the plasma composition was changed, the resulting layer thicknesses determined by spectral ellipsometry measurements are not equal but vary in the range from 100 to 140 nm. The passivation activation was achieved by annealing the layers on a hotplate in ambient air to 300 °C for 15 min.

Table 1
Labelling of the investigated samples, chosen to provide information about the gas flux ratio R_x used during deposition.

Sample (label)	R_{N2O} (%)	R_{CO2} (%)
N4.8	4.8	0
N9.1	9.1	0
N13	13	0
N16.6	16.6	0
C4.8	0	4.8
C7	0	7
C9.1	0	9.1
Reference	0	0

The microstructure of the layers as well as an estimate for incorporated nitrogen and oxygen was determined qualitatively with a FTIR setup (Vertex 80 from Bruker Optics) in terms of relative absorption strengths of selected bonds in the range of 500–2500 cm^{-1} with a resolution of 8 cm^{-1}. A baseline correction was applied to all spectra before multi-Gaussian fit procedures were performed on each of the two main absorption bands separately. The positions of the evaluated peaks as reported in the literature are depicted in Table 2. In order to compare the bond densities qualitatively, the relative absorption strength was determined by the ratio of the integral under the fitted Gaussian peak of interest and under the corresponding peak of a reference sample.

The refractive index variation within the layer as well as the layer thicknesses were determined using a Vertical VASE Rotating analyzer ellipsometer (J.A. Woollam Co., Inc.) operated in a spectral range of 500–2000 nm. The data (Ψ, Δ) were fitted by a graded Cauchy model, which considered the investigated layers as divided into 21 sublayers with fixed thickness, but individual homogeneous refractive indices to model variations of the optical constants within the layers, similarly to the approach in [19]. For the top surface a roughness layer was included in the model, which was simulated by an effective medium approximation of 50% layer material and 50% void.

Electronic transitions and effective minority carrier lifetimes were determined by SPV measurements of the light induced variation of surface or interface voltage, which is capacitively picked up in a metal-insulator-semiconductor configuration and amplified with a phase

Table 2
Literature values of the infrared active absorption peaks and corresponding bond vibrations of a-SiO_x and a-SiO_xN_y evaluated in this study.

Wavenumber [cm^{-1}] (from literature)	Bonds	Modes	Reference
640	Si-H / Si-H_2	wag / roll	[14]
780	Si-H / Si-O-Si	coupling of both bonds	[15]
840	Si-H_2	interaction between two Si-H_2 groups	[14]
850	Si-N	asymmetric stretch	[16]
890	Si-H_2	interaction between two Si-H_2 groups	[14]
980	Si-O-Si	asymmetric stretch	[15]
1107	O_i	interstitial oxygen	[17]
2000	Si-H	stretch	[18]
2100	Si-H_2 / Si-H_3	stretch	[18]