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Fundamental studies of hydrogen at the silicon / silicon nitride interface

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Abstract

The quality of the interface between silicon and a dielectric is one of the main influencing parameters for crystalline silicon surface passivation. In this work, this interface is examined by means of capacitance voltage (CV) and nuclear resonance reaction analysis (NRRA) measurements for SiN_x:H as well as SiO_2 capped SiN_x:H passivated p-type float zone silicon samples. Due to a highly sensitive NRRA measurement setup, very small differences in hydrogen concentration at the interface could be detected for the first time and a significant correlation between hydrogen concentration, interface state trap densities D_{it} and passivation quality is found. The results of this study present easily implementable processes to improve the quality of SiN_x:H surface passivation and process stability for solar cell and module production applications. First optimised industrial type Al-BSF p-type cells feature 2 mV and 0.5 mA/cm² gains in V_{oc} and j_{sc}, leading to efficiencies of up to 19.1%.

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Keywords: Passivation; silicon nitride; silicon oxide; semiconductor-insulator boundaries

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1. Introduction

Hydrogen is known to be a major influencing factor for silicon surface and bulk passivation. The publications of Lamers et al. [1,2] on SiN_x:H passivation indicate the interface between dielectric and silicon bulk to be the crucial location for surface passivation quality.

In this work, the SiN_x:H / Si interface is examined by means of NRRA and CV measurements. These investigations are performed on different plasma enhanced chemical vapour deposited (PECVD) dielectric layers and stacks consisting of a dense and well passivating amorphous hydrogenated SiN_x:H and a combination of this SiN_x:H and PECVD SiO_2 deposited on p-type float zone silicon (FZ-Si). The determined results of hydrogen concentration at the interface (NRRA) and density of fixed charges Q_{tot} and interface state trap densities D_{it} (CV) are correlated with effective minority carrier lifetime and sample preparation.

SiN_x:H is studied in this work because of its widespread usage in solar cell production. A deeper understanding of the mechanisms that lead to well passivating SiN_x:H layers is crucial for highly efficient solar cells and stable production processes.

2. Experimental details

For the experiments, p-type FZ-Si wafers of 2 Ωcm resistivity are used (thickness: 250 µm). After laser cutting and labelling, the samples are subjected to a chemical polishing/damage etch (~5 µm each side) followed by RCA cleaning [3]. SiN_x:H and SiN_x:H/SiO_2 stacks are deposited on both sides of the wafers in a lab-type direct-PECVD setup (Oxford Instruments Plasmalab System 100). The process gases used for SiN_x:H are SiH_4, NH_3 and N_2, and for SiO_2, SiH_4 and N_2O are used. As there is no evidence for cross contamination between the SiN_x:H and the SiO_2 deposition processes, stacked layers are deposited within one step at constant temperature. The dielectric layers and their thicknesses are depicted in Fig. 1. The thicknesses of the thin SiN_x:H layer and SiN_x:H/SiO_2 layer are chosen because of their relevance as anti-reflective coatings for solar cell processing. The thick SiN_x:H layer acts as a reference layer for best passivation without solar cell production relevance. All samples are exposed to an industrial-type co-firing process step at 855°C peak set temperature in a belt furnace.

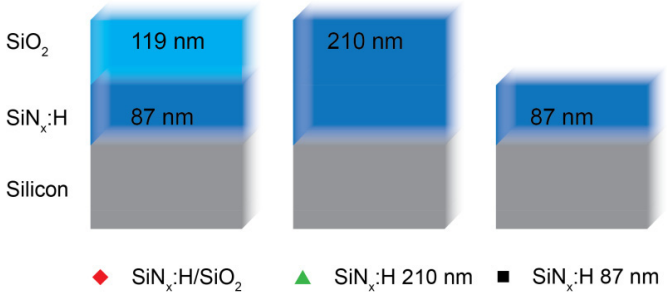

Fig. 1. Investigated dielectric layers, their respective thicknesses and the corresponding symbols for measurement data.

Effective minority charge carrier lifetimes (τ_{eff}) are measured via transient photoconductance decay technique by means of a WCT-120 tool from Sinton Instruments Inc. [4]. For comparability, all lifetimes are evaluated at an injection level of 10^{15} cm^{-3}.

After lifetime measurement the same samples are used for NRRA and CV measurements. CV measurements have been performed at 4Dimensions Inc. using a CVmap92A measurement setup. NRRA measurements have been performed at the Central Unit for Ionbeams and Radionuclides, RUBION at the University of Bochum. Fig. 2 illustrates the simplified measurement principle [5].

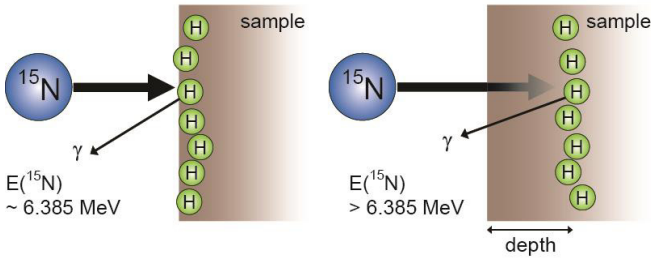

Fig. 2. Simplified NRRA measurement principle. Dependent on the detected gamma quanta from a ^{15}N particle beam of known kinetic energy and fluence, a [H] depth profile can be measured.

Two groups of industrial type solar cells are manufactured using 12.5×12.5 cm² boron-doped Czochralski-grown (Cz) silicon wafers (1.5 Ωcm, thickness: 200 µm) featuring a 50 Ω/sq $POCl_3$ emitter and a full area Al back surface field (BSF). The front side of the cells is passivated by a SiN_x:H single layer or a SiN_x:H/SiO_2 double layer antireflection coating (DARC), respectively.

3. Results

Table 1 displays the results from lifetime, CV and IV measurements. In this comparison, the thick SiNx:H layer exhibits the highest lifetime value and the lowest D_{it}.

Table 1. Effective minority charge carrier lifetime, CV measurement and best solar cell results.

Sample/dielectric	τ_{eff} (µs)	Q_{tot} (×10^{12} cm^{-2})	D_{it} (×10^{10} cm^{-2}eV^{-1})	V_{oc} (mV)	j_{sc} (mA/cm²)	η (%)
SiN_x:H 87 nm	722 ±36	2.5 ±0.3	leakage current	638	37.3	18.8
SiN_x:H 210 nm	1365 ±68	2.2 ±0.3	<1 - 1.6	-	-	-
SiN_x:H/SiO_2	1037 ±52	2.4 ±0.3	2.1 - 3.6	640	38.2	19.1

Q_{tot} for all samples is approximately the same within measurement uncertainty. Therefore, a correlation to lifetime values could not be found. The D_{it} values, however, reveal dependencies as expected. The SiN_x:H/SiO_2 sample exhibits a higher D_{it} value than the thick SiN_x:H sample. Due to leakage current, no D_{it} value could be calculated for the thin SiN_x:H sample, suggesting an even higher D_{it} value than found for the other samples.

A correlation of the τ_{eff} and bond densities of Si-H and N-H in the SiN_x:H bulk was presented in our earlier work [6]. In combination with the CV results a positive effect of the capping layer in respect to the interface passivation rather than to the density of fixed charges could be stated.

At a steady FF, solar cells using the SiN_x:H/SiO_2 ARC exhibit average improvements of 2 mV and 0.5 mA/cm² in V_{oc} and j_{sc}, leading to 19.1% efficiency for the best cell.

The NRRA measurements are depicted in Fig. 3. All measurements are normalized to the interface (0 MeV) and shown in relative kinetic energy of the ^{15}N atoms.

The thick SiN_x:H layer sample reveals the highest concentration of hydrogen close to the interface and in the silicon bulk. The thin SiN_x:H and the SiN_x:H/SiO_2 deposited samples feature comparable hydrogen concentrations in the silicon bulk. Close to the interface (0.05 MeV), however, the SiN_x:H/SiO_2 sample exhibits a slightly higher hydrogen content.

The combination of the results suggest that thicker PECVD SiN_x:H layers or SiNx:H layers capped with PECVD SiO_2, have more hydrogen available for an improved passivation or lower D_{it}, respectively. As Nickel et al. revealed, SiO_2 acts as a diffusion barrier for diffusion of hydrogen into silicon [7], so this effect might be due to the slowed down effusion of hydrogen from the SiN_x:H layer to the air due to thick SiN_x:H or added SiO_2, respectively.

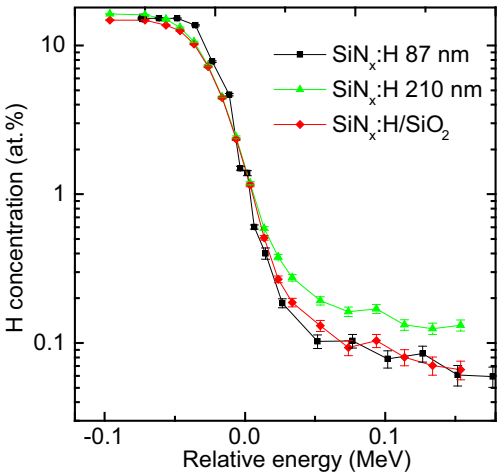

Fig. 3. NRRA measurement of hydrogen concentration after firing in the dielectric layers and silicon. x axis' zero is set to the interface between silicon and the dielectric.

Regarding solar cell production, the presented SiN_x:H/SiO_2 double ARC is favorable not only because of its better incoupling of light and better stability against thickness variations of the depositions [8], but also due to the improved surface passivation. In contrast to combinations with a thermal oxide layer, the presented stack is the more cost effective solution. The lower leakage current of SiN_x:H/SiO_2 compared to a thin SiN_x:H layer can also be advantageous for novel solar cell concepts.

4. Discussion about DARC on cell and module level

To discuss the optical effect of a DARC on cell and module level numerical simulations are performed [9]. In these simulations efficiencies of cells with SiN_x:H ($n_{600\ nm} = 1.95$) single layers (SARC) of different thicknesses alone, below 119 nm of SiO_2 ($n_{600\ nm} = 1.48$) (DARC), EVA ($n_{600\ nm} = 1.53$) and SiO_2 + EVA are investigated. The combinations without EVA represent cell level performance, whereas with EVA module level performance is represented. For the given efficiencies in Fig. 4 only optical effects are taken into account. Other cell parameters like FF, V_{oc} and shading are treated as constants.

SiN_x thickness (nm)	η SiN_x (%)	η SiN_x + SiO_2 (%)	η SiN_x below EVA (%)	η SiN_x + SiO_2 below EVA (%)
105	19.78	20.00	20.13	20.12
100	19.83	20.02	20.14	20.13
95	19.88	20.05	20.15	20.15
90	19.93	20.08	20.16	20.16
85	19.97	20.10	20.17	20.16
80	19.99	20.13	20.17	20.16
75	20.00	20.15	20.17	20.16
70	19.99	20.17	20.16	20.15
65	19.96	20.18	20.15	20.13
60	19.90	20.18	20.13	20.11
55	19.82	20.17	20.10	20.08
50	19.71	20.16	20.06	20.03
45	19.57	20.14	20.01	19.98
40	19.40	20.11	19.96	19.92
35	19.20	20.07	19.90	19.86
30	19.00	20.03	19.84	19.79

Fig. 4. Simulated efficiency table for different dielectric layer systems.

Fig. 4 reveals a strong dependence on the SiN_x:H layer thickness on cell level for a SARC. Within the chosen thickness range up to 1 $\%_{abs}$ in efficiency can be lost due to not optimized layer thickness. The loss is minimized with the addition of a SiO_2 capping layer. Here only 0.18 $\%_{abs}$ is lost. Thereby the process window dramatically widens for the DARC. In addition to the improved efficiency due to a better incoupling of photons into the Si bulk for optimized layer thicknesses, deposition recipes with more inhomogeneities (e.g. process time optimized or passivation optimized) are acceptable.

On module level however this advantage diminishes. There is even a small benefit for the SARC. However, it has to be taken into account how modules are made. Cells are binned according to j_{sc} and color. For SARC there is a large gain in j_{sc} from cell to module. This could lead to problems because in the module cells with suboptimal optics are limited by cells with suboptimal electrical properties, because they are connected in series. Thereby the binning of cells gets easier for DARC cells and the binning according to color might be unnecessary, because the color impression of DARC cells in modules is more homogeneous as well [7]. Taking the improved V_{oc} into account the temperature coefficient of the module can be slightly improved, leading to a minor efficiency gain with a simplification of the module production process.

5. Conclusion

The hydrogen content close to the silicon/dielectric interface is found to be a good measure for passivation quality of SiN_x:H coated silicon samples. With thicker SiN_x:H layers or the addition of a SiO_2 capping layer, the hydrogen content at the interface can be increased and thereby the passivation quality improved. With advantages in surface passivation, optics, cost and process stability the presented PECVD stack made of SiN_x:H/SiO_2 is favorable for efficient solar cell and module production.

Acknowledgements

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