HYDROGEN IN STACKED DIELECTRIC LAYERS

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ABSTRACT: Hydrogen plays a major role for passivation of silicon surfaces. The hydrogen needed for passivation is usually delivered by hydrogenated dielectric layers which are deposited on the silicon surface. The absolute concentration of hydrogen within the layers as well as the change in concentration and hydrogen bond structure due to firing or annealing steps are important factors for surface and volume passivation quality. Our recent work demonstrates major gains in passivation quality of stacked dielectric layers using a silicon oxide (SiO_2) capping layer compared to single layer systems [1,2]. As these stacked systems can be used as double layer anti-reflection coatings they are interesting for solar cell production. This study focuses on passivation layer stacks consisting of plasma-enhanced chemical vapour deposition (PECVD) hydrogenated silicon nitride (SiN_x) capped with PECVD SiO_2. Improved performance on stacked layer lifetime samples and solar cells on minority carrier lifetime level and V_{oc} compared to samples with single SiN_x layers, require a deeper look into the hydrogen kinetics and bonding structure. Fourier transform infrared spectroscopy (FTIR) and nuclear resonance reaction analysis (NRRA) reveal considerable differences in the bond density change due to firing and higher hydrogen concentrations at the silicon/dielectric interface of stacked systems compared to single layer anti-reflection coatings.
Keywords: passivation, PECVD, hydrogen

1 INTRODUCTION

The influence of the individual layers and their interaction within stacked dielectric layers is not yet well understood. As lifetime samples and solar cells show improved performances on minority carrier lifetime and V_{oc} level, respectively, a deeper look into the hydrogen kinetics and bonding structure is mandatory for these stacked systems.

SiO_2 layers can easily be implemented in a solar cell process as they can be produced with existing deposition equipment and almost no additional processing time nor additional processing costs.

This work reveals the important role of hydrogen for stacked layer systems for silicon surface passivation. The focus lies on how and why a stacked system can improve the interface and volume passivation quality in comparison to a single layer SiN_x layer by influencing the effusion of hydrogen from the SiN_x bulk.

2 EXPERIMENTAL DETAILS

To display the difference in passivation quality on cell level, 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 aluminium back surface field (BSF). The front side of the cells is passivated by a SiN_x single layer or a SiN_x/SiO_2 layer stack, respectively. SiN_x and SiN_x/SiO_2 stacks are deposited in a lab-type direct-PECVD setup (Oxford Instruments Plasmalab System 100). The process gases used for SiN_x are SiH_4 NH_3 and N_2, for SiO_2 SiH_4 and N_2O are used. As there is no evidence for cross contamination between the deposition processes, the complete stack is deposited within one step at a constant temperature. Thickness of the individual layers is optimised regarding best anti-reflectance properties on textured surfaces (solar cells) according to [3]. The shown cell parameters are measured prior to light induced degradation.

For the lifetime experiments, p-type float zone silicon (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 an RCA cleaning. SiN_x and SiN_x/SiO_2 stacks are deposited on both sides of the wafers in the same direct-PECVD setup used for the solar cells. The chosen thickness of the individual layers is identical to the ones used for the solar cells except for a reference layer of 210 nm thick SiN_x. In order to determine the influence of the industrial-type co-firing process required for the solar cells, some samples are exposed to an comparable firing step at 855°C peak set temperature in a belt furnace.

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

For the FTIR samples, chemically polished p-type FZ-Si wafers of 2 Ωcm resistivity are used (thickness: 250 μm) and the SiN_x/SiO_2 stacks as well as the SiN_x and SiO_2 single layers are deposited on both sides (SiO_2 as references). The thickness of the individual layers is the same as in the other experiments. Figure 1 depicts the deposited layers used in this work.
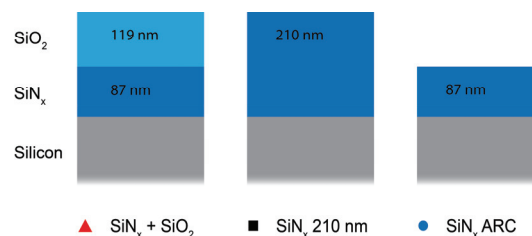

Figure 1: Dielectric layer systems and their names used in this work.

3 NRRA TECHNIQUE

The presence of hydrogen is a key influencing factor for the passivation of silicon surfaces. An excellent

technique for the depth dependent measurement of hydrogen concentration is nuclear resonance reaction analysis (NRRA). The measurements have been performed at the Central Unit for Ionbeams and Radionuclides, RUBION, at the University of Bochum.

NRRA for hydrogen is based on a resonant reaction of accelerated ^{15}N ions with atomic hydrogen. The reaction is described by

$$^{1}H(^{15}N,\alpha\gamma)^{12}C$$
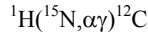
and has a sharp resonance at $E(^{15}N) = 6.385$ MeV. The amount of gamma quanta emerging from the reaction in relation to the nitrogen flux and kinetic energy compared to the values of a reference sample with known hydrogen content yields the hydrogen content in the layer of interest. A concentration depth profile is derived from the variation of the ^{15}N ions' kinetic energy. With higher energy, the resonant reaction occurs deeper within the sample as the energy of the ions is reduced by their penetration through the material. Figure 2 illustrates the principle [4].
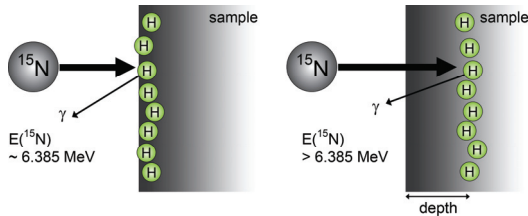
Figure 2: Simplified NRRA measurement principle. Dependent on the detected gamma quanta from a ^{15}N particle stream of known kinetic energy and flux, a hydrogen concentration depth profile can be calculated.

4 RESULTS

The V_{oc} measurements of the solar cells are depicted in Figure 3. Due to reduced reflectance compared to single layer SiN_x, the solar cells with a SiN_x/SiO_2 stack feature an average improvement of 0.5 mA/cm² in short circuit current density j_{sc} (not shown), the gain in open circuit voltage V_{oc} is around 3 mV (Figure 3). PC1D [5] simulations reveal that the increase in j_{sc} of 0.5 mA/cm² yields an increase in V_{oc} of only ~0.4 mV. Therefore, the additional gain (>2 mV) must be caused by an improved surface passivation of the solar cells by the stacked anti-reflection / passivation layer. A comparable gain in V_{oc} employing stacked layers was also observed in [6].
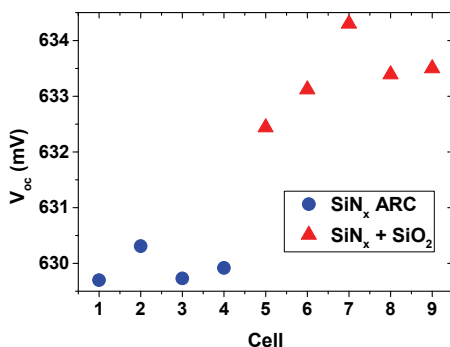
Figure 3: Solar cell results for single SiN_x and SiN_x/SiO_2 passivation layers. A clear improvement in passivation

quality (V_{oc}) for the SiN_x/SiO_2 system (right) compared to the single layer passivation (left) is observed.

The lifetime measurements confirm the gain in passivation quality for the stacked system compared to single layers with standard thicknesses (SiN_x ARC) (Figure 4). A SiN_x layer with a thickness above 200 nm displays the highest lifetime, but is not suitable for employment in solar cells as the reflection is too high. The symbols in Figure 4 represent the results for reference samples deposited together with the FTIR samples. The spread shows the range of lifetime values observed for these deposition processes carried out in earlier experiments.
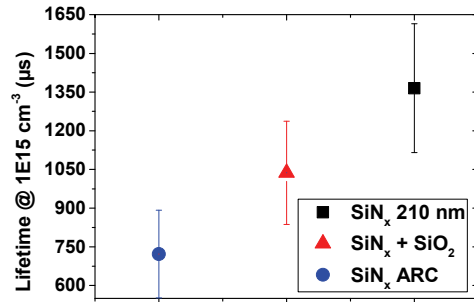
Figure 4: Effective minority charge carrier lifetimes of samples with single SiN_x layers and stacked SiN_x/SiO_2 systems, respectively, after a high temperature firing step.

For a more detailed insight into the hydrogen kinetics and bond structure, FTIR measurements are conducted on the samples as stated in Figure 1 before and after a high temperature firing step (Figure 5 and Figure 6). The bond densities are calculated according to [7].
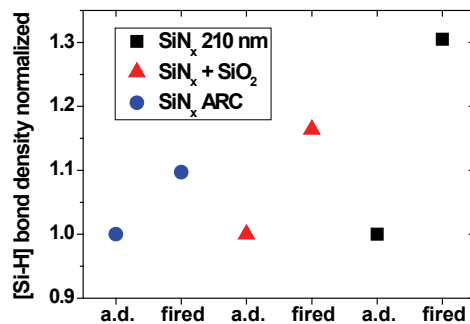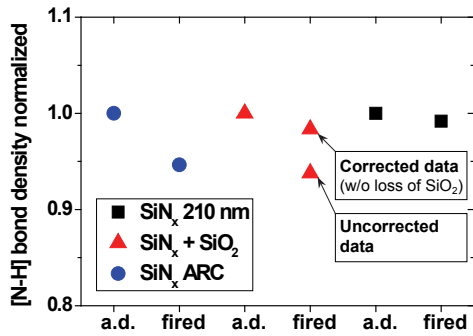

Figure 5: Si-H bond density determined by FTIR and normalised to the as deposited values for SiN_x single layers and a SiN_x/SiO_2 stack system as deposited (a.d.) and after a high temperature firing step.

In case of the stacked layer, the Si-H bond density increases more during firing, than it does for the ARC single layer. The thick SiN_x layer shows the largest increase. As pointed out in the work of Lenkeit about SiN_x single layers [8], an increase in Si-H bond density during a high temperature firing step is accompanied by an increase in effective minority carrier lifetime. This correlation is also observed here. Passivation of the interface is mainly due to the formation of Si-H bonds [9]

Lenkeit [8] also revealed that a decrease in lifetime can be but doesn't have to be correlated with a decrease

in N-H bond density. Albeit such a correlation is also found in this case as displayed in Figure 6.

For both cases (Si-H and N-H), the influence of H-bonding density changes within the SiO_2 layer is cross checked to avoid wrong conclusions. Therefore, SiO_2 layers of the same thickness deposited on FZ-Si wafers are included in the FTIR measurements. These layers are subjected to the same firing procedure. The finding is that for Si-H bond density the influence of firing is negligible on SiO_2, for N-H, however, most of the change in bond density is caused by changes in the SiO_2 bulk. The fact that there are N-H bonds in this layer might be caused by N_2O being used as a process gas.

Figure 6: Si-H bond density determined by FTIR and normalised to the as deposited values for SiN_x single layers and a SiN_x/SiO_2 stack system as deposited (a.d.) and after a high temperature firing step.

Taking the influence of SiO_2 into account and subtracting the change in N-H bonding density influenced just by the SiO_2 layer from the change of the stacked system, the decrease in N-H bond density is considerably reduced compared to the SiN_x ARC single layer.

To find out more about the distribution of the hydrogen within the layers and at the interface to the silicon wafer, NRRA hydrogen depth profiles were measured for the layer systems depicted in Figure 1, the profiles are depicted in Figure 7. All three samples are exposed to a high temperature co-firing step.
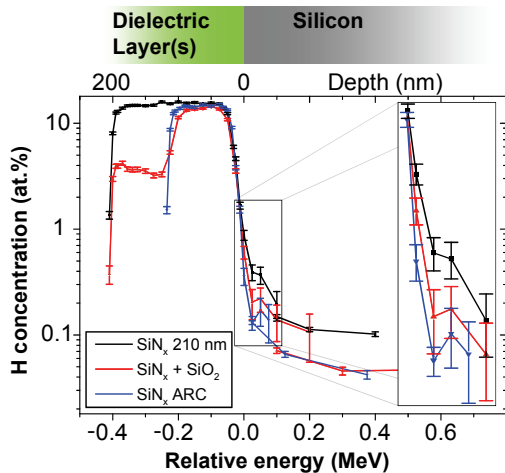
Figure 7: Hydrogen concentration determined by NRRA after firing in the dielectric layers and silicon. x axis' zero is set to the interface between silicon and the dielectric.

For convenience, the measurements are shifted in a way that the dielectric/silicon interface is set to the x-value zero. The error bars indicate the statistical error of the measurement. To lower the error, the flux of ^{15}N ions is increased for measurements in the silicon close to the interface. Here, the sample with the 210 nm thick SiN_x layer clearly reveals an increased concentration of hydrogen in the silicon. For the samples with the stacked system and the thin SiN_x single layer the concentration in the silicon seems to be comparable with a slight benefit for the stacked system. There seems to be a correlation between the SiN_x layer thickness and the hydrogen concentration in the silicon bulk near the interface.

At the interface, however, the stacked system exhibits a higher concentration of hydrogen. Taking the shown effective minority carrier lifetime into account where the stacked system lies in the middle between thin and thick SiN_x single layers, a correlation between the hydrogen concentration within the first few nanometers of silicon and effective minority carrier lifetime is found.

The presence of more hydrogen at the interface might be due to the slowed down effusion of hydrogen from the SiN_x layer to the ambient due to the SiO_2 layer.

Nickel et al. revealed SiO_2 acts as a diffusion barrier for diffusion of hydrogen into silicon [10]. As a higher hydrogen concentration at the dielectric/silicon interface is measured, the SiO_2 is likely to act as a barrier or even reflector that prevents the hydrogen effusion from the SiN_x layer. Thereby more released hydrogen (from the SiN_x layer) is available at the dielectric/silicon interface.

5 SUMMARY

Stacked dielectric layers which can be used as double layer anti-reflective coatings improve passivation quality in comparison to single PECVD SiN_x layer systems. A PECVD SiO_2 capping layer strongly influences the concentration and chemical bonds of hydrogen during a firing step. Bond densities of Si-H and N-H are changing in a way that is known to enhance effective minority charge carrier lifetime. NRRA measurements show higher hydrogen concentrations at the silicon / dielectric interface for these stacked systems as well.

SiO_2 is a diffusion barrier for hydrogen which leads to more available hydrogen in the SiN_x layer for silicon dangling bond passivation at the interface. SiO_2 layers for double layer anti-reflective coatings can easily be included in a cell process as they can be produced within existing deposition equipment with almost no additional process time and costs.

6 ACKNOWLEDGEMENT

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