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Double layers of ultrathin a-Si:H and SiN_x for surface passivation of n-type crystalline Si wafers

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Abstract

Surface passivation by double layers made of hydrogenated amorphous silicon (a-Si:H) and hydrogenated silicon nitride (SiN_x) on float zone n-type Si substrates was investigated. The thickness of the a-Si:H layers was varied from 0 to 4 nm and they were deposited at low temperature by plasma-enhanced chemical vapour deposition. The structure and composition of the double layers was determined by a combination of spectroscopic ellipsometry and glow discharge optical emission spectroscopy. The minority carrier effective lifetime and the uniformity of the surface passivation of the wafers were measured by calibrated photoluminescence imaging. The lifetime was observed to increase with increasing a-Si:H thickness. An excellent lifetime value of 7.3 ms was measured on the double layers with an a-Si:H layer thickness of 3.4 nm, corresponding to surface recombination velocity below 2 cm/s. Capacitance-voltage and conductance-voltage measurements were used to determine the densities of fixed charge and interface states at the interface between the Si substrate and the a-Si:H/SiN_x stacks. The fixed charge density of the initial SiN_x was positive, as expected. However, the overall fixed charge density of the double layers was observed to decrease when a layer of a-Si:H was inserted beneath the SiN_x, and eventually reaches negative values when the a-Si:H thickness exceeds 2 nm. The conductance-voltage measurements revealed that the interface state density (D_{it}) is significantly lowered when adding the ultrathin a-Si:H film between the substrate and the SiN_x layer, providing a significant improvement of the chemical passivation, thus reducing the overall surface recombination velocity.

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1. Introduction

Recently, several solar cells with efficiencies approaching or above 25% have been demonstrated. These, include the HIT solar cell from Panasonic with a conversion efficiency of 25.6%, and the TOPCon silicon solar cell from Fraunhofer ISE with an efficiency of 25.1%, both of which have been realized using stacks as surface or contact passivation material [1, 2]. It is well known that a-Si:H yields good surface passivation because of its low density of interface states resulting in good chemical passivation on silicon surfaces. However, a-Si:H shows poor thermal and UV stability and exhibits some parasitic optical absorption. [3] To overcome these limitations, stacks like SiO_x/SiN_x [4], a-Si:H/SiN_x [5,6] and a-Si:H/Al_2O_3 [7] have been developed for high efficiency solar cells. For the capping layer, low absorption, high stability, as well as high fixed charge are desirable properties. SiN_x is a prominent candidate because of its good thermal and temporal stability, tunable refractive index and a fairly high density of fixed, positive charge. Koyama et al. reported that a surface recombination velocity (SRV) of 1.5 cm/s and 9.0 cm/s could be obtained for n-type and p-type wafers, respectively, with a-Si:H/SiN_x stacks deposited by catalytic chemical vapor deposition (Cat-CVD). [8] A similar SRV value of 3.5 cm/s for plasma-enhanced chemical vapour deposition (PECVD) deposited a-Si:H/SiN_x stacks passivated n-type silicon has been obtained by Stepanov et al [9]. The passivation yielded by an a-Si:H/SiN_x stack is very sensitive to the a-Si:H layer thickness. [10] In this report, we focus on ultrathin a-Si:H films with a thickness between 0 and 4 nm capped by a SiN_x film with a thickness of 100 nm, which is good for avoiding parasitic absorption of a-Si:H.

2. Experiments details

In this work, double layers of a-Si:H/SiN_x, where the a-Si:H layer thickness was below 4 nm, were made. The thickness variation was controlled by adjusting the deposition time during the PECVD process and estimated based on predetermined deposition rates. The SiN_x layer thickness was kept constant at 100 nm while the a-Si:H thickness was varied from 0 to 4 nm. One 40 nm a-Si:H and one 100 nm SiN_x single layer were deposited for reference separately. The thicknesses were measured by variable angle spectroscopic ellipsometry (VASE). For the experiments, six halves of 4 inch float zone (FZ) n-type silicon wafers with a resistivity of approximately 2.8 Ωcm were used. The wafers were double-side polished with a thickness of 290 µm and a crystal orientation of (100). The double layers of a-Si:H/SiN_x were deposited on both sides of the wafers in a PlasmaLab 133 system from Oxford Instruments including a direct parallel plate reactor and an automatic wafer loading system. Before deposition, all wafers were cleaned in HF (5%) for 1 min, whereafter the a-Si:H films were deposited using a power density 9 mW/cm^2 and a temperature of 230 °C. In order to obtain a clean surface before deposition of the rear side, the wafers were subjected to a 5 s HF-dip before the second deposition of a-Si:H. In order to avoid cross contamination between a-Si:H and SiN_x, the PECVD was conditioned by performing a long (20 min) deposition of SiN_x on a dummy sample before the outermost 100 nm thick SiN_x layers were deposited on both sides with a power of 46.5 mW/cm^2 at 230 °C, the same deposition temperature as for the a-Si:H. After deposition, all wafers were cut into two pieces. One quarter was kept for lifetime measurements to determine temporal stability. Another quarter was used to deposit metal to form metal-insulator-semiconductor (MIS) structures for capacitance-voltage (C-V) and conductance-voltage (G-V) measurements.

The effective carrier lifetime was measured by photoluminescence imaging (PL-imaging) calibrated using the quasi steady-state photoconductance (QSSPC) method at an injection level of $10^{15}cm^{-3}$. VASE was used to characterize the film thickness and glow discharge optical emission spectroscopy (GDOES) was performed to investigate the composition of the samples as a function of thickness. The ellipsometry was performed using a variable angle spectroscopic ellipsometer from J. A. Woollam Co., Inc. A GDOES setup from Horiba Jobin Yvon was used to characterize the hydrogen depth profile of the samples. The C-V and G-V measurements were carried out at room temperature at a frequency of 100 kHz using a Keithley 4200-SCS semiconductor characterization system.

GDOES is a well-established spectrochemical approach for detecting trace elements. GDOES has many benefits including a high depth resolution, fast sputtering rate, low limits of detection and no need for high vacuum. [15] Here we applied GDOES to determine the H distribution in the c-Si/a-Si:H/SiN_x system for the first time.

3. Results and discussion

3.1. Passivation quality

Figure 1 shows the effective lifetime τ_{eff} of the wafers passivated by a-Si:H/SiN_x with a-Si:H thicknesses ranging from 0 to 4 nm. When there is no a-Si:H layer between c-Si and SiN_x, a low value of τ_{eff} of 20 µs is obtained at an injection level of 5×10^{14} cm^{-3}. After adding an a-Si:H film with a thickness of only 1.3 nm, τ_{eff} increases to 540 µs. As the thickness of the a-Si:H layer increases further, the τ_{eff} improves dramatically and reaches a very high value of 7.34 ms when the a-Si:H thickness is around 3.4 nm. Assuming infinite bulk lifetime (τ_b), we obtain a very low SRV of 2 cm/s from:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2SRV}{W} \tag{1}$$

where W is the thickness of wafer. Further increasing the thickness of the a-Si:H layer to 4 nm results in a slightly lower value of τ_{eff}, indicating that there is an optimal thickness of a-Si:H. A similar trend has been reported from other research groups [8].

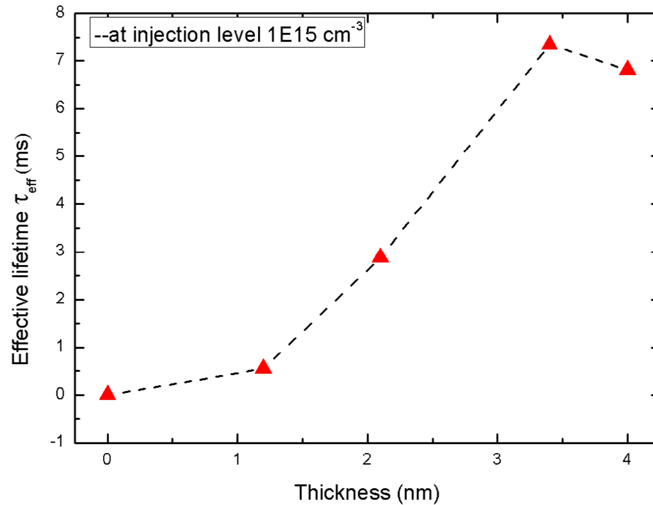

Fig. 1. Effective lifetime τ_{eff} as a function of a-Si:H thickness

3.2. Passivation mechanism

In order to better understand the passivation mechanism of these a-Si:H/SiN_x stacks, C-V and G-V measurements were performed. High frequency (100 kHz) C-V measurements were performed using voltages ranging from -4 V to +4 V for all samples. We assume that the a-Si:H/SiN_x stacks are good dielectric materials for a metal-insulator-semiconductor (MIS) structure, and that the fixed charge lies near the interface with the substrate. The density of fixed charge (Q_f) can be obtained by measuring the shift of experimental C-V curves along the voltage axis as compared to a theoretical curve. Assuming that the fixed charges are located at the interface to c-Si, Q_f can be expressed as

$$Q_f = \frac{C_i}{q}(\Delta\phi_{ms} - V_{fb}) \quad (2)$$

where C_i is the insulator capacitance, $\Delta\phi_{ms}$ the metal-semiconductor work function difference, V_{fb} the flat-band voltage and q the elemental electrical charge. [11]

The measured capacitance from inversion to accumulation conditions for samples with different a-Si:H thickness is shown in Figure 2 (a). For the single SiN_x passivation layer, a negative value of V_{fb} is observed, corresponding to a positive fixed charge, well in line with past reports. However, as the a-Si:H thickness increases, the measured V_{fb} shifts from -2.14 V for a single layer of SiN_x to +1.63 V for stacks with a 4 nm layer a-Si:H. This corresponds to a variation of fixed charge densities from positive ($+7.37\times10^{11}$ cm^{-2}) to negative (-6.7×10^{11} cm^{-2}). As the a-Si:H thickness increases, the effect of the positive charge from the initial SiN_x layer is suppressed, as shown in Figure 2 (b). A 1 to 2 nm SiO_x layer is often observed between SiN_x and c/Si, where donor like dangling bonds exist at the interface which influence the formation of positive fixed charge. When depositing a-Si:H between SiN_x and c-Si, H from a-Si:H will saturate some donor-like defects, leading to a decrease of the positive fixed charge. [12] In addition, the SiN_x is deposited at low temperature (230 °C) and is relatively weakly charged. Hence, defects at the interface between a-Si:H/c-Si can become dominant in this system. In a previous investigation by Olibet et al, the amphoteric nature of Si dangling bonds on a-Si:H passivated Si was suggested [13]. We suspect that with a limited a-Si:H (around 2 nm) layer, enough H from this layer could saturate SiO_x/c-Si interface donor-like defects, decreasing the positive charge, while the dangling bonds between a Si:H and c-Si result in the formation of a negatively charged dangling bond (D^-) when it is occupied by two electrons. Correlating with τ_{eff}, we see that the field effect passivation from the fixed charge in SiN_x decreases when the a-Si:H thickness increases from 0 nm to 2.1 nm. Thereafter, negative fixed charges form between the stacks and c-Si wafer when the a-Si:H thickness is further increased.

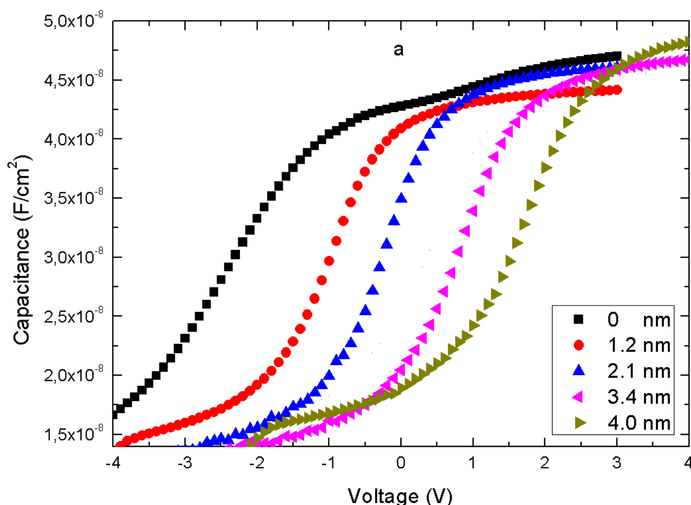

Fig. 2. (a) Capacitance as a function of bias voltage with a-Si:H thickness (b) Q_f as a function of a-Si:H thickness

Figure 3 (a) shows the results of G-V measurements for bias voltages from -4 V to +4 V for all samples. The single layer SiN_x sample shows a clear peak at -2.4 V corresponding to flat band conditions, which indicates a high density of interface states (D_{it}) at the interface. All samples with an a-Si:H layer inserted between the SiN_x and the Si wafer show much broader and lower peaks, indicating a lowering of the D_{it} at the interface. The single frequency method has been used to calculate D_{it} [14], as shown in Figure 3 (b). The value of D_{it} decreases clearly as the a-Si:H thickness increases. When the a-Si:H thickness increases from 0 nm to 1.3nm, D_{it} decreases from 9.55×10^{11} $cm^{-2}eV^{-1}$ to 1.3×10^{11} $cm^{-2}eV^{-1}$, indicating a good chemical passivation from a-Si:H. When the a-Si:H thickness further

increases, D_{it} decreases to 6.9×10^{11} $cm^{-2}eV^{-1}$ for an a-Si:H thickness of 3.4 nm, before it starts to increase. We see an optimal a-Si:H thickness for chemical passivation of around 2 nm.

The C-V and G-V results implies that for a-Si:H/SiN_x stacks on n-type silicon wafers, the chemical and field-effect play synergetic roles. The chemical passivation from ultra-thin a-Si:H layer (< 2 nm) plays an important role for passivation while negative charging from a-Si:H/SiN_x (> 2nm) further enhances the passivation of Si wafer.

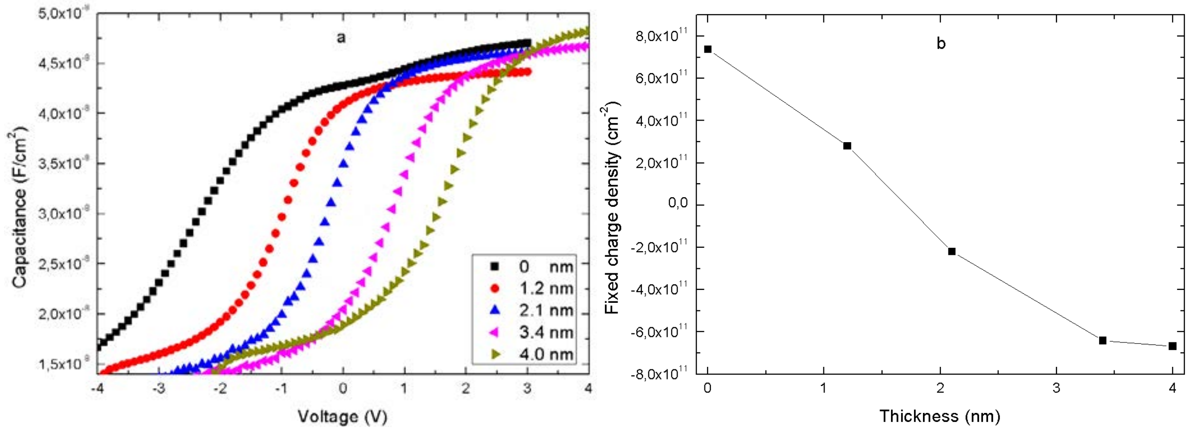

Fig. 3. (a) Conductance as a function of bias voltage with a-Si:H thickness variation (b) D_{it} as a function of a-Si:H thickness

3.3. Hydrogen depth profile from GDOES

Figure 4 (a) depicts the GDOES measurements of the hydrogen distribution from the surface to the substrate for the samples investigated, as well as the FZ-n-type Si reference sample. The X-axis represents the sputtering time and the Y-axis the emitted light intensity of H. Here we use the same sputtering setting for all samples with the same structure of SiN_x/a-Si:H/c-Si, which gives us qualitative results of the H distribution within this structure. It is possible to discriminate between the passivation stacks and the substrate Si wafer while it is more difficult to separate between SiN_x and the a-Si:H layer because of the low thicknesses. We need to adjust the sputtering setting to reduce the impact of H from the surface and within the chamber. As a result of different sputtering rate in SiN_x and the Si wafer, a high peak error is present in the first 0.1 s H depth profile of the reference n-type substrate. Figure 4 (b) shows the enlarged H depth profile at the a-Si:H/c-Si interface. A clear trend of increasing H concentration as the a-Si:H thickness increases at the a-Si:H/c-Si interface is observed. This is an important indication that H plays an important role in chemical passivation of the a-Si:H/c-Si interface.

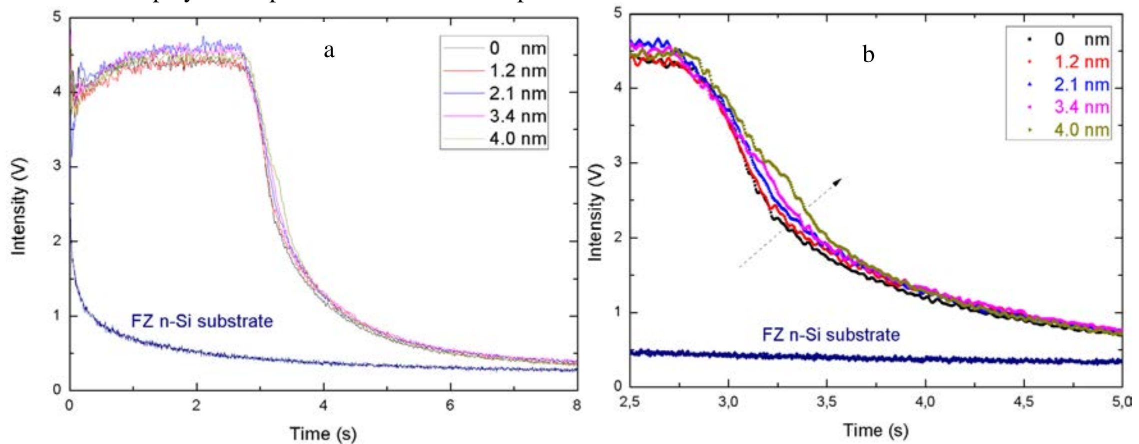

Fig. 4. Depth profile of SiN_x/a-Si:H/c-Si structure with a-Si:H thickness variation (a) from surface to substrate and (b) interface of a-Si:H/c-Si

4. Conclusion

Low temperature double layer a-Si:H/SiN_x stacks were used to passivate FZ-n-Si wafers. The a-Si:H thicknesses were varied from 0 nm to 4 nm. A very low SRV below 2 cm/s was obtained for stacks incorporating an a-Si:H layer with a thickness of 3.4 nm. Characterization results from C-V indicates that the overall fixed charge of the stack system switches from positive to negative polarity when increasing the a-Si:H thickness. G-V results show that D_{it} decreases with increased a-Si:H thickness. Furthermore, GDOES has been used on a-Si:H/SiN_x stacks for passivation for the first time. We observe an increase in the H concentration around the a-Si:H/c-Si interface with increasing a-Si:H layer thickness, further confirming the importance of chemical passivation from a-Si:H.

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