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Temporal stability of a-Si:H and a-SiN$_x$:H on crystalline silicon wafers

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Abstract

The temporal stability of single layer thin films of hydrogenated amorphous silicon (a-Si:H) and silicon nitride (a-SiN$_x$:H) passivated crystalline silicon wafers have been investigated over 18 months. The thin films were deposited at low temperature with plasma-enhanced chemical vapor deposition (PECVD) onto different substrates, including float zone (FZ) p-type and Czochralski (CZ) n-type silicon. For a-SiN$_x$:H, we investigate the temporal stability dependence on the flow rate of silane (SiH$_4$) used during deposition. This was varied from 13 sccm to 50 sccm. The thickness of the a-Si:H and a-SiN$_x$:H thin films was characterized by spectroscopic ellipsometry (SE), whereas the minority carrier effective lifetime (τ_{eff}) and the uniformity of the wafer were measured through carrier density imaging (CDI). We found that for both p-type FZ and n-type CZ silicon substrates, the a-Si:H passivation performance degrades after 150 h and reached a minimum value around 350 h, whereafter the lifetime recovered to a level of 1.1 ms (-16% compare to the initial state) and 1.6 ms (-4%), respectively. Similar trends were also seen on a-SiN$_x$:H passivated samples, but the lowest value was reached after around 550 h. For both p- and n-type substrates passivated by a-SiN$_x$:H passivation, as the flow rate of SiH$_4$ increased, the temporal stability of passivated samples enhanced.

Keywords: Temporal stability; a-Si:H; SiN$_x$; passivation ; PECVD

1. Introduction

As the technology continually improves, photovoltaic (PV) solar energy has rapidly increased its share of global electricity production [1]. Silicon based solar cells have been dominant (~90%) in the PV market for the past

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decades. Such solar cells have been successfully used in the power grid for over 25 years with acceptable levels of degradation [2]. Since the solar cells need to be used for long time, the temporal stability becomes more and more important. As the improvement of bulk silicon material continues, surface passivation techniques and materials have turned into an important limitation for silicon solar cell efficiency. The stability of the surface passivation materials also plays an important role for silicon solar cell products. Amorphous silicon nitride (a-SiN$_x$:H) has been widely used as an anti-reflection layer as well as surface passivation material for silicon solar cells [3]. In this report, the temporal stability and the effect of the flow rate of silane (SiH$_4$) on the temporal stability of the surface passivation yielded by a-SiN$_x$:H have been tracked for more than 18 months. Besides the a-SiN$_x$:H, hydrogenated amorphous silicon (a-Si:H) is also widely used in silicon based solar cells. It yields a good surface passivation and is used in high efficiency solar cells, e.g. the back contact heterojunction (BCHJ) solar cell, with the highest reported efficiency of 26.3 % on CZ n-type silicon wafers [4]. Such solar cells can employ a stack structure of silicon nitride and other layers passivating the front surface, as well as intrinsic amorphous silicon and doped amorphous silicon structure on the back side. This is mainly caused by the good chemical passivation provided by the low temperature deposited a-Si:H, which is related to many hydrogen atoms within the film saturating the dangling bonds at the silicon surface [5]. However, a-Si:H is also well known for its poor stability, e.g. the Staebler-Wronski (S-W) effect, degradation under light, as well as at higher temperature. Here, the long term stability of single layer a-Si:H passivated crystalline silicon (c-Si) samples has been investigated.

2. Experiments

Double-side polished, 4-inch p-type float zone (FZ) silicon and n-type Czochralski (CZ) wafers with <100> surface orientation, a resistivity of 3 Ωcm and a thickness of 280 µm and 300 µm, respectively, were used for this study. All wafers were rinsed by a 30 s dip in hydrofluoric acid (HF) immediately prior to the deposition of the intrinsic a-Si:H layer. For a-Si:H passivated samples, 40 nm thick layers of a-Si:H were deposited on both sides of all types of substrates at 200 °C by plasma-enhanced chemical vapor deposition (PECVD). For a-SiN$_x$:H passivated samples, 80 nm thick layers of a-SiN$_x$:H were deposited on both sides of the substrates using different flow rates of SiH$_4$ from 13 sccm to 50 sccm at 400 °C by PECVD. A lab scale PECVD, PlasmaLab 133 from Oxford Instruments, operating at 13.56 MHz, including a direct parallel plate reactor and an automatic wafer loading system, was used in this experiment. Both the a-Si:H and a-SiN$_x$:H deposition power were kept at 8 W. In order to get a clean surface before deposition of the rear side, the wafers were subjected to a short step of 5 s HF-dip before the second deposition of a-Si:H. Besides, one p-type FZ substrate was used to deposit the stacks of a-Si:H/a-SiN$_x$:H for comparison. After deposition, spectroscopic ellipsometry (SE) was used to measure the film thickness as well as the reflectance. The effective carrier lifetime was characterized by carrier density imaging (CDI) at 60 °C corresponding to an injection level of 10^{15} cm^{-3}. In order to track the temporal stability of all deposited samples, wafers were kept in a non-transparent box. The effective carrier lifetime was measured with CDI over a period of 18 months.

3. Results and discussions

3.1. Temporal stability of a-Si:H and a-SiN$_x$:H passivation on c-Si

Figure 1 shows the evolution of the measured effective lifetime over time of the a-Si:H and a-SiN$_x$:H passivated substrates over a period of 16000 h. For a-Si:H passivated samples, as shown in Fig. 1 (a), in the first 150 h after deposition, the measured lifetime of all passivated samples remains stable. Good passivation of all substrates is achieved, with the effective lifetimes for the p-type FZ and n-type CZ substrates reaching 1.3 ms and 1.7 ms, respectively. However, after 150 h, all samples show a declining trend. The lifetime of the n-type CZ samples is reduced to 1.5 ms (91% of original) whilst the lifetime of the p-type FZ samples is reduced to 1.0 ms (80% of original). Then after around 350 h, both FZ p- and CZ n-type samples show a slight increase in the lifetime and remain stable after 1050 h until 16000 h. The final value of lifetime for the n-type CZ samples is 1.6 ms (96% of original) and for the p-type FZ samples is 1.1 ms (84% of original). As both types of substrate do not exhibit light induced degradation (LID) [6], the observed degradation here is mostly caused by the passivation material a-Si:H, which could be related to the hydrogen rearrangement within a-Si:H under light [7]. Although all samples are stored

in an opaque box, they are exposed to the light when measuring the effective lifetime. Although the time required for each measurement is short, around 2 min, the light could still degenerate the amorphous silicon passivated samples [8].

Figure 1 (b) shows the effective lifetime of a-SiN$_x$:H passivated p-type FZ and n-type CZ substrates as a function of time, which gives a similar trend as the a-Si:H passivated samples. Both samples start degrading after 150 h and achieve the minimum value at around 550 h, with the effective lifetime of 0.04 ms (85% of original) and 0.32 ms (85% of original) on the p-type FZ and n-type CZ substrates, respectively. After 550h, the effective lifetime value increases until 1000h, whereafter it is stable. The last values are measured at 16000 h and show a slight decrease to 0.03 ms (75% of original) for the p-type FZ and 0.30 ms (78% of original) for the n-type CZ substrates.
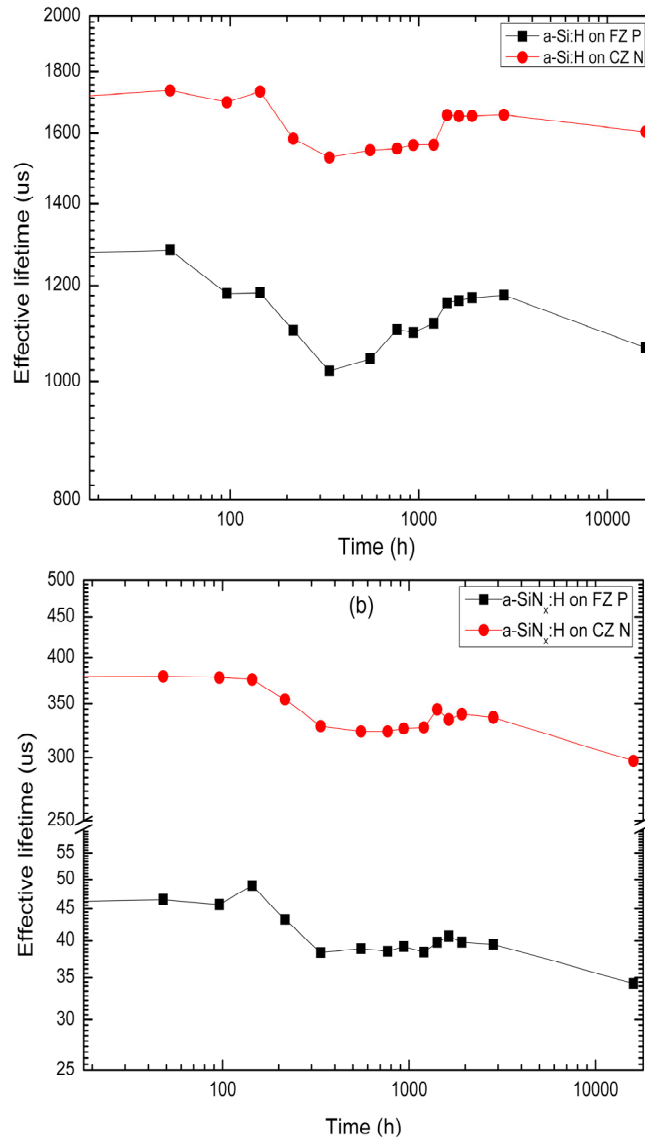

Fig. 1. (a) Temporal stability of a-Si:H and (b) a-SiN$_x$:H bifacial passivation on different types of c-Si substrates

From Figure 1, we see that both a-Si:H and a-SiN$_x$:H-passivated samples exhibit a degrading lifetime after around 150 h, whereafter they reach minimum values at 350 h and 550 h, respectively. Compared with the a-Si:H

samples, the a-SiN$_x$:H samples reach the minimum effective lifetime after a longer time, which could be explained by a more dense film of a-SiN$_x$:H than a-Si:H that limit the hydrogen movement under light [9]. Besides, for all passivated samples, we consider the last effective lifetime data with caution: since all samples have been measured over 20 times, some scratches appear and influence the measurements. However, even under these conditions, both a-Si:H and a-SiN$_x$:H passivated samples show a relative stable performance (difference to the stable value within 5%) after been kept in dark over 18 months, which also indicates that the samples passivated by a-Si:H and a-SiN$_x$:H could maintain the stable performance over long time. The main degradation occurs during these first 1000 h.

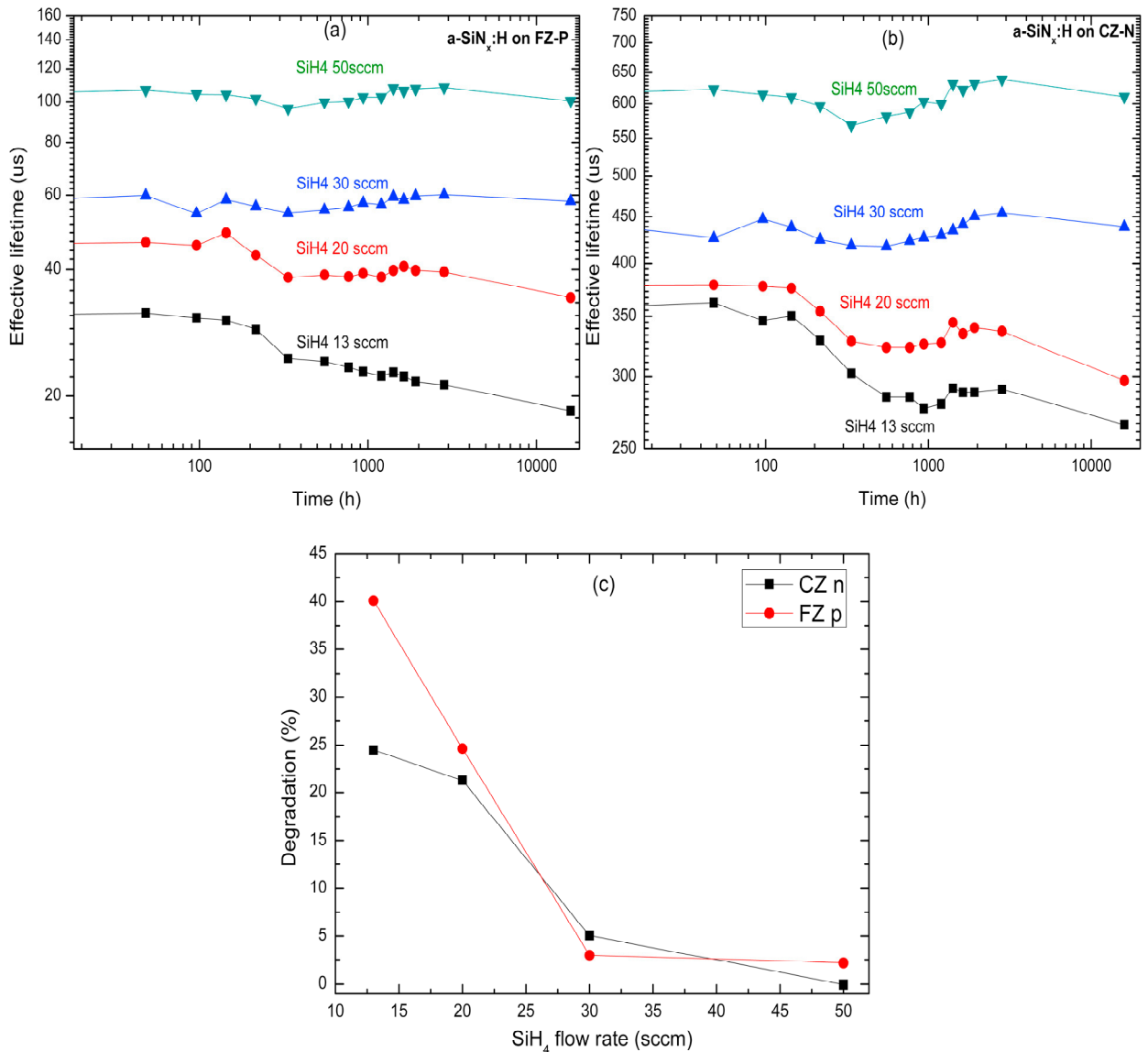### 3.2. Temporal stability of a-SiN$_x$:H with different SiH$_4$ flow rate passivated on c-Si

Fig. 2. Temporal stability of a-SiNx:H bifacial passivation on both FZ p type (a) and CZ n type (b) c-Si as a function of SiH4 flow rate variation. (c) Degradation percentage of both a-SiNx:H passivated CZ n- and FZ p- type substrates

Figure 2 shows the effective lifetime over time of the a-SiN$_x$:H passivated p-type FZ (a) and n-type CZ (b) substrates over 16000 h. The films shown here were deposited using flow rates of SiH$_4$ varying from 13 sccm to 50 sccm during deposition. For the p-type FZ substrates, as the flow rate of SiH$_4$ increases from 13 sccm to 50 sccm, the initial effective lifetime of samples increases from 0.031 ms to 0.1 ms, which could be caused by more hydrogen passivating the unsaturated dangling bonds with higher SiH$_4$ flow rate [10]. On the n-type CZ samples, a similar trend is also found: the effective lifetime of SiH$_4$ flow rate at 13 sccm with 0.35 ms increases to 0.61 ms at 50 sccm.

The temporal stability of the a-SiN$_x$:H passivated samples is enhanced as the flow rate of SiH$_4$ increases. For the p-type FZ substrates, when the flow rate is 13 sccm, the effective lifetime decreases rapidly from 0.031 ms to 0.018 ms after 100 h and keeps degrading over long time. The samples deposited with a flow rate of SiH$_4$ of 20 sccm exhibits an effective lifetime degradation lower than that of the samples deposited at 13 sccm. The samples deposited with a flow rate of 30 sccm show no overall degradation. When the flow rate is 50 sccm, the effective lifetime remains in the same level as that measured on the as-deposited samples, i.e. 0.1 ms. The same trend also can be found on n-type CZ samples. A low flow rate of 13 sccm SiH$_4$ results in the effective lifetime decreasing from 0.35 ms to 0.27 ms, while a high flow rate of 50 sccm results in a stable lifetime value of around 0.61 ms. Figure 2 (c) presents the degradation percentage of the effective lifetime after 16000 h compared to the as-deposited states. We find that when the flow rate of SiH$_4$ is lower than 30 sccm, the long term stability of a-SiN$_x$:H passivation is reduced by more than 20% after been kept in the dark over 1000 h, while the samples deposited with flow rate of SiH$_4$ of 30 sccm shows a degradation of the passivation performance below 5%.

3.3. Temporal stability of a-Si:H/a-SiN$_x$:H stacks on p type FZ c-Si
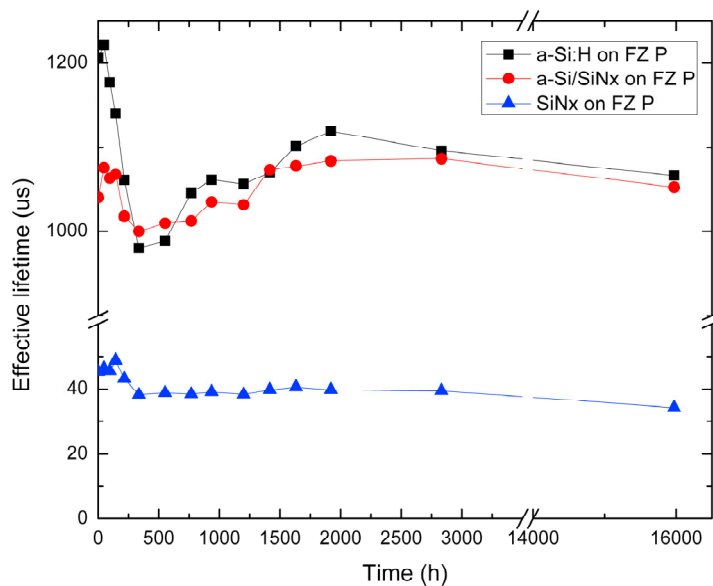

Fig. 3. Temporal stability of a-Si:H, a-SiN$_x$:H and their stacks (a-Si:H/a-SiN$_x$:H) bifacial passivation on FZ p type substrates

We also deposited a stack passivation system consisting of a-Si:H (40 nm) and a-SiN$_x$:H (80 nm) on the p-type FZ silicon substrates. In this experiment, the flow rate of SiH$_4$ was kept at 20 sccm. Figure 3 shows the effective lifetime as a function of time for all three different passivation systems on the p-type FZ substrates over 16000 h. It shows that in the first 500 h, all three passivation systems undergo a degradation, thereafter the lifetime of the 40 nm a-Si:H and a-Si:H/a-SiN$_x$:H stack passivated samples recover to 85% and 100% of the original value, respectively, and maintain this passivation over 18 months. However, single layer a-SiN$_x$:H passivated samples show little recovery and keep stable at 85% of the original value. This degradation could be related to the weak bonds of Si-H within the a-Si:H films, which can be influenced by light and temperature [11,12]. Although our samples were kept

in the dark most of time, when we use CDI measure the effective lifetime, all samples are exposed to light and a hot (60 °C) sample holder. This may affect the hydrogen structure at the a-Si:H/c-Si interface. Compared to the results reported by other groups, our 40 nm a-Si:H passivation shows quite good temporal stability, mainly because of thicker films [13,14]. In our previous experiments, we have observed that the temporal stability of a-Si:H passivated samples increases with the a-Si:H thickness [15]. When the thickness of a-Si:H exceeds 20 nm, enough hydrogen is probably present at the a-Si:H/c-Si interface, making the passivation less sensitive to environmental light or temperature. Besides that, compared to the single layer passivation, the samples passivated by a-Si:H/a-SiN$_x$:H stacks show better temporal stability, with little degradation over 18 months. We believe this is caused by two factors. The buffer layer a-Si:H is quite thick, around 40 nm, and less sensitive to environmental effects. Secondly, the capping layer a-SiN$_x$:H acts as a blocking layer for possible hydrogen effusion out of passivation stacks, further improving the temporal stability of this passivation system.

4. Conclusions

In this work, the effective lifetime of both 40 nm a-Si:H and 80 nm a-SiN$_x$:H single layer passivated p-type FZ and n-type CZ c-Si wafers have been tracked over 18 months. Both passivation systems show degradation in the first 500 h, which can be related to the hydrogen movement under light or other environmental effects. The effect of the flow rate of SiH$_4$ used during a-SiN$_x$ deposition on the temporal stability has been investigated. The stability is enhanced as the flow rate of SiH$_4$ increases. Furthermore, by combining a-S:H and a-SiN$_x$:H forming the a-Si:H/a-SiN$_x$:H stack passivation system on p-type FZ c-Si substrates, we found that this stack shows little degradation up to 1000 h and maintains a good performance after the full 18 months.

Acknowledgements

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