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Influence of a-Si:H deposition temperature on thermal stability of a-Si:H/SiN_x:H stacks

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ABSTRACT

A hydrogenated amorphous Si (a-Si:H) film, combined with a silicon nitride (SiN_x:H) capping layer and a post-deposition anneal, can hugely enhance the surface passivation on crystalline silicon wafers. In this work, the influence of various deposition temperatures of a-Si:H films on the thermal stability of a-Si:H/SiN_x:H stacks and a possible mechanism are discussed. Both minority carrier lifetime measurement and grazing-angle XRD were employed to study the thermal stability of a-Si:H/SiN_x:H stacks, and the results are interpreted in terms of dihydrides concentration and epitaxial crystallization. With an appropriate thermal treatment, the a-Si:H film deposited at 130°C and capped by SiN_x:H showed better passivation performance than 200°C-deposited a-Si:H/SiN_x:H stacks, but under an excessive thermal budget the former showed more severe degradation of carrier lifetime. The more dihydride-rich composition within 130°C-deposited a-Si:H/SiN_x:H stacks could be regarded as providing more effective intermediates for hydrogen interchanges, but on the other hand, it is also more susceptible to epitaxial crystallization.

Introduction

The goal of grid parity is leading to the development of cells with thinner crystalline-Si wafers in an attempt to reduce costs. The use of thinner cells usually results in lower efficiency because more light is able to reach the rear surface of the cell where many trapping sites exist. These trapping sites, which include defects and dangling bonds, act as recombination centres for photo-generated carriers in the Si substrate [1]. Therefore, to improve the efficiency of thin solar cells, good surface passivation is vital to reduce the surface recombination, especially for the rear surfaces. Thermally-grown silicon dioxide (SiO_2) layers provide a very good and thermally stable passivation, but they are prepared by a long and energy-intensive high temperature process, which is unfavourable for mass production [2]. Furthermore, this high-temperature process is extremely detrimental for block-cast multicrystalline silicon [3,4]. Considering quality degradation of wafer materials, a passivation layer that can be deposited at lower temperatures is preferable. Plasma-enhanced chemical vapour deposition (PECVD)-SiN_x films are typically fabricated by a low-temperature process (approx. 300–400°C). They provide very good passivation quality [5–7], but the thermal stability is not as good as SiO_2 layers. Furthermore, cells made from p-type wafers and passivated with nitrogen-rich SiN_x films typically suffer from an inversion layer which is shunted by the local contacts [8]. As the nitrogen content in the SiN_x layer was reduced to get silicon-rich SiN_x layers, the overall defect density was found to decrease. In the extreme case that nitrogen is totally removed, amorphous silicon layers should be formed with the lowest defect density [9]. This intrinsic hydrogenated amorphous silicon (a-Si:H) shows several advantages.

First of all, this passivation film is deposited by PECVD in the temperature range between 200°C and 250°C. The much lower process temperature reduces both energy consumption and degradation of wafer material quality caused by impurity diffusion. Secondly, a-Si:H films can result in the same low effective surface recombination velocity as thermal oxidation [10] and show no parasitic shunting. Therefore, surface passivation by a-Si:H is an attractive candidate for high-efficiency silicon solar cells.

> "In this work, 5-6Ωcm B-doped p-type Cz wafers were used for deposition of dielectric layers and the measurement of minority carrier lifetime."

Even though surface passivation with a-Si:H shows many advantages, it is not without its drawbacks. Quality of passivation with a-Si:H films is highly sensitive to thermal processes. Since process steps such as contact annealing or even screen-printing require a certain thermal stability of the passivation layer, many researchers prefer to focus their study on improving the thermal stability of a-Si:H films for better surface passivation. Plagwitz et al. [11] and Bentzen et al. [12] showed that depositing a silicon nitride (SiN_x) layer on top of the a-Si:H film as a capping layer can improve the thermal stability of the surface passivation. On the basis of this discovery, S. Gatz et al. [13] revealed that the thermal stability of the surface passivation by a-Si:H/SiN_x stacks can be enhanced by increasing the deposition temperature of the SiN_x layer from 300°C to 400°C because of the increasing density of the SiN_x capping layer.

In this work, several concepts to improve thermal stability of surface passivation by a-Si:H/SiN_x stacks are discussed. The SiN_x capping layer is deposited by PECVD at 450°C. The results confirmed that SiN_x-capped a-Si:H films show better thermal stability as compared with a single a-Si:H layer. The effect of deposition temperature of a-Si:H films on the thermal stability of a-Si:H/SiN_x passivation stacks is also discussed in this study.

Experimental details

In this work, 5-6Ωcm B-doped p-type Cz wafers were used for deposition of dielectric layers and the measurement of minority carrier lifetime. KOH chemicals were employed for the fabrication of shiny wafer surface and followed by diluted HF dipping prior to the film deposition. Subsequently, 27.12MHz PECVD systems with H_2 and SiH_4 as the precursor gases were utilized for the deposition of a-Si:H film, followed by the deposition of an SiN_x:H layer using precursor gases of NH_3 and SiH_4. All a-Si:H/SiN_x:H stacks were deposited on both surfaces of the samples, and SiN_x:H layers were deposited with film thickness of 80nm at a temperature of 450°C. Film thickness and deposition

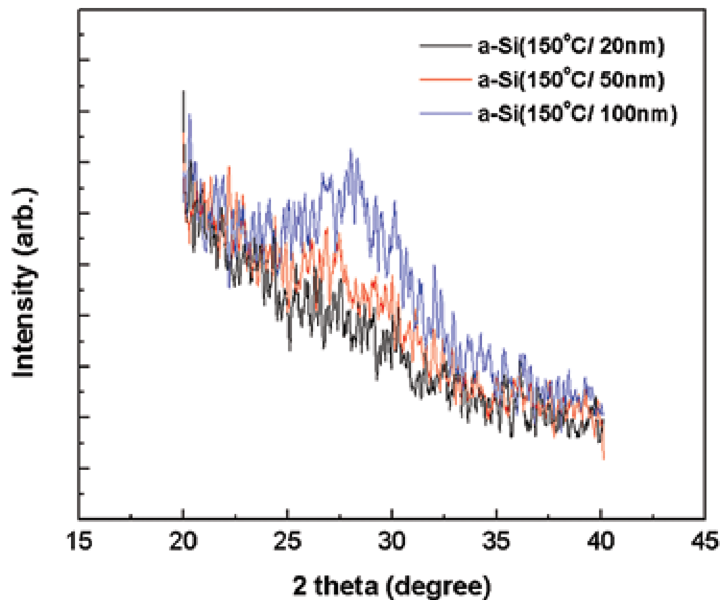

Figure 1. XRD spectra for amorphous silicon films deposited at 150°C with thickness of 20nm, 50nm and 100nm on p-type (100) polished wafers.

temperature of a-Si:H layers were varied from 20nm to 100nm and 110°C to 200°C, respectively. Additionally, in order to measure the extent of crystallinity of a-Si:H films under various thermal conditions, p-type polished wafers with equal size of 1cm^2 were used for XRD monitoring on the same film stacks.

Firstly, we measured samples with a-Si:H film thickness of 20nm, 50nm and 100nm by grazing-angle XRD to look for the sufficient signal of crystallinity. Then, with the selected sampling thickness, various deposition temperatures of a-Si:H layer and different post-deposition RTA (rapid thermal anneal) temperatures were considered to check the phase of crystallization by XRD. In the meantime, micro-PCD was employed in this work to measure the minority carrier lifetime for shiny surface-based samples.

Results and discussion

Thickness dependence on XRD

Fig. 1 shows that the diffraction signals from the crystallized orientation phase (111) of a-Si:H film at a diffraction angle of 2θ~ 28 degree were more and more pronounced with increasing thickness of a-Si:H film. The broad peaks indicate the weak crystallinity of a-Si:H film even with 100nm thickness. For subsequent tests, 100nm a-Si:H layers were used, partly due to the better XRD signal, and partly due to good passivation performance of a-Si:H of such thickness. Mitchell [14] has worked on thick a-Si:H film capped onto c-Si wafers as a passivation layer and concluded that a 200nm-thick a-Si:H layer has a deleterious effect on surface passivation, and that an a-Si:H layer with thickness around 100nm can achieve an optimal passivation property by providing more atomic hydrogen, evidenced by higher concentration of monohydrides and dihydrides in the FTIR spectra.

Temperature dependence on carrier lifetime and XRD

The evolution of crystallinity of a-Si:H films under various thermal treatments and the associated influence on thermal stability of a-Si:H/SiN$_x$:H stacks is of great interest. Wang [15] reported on an investigation into the use of the a-Si:H layer in silicon heterojunction solar cells on p-type crystalline silicon wafers. The dramatic effects of crystallinity on the SHJ solar cell's performance were summarized such that epitaxial growth of crystalline silicon will easily take place over a specific thermal budget, and low temperature deposition (<150°C for (100) and <200°C for (111)) of the a-Si:H layer is recommended for the growth of abrupt and flat interface at the heterojunction. Our measurement results of minority carrier lifetime by micro-PCD on samples with 130°C, 150°C, 170°C and 200°C as various deposition temperatures (see Fig. 2) indicate a progressively better passivation performance with lower deposition temperature, and such results are consistent Wang's findings [15]. From XRD spectra shown in Fig. 3, however, higher diffraction intensity around phase (111) of the epitaxial-grown a-Si:H layer is not observed as expected on samples with higher deposition temperature. This may indicate that a slight difference of a-Si:H crystallinity among various deposition temperatures from 130°C to 200°C cannot be readily revealed by XRD spectra.

Nevertheless, the influence of various crystallinity factors relevant to different deposition temperatures of a-Si:H films on passivation performance may not necessarily be mainly attributable to the epitaxial growth at the interface of heterojunction. More active interchanges of atomic hydrogen within dihydride-rich a-Si:H films deposited at 130°C, compared to that at 200°C, could be another dominant factor for the better passivation effects instead. Generally, dihydrides ratio for 130°C-deposited a-Si:H films estimated from FTIR results is 1.5 to 2 times as much as that for 170°C, and such dihydride-rich a-Si:H films could contain more porous Si-H bonding with which less thermal activation energy of surface

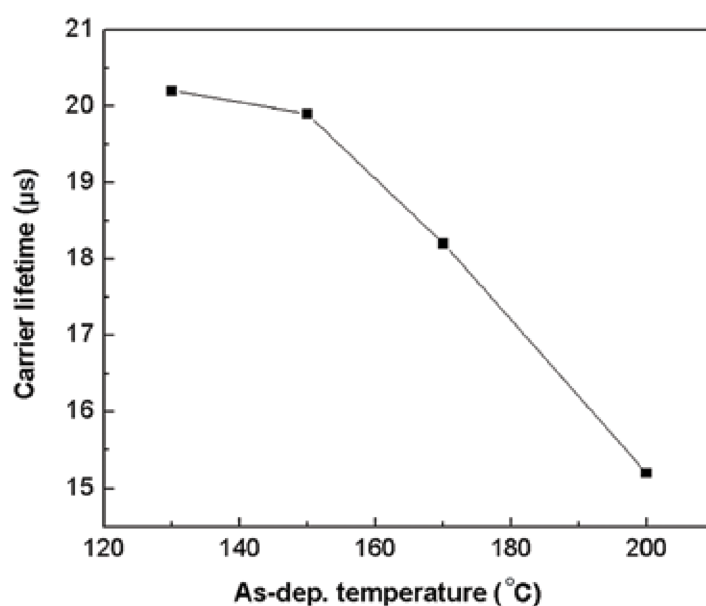

Figure 2. Minority carrier lifetime measured by micro-PCD for amorphous silicon films deposited at 130°C, 150°C, 170°C and 200°C with thickness of 100nm on p-type (100) Cz shiny wafers.

Cell Processing

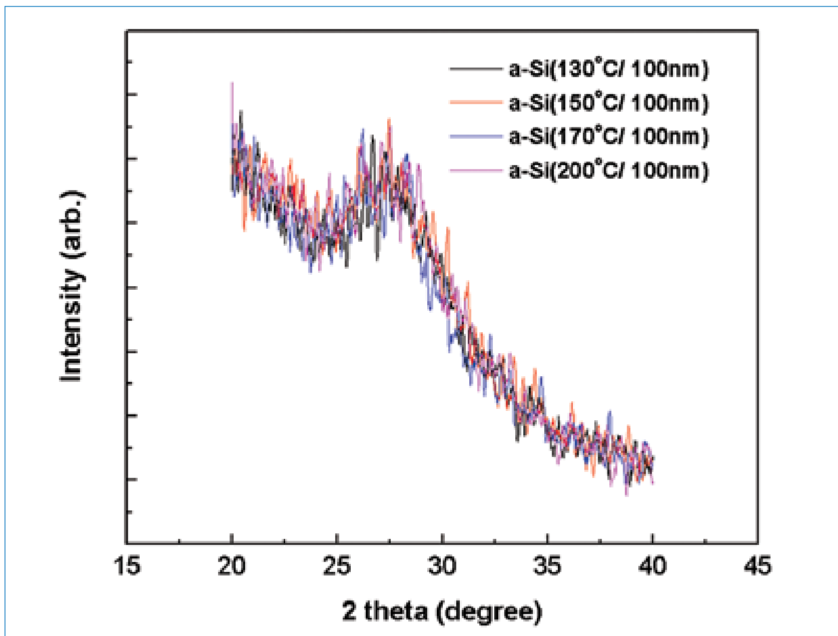

Figure 3. XRD spectra for amorphous silicon films deposited at 130°C, 150°C, 170°C and 200°C with thickness of 100nm on p-type (100) polished wafers.

passivation would be required. Mitchell [1] also reported that, based on FTIR results before and after thermal anneal, dihydrides showed potential for surface passivation since the concentration of dihydrides was reduced after an effective thermal treatment. The results imply that atomic hydrogen under thermal diffusion can interchange between the easily-broken Si-H_2 bonding and those that already exist near the interface of c-Si surface. After an effective surface passivation under thermal treatment, Si-H_2 bonding could be structurally transformed to Si-H and crystalline silicon, leading to the reduction of Si-H_2 concentration. In the case of as-deposited dihydride-rich a-Si:H films prior to thermal treatment, nevertheless, Si-H_2 bonding still plays an important role in the interchange of atomic hydrogen and behaves like intermediates for hydrogen passivation during the process of deposition.

Thermal stability of as-deposited a-Si:H

As published elsewhere [12], post-deposition thermal anneal upon passivation layers with a-Si:H/SiN_x:H structure can further enhance surface passivation performance. If one simply applies a-Si:H/SiN_x:H stacks as backside passivation layers on traditional solar cells, the degradation of cell performance caused by high thermal budget of the fabrication process is a major problem. To study this issue, post-deposition RTA with ambiance of forming gas was employed in this work to check the thermal stability.

Two deposition temperatures of a-Si:H films, 130°C and 200°C, were selected to investigate whether the as-deposited composition of a-Si:H films would account for the thermal stability of a-Si:H/SiN_x:H stacks. Effects of five-minute RTA treatment on three kinds of samples: single layer-passivated a-Si:H (130°C/100nm); dual a-Si:H (130°C/100nm)/SiN_x:H (450°C/80nm) stacks; and dual a-Si:H (200°C/100nm)/SiN_x:H (450°C/80nm) stacks are summarized in Fig. 4. Without the SiN_x:H capping layer on a-Si:H films, the carrier lifetime before and after annealing showed comparable values for 150°C anneal, but severe degradation occurred after annealing at 250°C and 350°C. This suggests that atomic hydrogen originating from a-Si:H layers not only thermally diffused toward the crystalline silicon interface but also simultaneously diffused out of the stacks to the atmosphere. When annealing over the thermal criteria of deposition temperature, out-diffusing hydrogen may dominate the interaction so that large parts of broken dangling bonds would not be passivated.

> "Post-deposition thermal anneal upon passivation layers with a-Si:H/SiN_x:H structure can further enhance surface passivation performance."

In addition to the dependence of anneal temperature, the anneal duration is also a key factor. In our previous study, single layer-passivated a-Si:H deposited at 130°C, 150°C and 170°C with RTA of 250°C for three minutes can all achieve improvement of carrier lifetime by more than a factor of two. Even with annealing over the deposition temperature, effective thermal treatment can be achieved under the proper control of thermal budget. As a result, investigations seeking for the optimal duration of RTA shall be further included as future works.

Thermal stability of a-Si:H/SiN_x:H stacks

With SiN_x:H films served as capping layers on a-Si:H films, surface passivation effects can be enhanced due to more inward diffusion of atomic hydrogen. At anneal temperature of 400°C, which is lower than SiN_x:H deposition temperature of both samples (with underneath layers of 130°C and 200°C-deposited a-Si:H films), comparable carrier lifetime changes were evident, which is most likely due to insufficient thermal activation energy.

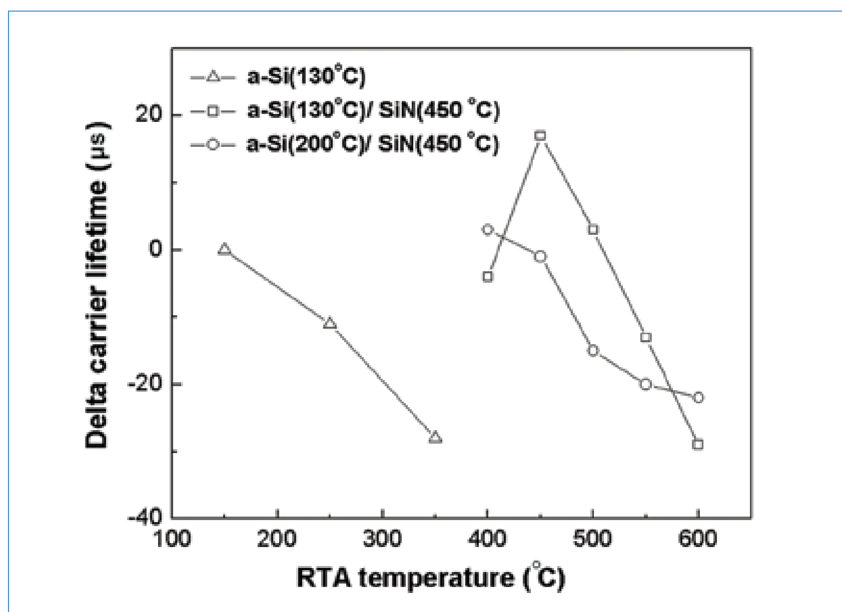

Figure 4. Minority carrier lifetime changes before and after RTA for three kinds of sample: c-Si/a-Si:H (130°C/100nm); c-Si/a-Si:H (130°C/100nm)/SiN_x:H (450°C/80nm); and c-Si/a-Si:H (200°C/100nm)/SiN_x:H (450°C/80nm).

Mitchell's study [1] about the estimation of thermal activation energy for hydrogen passivation indicated that for a single a-Si:H layer, anneal temperature near to or higher than the deposition temperature can accelerate the reaction. In this work, however, the predominant element determining the thermal activation energy of a-Si:H/SiN_x:H stacks is the deposition temperature of the SiN_x:H capping layers. The alternation of the thermal activation threshold from the deposition temperature of a-Si:H to that of SiN_x:H occurs when the process of as-deposited a-Si:H films is subsequently followed by the SiN_x:H capping process.

At anneal temperature of 450°C, 130°C-deposited a-Si:H stacks showed more carrier lifetime improvement than that of 200°C-deposited ones. The effectiveness of carrier lifetime improvement at anneal temperature of 450°C for the 130°C-deposited a-Si:H sample is, as discussed, probably attributed to the abundance of dihydrides. The threshold criteria of thermal activation for a-Si:H/SiN_x:H stacks should be, as mentioned, near the deposition temperature of SiN_x:H so that the anneal temperature of 450°C can activate atomic hydrogen within SiN_x:H films and then successively interchange with those located in a-Si:H films. As a result, for a-Si:H/SiN_x:H stacks, the effective anneal treatment should rely not only on exceeding activation criteria of SiN_x:H deposition temperature, but also on a sufficient concentration of atomic hydrogen originating from a-Si:H films.

"The abrupt drop of carrier lifetime for 130°C-deposited a-Si:H stacks with anneal temperature increasing to 600°C is apparently attributed to the formation of epitaxial crystallization."

Beyond an anneal temperature of 500°C, however, carrier lifetime of 130°C-deposited a-Si:H stacks showed more degradation with increasing anneal temperature. The XRD spectra depicted in Fig. 5 showed no obvious diffraction signals of a-Si:H crystalline phase, except for the sample of 130°C-deposited a-Si:H stacks annealed at 600°C. The XRD spectra indicated that the abrupt drop of carrier lifetime for 130°C-deposited a-Si:H stacks with anneal temperature increasing to 600°C is apparently attributed to the formation of epitaxial crystallization even though such diffraction signals are not observed at anneal temperature of 500°C and 550°C. As for 200°C-deposited a-Si:H stacks, the lifetime change from anneal temperature of 500°C to 600°C showed smoother dependence than those deposited at 130°C, which is consistent with the outcome that each corresponding XRD spectrum showed no obvious crystallization phase. As a result, the causal relationship between the lifetime degradation at an excessive thermal treatment and the formation of epitaxial crystallization can be reasonably speculated. Furthermore, regarding the role of dihydrides as intermediates of hydrogen interchanging therein, even though Si-H_2 bonding could potentially provide a better surface passivation, it is also susceptible to epitaxial crystallization under an excessive thermal budget.

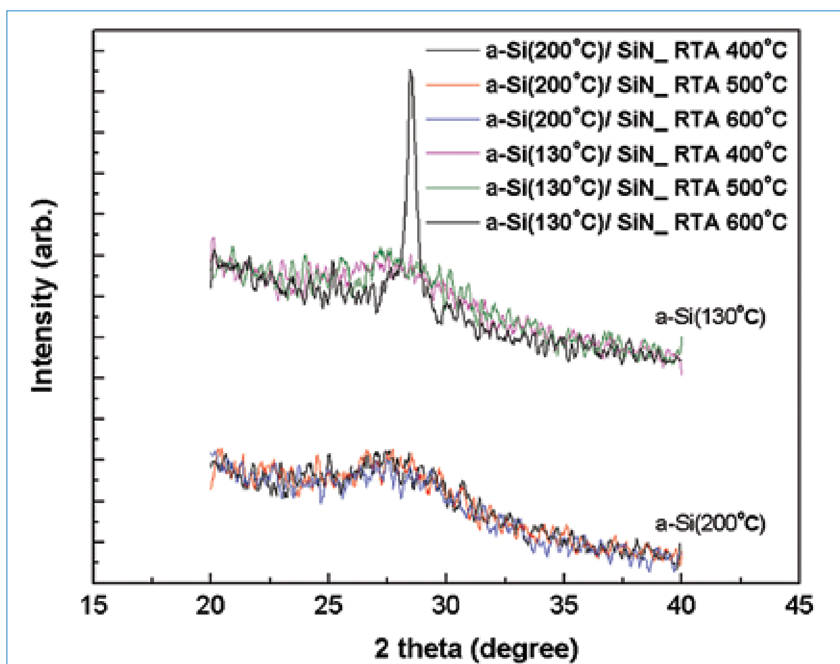

Figure 5. XRD spectra for 130°C and 200°C-deposited a-Si:H dual stacks (a-Si:H/SiN_x:H) with RTA 400°C, 500°C and 600°C.

While the results of carrier lifetime changes under various thermal treatments could be consistently interpreted in terms of the formation of epitaxial crystallization, a couple of points are worthy of further investigation in order to achieve better thermal stability of the passivation stacks. Firstly, the recipe of SiN_x:H film deposition needs to be optimized, to diminish the plasma damage upon a-Si:H film surface and to supply more atomic hydrogen with a lower thermal activation energy. Secondly, thermal profile (temperature vs. duration) of the entire fabrication process needs to be carefully designed, in order to avoid either insufficient or excessive thermal treatment.

Conclusions

For single-layer a-Si:H films, the higher lifetime improvement provided by films deposited at lower temperatures (e.g. 130°C) could be attributed to their dihydride-rich composition, supplying a higher concentration of atomic hydrogen and providing a lower thermal activation energy of hydrogen passivation. Compared with the single a-Si:H layer, the a-Si:H/SiN_x:H stack showed better surface passivation performance, and the carrier lifetime can be further improved by an adequate thermal treatment (450°C/five minutes). The more pronounced improvement for 130°C-deposited a-Si:H/SiN_x:H stacks is again consistent with the possibility that dihydride-rich structures could contribute hydrogen to enhance passivation. Furthermore, the thermal activation threshold changed from the deposition temperature of a-Si:H to that of SiN_x:H when the SiN_x:H capping layer was deposited on top of the a-Si:H films. When excessive thermal annealing (600°C/five minutes) was applied, carrier lifetime showed more severe degradation for 130°C-deposited a-Si:H stacks, and the phase signals of epitaxial crystallization of a-Si:H films revealed by XRD spectra also demonstrated the detrimental effect on surface passivation. As a result, even though Si-H_2 bonding could potentially provide better surface passivation, it is also more susceptible to the epitaxial crystallization under an excessive thermal budget.

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