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Instability of dielectric surface passivation quality at elevated temperature and illumination

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Abstract

Hydrogenated silicon nitride and aluminum oxide passivation layers were deposited on boron doped floatzone silicon wafers that underwent a high temperature firing step. The passivation quality was monitored during thermal treatment at 75°C, 150°C and 250°C in darkness or under illumination. It was found that the passivation quality of the specific layers under investigation is far from stable in the course of time showing both deterioration and improvement features on a time scale of minutes to weeks. Furthermore, it was found that these changes occur in both darkness and under illumination, whereupon (stronger) illumination accelerates the changes. Via corona charging and capacitance voltage experiments it could be shown that the observed changes in the short term are mainly caused by changes in the chemical passivation quality.

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1. Introduction

In recent years, degradation of bulk quality (meaning charge carrier lifetime) has become a severe handicap for the ever increasing conversion efficiencies of wafer-based silicon solar cells, especially with regard to new cell concepts like PERC (passivated emitter and rear cell) relying strongly on a high bulk quality due to superior surface passivation layers. This accounts especially for the well-known boron-oxygen related degradation [1] and the more recently discovered mc-PERC degradation [2,3,4], both being light-induced degradation (LID) mechanisms [5].

However, it is often forgotten or thought of as irrelevant that passivation layers are not by definition immune to changes induced by (even low) temperature, illumination and more general the presence of excess charge carriers, or in other words factors being present every day in the solar cell's real outdoor life. And yet instability of passivation can be a real show stopper especially for the PERC concept and can strongly interfere with any investigation

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targeting on high bulk lifetime or separation of bulk and surface properties. This is especially true for long-term experiments examining topics such as the stability of samples whose boron-oxygen defects have been deactivated via regeneration [6] or degradation experiments on multicrystalline material where changes in the bulk might easily be obscured by changes in the passivation layer.

There are indicators that the passivation quality of different dielectric layers changes over time. For example, already during storage in darkness the surface recombination velocity (SRV) increases significantly for samples with a thermally grown silicon oxide (SiO_x) layer on boron doped silicon and on boron emitters, but interestingly not on phosphorous emitters [7]. Concerning annealed aluminum oxide ($\text{AlO}_x\text{:H}$) layers, it was observed that already at low temperatures and illumination, changes occur [8]. It is also known that samples passivated with hydrogenated silicon nitride ($\text{SiN}_x\text{:H}$) and treated at 400°C show a strong degradation in effective lifetime, while a thin thermally grown SiO_x layer below the $\text{SiN}_x\text{:H}$ increases the stability significantly [9]. For short illumination times, a light induced curing effect can be observed in samples with thin chemically grown SiO_x layers [10]. There is also some evidence that thin native SiO_x layers grown at room temperature before $\text{SiN}_x\text{:H}$ deposition lead to an increased stability under long term illumination in n-type FZ samples [11]. One of the few stability investigations on fired $\text{AlO}_x\text{:H}$ or $\text{SiN}_x\text{:H}/\text{AlO}_x\text{:H}$ samples found that the samples react to an annealing as well as to illumination treatments [12].

But little is known about the long term behavior of the surface passivation quality of samples that underwent a high temperature firing step and were treated at elevated temperatures and illumination simultaneously, as commonly found in LID experiments. To the knowledge of the authors, this is the first detailed investigation done under these conditions. To examine their long term behavior, different dielectric layers were deposited on floatzone (FZ) silicon substrates, known to exhibit a high bulk lifetime, and subsequently exposed to elevated temperature and illumination conditions.

2. Experimental approach

To find out which parameters have a strong influence on the temporal evolution of a sample, many parameters of sample preparation were varied, leading to a rather big range of processing conditions. As can be seen later, only a small part of these processing parameters has a significant influence on the temporal evolution of the samples. To allow for easier reading, only the important details are given in the text, while the complete processing details are described in the captions of the figures.

All samples were fabricated using $1\ \Omega\text{cm}$ p-type FZ-Si base material of thickness $250\ \mu\text{m}$. They received either a Piranha clean, an RCA clean or no clean at all. Samples that received a cleaning underwent a dip in hydrofluoric acid (HF dip) before passivation layer deposition. On some samples, a thin SiO_x layer ($\sim 1\ \text{nm}$) was chemically grown before $\text{SiN}_x\text{:H}$ deposition. Two types of hydrogenated $\text{SiN}_x\text{:H}$ were used with deposition parameters as applied for solar cell processing (thickness $d\approx 75\ \text{nm}$, refractive index $n\approx 2.0$ at $633\ \text{nm}$), one deposited in a plasma-enhanced chemical vapor deposition (PECVD) with indirect plasma (type 1), the other in a PECVD with direct plasma source (type 2). The type 1 deposition was always used for samples with a passivation stack consisting of a thin layer of $\text{AlO}_x\text{:H}$ ($\sim 5\ \text{nm}$) covered with $\text{SiN}_x\text{:H}$. The $\text{AlO}_x\text{:H}$ layer was deposited using atomic layer deposition (ALD).

The samples were divided into subgroups of different firing conditions with measured peak sample temperatures reaching either 750°C , 800°C or 830°C , respectively. Immediately after firing, samples were stored in the dark until measurement series were performed.

The samples were then treated at temperatures of either 75°C , 150°C or 250°C . Some samples were kept in the dark while others were constantly being illuminated using a tungsten halogen incandescent lamp. To investigate the changes in passivation quality, different methods were used. The first was a measurement of the photoconductance decay (PCD) at room temperature (RT-PCD) using a Sinton lifetime tester (WCT 120). Temperature and illumination treatment was shortly paused for these samples. Secondly, photoconductance decay measurements at elevated temperature were performed (ET-PCD). In this case, the PCD measurement was carried out at the same temperature at which the sample was treated, allowing for an automated measurement with only a short break in illumination during the measurement. Although the absolute values of measured effective lifetimes differ at elevated temperatures, the curve shapes of ET-PCD and RT-PCD measurements show the same qualitative behavior. All PCD measurements were evaluated at an injection level of $\Delta n = 1\cdot 10^{15}\ \text{cm}^{-3}$.

On some samples, corona charging and capacitance-voltage (CV) experiments were carried out. The corona charging experiments were done with a setup comparable to the one described in [13]. For CV measurements, a mercury probe was used. This allowed for measurements of lifetime samples during degradation treatments without the need of permanently adding a metal electrode.

3. Results and discussion

3.1. Treatment at 75°C

Fig. 1a shows ET-PCD measurements of two $\text{SiN}_x\text{:H}$ samples treated at 75°C under illumination. As can clearly be seen, both samples show a significant change of effective lifetime values both in time frames of minutes as well as in time frames of weeks. These two samples differ in many processing details, such as pre-clean conditions and silicon nitride deposition technique. Additionally, they were fired at different peak temperatures (750°C and 800°C). Nevertheless, both curves match qualitatively in the beginning and even quantitatively in the final exponential decline of effective lifetime values.

To closer investigate the influence of the firing step on the observed behavior, two $\text{SiO}_x/\text{SiN}_x\text{:H}$ samples were processed identically and fired at different temperatures. The resulting RT-PCD measurements shown in Fig. 1b (red, orange) show again a similar splitting of the two curves in the short term and converging curves in the long term behavior.

It is interesting to note that the final decline of the samples is approximately as steep as in Fig. 1a. This is contrary to the expectation that a thin chemically grown SiO_x layer below the $\text{SiN}_x\text{:H}$ of the samples in Fig. 1b would be slowing down the long term degradation as was observed in [9, 11]. An intermediate layer of aluminum oxide in an $\text{AlO}_x\text{:H}/\text{SiN}_x\text{:H}$ stack, however, does exert a strong effect on the sample evolution (blue data). As can be seen, this sample shows a different behavior under the given degradation conditions and no final exponential decline is visible in the observed time frame.

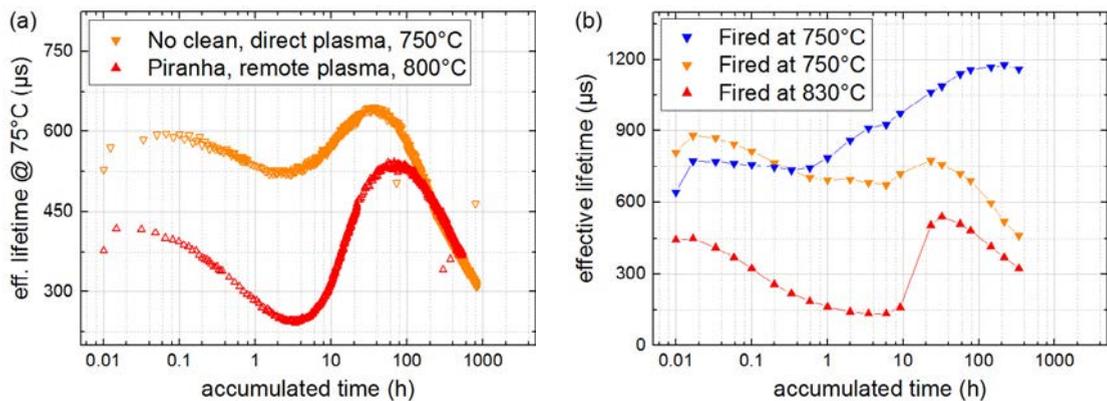


Fig. 1. (a) ET-PCD measurements of the effective lifetime of two $\text{SiN}_x\text{:H}$ samples during heat treatment at 75°C under illumination of ~ 0.65 suns. One sample received no cleaning step and no HF dip before deposition of $\text{SiN}_x\text{:H}$ (type 2) and was fired at 750°C (orange). The other sample received a Piranha clean before deposition of $\text{SiN}_x\text{:H}$ (type 1) and was fired at 800°C (red); (b) RT-PCD measurements of two $\text{SiN}_x\text{:H}$ (red, orange) and one $\text{AlO}_x\text{:H}/\text{SiN}_x\text{:H}$ sample (blue). The $\text{SiN}_x\text{:H}$ samples differ only in the applied firing profile. Both received an RCA clean and a thin oxide layer (~ 1 nm) was chemically grown before $\text{SiN}_x\text{:H}$ deposition (type 2), whereas the $\text{AlO}_x\text{:H}/\text{SiN}_x\text{:H}$ sample received a Piranha clean before layer deposition. Downward triangle symbols imply 750°C peak firing temperature whereas upward symbols denote 830°C. Lines only serve as a guide to the eye.

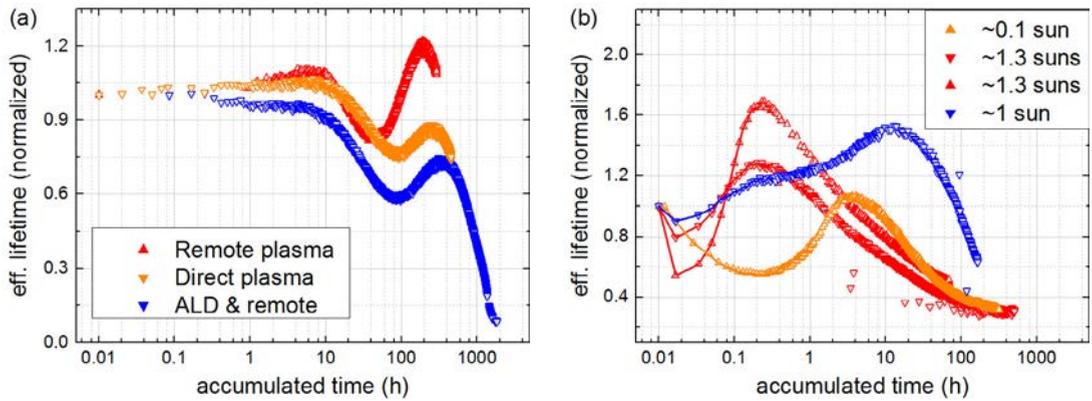


Fig. 2. (a) ET-PCD measurements of the effective lifetime of two SiN_x:H (red, orange) and one AlO_x:H/SiN_x:H sample (blue) during heat treatment at 150°C in darkness. All samples received a Piranha clean. The two SiN_x:H samples differ in deposition technique and firing conditions. Upward symbols indicate 800°C peak firing temperature, downward symbols 750°C; (b) ET-PCD measurements of three SiN_x:H (red, orange) and one AlO_x:H/SiN_x:H sample (blue) at 150°C under different illumination settings. All samples received a Piranha clean. The SiN_x:H samples were identically processed (type 2) but fired differently. Downward symbols indicate a peak firing temperature of 750°C, upward symbols stand for 800°C. Lines only serve as a guide to the eye.

3.2. Treatment at 150°C

According to Fig. 2a, also a treatment in darkness at 150°C leads to changes in passivation quality. But compared to the measurements under illumination, the temporal evolution of the samples progresses slower: While the minima are reached in a couple of hours for samples treated at 75°C under illumination, the minima are only reached after around 100 hours for samples treated at 150°C in the dark. Still, the shape of the curves is similar to the ones seen in Fig. 1. Interestingly, in darkness there is no big difference in the time scales of degradation when comparing SiN_x:H samples (red, orange) with AlO_x:H/SiN_x:H samples (blue). But it can still be seen that a sample fired at higher temperature exhibits more pronounced changes in the short term (red). This sample also shows a rather low effective lifetime after firing and this might be the reason why the sample is able to recover to better effective lifetime values after around 200 h. In the long term, all samples show a strong degradation as already seen in the measurements at 75°C.

When combining a temperature of 150°C with illumination, the temporal evolution of the samples speeds up significantly as can be seen in Fig. 2b. Comparing measurements of SiN_x:H samples at weak illumination (orange) and at stronger illumination (red), a big influence of illumination intensity on the velocity of the temporal evolution is apparent. For the samples under strong illumination, saturation is reached after less than 1000 h. In accordance with the measurements at 75°C, an aluminum oxide layer between silicon and silicon nitride again slows down the temporal evolution significantly (blue). But in contrast to Fig. 1b, in Fig. 2b it can be seen that also an AlO_x:H interlayer does not prevent the final decline of effective lifetime, but only delays it.

3.3. Treatment at 250°C

Up to this point, increasing temperature and illumination accelerated the process under investigation, so it is an interesting question if a further increase in temperature has a similar effect. In Fig. 3a, RT-PCD measurements of two SiN_x:H samples are shown. Both samples were processed in the same way and were treated at 250°C. One sample was illuminated with approximately 1 sun intensity (red) while the other one was treated in darkness (black). Besides the effective lifetime values of the illuminated sample being constantly higher than those of the sample kept in darkness, the characteristic shape of the curves is similar for both conditions (with the exception of the first 0.2 h where the lack of data points does not allow a comparison of the curves). The sample under illumination shows only a moderate acceleration in reaching the first minimum, afterwards the time scales of both curves are very similar. This is in strong contrast to the measurements shown before, where illumination drastically speeded up the temporal evolution of a sample. As a consequence, the illuminated sample at 250°C needs more time to reach the minimum in

effective lifetime compared to an illuminated sample at 150°C. Additionally, at 250°C the final decline is generally much less steep and even after around 2000 h of degradation, no saturation is visible. The only acceleration in temporal evolution can be seen in darkness: at 250°C the first minimum is reached significantly earlier compared to measurements at 150°C.

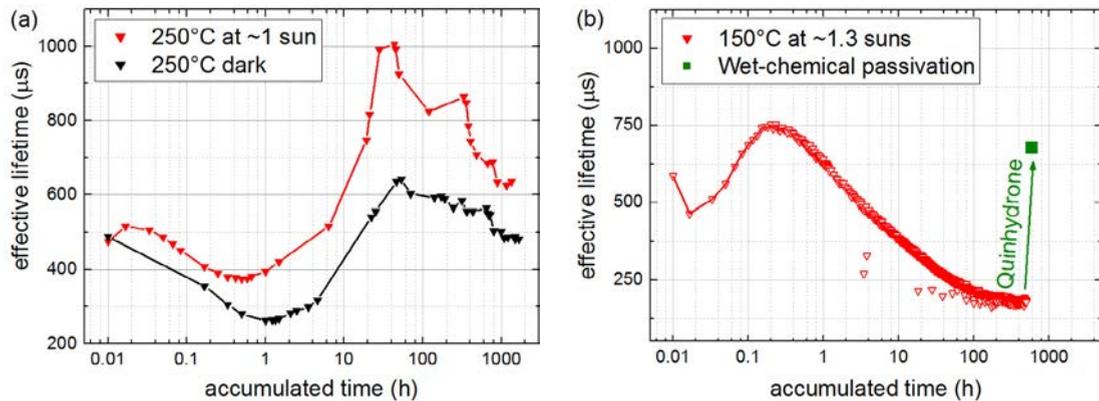


Fig. 3. (a) RT-PCD measurements of the effective lifetime of two samples during heat treatment at 250°C. One sample was kept in the dark (black), one was illuminated at ~1 sun (red). Both samples were identically processed, using a Piranha clean, a type 2 deposition and 750°C peak firing temperature. Lines only serve as a guide to the eye; (b) ET-PCD measurement of the effective lifetime of a $\text{SiN}_x\text{:H}$ sample during heat treatment at 150°C under illumination of ~1.3 suns (red). The sample was processed using a Piranha clean and a type 2 deposition. After the red curve was measured, the silicon nitride was removed by an HF dip followed by a new Piranha clean. Then, a wet-chemical quinhydrone passivation was deposited and effective lifetime was measured (green). Lines only serve as a guide to the eye.

3.4. Wet-chemical passivation after degradation treatment

To clarify whether the observed degradation is happening at the surface, one of the samples shown earlier in Fig. 2b had its $\text{SiN}_x\text{:H}$ layer removed by an HF dip after reaching saturation. Afterwards, the sample received a Piranha clean and was wet-chemically passivated using quinhydrone. As can be seen in Fig. 3b, the effective lifetime with the wet-chemical passivation is much higher than the one at the end of the degradation treatment. Additionally, an $\text{AlO}_x\text{:H/SiN}_x\text{:H}$ sample degraded at 150°C in darkness also had its passivation layers replaced with the same procedure and showed also a substantial increase in effective lifetime (data not shown). Therefore it can be concluded that the bulk of the samples remained rather unaffected and the observed effect is happening very close to the sample surface.

3.5. Corona charging and capacitance-voltage experiments

To get some first insight on what is happening at the surface of the samples, corona charges were deposited using a corona discharge. By constantly depositing small amounts of charge at both surfaces, a minimum of the measured effective lifetime can be reached in which the deposited negative corona charges compensate the fixed positive charges present in the $\text{SiN}_x\text{:H}$. In that way the field effect passivation of the sample is neutralized and the remaining effective lifetime value is a measure of chemical passivation quality. After the measurement, the charges can easily be removed using de-ionized water.

The $\text{SiN}_x\text{:H}$ sample in Fig. 4a received a thermal treatment in the dark at 250°C, but additionally the corona charging analysis was carried out at five distinctive points of the curve. The resulting effective lifetime values, which are characteristic for the chemical passivation of the sample, are shown in red. Both measured lifetime curves, determined in the corona charged (red) and uncharged (black) state, show a similar behavior during the first part of the treatment. This indicates that the chemical passivation decreases and recovers during this part of the treatment. Thereafter, the chemical passivation still increases in quality, while the overall uncharged effective lifetime of the sample (black) drops again, suggesting a loss of charge in the $\text{SiN}_x\text{:H}$.

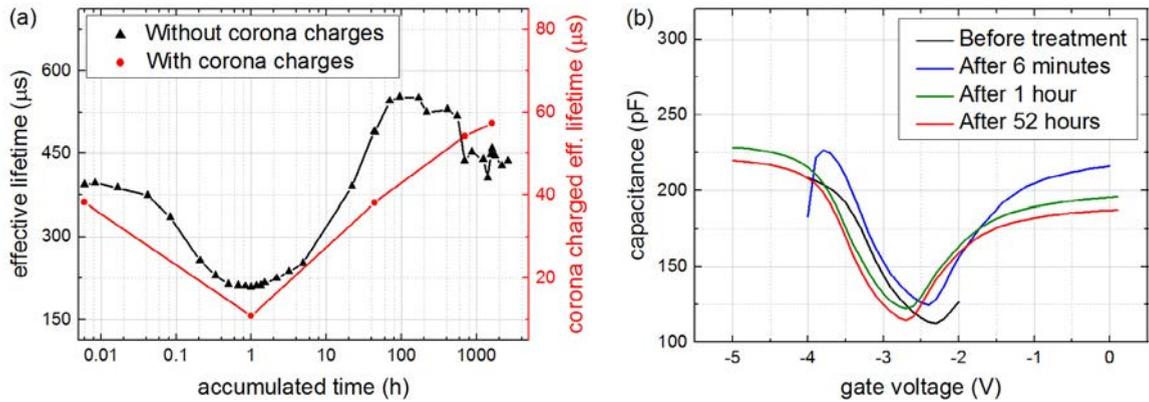


Fig. 4. (a) RT-PCD measurement of the effective lifetime of a $\text{SiN}_x\text{:H}$ sample during heat treatment at 250°C in darkness (black). The sample was processed using a Piranha clean, a type 2 deposition and a peak firing temperature of 800°C . At five points during heat treatment, corona charging experiments were conducted to compensate the field effect passivation. After corona charging, effective lifetime was measured again (red); (b) CV measurements taken during a heat treatment of a $\text{SiN}_x\text{:H}$ sample treated at 250°C in darkness. The CV measurements were each taken at a new position on the sample surface. The investigated sample received an RCA clean and a thin oxide layer was chemically grown before $\text{SiN}_x\text{:H}$ deposition (type 2). The sample was fired at a peak temperature of 830°C .

To investigate a possible change in fixed charge density during degradation treatments, CV measurements were carried out in order to directly quantify the fixed charges of the investigated layers. Similar to the corona charging experiments, the CV measurements were performed at four selected points of the degradation curve of another $\text{SiN}_x\text{:H}$ sample. Like before, the sample was degraded at 250°C in darkness. The resulting CV curves are shown in Fig. 4b. As can be seen, there are only minor shifts on the voltage axis which correspond to only small changes in the fixed charge density of the $\text{SiN}_x\text{:H}$ layer. This is in good agreement with the observation that the duration of corona charging needed to reach the minimal effective lifetime did not change much during the degradation treatment.

It should be emphasized that every new CV measurement was performed at another point of the sample surface because every measurement damages the sample surface to some extent. It is therefore likely that the measured curves differ over a small range because the sample surface is not perfectly homogeneous. Also, the voltage range was not the same in each measurement, which might also influence the resulting curves [14]. To take these effects into account, an identically processed sample was not degraded but measured at the same time intervals as the degraded sample (data not shown). Also the non-degraded sample showed small shifts of similar magnitude as the ones observed in the degraded sample. It can therefore be assumed that in the short term behavior the field effect passivation of the sample is not changing significantly.

The effect of charge in the long term has not yet been investigated. Since the final decline in effective lifetime is not strongly pronounced at 250°C , it is necessary to perform measurements on the long term behavior at lower temperatures. Performing corona charging and CV experiments at lower temperatures is also important to decide, whether the mechanism at lower temperatures and under illumination is indeed comparable to the one observed at 250°C in darkness.

4. Conclusions

In summary, it can be stated that the dielectric passivation layers under investigation show strong changes in passivation quality under the influence of elevated temperature and illumination. It is remarkable that, independent of different pre-cleaning procedures and deposition techniques, a very similar degradation behavior is observed. While the firing conditions have a strong influence on the short term behavior of a sample, they have no significant effect in the long term. Regarding the long term behavior, the chosen layer combination exerts the strongest effect. As could be seen, intermediate $\text{AlO}_x\text{:H}$ layers between silicon bulk and $\text{SiN}_x\text{:H}$ improve the long term stability of lifetime samples, whereas thin chemically grown SiO_x layers did not change the long term behavior significantly.

Concerning the degradation conditions, it can be concluded that stronger illumination generally speeds up the temporal evolution of the investigated samples, especially at low temperatures. Increasing the temperature tends to accelerate the short term behavior of the samples, especially in darkness. But with respect to the long term behavior, the fastest degradation is seen at 150°C. Raising the temperature to 250°C significantly slows down the final decline in measured effective lifetime values.

To gain a better understanding of the degradation mechanisms at play, corona charging and CV experiments were conducted. The measurements indicate a strong change of chemical passivation quality during a degradation treatment in the short term, while the field effect passivation remains rather unaffected. This also explains why dielectric layers with both negative and positive fixed charges exhibit a similar degradation behavior.

The magnitude of the changes in effective lifetime is so significant that it is definitively advised to check for this effect when performing experiments aimed at effects happening in the silicon bulk.

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