INVESTIGATIONS OF HIGH REFRACTIVE SILICON NITRIDE LAYERS FOR ETCHED BACK EMITTERS: ENHANCED SURFACE PASSIVATION FOR SELECTIVE EMITTER CONCEPT (SECT)

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ABSTRACT: The application of selective emitter solar cells via emitter etching has already shown its potential as an industrial type solar cell concept. Thereby the surface passivation of etched back emitters plays an important role. In this work the possibilities for enhanced surface passivation are investigated by using single and double layered high refractive PECVD SiN_x layers. QSSPC, ellipsometry and FTIR measurements were performed on FZ wafers to determine the critical thickness of the high refractive SiN_x for an improved hydrogen passivation. The studies were also focused on the firing stability of the passivation quality. Finally, optimized single as well as high refractive double SiN_x layers were applied on selective emitter solar cells. The Selective Emitter ConcepT (SECT) solar cells show an increase of the open circuit voltage, which is related to the improved surface passivation. The highest V_{oc} value of 642 mV was obtained with a high refractive double layered SiN_x on large area screen printed Cz solar cells. Compared to reference solar cells an average gain of $0.6\%_{abs.}$ was achieved on SECT solar cells. The cell efficiency of 19.0% for screen printed SECT-solar cells with full area Al-BSF shows that a further improved surface passivation is possible and can increases cell performance of selective emitter solar cells.
Keywords: Selective emitter, passivation, high refractive silicon nitride, PECVD

1 INTRODUCTION

For an industrial-type screen printed crystalline silicon solar cell with n-doped emitter, the emitter saturation current density is one of the efficiency limiting features. In order to reduce the recombination rate in the emitter, a hydrogen-rich PECVD (plasma enhanced chemical vapour deposition) silicon nitride (SiN_x) is most commonly applied for surface passivation [3]. Apart from this, it serves as a reservoir of hydrogen and is used as an anti-reflection coating for industrial solar cells.

In the frame of this work the quality of the surface passivation of high refractive PECVD SiN_x layers on etched back emitters will be studied. The etched back emitter is applied for screen printed solar cells via a Selective Emitter ConcepT (SECT) [1]. The SECT solar cell has a highly doped emitter under the metallization and a lightly doped emitter between the front side metallisation. This kind of cell structure is realized by a masking and etching step [1]. Thereby the high phosphorus concentration at the emitter surface is reduced by a wet chemical process.

Such an etched back emitter structure allows for improved surface passivation by means of the reduction of Auger and SRH (Shockley Read Hall) recombination.

In earlier investigations we were already able to show that a variation of the PECVD SiN_x deposition parameters has a strong effect on surface passivation, particularly with etched back emitters [1]. With n-doped emitters that were etched back from 40 Ω/□ to 80 Ω/□ we measured a significant increase in the effective lifetime of symmetrically passivated samples, indicating a better surface passivation quality.

One of the aims of this study is to determine the optimal thickness of the high refractive index SiN_x layer with which we can achieve improved surface passivation and low absorption in the short wavelength range of an etched back emitter.

The studies of the highly refractive single SiN_x layers for etched back emitters are supported by QSSPC and ellipsometry measurements before and after firing. Similar investigations were also carried out on double layered SiN_x layers including a high refractive nitride layer.

Finally, the studied layers were transferred to the SECT- and reference solar cell process. Thereby the potential of hydrogen rich SiN_x for surface passivation and anti-reflection coating has been shown.

2 SINGLE LAYER SiN_x ON ETCH BACK EMITTERS

The variation of the parameters of the PECVD SiN_x deposition has been limited to the gas flow rate of silane SiH_4 to ammonia NH_3 and the deposition time. The samples used for this investigation were p-type float zone wafers with $R_{base} = 0.5\ \Omega cm$. After cleaning, a heavily doped $POCl_3$-diffusion ($R_{sheet} = 30\ \Omega/\Box$) was carried out. Then the emitter was etched back to $R_{sheet} = 80\ \Omega/\Box$ in a wet chemical step. After that, the samples were symmetrically passivated by different PECVD SiN_x layers. Finally, the emitter saturation current density j_{0E}, thickness d, refractive index n, extinction coefficient k and several hydrogen- and Si-N bond densities were measured by QSSPC measurements in high injection condition, ellipsometry and FTIR before and after firing in a belt furnace.

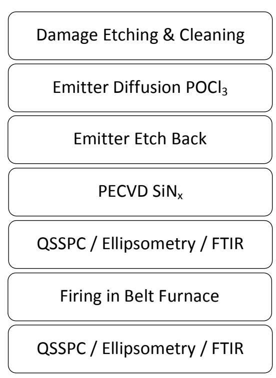

Figure 1: Processing sequence of symmetrically passivated samples on etched back emitters.

Figure 2 shows a comparison between the j_{0E} values of etched back emitters using high refractive SiN_x layers before and after firing compared with a PECVD SiN_x layer with a refractive index of 2.0 ($\lambda = 633$ nm) and a thickness of about 75 nm. By varying the SiH_4/NH_3 ratio, the refractive index of the SiN_x layer can be controlled. The thickness was changed via the deposition time.

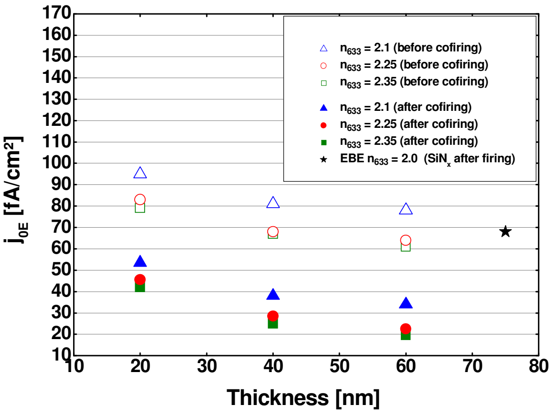

Figure 2: QSSPC measurements of etched back emitters in high injection on different high refractive PECVD SiN_x layers with different thicknesses before and after firing. The j_{0E} values of all samples decreased after firing. Furthermore, a reduction of the j_{0E} value with increasing thickness and increasing refractive index was obtained.

The j_{0E} values of all passivated samples with a high refractive SiN_x layer could be further decreased after firing. Thus the temperature stability of the highly refractive SiN_x after firing is shown as well in Fig. 2.

We could show that a thickness of of 20 nm and a refractive index of $n_{633} > 2.2$ are sufficient to achieve values of emitter saturation current densities of less than 50 fA/cm². Furthermore, a reduction of the j_{0E} value can be observed with increasing layer thickness. Thereby we conclude that further changes of the SiH_4/NH_3 to even higher refractive indices do not cause any significant further decrease in the j_{0E} values. QSSPC measurements of a SiN_x layer with a refractive index of $n_{633} = 2.35$ and a layer thickness of 60 nm show the lowest j_{0E} value of 19 fA/cm² on an etched back emitter with a sheet resistance of 80 Ω/□.

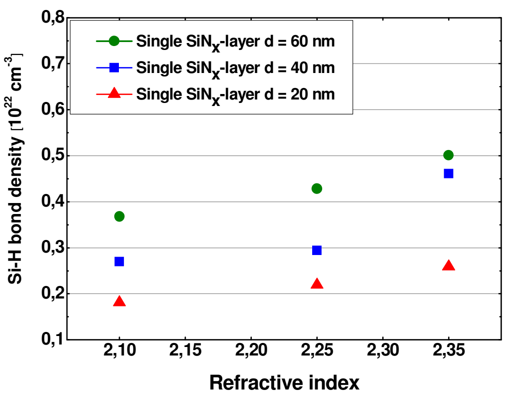

Figure 3: FTIR measurements (Si-H bond density) of symmetrically passivated samples with etched back emitters and different PECVD SiN_x depositions. The Si-H bond densities increase with increasing thickness and increasing refractive index of the single SiN_x layer.

In order to obtain a correlation between the j_{0E} values and the hydrogen bond density of the studied PECVD SiN_x films, Fourier Transform Infrared (FTIR) spectroscopy in the range of 4000 to 800 cm^{-1} has been carried out. For the baseline absorption a reference sample without SiN_x layer was used. For the quantitative determination of the bond density, the detected absorption was integrated over the wavenumber and calculated considering thickness, optical property and cross section of the specific bond type in silicon.

The FTIR absorption spectrum shows well-defined monohydrated hydrogen peaks at 3300 cm^{-1} (N-H) and at 2200 cm^{-1} (Si-H). The quantitative evaluation of the N-H bond densities turned out to be difficult due to the thin layers.

Fig. 3 shows an increase in the Si-H bond density due to an increase in the refractive index which corresponds to the increase of the SiH_4 ratio during PECVD SiN_x deposition and the thickness of the SiN_x films. A similar result was also observed for the Si-N bond densities.

3 DOUBLE LAYER SiN_x ON ETCH BACK EMITTERS

In the next experiment the electrical as well as optical characteristics and the density of the hydrogen and nitride bonds of double layered SiN_x films were studied on etched back emitters.

For this the thicknesses were adjusted so that they could be applied as anti-reflection coatings for solar cells. The double layer SiN_x consists of a high refractive SiN_x ($n_{633} = 2.25$) layer with the variable thickness d_1 and a second SiN_x layer ($n_{633} = 1.95$) on top of it.

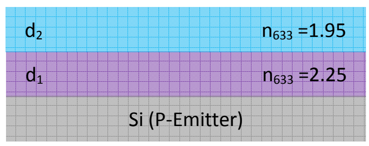

Figure 4: Sample structure of double layered SiN_x.

The samples used for this investigation were p-type float zone wafers with $R_{base} = 1.5$ Ωcm. After an alkaline damage etch, a $POCl_3$ diffusion ($R_{sheet} = 30$ Ω/□) was carried out, then the emitter was etched back from 30 Ω/□ to 65 Ω/□ in a wet chemical step [2]. After that step, the samples were symmetrically passivated by different PECVD SiN_x layers. Thereby double layered SiN_x structures were realized by changing the SiH_4/NH_3 ratio during the deposition. Finally, the emitter saturation current density j_{0E}, the thickness d, the refractive index n, the extinction coefficient k and several hydrogen and nitride bond densities were measured by QSSPC measurements in high injection condition, ellipsometry and FTIR before and after firing.

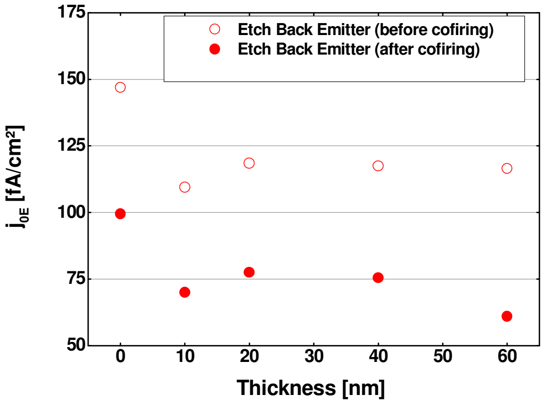

Figure 5: J_{0E} measurements of etched back emitters as a function of the thickness of the high refractive SiN_x layer (d_1, $n_{633} = 2.25$). The j_{0E} values of all samples decrease after firing. A thickness of 10 nm high refractive SiN_x reduces significantly the j_{0E} value ($\Delta j_{0E} = 30$ fA/cm²).

In Fig. 5 the j_{0E} values of etched back emitters are shown as a function of the thickness of the high refractive SiN_x layer (d_1, $n_{633} = 2.25$) before and after firing. The j_{0E} value decreases on all samples after firing, whereby the firing stability of the passivation layer is ensured at temperatures above 800°C. Concerning the double layer stack, the thickness of the high refractive SiN_x ($n_{633} = 2.25$) has no significant influence on the j_{0E} values of etched back emitters in the range of 10 nm to 40 nm. It can be seen that with double SiN_x stacks very low j_{0E} values can be achieved already with a thickness of the high refractive layer of only 10 nm.

A comparison of Fig. 5 with Fig. 2 shows that single layered SiN_x still results in lower j_{0E} values. On one hand, this is due to the alkaline damage etching of the float zone samples in the second group, but above all due to the different emitter etching (R_{sheet} single SiN_x layer, Fig. 2 = 80 Ω/□, R_{sheet} double SiN_x layer, Fig. 5 = 65 Ω/□).

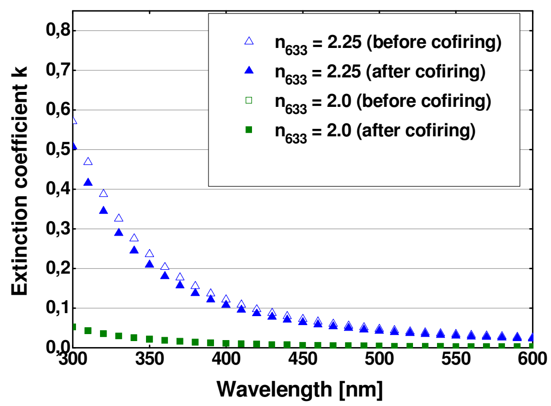

Figure 6: The extinction coefficient k in the wavelength range 300-600 nm as a function of the refractive index of SiN_x before and after firing. The extinction coefficient k increases with higher refractive index.

The dependence of the extinction coefficient k on the refractive index of the SiN_x layer before and after firing is illustrated in Fig. 6. Thereby it can be deduced that the extinction coefficient varies depending on the SiN_x deposition conditions. The extinction coefficient of both groups shows no significant change after firing.
The determination of the optical constants (n, k) was carried out by modeling and fitting of the measured data with the Cauchy model.

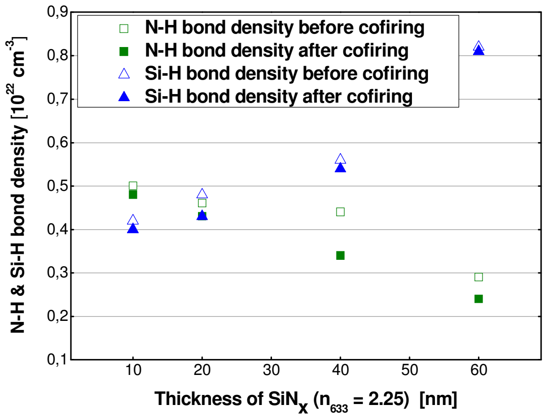

Figure 7: N-H and Si-H bond densities as a function of the thickness of the high refractive SiN_x layer before and after firing. N-H and Si-H bond densities decrease after firing. The increase of Si-H bond densities with increasing thicknesses is due to the Si concentration in the high refractive SiN_x layer. N-H bond densities show an inverse behavior.

FTIR measurements show that an increase in the thickness of the first high refractive SiN_x layer increases the Si-H bond densities. This is attributed to the increased SiH_4 content in the SiN_x layer. An inverse behavior was observed with the N-H bond densities.

With regard to the high refractive SiN_x double layer, it was found that the density of N-H and Si-H bonds decreases after firing, probably because of breaking of bonds at high temperature.

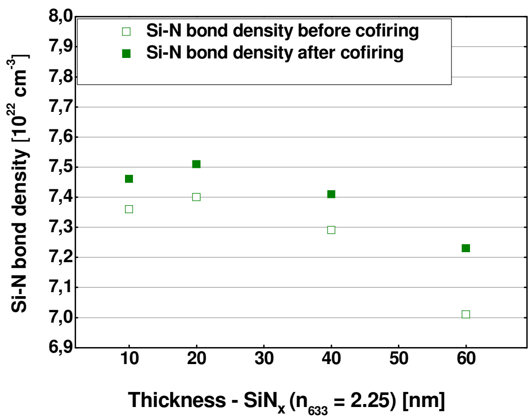

Figure 8: Si-N bond densities as a function of the thickness of the high refractive SiN_x layer before and after firing. Si-N bond densities of all samples increase after firing.

Fig. 8 displays the increase of Si-N bond densities of all samples after firing. The influence of the layer thickness is correlated with the N-H densities in Fig. 7 for a thickness above 20 nm.

4 SOLAR CELL PROCESS

Based on the above mentioned studies of high refractive SiN_x double layers, a solar cell process was carried out on 125x125 mm² Cz wafers with a bulk resistivity of about 2.8 Ωcm. After texturization and cleaning, the batch was divided into two main groups. On the first group a $POCl_3$ emitter ($R_{sheet} = 45\ \Omega/\square$) was carried out. The second group included masking via screen printing, emitter etch back via porous Si formation and the wet chemical removal of the mask and the porous silicon (SECT) as described in [1]. The emitter of the SECT solar cells were etched back from 30 to 65 Ω/□. Then both groups received several double layered PECVD SiN_x depositions. The influence on the IV parameters of the SECT and reference solar cells was studied by the variation of the first high refractive SiN_x layer ($n_{633} = 2.25$). Finally, all solar cells were contacted by screen printing, cofired and edge isolated at last. The rear side contained a full area Al-BSF.

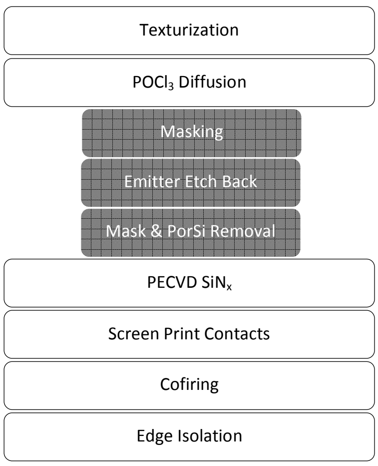

Figure 9: Processing sequence of selective emitter SECT and reference solar cells. The grey boxes illustrate the additional steps for the SECT solar cells.

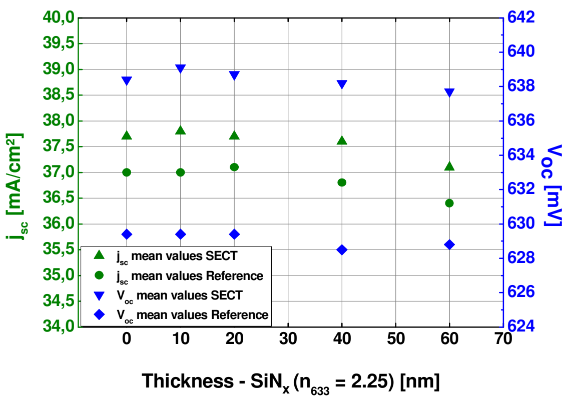

Figure 10: The mean IV parameters j_{sc} and V_{oc} of SECT and reference solar cells (averaged over 10 solar cells) as a function of the thickness of the high refractive SiN_x layers (d_1, $n_{633} = 2.25$).

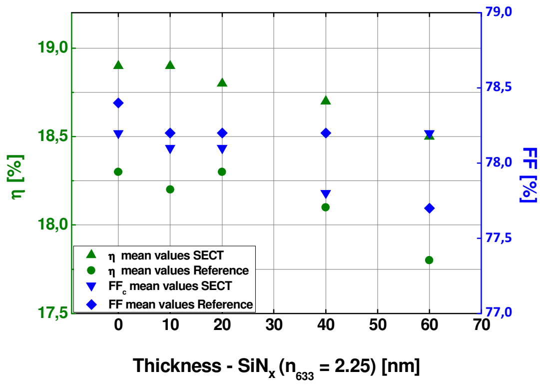

Figure 11: The mean IV parameters η and FF of the SECT and reference solar cells (averaged over 10 solar cells) as a function of the thicknesses of the high refractive SiN_x layers (d_1, $n_{633} = 2.25$).

The application of a high refractive double SiN_x layer has, as expected, no significant influence on the V_{oc} value for the reference solar cells. The mean V_{oc} value of the SECT cells with a 10 nm high refractive SiN_x layer is slightly improved compared to the SECT cells with a single layer SiN_x, whereby the highest V_{oc} value of 642 mV was obtained with a layer thickness of 10 nm of the high refractive SiN_x ($n_{633} = 2.25$).

The loss in j_{sc} at a thickness of the first high refractive SiN_x layer of more than 40 nm is attributed to the strong increase of the absorption in the UV wavelength range.

One of the remaining open questions concerns the interaction of the silver paste with the optimized highly refractive SiN_x layer during the cofiring step. Fig. 11 shows no significant loss in fill factor, even if Si-rich high refractive SiN_x layers were applied on the solar cells.

In average the optimized SECT selective emitter solar cells have achieved a gain in efficiency of $0.6\%_{abs.}$, which is a noteworthy result. The highest level of efficiency for the best cells of 19.0% was achieved with both the optimized single layer SiN_x but also with the high refractive double SiN_x layer on selective emitter solar cells.

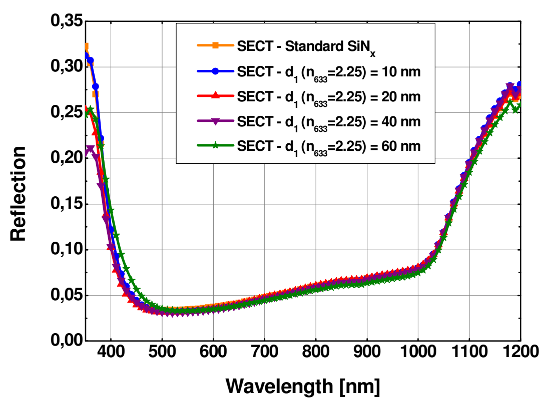

Figure 12: Comparison of the reflection of SECT solar cells with different thickness of the high refractive SiN_x layers (d_1, $n_{633} = 2.25$).

In the above comparison of the reflection of the SECT solar cells, it can be seen that double SiN_x layers may lead to a decrease in reflection in the short wavelength range (350 nm < λ < 550 nm). This effect can be attributed to increased absorption, which is amplified by the thickness of the high refractive SiN_x layer. The shift of the minimum in reflection for the 60 nm high refractive SiN_x layer (green stars) is due to the not optimal total thickness of the SiN_x layer, which shifts the minimum of the reflection curve. The reduction of the reflectivity in the short wavelength range could also be caused by the improved light trapping due to the gradient of the refractive index in the double layer SiN_x. On the other side, a reduced reflection in the long wavelength range (800 nm < λ < 1200 nm) can be obtained. This behaviour could be explained by the increased angle of incidence of long wavelength light on the pyramid texture of the rear side.

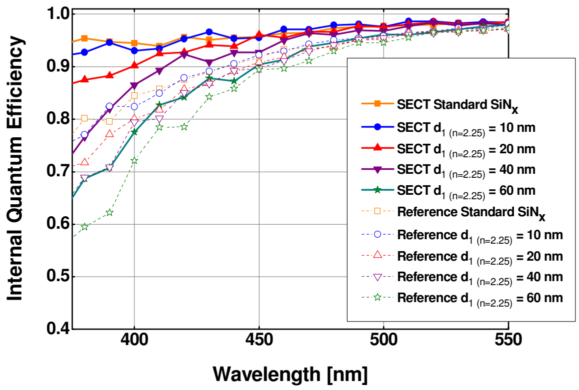

Figure 13: Comparison of the internal quantum efficiency of SECT and reference solar cells with different thicknesses of the high refractive SiN_x layer (d_1, $n_{633} = 2.25$).

The reduction of the internal quantum efficiency with the thickness of the first Si-rich high refractive SiN_x layer can be demonstrated with Fig. 13. Here the selective emitter SECT as well as the reference solar cells display a decrease in IQE with increasing thickness of the high refractive SiN_x. This result, which is to be expected, can be explained by the law of Lambert-Beer, which in this case describes the photon intensity loss by photon absorption in the thin SiN_x layer.

$$A(\lambda) = A_0(\lambda) \cdot e^{-\alpha(\lambda)d}$$

$$\alpha(\lambda) = \frac{4\pi \cdot k(\lambda)}{\lambda}$$

α: Absorption coefficient
A_0: Absorption in the substrate
A: Absorption in the SiN_x
d: Thickness of the SiN_x layer
k: Extinction coefficient

The photon absorption increases above all in the short wavelength range (increased extinction coefficient *k*) with increasing thickness of the absorbing Si-rich high refractive SiN_x layer.

5 CONCLUSION

In conclusion, the single SiN_x layer on etched back emitters ($R_{sheet} = 80\Omega/\square$) showed a very low j_{0E} value of 19 fA/cm². The studies and optimizations of double layered SiN_x on etched back emitters ($R_{sheet} = 65\Omega/\square$) showed that already 10 nm of high refractive SiN_x layer ($n_{633} = 2.25$) reduces the j_{0E} from 100 fA/cm² to 70 fA/cm².

QSSPC measurements before and after firing showed the firing stability of the high refractive double layered SiN_x. With FTIR absorption measurements the change of hydrogen and nitride bond densities before and after firing were studied.

The results of the previous investigations were successfully transferred to industrial type selective emitter solar cells (SECT), whereby a gain in efficiency of $0.6\%_{abs.}$ was achieved compared to reference solar cells. The best V_{oc} value of 642 mV and a maximum cell efficiency of 19.0% for SECT solar cells with a full area Al-BSF show the potential of surface passivation on selective emitter solar cells.

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