HIGH LIFETIME ON N-TYPE SILICON WAFERS OBTAINED AFTER BORON DIFFUSION

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ABSTRACT: For the formation of emitters or back surface fields by means of diffusion the influence of a high temperature processes on the bulk lifetime of Cz-Si wafers has to be understood. Here we present experiments of such heat treatments over a temperature range from 850°C to 960°C employing lifetime samples of neighboring n-type and p-type Cz wafers. In a second experiment we investigated the influence of the wafer origin from ingots and compared 2 Cz-ingots from different feedstock material side by side. The results were measured using the QSSPC technique and μW-PCD lifetime mapping.

1 INTRODUCTION

The interest in n-type base material is ever increasing since a few pioneering works \cite{1,2,3} have pointed out its advantages for solar cell production. Slowly the scope of silicon based cell concepts use such material. The well known tolerance over common metal impurities and lack of lifetime degrading boron-oxygen complexes make it well suited for an industrial application \cite{4}. An important step towards boron emitter formation, as well as the boron back surface field (BSF) formation in a standard p-type process is the understanding of boron diffusion and its effects on the lifetime. Contrary to the common belief to degrade carrier lifetimes \cite{5}, in this paper we demonstrate some examples of high temperature processes, such as boron diffusion, that actually improve the bulk properties. Alongside with boron diffusion we compare the effects of pure nitrogen annealing and phosphorous diffusion in the relevant temperature regime (850°C-960°C) using n-type and p-type Cz wafers. In a second step we chose solely n-type wafers from ingots grown from different quality feedstocks, and compared their performance after exposure to high temperatures using the same process conditions as before. The methods that are used can all be found in an industrial environment today, thus our results are of great relevance not only for the general understanding but also for our industry partners.

2 EXPERIMENT

In a first experiment neighboring, large area wafers were selected from an n-type ingot and from a p-type ingot grown under industrial conditions at Bosch Solar Energy AG. The as-cut base resistivity was determined to be in the range of around 2.5 Ωcm for n-type wafers and 8.5 Ωcm for wafers of the p-type ingot. Values are taken before any processing steps so include the influence of thermal donors. All wafers were chemically etched to remove the saw damage and subsequently divided in three groups.

The first one was the reference group and did not get any high temperature treatment. The second and third group were submitted to either boron diffusion or annealing under nitrogen atmosphere respectively. Process temperatures in the industrial type quartz tube furnace were set to 850°C, 900°C, 930°C and 960°C. For the boron diffusion a BBr\textsubscript{3} source was used. Afterwards the wafers have undergone another chemical etching step in order to remove both the oxide and diffused layers. Hydrogenated silicon nitride (SiN\textsubscript{x}:H) layers were deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) on both sides of the wafers as a passivation layer and then they were submitted to a firing step. Figure 1 shows the process sequences for both groups respectively.

3 RESULTS AND DISCUSSION

3.1 n-type and p-type comparison

The effective bulk lifetime was analyzed using μW-PCD mapping and QSSPC measurements at the center of each wafer. Figure 2 illustrates the lifetime results. For simplicity reasons only the highest and lowest process temperatures are shown.

The lifetime improvement over the whole area becomes obvious for the n-type wafer when looking at the lifetime maps. The p-type wafers on the other hand tend to be negatively affected with increasing process temperature. We see a correlation of the lifetime behavior with the change in the resistivity as it is also predicted by the SRH theory for low injection levels.

From the lateral patterns in figure 2 we deduct that effects of the simple passivation method used here come into play and might limit the lifetimes.

The lifetime of p-type minority charge carriers are...
already initially lower, but especially on the processed samples. However even if we compensate for the difference in the diffusivity coefficient of the electrons and holes, significantly higher diffusion lengths of minority charge carriers, as can be seen in figure 3, are measured on n-type wafers after the high temperature process. These results indicate that boron diffusion can be performed without degrading bulk lifetime in an industrial solar cell process, and it demonstrates high lifetime and high temperature stability of n-type wafers as needed in a potential application. The solar cell results based on these materials are presented at 2D0.2.2

The substantial increase in lifetime on n-type substrates is observed for both, samples with boron diffusion and annealing or either boron or POCl₃ diffusion step and reference group.

The results for all temperatures are summarized in figure 3 in form of effective lifetime values and effective diffusion lengths.

### 3.2 Comparison of ingot quality

Here we selected wafers from the top, middle and bottom region of two different n-doped Cz crystals respectively. Both crystals were intentionally doped to gain a base resistivity of about 2.5 Ωcm. The difference between the crystals is the feedstock of different quality. One ingot was made from higher quality feedstock (hereafter A1) while the second one was made from feedstock of comparable quality as feedstock commonly used in today’s industry processes (hereafter B1).

We were interested in a side by side comparison of the high temperature effects on lifetime samples given the different quality of the base material. The influence of the origin of the wafer within the ingot was also under investigation. Groups of wafers from the different positions were processed under the same conditions. In figure 4 we give a set of exemplary results from both ingots and all high temperature processes. Here we limit ourselves to the depiction of the middle region of both ingots but corresponding results have been found in samples from other parts of the respective ingot. The samples were prepared following the process sequence outlined in section 2.

![Figure 2: µW-PCD lifetime mapping of the n-type (left) and p-type (right) wafers that received boron diffusion with the lifetime mapping of an initial wafer (without diffusion).](image1)

![Figure 3: Average values of effective lifetime of the passivated wafer and corresponding diffusion length, deducted from µW-PCD mapping of the n-type (circles) and p-type (squares) wafers that received an annealing or either boron or POCl₃ diffusion step and reference group.](image2)
As can be seen from figure 4 the ingots perform comparably well after these high temperature steps. What is remarkable is that even the production ingot B1 yielded high lifetimes after phosphorous diffusion at 850°C and also after boron diffusion at 960°C, which are common processing temperatures. The observations from the first part of the experiment are widely reproduced for the case of n-type base material which emphasizes our earlier findings. Again we suspect the reason for the substantial increase in bulk lifetime in the increase of base resistivity. The top part of an ingot usually contains a high amount of incorporated oxygen. The large resistivity shift in the top part of the ingots A1 and B1 can be explained by annealing of oxygen related defects.

**Figure 4:** \(\mu W\)-PCD lifetime mapping of samples of the middle region of B1 ingot (left) and A1 ingot (right) wafers from the middle region that received boron diffusion with the lifetime mapping of an initial wafer (without diffusion).

3.3 Crystal defects triggering lifetime decay

On few samples originating from the very top of the A1 crystal we observed a pattern of concentric rings of significantly reduced lifetime after processing. A graphical representation of this effect is given in figure 6.

**Figure 6:** \(\mu W\)-PCD lifetime mapping of samples from top region of the A1 ingot after Boron diffusion at 960°C (left) and nitrogen annealing at the same temperature (right)

We observed this phenomenon on similarly processed top-region Cz-wafers from other manufacturers. Therefore we conclude its great relevance for the suppliers of such material. We suspect a configuration of grown in intrinsic defects and defect clusters as at the core of the problem [7,8,9]. It has been show in literature that a certain constellation of parameters can, during crystallization, cause similar characteristic defects. These defects are known to act as a sink for impurity atoms and thus are believed to enhance formation of oxygen complexes. We put this topic up for discussion and will continue research in this field.

4 CONCLUSION

No degradation of the bulk lifetime was observed after boron diffusion or annealing in nitrogen on n-type Cz-Si wafers. Furthermore, an improvement of the bulk lifetime could be observed after high temperature step as compared to the initial lifetime. This improvement is not attributed to a possible metal gettering effect of boron since neighbouring wafers that received only the tempering step in nitrogen show the same behaviour.

For p-type Cz-Si wafers, a different behaviour was observed: high temperature steps have a moderate impact on the bulk lifetime regardless of the process performed. Nevertheless, the lifetime values are significantly lower than those measured on n-type Cz-Si wafers resulting in significantly higher diffusion lengths of minority charge carriers on n-type wafers after the high temperature process. Together with the results of the second experiment which widely reproduced the observations made for n-type wafers, the superiority of n-type Cz-substrates over p-type as base material for an application in a standard process with diffused boron emitter could be shown. By using large area (241cm²) wafers we could demonstrate that even a low cost feedstock material has the potential for a long-term stable high efficiency n-type solar cell. The solar cell results based on these materials are presented at 2DO.2.2.

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REFERENCES