Hydrogen passivation of B-O defects in Czochralski silicon

Brett J. Hallam*1, Stuart R. Wenham1, Phillip G. Hamer1, Malcolm D. Abbott1, Adeline Sugianto1,2, Catherine E. Chan1, Alison M. Wenham1, Mitchell G. Eadie1, GuangQi Xu1

1School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Kensington NSW 2052, Australia
2now with Suntech Power Holdings Co., Ltd, 17-6 Chang Jiang South Road, New District, Wuxi 214028, China

Abstract

We report on hydrogen passivation of boron-oxygen defects through manipulation of the hydrogen charge states within the silicon. Standard hydrogenation processes which do not control hydrogen charge states do not appear to passivate a significant quantity of boron-oxygen defects and may result in a reduction in lifetime for wafers with high boron doping concentrations. An improved hydrogenation process through charge state manipulation is observed to lead to substantial improvements in the lifetimes of standard 2 Ωm commercial grade boron-doped Czochralski wafers and experimental compensated 2 Ωm Czochralski grown wafers. The passivation of boron-oxygen defects using hydrogen is a fully reversible process, and hence subsequent processes can lead to a net reactivation of boron-oxygen defects if there are insufficient quantities of atomic hydrogen in the correct charge state. Though improved hydrogenation, independently confirmed open circuit voltages in excess of 680 mV are demonstrated on solar cells fabricated using standard commercial grade boron-doped Czochralski grown wafers on an industrial production line.

© 2013 The Authors. Published by Elsevier Ltd. Open access under CC BY-NC-ND license. Selection and/or peer-review under responsibility of the scientific committee of the SiliconPV 2013 conference

Keywords: hydrogen passivation, Czochralski silicon, boron-oxygen defect, light-induced degradation

1. Introduction

Lifetime degradation in boron-doped Czochralski (CZ) is widely reported throughout the literature to result from the formation of boron oxygen (B-O) complexes [1-5]. Whilst the degradation associated with the formation of B-O complex is often referred to as ‘light induced degradation’ (LID), the defect
generation rate only weakly depends on illumination intensity for intensities greater than 1 mW/cm² [2,6], and can occur in the dark for temperatures above 300K in the absence of an applied bias [7].

Furthermore, the defect formation rate is determined by the total recombination rate and hence dependent on the total minority carrier concentration [7]. Subsequently, the current understanding is that the formation of the B-O complex is a recombination enhanced diffusion process [8]. In this process, the minority carriers are not directly involved in the defect formation, but rather the energy released from minority carriers during the recombination process activates the diffusion of the interstitial oxygen dimer O2i which is then captured by a substitutional boron atom Bs, forming the BsO2i complex [7]. After the BsO2i dissociate with annealing in the dark, the Bs and O2i are still typically present in the silicon and hence can form once again under further illumination or minority carrier injection [9].

For lifetime degradation, Bothe et al. observed a fast and slow process occurring in parallel with the fast process occurring in the first few minutes whilst the other process takes several hours. Initially these two processes show two different states, however for longer times a subsequent reaction appears to transform both into a final state of the slow asymptotic process [10]. This observation suggests multiple stable states of the BsO2i complex in agreement with theoretical predictions from Adey et al. [11].

1.1. Recovery and permanent deactivation of boron-oxygen defects

Whilst annealing in the dark at temperatures above 170°C are reported to fully reverse the effects of LID [1-5,9], the lifetimes in the non-degraded state are typically substantially lower than that of boron-doped FZ or gallium-doped CZ wafers [9,12].

Several approaches such as high temperature oxidations and anneals have been observed to increase the stable lifetime of boron-doped CZ wafers through permanent deactivation of B-O defects if heating and cooling regimes are performed correctly although not completely avoid it [3,12-17]. Phosphorus diffusions also reported to increase the stable lifetime of boron-doped CZ wafers and accelerate the deactivation process of B-O defects [9,18-19]. However other reports suggest phosphorus gettering has no direct impact on LID, with the same reduction in metastable defect concentration occurring from high temperature oxidations, or lengthy low temperature anneals [20].

Similarly to the formation of the B-O complexes which can be enhanced with illumination, the rate of B-O complex defect passivation can be enhanced by minority carrier injection from illumination. Recent work with simultaneous 1-sun illumination and thermal annealing at temperatures of 70-160°C is reported to permanently deactivate the B-O complex [21-22] and discuss the presence of a third ‘regenerated’ state of the B-O complex. Lim et al. also report permanent deactivation of the B-O complex using this method, however at higher temperatures in the range of 160-215°C. In this work, a theoretical model is introduced suggesting the presence of an unknown atom X which forms a recombination-inactive complex with the oxygen dimer, XO2i [9].

1.2. Hydrogen in silicon

The properties and interactions of hydrogen in silicon have been widely studied over multiple decades with beneficial effects shown as early as 1976 [23]. However the diffusion and passivation mechanisms of hydrogen, and dependence on material parameters appear to be poorly understood with many contradictory theories, and large variations in the results and subsequent interpretations reported in the
literature [24-28]. The complications arise in that atomic hydrogen interacts with the lattice and virtually all impurities and defects within the silicon [29], the difficulty of measurement/detection of hydrogen in silicon and the fact that hydrogen can be incorporated into films unintentionally during a variety of processing steps [26,30].

The diffusivity of hydrogen is affected by temperature, electric fields, crystallographic defects and the type and concentration of almost all impurities and defects within the silicon [25,27,32-36]. As a result many experiments and theories yield conflicting results and an uncertainty in the diffusivity of hydrogen with variations of more than five orders of magnitude for a given temperature [27-28,37-38].

Perhaps one of the most underestimated properties of hydrogen in silicon is its ability to assume different charge states, hence hydrogen can take on a positive (H⁺) neutral (H⁰) or negative (H⁻) charge state [28,39]. Due to interactions, large differences are observed for the mobility of the various charge states within crystalline silicon. For example, H⁰ is not affected by electric fields and charge effects within the silicon, and has a diffusivity five orders of magnitude higher than that of H⁺ [40]. Furthermore, the diffusivity of H⁺ is substantially smaller than that of H⁻ [39].

The ability of hydrogen to assume different charge states has important implications for the passivation of impurities and defects within silicon. Certain defects can only be passivated by a certain charge state of hydrogen and require the presence of electrons to allow the passivation process to occur. A number of authors have offered interpretations of hydrogen passivation mechanisms in silicon. However attempts to explain observed results have led to a number of contradictory assumptions of the charge state of hydrogen and hence the passivation reactions which can take place [38,41-42].

1.3. Hydrogen passivation of boron-oxygen defects

Whilst it has been reported that hydrogen plays no role in the deactivation of B-O defects [13], recent studies have observed that wafers passivated by plasma enhanced chemical vapor deposited (PECVD) SiN containing hydrogen show degradation and subsequent regeneration with exposure to illumination, whilst wafers passivated by low pressure chemical vapor deposited (LPCVD) SiN not containing hydrogen show degradation but no subsequent regeneration of the minority carrier lifetime [43]. Hence hydrogen plays a critical role in the regeneration process for B-O complexes. This effect has also been observed by other authors who indicate a strong correlation between the hydrogen content in the SiN layer and the regeneration process [44-45].

However Lim et al. indicate that hydrogen content in the dielectric layer alone does not influence the deactivation process, but the rate of deactivation is inversely proportional to the O₁ concentration, total boron concentration and is adversely affected by the presence of thermal donors [46]. Furthermore, the saturation value of the recovered lifetime decreases with increasing O₁ concentration. As a result, Lim questions the role of hydrogen in the regeneration process. Lim's results, in conjunction with earlier reports of lower lifetimes in the non-degraded state of boron-doped CZ silicon compared to boron-doped FZ, or gallium doped CZ wafers in several studies suggest that B-O associated defects may still be present in what is widely referred to as the non-degraded or regenerated states.

In this work, we demonstrate that by controlling the charge state of hydrogen, a more effective passivation of B-O defects can result.
2. Experimental details

Standard commercial grade 2 Ωcm boron-doped CZ (B-CZ), standard commercial grade gallium-doped CZ (Ga-CZ) wafers, 1 Ωcm boron-doped FZ (B-FZ) wafers and experimental compensated boron-doped p-type CZ (CB-CZ) wafers with a boron concentration of approximately 1x10^{17}/cm^3 and phosphorus compensation to result in a resistivity of approximately 2 Ωcm grown by Apollon Solar and purified using the PHOTOSIL process [47] are used in this work. Wafers are saw-damage etched, RCA cleaned and HF dipped prior to the deposition of SiN layers in a Roth&Rau remote microwave PECVD system. Injection level dependent (ILD) effective minority carrier lifetime (τ_{eff}) curves and 1-sun implied open circuit voltages (V_{OC}) are obtained using the quasi-steady-state photoconductance (QSS-PC) and quasi-steady-state photoluminescence (QSS-PL) methods [48-50].

Two different hydrogenation processes are applied in this work. For process P1, conventional hydrogenation conditions are used whereby there is no attempt to control the hydrogen charge state and hence results in a hydrogen charge state which is not favourable for the passivation of defects such as the B-O complex. For process P2, the charge state of the hydrogen is controlled to enhance passivation. For both processes, atomic hydrogen from identical dielectric layers of PECVD SiN is the only source of hydrogen for the passivation process. Subsequently, the wafers are re-measured using the aforementioned techniques.

Solar cells are also fabricated on the B-CZ wafers and processed in an industrial environment using standard commercial production equipment. The wafers are anisotropically textured to expose the (111) planes followed by a phosphorus emitter diffusion with a resultant sheet resistance of 100-150Ω/□ after the subsequent chemical edge junction isolation process which simultaneously planarises the rear surface and performs a slight etch back of the front surface to reduce the surface concentration of phosphorus. The front and rear dielectric layers are deposited using an industrial Roth&Rau remote microwave PECVD system.

A commercially available boron spin-on dopant source from Filmtronics is spun onto the rear surface at 2000 RPM for 20s. Laser doping is performed on the rear surface using a 15W 532nm Spectra Physics Millennia Prime laser with a processing speed of 0.5m/s. The advanced hydrogen process P2 is applied after the laser doping process to passivate laser induced defects, B-O complexes and other defects within the device. The p-type metal contact is formed by aluminium is sputtering and the n-type contacts are formed using the PLUTO process [51].

3. Results and discussion

3.1. Improved passivation of boron-oxygen defects through advanced hydrogenation

The PECVD system used in this work incorporates a thermal process after the deposition of the dielectric layer. This process starts at the deposition temperature of 400°C and ramps down to a temperature of 250°C over approximately 30 minutes before the samples are unloaded. According to literature, the thermal treatment above 170°C should result in the lifetime of the B-CZ and CB-CZ wafers being in a non-degraded state [4]. However, directly after the deposition of the SiN, the shape of the τ_{eff} curves on B-CZ and CB-CZ wafers greatly varies from that obtained on Ga-CZ or B-FZ wafers (see Fig. 1). The lifetime of the CB-CZ wafers is also much lower than that of the B-CZ wafers, possibly due to an increased B-O defect concentration due to the higher B concentration. For the B-CZ wafers, the lower
lifetimes are observed for excess minority carrier concentrations ($\Delta n < 2\times 10^{16} /\text{cm}^3$) whilst for the CB-CZ wafers, the lower lifetimes occur for $\Delta n < 1\times 10^{16} /\text{cm}^3$.

Fig 1. Injection level dependent lifetime curves extracted from QSS-PC and QSS-PL before and after hydrogenation processes on (a) 1 $\Omega$cm boron-doped FZ wafers, (b) 2 $\Omega$cm gallium-doped CZ wafers, (c) 2 $\Omega$cm boron-doped CZ wafers and (d) 2 $\Omega$cm compensated boron-doped CZ wafers.

After a standard hydrogenation process (P1), the $\tau_{\text{eff}}$ of B-FZ, B-CZ and Ga-CZ wafers improve for all injection levels. However, B-CZ wafers show little improvement for $\Delta n > 1\times 10^{13} /\text{cm}^3$. In addition, the $\tau_{\text{eff}}$ of CB-CZ wafers decreases for all injection levels. This suggests B-O defects are still present in the wafers, particularly for the CB-CZ wafers with higher B concentrations and lower $\tau_{\text{eff}}$ than that of the B-CZ wafers. Subsequently, it appears that the standard hydrogenation process P1 may enhance the recombination activity of B-O complexes. For the B-CZ wafers, the reduction in recombination activity of other defects as observed in the Ga-CZ wafers may be partially counteracted by an increased recombination activity of the B-O complexes. For the CB-CZ wafers, due to the much higher initial recombination activity presumably due to a higher B-O defect concentration, the increased recombination activity of the B-O defects through process P1 completely outweighs any increase in lifetime through the reduction in recombination activity of other defects. This phenomenon is noted by several authors on multi-crystalline silicon and upgraded metallurgical grade (UMG) CZ silicon with differing responses of wafers to hydrogenation throughout the ingot [52-53]. It appears that this differing response is due to changes in the fractional charge state concentrations which result from differing concentrations of
impurities throughout the ingot and the subsequent changes to the diffusivity and reactivity of the atomic hydrogen.

After a modified hydrogenation process (P2) implemented by controlling the charge state of the atomic hydrogen to enhance its mobility and reactivity, the B-FZ wafers show no improvement in $\tau_{\text{eff}}$. In fact, the $\tau_{\text{eff}}$ of such wafers slightly reduces for $N < 1 \times 10^{16}/\text{cm}^3$.

On Ga-CZ wafers, only a small increase in $\tau_{\text{eff}}$ is observed for $\Delta n$ in the range of $1 \times 10^{12} - 1 \times 10^{16}/\text{cm}^3$, however the B-CZ show a substantial increase in $\tau_{\text{eff}}$ over the same range of $\Delta n$. In addition, substantial improvements in the $\tau_{\text{eff}}$ are observed for the CB-CZ wafers over all injection levels. Hence it appears that process P2 passivates a number of B-O defects which a typical hydrogenation process such as process P1 fails to passivate. This suggests that the charge state of hydrogen is of significant importance to passivate B-O defects. At this stage, base on the model suggested by Lim et al., it would appear that atomic hydrogen is binding to the O$_2^+$ to create a recombination inactive complex [9]. In Münzer's work, it is suggested that the electron of diffusing hydrogen interacts with the oxygen’s positively charged region to neutralize the positive space charge, however no mention is given to the charge state of hydrogen [43]. Based on our results with increases in the concentration of both $H^0$ and $H^-$ by the charge state control in process P2, in order to achieve charge neutrality of the O-H complex it would appear likely that $H^-$ is involved in the deactivation process.

### 3.2. Reversibility of hydrogen passivation

Whilst other papers report permanent deactivation of B-O defects through hydrogenation [43-44,46], it is observed that the hydrogen passivation of the B-O defects is indeed reversible. From the $\tau_{\text{eff}}$ obtained from applying process P2, subsequent processing with hydrogenation process P1 reverts the lifetime back to the previous $\tau_{\text{eff}}$ determined by the use of the initial process P1, whilst a further anneal using process P2 once again passivates the B-O defects leading to substantial increases in $\tau_{\text{eff}}$.

The hydrogen passivation of B-O defects appears to be a two way process, in which B-O defect deactivation and reactivation are occurring simultaneously. Hence careful attention must be made to ensure the right mobility and reactivity of the hydrogen to result in a net passivation of the B-O and presumably other defects within the silicon. Therefore, if conditions during subsequent processing result in the atomic hydrogen being in an unsuitable state to re-passivate a sufficient quantity of defects which are reactivated during such processes, a net reactivation of the B-O defects may result. Fig. 2(a) shows the ILD $\tau_{\text{eff}}$ of B-O defects of B-CZ wafers subjected to additional hydrogenation processes with the legend indicating the sequential order of the processes, showing complete reversibility between the $\tau_{\text{eff}}$ obtained after processes P1 and P2. Similarly Fig. 2(b) shows the 1-sun $iV_{OC}$ of the various wafer types. It is observed that B-CZ and CB-CZ wafers show increases in $iV_{OC}$ of approximately 15 mV and 70 mV respectively between process P1 and process P2 through a more effective passivation of the B-O defects, whilst no improvements are observed for the Ga-CZ and B-FZ wafers.

It appears that in order to get effective hydrogenation of B-O defects, a number of factors should be considered. The hydrogen should be in the correct charge state to increase its mobility to allow it to move into and throughout the bulk of the silicon and subsequently react to deactivate the B-O complexes. During subsequent thermal processes, a sufficient concentration of hydrogen must be in the correct charge state such that any thermally reactivated B-O defects can be re-passivated by the atomic hydrogen, therefore not leading to a net reactivation of B-O defects during the process. It is also essential that the
solar cell structure avoids the formation of hydrogen sinks which may generate molecular hydrogen, and therefore reduce the concentration of atomic hydrogen in the silicon available to passivate such defects.

![Injection level dependent lifetime curves extracted from QSS-PC and QSS-PL before and after hydrogenation processes on 2 Ωcm boron-doped CZ wafers showing the reversibility of the effective lifetime and 1-sun $V_{oc}$ extracted from QSS-PC on various wafers before and after hydrogenation. The legend indicated sequential order of the processes.](image)

3.3. Application of the advanced hydrogenation process to solar cells

Hydrogen passivation of B-O defects appears to be a complex process with multiple interactions occurring within the device. The effectiveness of passivation depends on a number of factors, which for example can influence the release of atomic hydrogen from dielectric layers, mobility of hydrogen throughout the device, reactivity and ability of the atomic hydrogen to passivate B-O defects, reactivation of defects during subsequent processing or the formation of molecular hydrogen and therefore loss of atomic hydrogen from the silicon. Using the advanced hydrogenation process based on controlling the charge state of the atomic hydrogen (process P2), we fabricate large area industrial PERL solar cells on standard commercial grade boron-doped CZ silicon wafers. Through the hydrogen passivation of B-O defects, we demonstrate at the end of processing, and independently confirmed open circuit voltages and short circuit current densities of 681 mV and 40.0 mA/cm² respectively [54].

4. Conclusion

Recent developments for the permanent deactivation of B-O defects have highlighted the role of hydrogen in the deactivation process, although indicating that hydrogen content alone does not influence the deactivation process. In general, the diffusion and passivation properties of hydrogen in silicon appears to be poorly understood with many conflicting reports in the literature. Perhaps the most underestimated property of atomic hydrogen in silicon is its amphoteric nature, which has important implications for hydrogen diffusion and defect passivation, with a difference of more than five orders of magnitude in hydrogen diffusivity for the different charge states. In addition, certain defects require the presence of electrons in order to be passivated and hence require hydrogen to be in a certain charge state.

In this work, it is observed that standard hydrogen passivation processes do not appear to passivate a significant quantity of B-O defects, and for CB-CZ wafers with B doping concentrations of approximately
1x10^{17}/cm^3, a standard hydrogenation process appears to enhance recombination due to B-O defects. The hydrogenation process used greatly impacts on the effectiveness of the hydrogen passivation of B-O defects through enhancements of the mobility and reactivity of the atomic hydrogen, whilst B-FZ and Ga-CZ fail to show improvements in $\tau_{\text{eff}}$. The hydrogen passivation of B-O defect appears to be a fully reversible process in which the deactivation and reactivation of B-O complexes occurs simultaneously. Therefore during subsequent processes, if conditions do not provide sufficient quantities of hydrogen in the correct charge state, a net reactivation of B-O defects may occur. At this stage it is unclear whether the enhanced $\tau_{\text{eff}}$ from reduced recombination activity of B-O defects comes from atomic hydrogen bonding to the B₅O₂ or B₅O₂⁻ complexes.

Incorporating the advanced hydrogenation process for B-O defects into a production sequence for industrial PERL type solar cells with laser-doped p-type contacts on standard commercial grade B-doped CZ wafers has resulted in independently confirmed $V_{OC}$ and $J_{SC}$ of 681 mV and 40 mA/cm² respectively. This suggests that with appropriate fabrication sequences, hydrogen passivation of B-O defects can be retained through metallisation processes and result in bulk lifetimes in excess of 500 μs.

Acknowledgements

The authors would like to acknowledge the support of Suntech Power for allowing access to an industrial research production line for this work, Roth&Rau for the use of laboratory and industrial plasma enhanced chemical vapor deposition (PECVD) tools used in this work, Apollon Solar for growth and donation of wafers from an experimental CZ ingot, and the Australian Government through the Australian Renewable Energy Agency (ARENA). The Australian Government, through ARENA, is supporting Australian research and development in solar photovoltaic and solar thermal technologies to help solar power become cost competitive with other energy sources. The views expressed herein are not necessarily the views of the Australian Government, and the Australian Government does not accept responsibility for any information or advice contained herein.

References


