Understanding of the RTP-assisted Reduction of Hydrogen Dissociation from Defects in EFG Si

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ABSTRACT

This paper shows that very short, one second, firing of screen-printed Al on the back and SiN_x anti-reflection coating on the front can significantly enhance the bulk lifetime in EFG Si through SiN_x-induced hydrogenation of defects. This process improved average minority carrier lifetime from 3 μs to 93 μs, resulting in the open-circuit voltages as high as 613 mV. It is proposed that rapid firing at an appropriate temperature enhances the retention of hydrogen at defect sites by minimizing the hydrogen dissociation from defects. This is supported by a combination of simulations and experiments which reveal that the dissociation of hydrogen is extremely rapid at or below firing temperature of 700°C.

1. Introduction

Edge-defined Film-fed Grown (EFG) ribbon Si is one of the promising materials for cost effective PV because it eliminates the kerf loss and the mechanical sawing. However, EFG Si suffers from relatively high concentration of impurities and crystallographic defects, such as dislocations, twins, and grain boundaries. These defects lead to very low as-grown minority carrier lifetime, typically less than 3 μs, which is not sufficient for high efficiency cells (>15%). Therefore, it is necessary to enhance the bulk lifetime during the cell processing to reach the full potential of EFG Si for cost effective PV.

It is well known that SiN_x-induced hydrogen passivation of defects plays an important role in enhancing the bulk lifetime in ribbon Si. However, it is critical to optimize the firing process to achieve high retention of atomic hydrogen at the defect sites. This study shows the merit of rapid firing of screen-printed contacts for achieving significant lifetime and cell performance enhancement in EFG cells.

2. Experiment

In this study, simple n^+-p-p^+ planar solar cells were fabricated with screen-printed Al on the back and Ag grid on the front. EFG wafers were provided by RWE Schott Solar, Inc. Nine 4 cm^2 cells were fabricated and isolated by dicing saw. The EFG Si had resistivity of 3~5 Ω-cm and thickness of 300 μm. After the initial cleaning process, the wafers were phosphorus diffused to form 50 Ω/sq. emitter. A SiN_x anti-reflection (AR) coating with a thickness of 800Å and index of 2.0 was deposited in a low frequency PECVD reactor. A commercial Al paste was screen-printed on the back followed by an anneal in a rapid thermal processing (RTP) system at 725, 750, 775, 800, and 825°C for 1 second in conjunction with temperature ramp-up rate of 100°C/sec and cooling rate of 40°C/sec. The Ag grid was also screen-printed and fired in the RTP system at 700°C for 1 second with similar ramp-up and cooling rates. A forming gas contact anneal was performed at 400°C for 15 min at the end. Light and dark I-V measurements were performed to extract the cell performance parameters. Finally, cells were stripped down to bare Si and minority carrier lifetime was measured at an injection level of 10^{15} cm^{-3} using quasi-steady-state photoconductance (QSSPC) technique [1].

3. Results and Discussion

Table 1 shows the average values of V_{OC}, J_{SC}, FF, and efficiency for each firing scheme. Average values were determined from four EFG wafers or 36 cells. Table 1 shows that firing at 775°C for 1 second gave maximum V_{OC} (600 mV).

Table 1: Average cell parameters and average lifetime for each firing scheme, firing time was 1 second for all cases

	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	τ (μs)	Eff. (%)
725°C	587	33.8	0.74	68	14.6
750°C	589	33.8	0.74	84	14.7
775°C	600	34.1	0.75	93	15.3
800°C	596	34.0	0.72	74	14.6
825°C	579	32.4	0.72	50	13.5

To verify that this optimal firing condition also enhances bulk lifetime, QSSPC lifetime measurements were performed at several different locations on each wafer, after stripping the cell down to bare Si, to extract the average lifetime. An average lifetime of 93 μs was achieved with a maximum of 169 μs at the peak firing temperature of 775°C for 1 second. Table 1 also shows that the average lifetime decreased to 74 μs at a firing temperature of 800°C and 50 μs at 825°C firing. It is proposed that this is the result of reactivation of hydrogenated defects at high annealing temperature. Degree of hydrogenation is the result of competition between the supply of hydrogen atoms to the defects from SiN_x layer and the dissociation of hydrogen from the defects. These two processes happen

simultaneously at the hydrogenation temperature. To support and quantify the hydrogen dissociation process, hydrogenated samples were etched down to bare Si to remove the hydrogen supply and were annealed in RTP in the temperature range of 400-700°C for 1 second to study the reactivation of defects. Experimental data in figure 1 shows a rapid decrease in lifetime above 550°C. After 700°C/1 sec firing, lifetime dropped from 83 μs to 7 μs due to hydrogen dissociation from the defect sites. In the literature, annealing-induced reactivation of defects is described by the equation,

$$\ln\frac{N_O}{N} = t\nu\exp\frac{E_D}{kT} \qquad (1)$$

where N_O and N are passivated defects before and after annealing, t is the annealing time, υ is the attempt frequency (10^{13}~10^{14} sec^{-1}), E_D is the activation energy and T is the annealing temperature [2]. Figure 1 shows the normalized lifetime (τ_f/τ_i), where τ_i and τ_f are the lifetimes before and after annealing of hydrogenated samples. Figure 2 shows the experimental and simulation results obtained using Eq. (1) for 1 second annealing and two different E_D values corresponding to hydrogen dissociation from metallic impurities (E_D~2.3eV) and dislocations (E_D~3.1eV) [2]. Next, the measured lifetime data was plotted on this map, assuming N_O' and N' are the unpassivated defects before and after annealing, which limit the lifetime, and N_T is the unpassivated defect concentration when all the defects are reactivated and lifetime does not decrease with further annealing.

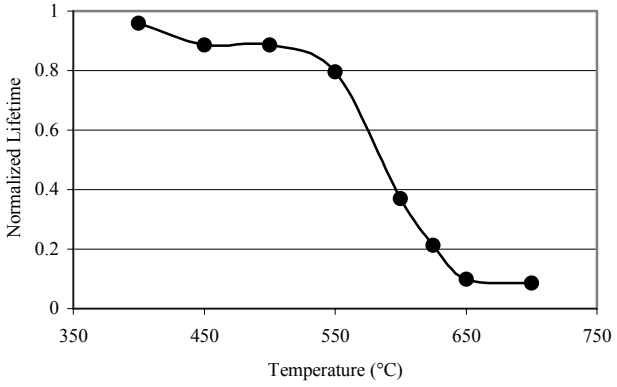

Figure 1: Normalized lifetime (τ_f/τ_i) as a function of temperature for 1 second annealing

$$\frac{N}{N_O} = \frac{\text{number of passivated defects after annealing}}{\text{number of passivated defects before annealing}} = \frac{N_T - N'}{N_T - N_O'} \qquad (2)$$

Assuming that τ is inversely related to the active defect concentration, the fraction of passivated defects can be expressed by

$$\frac{N}{N_O} = \frac{1/\tau_o - 1/\tau_f}{1/\tau_o - 1/\tau_i} \qquad (3)$$

In this study, τ_o was ~7 μs and the attempt frequency, υ, was set to 1.0×10^{14} sec^{-1}.

Using the above relationship, it is found that the plot of N/N_O from the experimental data falls in between the impurity-hydrogen and dislocation-hydrogen dissociation curves. This suggests the reactivation of passivated impurities, dislocations, or decorated dislocations during the annealing process. This plot gives the activation energy, E_D, of 2.55 eV.

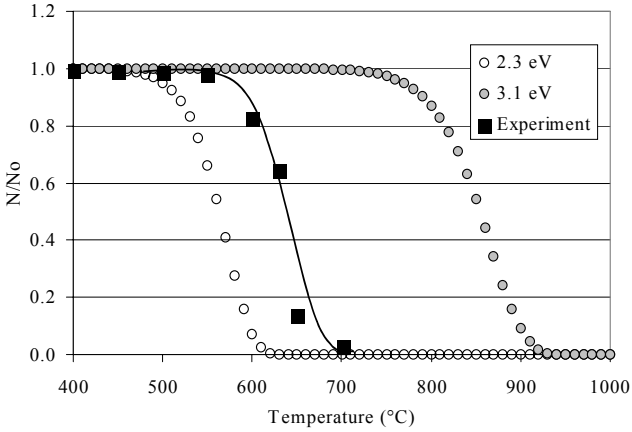

Figure 2: Simulations and experimental data showing fraction of passivated defect as a function of annealing temperature

4. Conclusion

It is found that the simultaneous firing of SiN_x and Al at an optimal temperature for very short time (1 second) significantly enhances minority carrier lifetime in EFG Si. This is due to the competition of hydrogen supply and dissociation to and from the defect sites. It is critical to find the optimal firing temperature and time to maximize the minority carrier lifetime by hydrogen passivation of defects. Maximum V_{OC} and average lifetime of 613 mV and 93 μs, respectively, were achieved by understanding and minimizing the dissociation of hydrogen from defects during the hydrogenation process.

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