

Improvement of Commercial Silicon Solar Cells with n^+ -P- n^+ Structure using Halogenic Oxide Passivation

K. Chakrabarty, D. Mangalaraj, Kyunghae Kim, J. H. Park, and J. Yi*
*School of Electrical and Computer Engineering, Sung Kyun Kwan University,
Chunchun-dong, Jangan-gu, Suwon, Kyunggi-do 440-746, Korea*

*E-mail : yi@yurim.skku.ac.kr

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This paper describes the effect of halogenic gettering during oxide passivation of commercial solar cell with the n^+ -p- n^+ structure. In order to study the effect of halogenic gettering on n^+ -p- n^+ structure mono-crystalline silicon solar cell, we performed conventional POCl_3 diffusion for emitter formation and oxide passivation in the presence of HCl vapors. The n^+ -p- n^+ structure based silicon solar cells were found to have higher short circuit current and minority carrier lifetime. Their performance was also found to be superior than the conventional n^+ -p- p^+ structure based mono-crystalline silicon solar cell. The cell parameters of the n^+ -p- p^+ and n^+ -p- n^+ structure based cells, passivated by HCl assisted oxidation were measured. The improvement in I_{sc} was attributed to the effect of the increased diffusion length of minority carriers, which came from the halogenic gettering effect during the growth of passivating oxide. The presence of chlorine caused gettering of the cells by removing the heavy metals, if any. The other advantage of the presence of chlorine was the removal of the diffusion induced (in oxygen environment) stacking faults and line defects from the surfaces of the silicon wafers. All these effects caused the improvement of the minority carrier lifetime, which in-turn helped to improve the quality of the solar cells.

Keywords : HCl assisted passivation, n^+ -p- n^+ solar cell, Spectral response

1. INTRODUCTION

The commercial solar cells are generally made using p type Cz crystalline silicon having $\langle 100 \rangle$ orientation. The standard practice for the fabrication of commercial silicon solar cell is to employ n^+ -p- p^+ structure, in order to get a better back surface field effect[1,2]. The contacts are made by screen-printing with silver paste for front contact and silver-aluminium paste for back contact and the subsequent sintering at 700 °C in the ambient of dry air. The aluminium present in the paste used for making back contact converts the back surface into p^+ layer. This develops a low-high junction at the back, which in turn gives the back surface field effect. This process of making low-high junction at the back needs complete coverage of the back surface with silver-aluminium paste [3], which involves high costs and so not desirable for industrial production of solar cell. To get rid of this problem, some industries started using aluminium paste for low-high junction and the back bus bar contact was made using silver paste. This process needed one additional step of screen-printing of bus bar at the back,

yet there was no significant cost reduction[4].

Many researchers have developed a new structure for solar cell made using multi-crystalline silicon substrate, having n^+ -p- n^+ double-sided junction. The rear n^+ layer is shorted to the front n^+ layer through a third contact. The third contact can be avoided by joining the two n-type regions through the substrate as in the polka-dot cell. We have developed a n^+ -p- n^+ structure having a floating n^+ region at the backside surrounded by p^+ grided back contact using silver-aluminium paste. This is essentially a combination of n^+ -p- p^+ and n^+ -p- n^+ structures with common n^+ front emitter. For the sake of convenience we shall however refer it as n^+ -p- n^+ structure.

Surface represents rather severe discontinuities in the crystalline structure of silicon. Consequently, quite a high density of allowed energy levels or surface states occurs on the surface, at energies corresponding to the forbidden gap. The surface states have an enormous effect on any metal to semiconductor contact. Electrons in the conduction band will try to fill the surface states, until the highest filled surface state coincide with the Fermi level. Thus a potential drop is built and causes a rectifying

contact[5,6]. This adverse effect of the surface states can be reduced considerably by growing a thin layer of oxide on the surface. The semiconductor-insulator-metal contact causes the movement of the carrier through tunneling and thus the presence of rectifying contact can be avoided. During the growth of oxide, the interface between the oxide and the underlying silicon moves deeper into the bulk. This displacement of the interface to clean region within the bulk is believed to be one of the major factors, which contribute to the high level of passivation provided by this approach. For this growth of oxide formation, an extra high temperature step is required, because the growth rate of the dry silicon dioxide is very small.

An extra step of high temperature process of solar cell (a minority carrier device) will reduce the lifetime of minority carriers. The oxide layer formed by any relatively low temperature wet oxidation process is porous in nature and does not show much improvement. If the surface states of the solar cells are not passivated, they trap other impurities as well as carriers to cause a remarkable reduction of minority carrier lifetime and collection probability. To overcome these problems, in the present study, we have used HCl assisted oxidation process for the passivation of front surface. Oxide was grown before making metallic contacts. Unlike the usual process of chlorinated oxidation by using 2% dry HCl gas we have bubbled the oxygen through the hydrochloric acid[7].

2. EXPERIMENTAL

A few batches of 100 mm diameter silicon solar cells were fabricated using <100> oriented Cz grown p-silicon wafers (area = 78.6 cm² and resistivity = 1.2 Ω-cm). Prior to diffusion the wafers were textured to reduce reflectivity. The n⁺ layer was formed on both sides of the wafers by (putting single wafer in each slot of the boat) conventional phosphorous diffusion using a POCl₃ source. Prior to metallization the cells were divided into two groups. One group of the cells were passivated by carrying out dry oxidation and the other by carrying out oxidation, in HCl / O₂ ambient by bubbling oxygen through hydrochloric acid (HCl). Both the front silver (Ag) contact and the back grided silver-aluminium (Ag / Al) contacts were made by screen-printing, followed by sintering at 725 °C for a few minutes. The n⁺ front emitters of both types of the cells were passivated with SiO₂ layer using HCl assisted oxidation process before making the metallic contact. I-V characteristics of the cells were measured at 25 °C under dark and under simulated AM 1.5 condition at 100 mW/cm² intensity. Beside this, the spectral response and diffusion length measurement were also carried out to evaluate the performance of n⁺-p-n⁺ structure based large

area cells as well as that of the conventional n⁺-p-p⁺ structure based cells.

3. RESULTS AND DISCUSSION

Figure 1 shows the I-V characteristics curves of typical solar cells having n⁺-p-n⁺ structure (-●-) and n⁺-p-p⁺ structure (-○-).

The spectral response curves of these cells are shown Fig. 2. The values of short circuit current (I_{sc}), open circuit voltage (V_{oc}), curve factor, dark saturation current (I₀), series resistance (R_s), shunt resistance (R_{sh}) and minority carrier diffusion length are presented in Table 1.

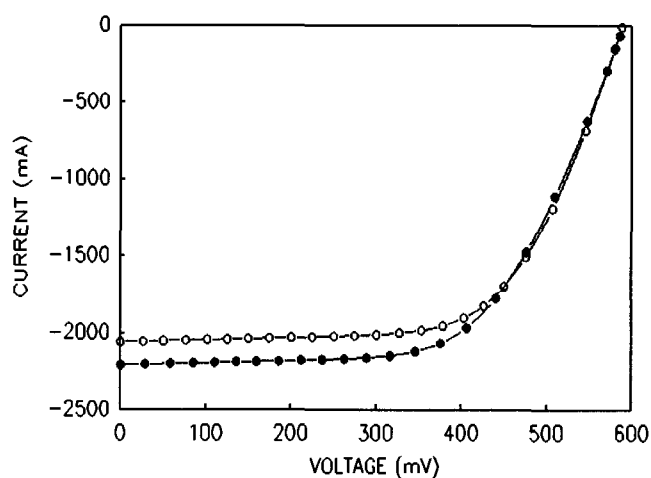


Fig. 1. I-V Characteristics of silicon solar cells with fully back covered n⁺-p-p⁺ structure (-○-) and grided back contact n⁺-p-n⁺ structure (-●-).

It is observed, from Table 2 and Fig. 1, that the short circuit current of n⁺-p-n⁺ structure based cell is higher than that of the cell having the conventional n⁺-p-p⁺ structure. It is also seen that in n⁺-p-n⁺ structure based cell, the reverse saturation current was smaller, whereas its series resistance was higher. The larger series resistance inevitably led to low curve factor value. A part of the series resistance is contributed by the pressure contact used for the measurement. But the smaller back metal coverage is the major cause of the series resistance. From the spectral response curves of n⁺-p-n⁺ and n⁺-p-p⁺ structure based cells (Fig. 2.) it can be observed that the mid and long wavelength response of the cell having n⁺-p-n⁺ structure is better than that of the n⁺-p-p⁺ based cell. This could be due to the larger value of diffusion length and the smaller value of back recombination velocity (S_B) of minority carriers in the p-base region of those cells.

Table 1. Cell parameters of the $n^+ - p - p^+$ and $n^+ - p - n^+$ structure based cells. The front surface of the cells were passivated with SiO_2 layer grown of HCl vapors.

Cell Structure	I_{sc} (A)	V_{oc} (mV)	I_0 (A)	n Factor	Curve Factor	R_s (m Ω)	R_{sh} (Ω)	Diff.Length (μm)
$n^+ - p - p^+$	2.06	588	4.4×10^{-10}	1.03	0.64	45	25.8	150
$n^+ - p - n^+$	2.21	589	2.3×10^{-10}	1.00	0.62	53	12.8	173

Table 2. Parameters of $n^+ - p - n^+$ cells passivated by dry oxidation and HCl assisted oxidation.

Type of Oxidation	I_{sc} (A)	V_{oc} (mV)	I_0 (A)	n Factor	Curve Factor	R_s (m Ω)	R_{sh} (Ω)	Diff.Length (μm)
Dry	1.96	582	5.3×10^{-10}	1.03	0.63	51	11.9	130
HCl	2.21	589	2.3×10^{-10}	1.03	0.62	53	12.8	173

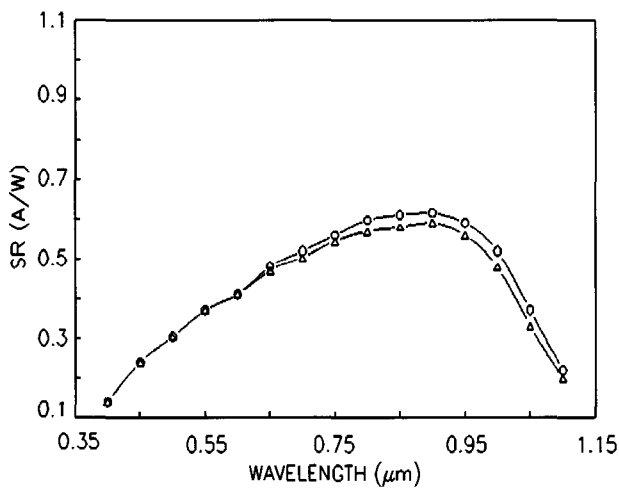


Fig. 2. Spectral response curves of solar cells with $n^+ - p - p^+$ structure (Δ -) and with $n^+ - p - n^+$ structure (o-). Both the cells were passivated with HCl assisted oxide.

It may have had its origin in the halogenic gettering effect at the backside during the $POCl_3$ diffusion [8-9].

Because of the exposure of both sides of the Si wafer to chlorine (generated during $POCl_3$ diffusion) the gettering effect takes place, which increases the minority carrier diffusion length and subsequently causes improvement in long wavelength spectral response. This fact is supported by the observed higher minority carrier diffusion length of the cells (Table 1).

This improvement in I_{sc} as well as in spectral response can also be attributed partially to lower recombination velocity of the carriers at the back floating n^+ region. On the other hand, in the $n^+ - p - p^+$ structure based cells, $p - p^+$ type of low high junction is formed at the back and this can give rise to defects states at the base region which is responsible for lower diffusion length of the minority

carriers. Fig. 3 shows the I-V characteristics of typical solar cells having $n^+ - p - n^+$ structure. The observed spectral response curves are shown in Fig. 4. In both the figures, one curve represents the cell passivated by dry oxidation and the other represents the cell passivated by HCl assisted oxidation.

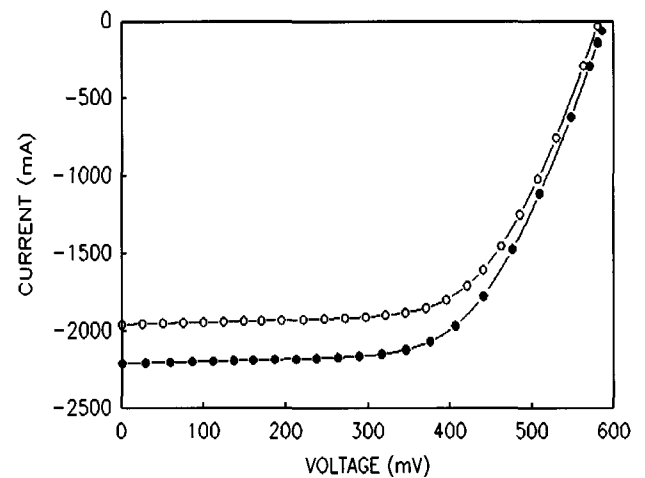


Fig. 3. I-V characteristics of dry oxide passivated solar cell (o-) and HCl oxide passivated solar cell (•-). The cells have $n^+ - p - n^+$ structure with an area of 78.6 cm^2 .

The measured values of I_{sc} , V_{oc} , I_0 , curve factor, R_s , R_{sh} and diffusion length are shown in Table 2. From this table it is clear that the HCl assisted passivating oxide cells have the higher values of I_{sc} , V_{oc} as well as curve factor. It is also observed that the diffusion length of the minority carrier is more for the cell having HCl assisted passivating oxide, which is supported by the improved spectral response of such type of cell in the mid and long wavelength region.

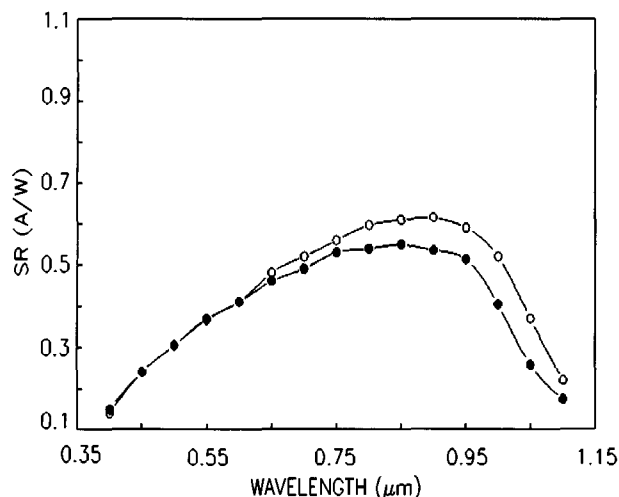


Fig. 4. Spectral response of HCl assisted oxide passivated solar cell (○) and dry oxide passivated solar cell (●). The cells have $n^+ - p - n^+$ structure with an area of 78.6 cm^2 .

The improvement in I_{sc} can be attributed to the effect of the increased diffusion length of minority carriers, which comes from the halogenic gettering effect during the growth of passivating oxide. The presence of chlorine causes gettering of the cells by removing the heavy metals, if any. The other advantage of the presence of chlorine is the removal of the diffusion induced (in oxygen environment) stacking faults and line defects from the surfaces of the silicon wafers. All these effects caused the improvement of the minority carrier lifetime, which intern helps to improve the quality of the solar cells.

4. CONCLUSION

The $n^+ - p - n^+$ structure based silicon solar cells were found to have higher short circuit current and minority carrier lifetime and their performance was superior to the conventional $n^+ - p - p^+$ structure based solar cells. This can be attributed to the halogenic gettering at the backside during the POCl_3 diffusion, which increased the minority carrier diffusion length and caused improvement in long wavelength spectral response of the cells. The study on the cells having front surface oxide passivation with thermal oxide and HCl assisted grown oxide showed that I_{sc} , V_{oc} as well as curve factor values were higher for the cell having HCl assisted passivating oxide. It is also observed that the diffusion length of minority carrier is more for the cell having HCl assisted passivating oxide, which is supported by the improved spectral response of such type of cell in the mid and long wavelength region. Summarily it can be concluded that monosilicon solar cells with $n^+ - p - n^+$ structure having HCl assisted oxide

passivation layer are the better candidates for the fabrication of commercially viable solar cells.

REFERENCES

- [1] G. C. Sun, J. C. Bourgoin, N. de Angelis, M. Yamaguchi, A. Khan, T. Takamoto, and O. Gilard, "Metastability effects in InGaP solar cells," *Solar Energy Materials and Solar Cells*, Vol. 75, p. 293, Jan. 2003.
- [2] A. P. Gorban, A. V. Sachenko, V. P. Kostilyov, and N. A. Prima, "Effect of excitons on photoconversion efficiency in the $p^+ - n - n^+$ and $n^+ - p - p^+$ structures based on single-crystalline silicon", *Semiconductor Physics, Quantum Electronics & Optoelectronics*, Vol. 3, p. 323, 2000.
- [3] L. M. Porter, A. Teicher, and D. L. Meier, "Phosphorus-doped, silver-based pastes for self-doping ohmic contacts for crystalline silicon solar cells," *Solar Energy Materials and Solar Cells*, Vol. 73, p. 209, 2002.
- [4] P. Panek, M. Lipiski, R. Ciach, K. Drabczyk, and E. Bielaska, "The infrared processing in multicrystalline silicon solar cell low-cost technology," *Solar Energy Materials and Solar Cells*, Vol. 76, p. 529, 2003.
- [5] K. Laihem, R. Cherfi, and M. Aoucher, "Hydrogen interaction on metal / hydrogenated amorphous silicon Schottky structures: adsorption / desorption effects," *Thin Solid Films*, Vol. 383, p. 264, 2001.
- [6] J. A. del Alamo, J. Van Meerbergen, F. D'Hoore, and J. Nijs, "High-low junctions for solar cells applications", *Solid-State Electronics*, Vol. 24, p. 533, 1981.
- [7] J. Muller, G. Schope, O. Kluth, B. Rech, M. Ruske, J. Trube, B. Szyszka, X. Jiang, and G. Brauer, "Upscaling of texture-etched zinc oxide substrates for silicon thin film solar cells," *Thin Solid Films*, Vol. 392, p. 327, 2001.
- [8] M. Lipiski, P. Panek, Z. witek, E. Betowska, and R. Ciach, "Double porous silicon layer on multicrystalline Si for photovoltaic application," *Solar Energy Materials and Solar Cells*, Vol. 72, p. 271, 2002.
- [9] B. C. Chakravarty, P. N. Vinod, S. N. Singh, and B. R. Chakraborty, "Design and simulation of antireflection coating for application to silicon solar cells," *Solar Energy Materials and Solar Cells*, Vol. 73, p. 59, 2002.