RAPID THERMAL OXIDATION OF HEAVILY DOPED SILICON FOR ADVANCED SOLAR CELL PROCESSING

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ABSTRACT

Crucial steps in solar cell processing such as emitter diffusion and surface oxide passivation have been carried out by rapid thermal processing (RTP). Rapid thermal diffusion (RTD) of boron into silicon from APCVD borosilicates has been studied. Rapid thermal oxidation (RTO) of the heavily B-doped surfaces of these shallow junctions (0.2 µm) has been studied in view of applicability of this technique in solar cell processing. These shallow diffusions have excellent lateral uniformity over large areas and have high surface concentrations depending on the APCVD deposition conditions and on RTP conditions. The surface passivating oxides resulting from the RTO are exceptionally thick in case of heavy boron diffused surfaces. RTO does not cause considerable drive-in of the diffused junction profiles. In the contrary, the thick RTO oxides considerably reduce the surface concentration, thereby reducing the heavy doping effects in the junctions, making them more suitable emitters for devices such as solar cells. p^+nn^+ solar cells have been fabricated on n-type CZ silicon wafers by RTD of boron followed by RTO. The cells result in conversion efficiencies as high as 16.2%. The passivation effect of RTO oxides have been investigated by analysing RTO MOS capacitors and are compared to conventional furnace oxides.

Introduction

Low thermal budget $\{\int T(t).dt\}$ processing based on RTP is essentially becoming an advantageous alternative for conventional furnace processes in microelectronic and optoelectronic applications. The often-cited advantages of RTP include low cost, low overall thermal budget, low power consumption and high throughput. RTP yields device quality silicon dioxide (SiO_2) and junctions of good characteristics[1,2]. Complete devices such as high speed bipolar transistors have already been fabricated by RTP [3]. Another possible sub-field of RTP applications is photovoltaic solar cells, where the processing cost is a very significant part of the device cost. Optical processing has been suggested as a cost-effective metallization technique for solar cells [4]. Solar cell emitters are generally shallow (<.5 µm) and therefore can be formed by RTD. In fact, shallower and steeper junctions enhance the minority carrier collection efficiency of emitters (for short wavelength illumination, 0.35 to 0.6 µm) because of the built-in electric field resulting from doping gradient and due to reduced minority carrier recombination in the bulk of the emitter. On the other hand, heavy doping effects at the surface tend to increase the surface states thereby enhancing the minority carrier recombination at the surface. This will reduce the effectiveness of any passivation layer at the emitter surface. Conventional furnace processes are well-established for optimal junction formation and surface passivation, but with a disadvantage of a larger thermal budget compared to RTP. The RTP-induced diffusions and oxidations take place in a much shorter time (in tens of seconds) compared to furnace processes, and the enhanced kinetics are explained to be due to certain photo-chemical reactions involving spectra of UV and VUV radiations which are a significant part of RTP optical lamps[5]. However, it is possible that, in the case of RTP, very high cooling rates and high quench temperatures can freeze process-induced and grown-in impurities that can decorate defects or occupy electrically active states. This might reduce the minority carrier lifetime and hence can be a disadvantage for devices such as solar cells. But, on the other hand, enhancement of RTP induced gettering of transition metals over mechanical or laser damaged areas in silicon has been reported[6]. Further, an increase in bulk lifetime in silicon has been observed after RTD of dopants such as P or Al, due to gettering [7]. Therefore, a proper RTD junction formation

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scheme followed by a surface passivation scheme by RTO, can yield emitters which are compatible for solar cell applications with a lower thermal budget. RTO of phosphorous diffused silicon surfaces has been previously studied[8]. In this work, we study the RT-diffusion of boron in n-type silicon. Further we investigate the RTO of such heavily doped RT-diffused surfaces and the reduction in surface concentration that makes them more suitable for p^+n solar cell emitters. We also report on small area (4 cm^2) solar cells fabricated by RT diffusion of boron into 4 Ω-cm, n-type CZ silicon followed by RTO of the boron-diffused surface. The RTO Si-SiO_2 interfaces are also characterized by MOS capacitors made on p-type bare silicon and are compared with furnace oxides.

Experimental

(i) RTD of boron.

The diffusion source used for RTD B-diffusion is the APCVD deposited borosilicate glass (BSG). The precursor gases used were SiH_4, B_2H_6, and O_2. The deposition temperature was ≈ 400°C. The deposition rate was around 1000Å/min., with the following reactions taking place.

$$SiH_4 + O_2 \longrightarrow SiO_2 + 2H_2$$
$$2B_2H_6 + 3O_2 \longrightarrow 2B_2O_3 + 6H_2$$

The composition B_2O_3:SiO_2 in the deposited BSG could be changed by varying the flows of reaction gases SiH_4 and B_2H_6. We have used two different B_2H_6/SiH_4 flow ratios (R) 1.0 and 0.7. After the deposition of approximately 5000Å of BSG, RTD is carried out in dry N_2 ambient in a HeatPulse 610 (AG Associates) RTP furnace, which consists of a quartz process tube in which the sample is held horizontally, supported on a 3-pin quartz tray. The sample is illuminated from the top & bottom by two sets of tungsten halogen lamps. The temperature is monitored by an infrared pyrometer. The typical heating and cooling rates were in the range of 100°C/sec. After the diffusion the remaining silicate glass was stripped off by HF and the junctions were characterized by 4-point probe sheet resistance measurements and SIMS analysis. Several experiments were carried out varying RTD temperatures and durations.

(ii) RTO of heavily B-doped silicon surfaces and of bare p-silicon.

Some of the samples with heavy B diffusions at the surface were subjected to RTO in the same reactor in dry O_2 ambient. Prior to RTO, any remaining silicates on the samples were removed and the samples underwent a standard cleaning. The oxide thickness was measured by ellipsometry, and, after removing the RT-oxides, SIMS analysis was performed on some samples to see any redistribution in the existing RTD profiles. Some bare p-type silicon samples without diffusion were also RT-oxidized and MOS capacitors (MOSC) were fabricated by evaporating 7000Å aluminum on the RT-oxide. Another set of control MOSC's were fabricated using conventional furnace oxidation. High frequency (100kHz) and quasi-static (1 volt/sec.) C-V measurements were performed in order to determine the interface trap density (D_{it}) at the Si-SiO_2 interface for both RT- and furnace- MOSC's.

(iii) Solar cell fabrication.

Small area (4cm^2) solar cells were fabricated on n-type CZ wafers which initially had a furnace phosphorous diffusion (n^+) on the rear contact side (for the back surface field and for good contacting) before starting the RT process. The subsequent processing was in the following sequence: (i) deposition of APCVD borosilicate on the front side, (ii) RTD boron diffusion at 1000°C, 50sec.for emitter formation, (iii) RTO at 950°C, 50sec. for emitter surface passivation, (iv) metallization, (v) e-beam evaporation of ZnS for antireflection coating. Control cells were also fabricated with RTD B-diffusion followed by conventional furnace oxidation (900°C, 7 minutes, with a slow ramp down of -2°C/min.) instead of RTO.

Results and Discussion

Figure 1 shows the variation in sheet resistance of RTD boron-diffused layers with duration of diffusion. The lateral uniformity was very good (<5% variation) over 4-inch wafers. The SIMS analysis of the RTD boron diffused samples show very high surface concentrations (N_S) and shallow junctions (< 0.2 µm). In figure 2, we show the influence of B_2O_3 concentration in the initial BSG on the RT-diffused profiles for two different B_2H_6/SiH_4 ratios (R). The boron rich BSG results in a surface layer of unusually high boron concentration. This is probably due to a boron-rich Si phase (SiB_6 or SiB_4) as suggested in [9].

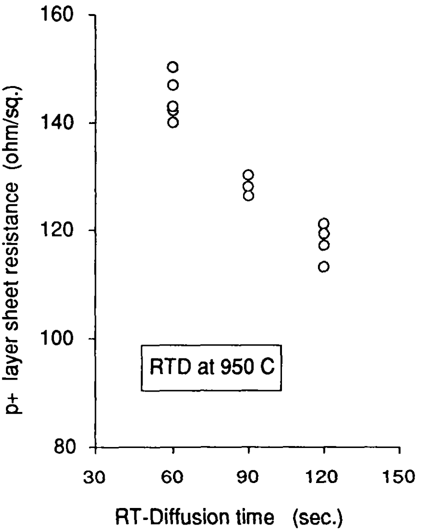


Figure 1. Variation of the p^+ layer sheet resistance with the duration of RT-diffusion.

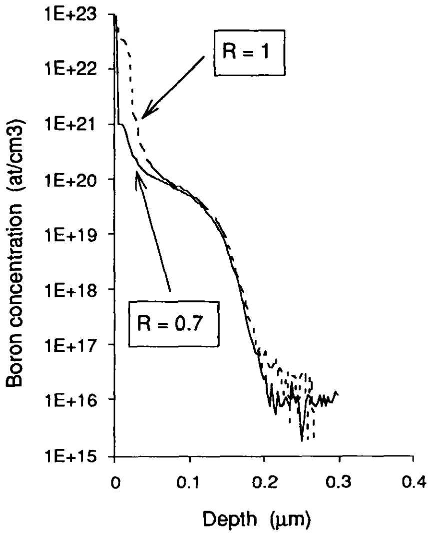


Figure 2. Influence of the B_2O_3 concentration in the initial BSG on the RT- diffusion profile. (R = gas flow ratio, B_2H_6/SiH_4 during APCVD deposition) RTD at 1000°C, 50 sec.

Figure 3 shows the strong dependence of the p^+ layer sheet resistance on the RTD temperature. The RTO of B-diffused samples result in increased sheet resistance with a largely reduced surface concentration (N_S) (figures 3, 4). One of the boron profiles before and after RTO is shown in figure 4. The oxide thickness in this case was exceptionally high ≈450 Å for the RT oxidation of 950°C, 50 seconds. It indicates that part of the heavily doped region might have been consumed in the RT-oxidation process. The slight deepening of the B-profile can be due to the enhanced B-diffusion that can be attributed to the generation of excess Si self-interstitials at the Si-SiO_2 interface during the oxidation process. Out-diffusion of boron at the surface can also be seen in the figure. The reduction in N_S and slight increment in junction depth after RTO, can make RT-diffused junctions more suitable for devices such as solar cells.

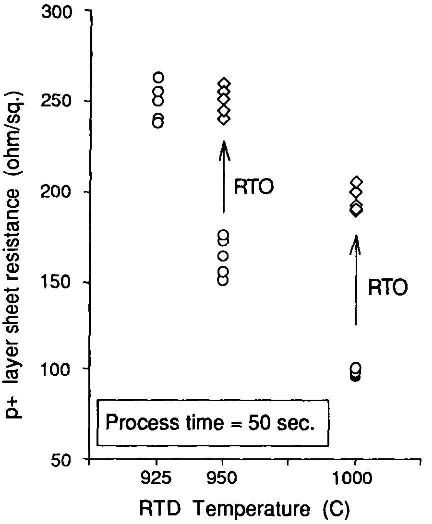


Figure 3. Dependence of B-diffused layer sheet resistance on RTD temperature (circles), and the change after RTO of 950°C, 50 sec. (diamonds)

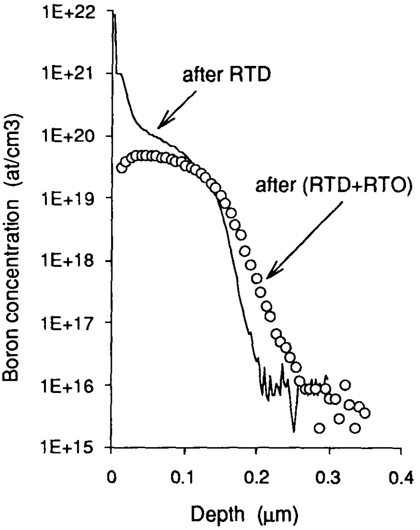
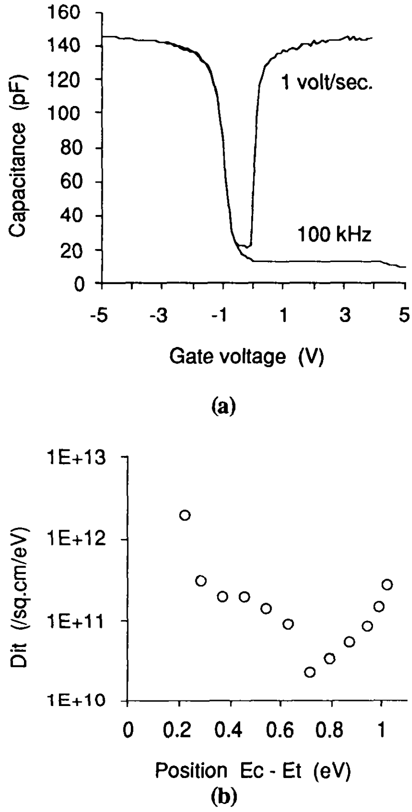


Figure 4. RT-diffused boron profiles before (solid line), and after (circles), RTO. The RTD was at 1000°C, 50 sec., RTO at 950°C, 50 sec.

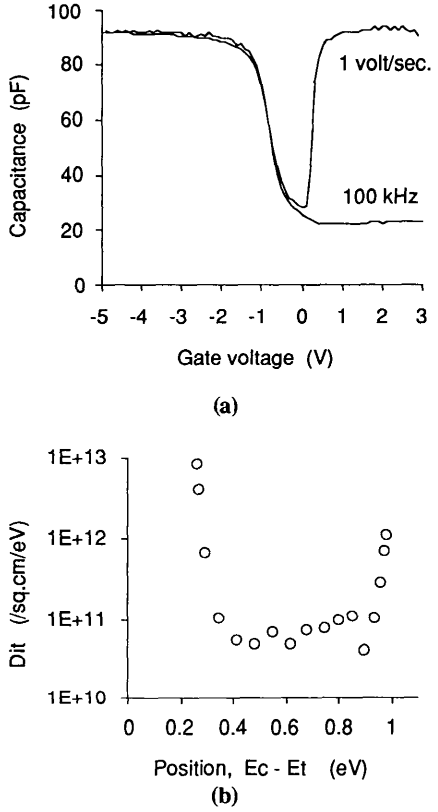
Figures 5a and 6a show the high frequency and quasi-static C-V measurements performed on MOS capacitors with RT and furnace oxides. As the p-type Si wafers used for the MOS-C had a moderate base doping level (0.5 Ω-cm), the RTO temperatures had to be raised to obtain gate oxides in the range 40-50 Å. The analysis of the C-V curves shows $D_{it} < 10^{11}$ cm^{-2}eV^{-1} near midgap for both RT and furnace oxides (figures 5b, 6b). This further emphasizes the possibility of using RT oxide passivation for solar cell emitter surfaces. Even though such low D_{it} values cannot be obtained in a diffused emitter surface of relatively higher N_S, the comparison with furnace oxides shows that the RT-oxide passivation can be as effective as a conventional furnace oxide passivation.



(a)

(b)

Figure 5. (a) High frequency and quasi-static C-V curves of a MOSC with RTO gate oxide (RTO done at 1000°C, 30sec., oxide thickness = 52Å, substrate: 0.5 Ωcm p-type FZ silicon), (b) Distribution of D_{it} for the RTO MOSC.



(a)

(b)

Figure 6. (a) High frequency and quasi-static C-V curves of a MOSC with furnace gate oxide (oxidation at 900°C, 45 min., oxide thickness = 194Å, substrate: 0.5 Ωcm p-type FZ silicon), (b) Distribution of D_{it} for the furnace oxide MOSC.

Finally Table I compares the performance of the 4cm^2 p^+nn^+ solar cells fabricated using RTD and RTO (cell type "A") with other control cells. The performance of the type-A device (Figure 7) is as good as that of the type-B device which had an RT-diffused boron emitter and conventional furnace oxide passivation. The short circuit current and the conversion efficiency are very comparable in both type- A, and B cells. On the other hand, the type-C device which had only RT boron diffusion but no surface oxide passivation shows a poor performance due to enhanced minority electron recombination at the heavily doped emitter surface. This further evidences the advantages brought about by the RT-oxide passivation.

Table I. Performance of different RTP solar cells: **A** = RT diffusion + RT oxidation, **B** = RT diffusion + furnace oxidation, **C** = RT diffusion + no oxidation.

	CELL TYPE		
	A	B	C
Cell Parameter			
short circuit current (mA/cm^2)	35.8	35.4	34.2
open circuit voltage (mV)	591	598	581
fill factor (%)	76.6	77.7	78
efficiency (%)	16.2	16.4	15.5

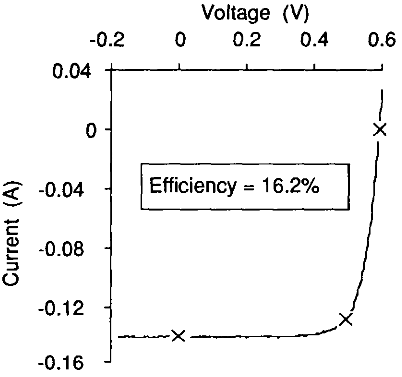


Figure 7. Illuminated I-V characteristics of a 4 cm^2 solar cell fabricated with RTD boron emitter and with RTO surface passivation.

Conclusion

Rapid thermal diffusion of boron into silicon has been investigated from APCVD deposited silicates. RTO of these heavily doped shallow junctions has been studied for possible application of RTP technology for solar cell processing. Highly efficient devices have been fabricated on n-type CZ silicon by combining RTD and RTO. A well-optimized RTP technique can replace conventional furnace processes, resulting in a considerably low thermal budget process and, at the same time, yielding highly efficient devices.

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