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# Silicon gettering: Some novel strategies for performance improvements of silicon solar cells

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This paper reports the recent performance improvements in crystalline silicon solar cells. These have been achieved by a combination of two mechanisms. One is related to the solar cell design which consists of grooving silicon substrates to obtain a structure suitable to perform an efficient gettering process. The proposed structure consists of buried emitter contacts rear locally diffused. Chemical-vapour etching has been used in the process sequence both to realize buried contacts and opening periodic arrangement of small deep grooving holes, for local aluminum diffusion. The second consists to perform a gettering sequence by Rapid Thermal (RT) heat treatments of *p*-type silicon in an infrared furnace, in controlled silicon tetrachloride ($SiCl_4$) and $N_2$ gas atmosphere. The resulting silicon shows an increase of minority drift mobility determined by Hall Effect to reach 1417 cm$^2$ V$^{-1}$ s$^{-1}$, and a decrease in resistivity over 40 $\mu$m on both sides of silicon substrates. Moreover, Light Beam Induced Current (LBIC) investigations show an improvement of diffusion bulk lengths ($L_n$) to ward 210 $\mu$m as compared to silicon starting substrates.


## 1. Introduction

Two of the challenges of present-day semiconductor technology are the development of a device design and gettering technique, that are compatible with silicon based industry. Concerning the field of solar electricity various types of efficient silicon solar cells were proposed. Examples of such cells are the buried contact (BC) cell [1], the passivated emitter rear locally-diffused (PERL) or passivated emitter rear totally-diffused (PERT) cells [2, 3], and the obliquely evaporated contact (OECO) metal-insulator-semiconductor (MIS)–$n^+$ cell structure [4]. However, to improve purity requirements, over eight years several gettering methods have been used to reduce impurities concentrations [5, 6]. In this context, aluminum and phosphorus gettering are widely integrated in the process sequence of silicon solar cell technology [7, 8]. In this present paper, new combined gettering and grooving procedures for solar cells prepared from Czochralski silicon (Cz-Si) have been considered. Gettering has been performed by using porous silicon (PS) as sacrificial thin layer followed by photothermal treatments under silicon tetrachloride /Nitrogen ($SiCl_4/N_2$) atmosphere. The investigated solar cell structure was done using chemical vapour-etching from $HNO_3$/HF based solutions, as grooving tool [9]. It was outlined, that the novel purification process enhance most importantly the mobility of majority carriers and the bulk diffusion length as regard to starting silicon material.

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## 2. Experimental procedures

### 2.1. Gettring

The starting material is Cz solar grade (SG), (100) oriented, *p*-type boron doped silicon wafers, with a resistivity ranging from 1 to 3 Ω cm and a thickness of about 450 $\mu$m. A thin porous layer was elaborated on both sides of the sample using the stain-etching technique in a (HF (40%): $HNO_3$ (65%): $H_2O$) solution with (1:3:5) volume composition. The next step consists to heat samples in an infra-red furnace under $SiCl_4/N_2$ atmosphere at various temperatures (from 850 to 1000°C) and for various annealing durations (from 30 to 90 min). After this step, the samples were successively steeped in diluted HF solution, to remove oxide, and NaOH to remove the sacrificial PS layer acting as getter region. Finally, Van Der Pauw method, Hall effect and Light Beam Induced Current (LBIC) characteristics of Metal/Insulator/silicon (MIS) structures were used to extract bulk diffusion lengths.

### 2.2. Processing sequence of BC rear locally-diffused silicon solar cells

The main features of the cell structure are the periodic deeply grooved holes at the back side and the buried emitter contacts. The CVE method allows grooving silicon substrates with various shapes and sizes. A photosensible resin film was used to mask regions against vapours etching. In Fig. 1, holes with hemispherical shapes were shown. Fig. 2 shows two grooves for buried contacts in monocrystalline silicon. Then, from these micrographs, one can deduce that there is no effect which limits the grooves depth. Hence, it will be recommended to optimize the holes sizes which led the best performances. This cell structure seems to be very suitable to an effective gettering step according to the procedures given in Section 2.1 under the optimized conditions. It may be possible to purify the entire active cell areas including the emitter and a large part of the base, according to the purified depth ensured by PS/ $SiCl_4/N_2$photo-thermal gettering. The Al-P co-diffusion technique was used to form the emitter and the back surface field of the cell. The aluminum is thermally evaporated; the phosphorus was injected from $POCL_3$ solution in a gas phase, and the co-diffusion was taken out in resistive tubular furnace at temperatures below 850°C. After, the cells were cleaned in HCl acid solution. The *n*- and *p*-grids were made by screen-printing.

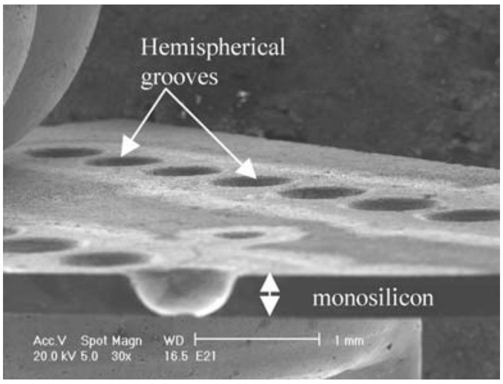


*Figure 1* SEM Cross section view of vapours etching grooved holes from $HNO_3$:HF = 1/2 volume composition.

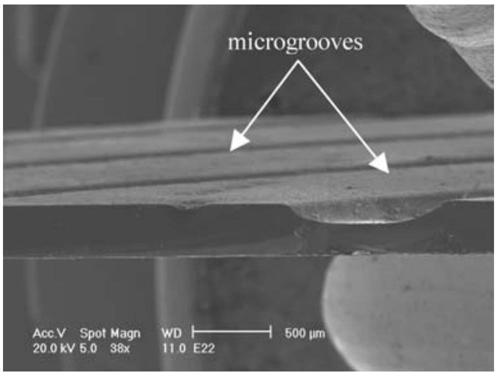


*Figure 2* SEM cross section view of vapours etching grooves for buried contacts.

## 3. Results and discussions

After removing the porous silicon the resistivety was measured using Van Der Pauw method. Fig. 3 shows that the resistivity decreased for a sample treated in an infrared furnace at 950°C under $SiCl_4/N_2$ ambient as compared to untreated one, over a depth of about 40 $\mu$m on each side of the wafer. At a first sight, this resistivity reduction could be due to impurities migration, during the process, from the bulk towards the porous silicon layer as has been reported elsewhere [10]. Silicon tetrachloride like chlorine is known to react with metallic impurities (Al, Ca and Mg) [11]. In fact, at high temperatures metallic impurities decomposes silicon tetrachloride to form silicon and metallic chlorides. All metallic chlorides were formed in gas form, and vanish easily. Fig. 4 shows the variation of the mobility as a function of annealing temperature (measured using the Hall effect technique). The results show that the mobility increases by increasing annealing temperature and duration. It reaches a maximum of 1417 $cm^2V^{-1}s^{-1}$for the sample annealed at temperature of 1000°C during 90 min in a $SiCl_4/N_2$ atmosphere. The increasing in mobility is due to the reduction in the impurity concentrations, and the defects concentrations in the material.

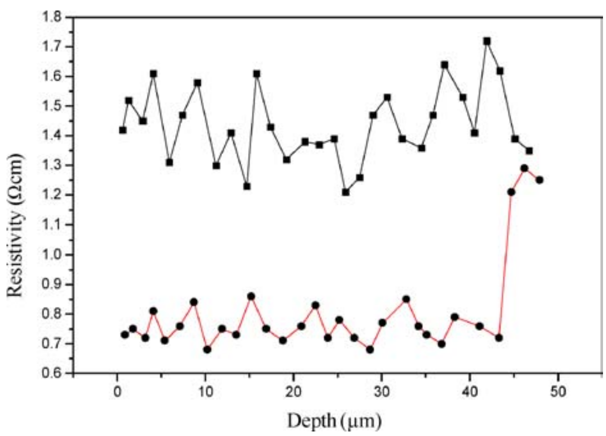


*Figure 3* Variation of the resistivety with depth for an untreated sample (square) and an annealed sample at 950°C for 60 min in $SiCl_4/N_2$ atmosphere (circle).

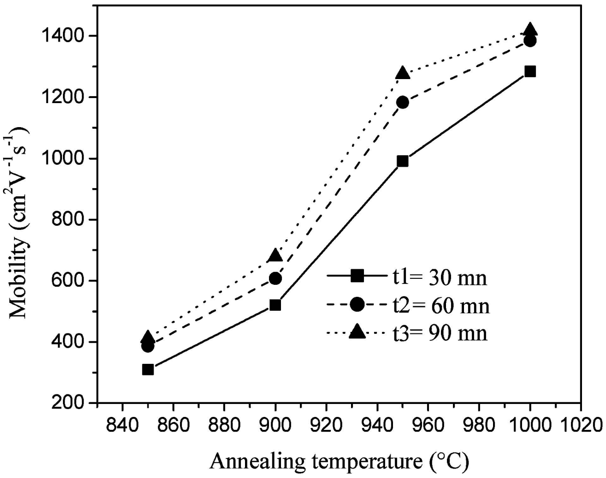


*Figure 4* Variation of the mobility versus annealing temperature for various annealing times under a $SiCl_4/N_2$ atmosphere.

The Table I shows the majority carrier mobility values for four different samples. We observe that an enhancement on the mobility for the third sample due to the diffusion of impurities from the bulk to reach the porous silicon layer where they are localized. For the last sample the addition of silicon tetrachlorine during the treatments has to increase the mobility about tow order compared with the preceding sample. This supplementary enhancement of mobility is due to the reaction of silicon tetrachloride with impurities confined in the porous layer and attraction of additional impurities to the surface.

The diffusion length of minority carriers in samples treated under different conditions is examined by Laser Beam Induced Current (LBIC). Current profiles are recorded in planar configuration. Results show a clear improvement of photo-current if samples are treated in

TABLE I The effect of different treatment conditions on the mobility of majority charge carriers

| Sample number | Treatment conditions | Mobility ($cm^2\ V^{-1}\ s^{-1}$) |
|---|---|---|
| 1 | Untreated sample | 97.7 |
| 2 | Sample without porous layer treated at 1000°C in $N_2$ atmosphere for 90 mn | 132 |
| 3 | Sample with porous layer treated at 1000°C in $N_2$ atmosphere for 90 mn | 709 |
| 4 | Sample with porous layer treated at 1000°C in $SiCl_4/N_2$ atmosphere for 90 mn | 1417 |

TABLE II The effect of different treatment conditions on the bulk diffusion lengths

| Sample number | Treatment conditions | Diffusion length ($\mu$m) |
|---|---|---|
| 1 | Untreated sample | 86 |
| 2 | Sample without porous layer treated at 1000°C in $N_2$ atmosphere for 90 mn | 150 |
| 3 | Sample with porous layer treated at 1000°C in $N_2$ atmosphere for 90 mn | 180 |
| 4 | Sample with porous layer treated at 1000°C in $SiCl_4/N_2$ atmosphere for 90 mn | 210 |

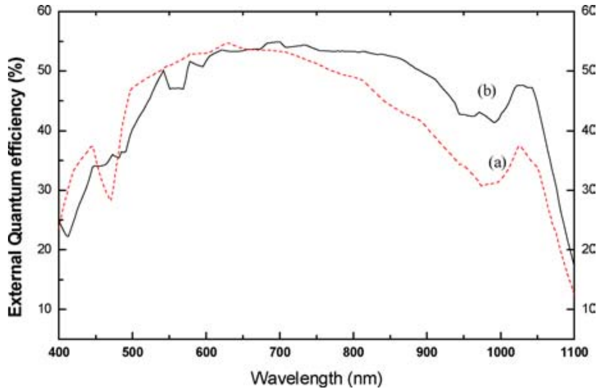


*Figure 5* External Quantum Efficiency; (a) untreated cell, (b) gettered cell.

$SiCl_4/N_2$ atmosphere (Table II) and when the annealing duration is increased. The values of the bulk diffusion are extracted by adjusting the theoretical LBIC profiles to experimental ones [12]. The external quantum efficiency investigations show an enhancement of photo generated electron in the base regions Fig. 5. These improvements may be due to the increase of intrinsic bulk diffusion lengths of photo-generated electron in the base region.

## 4. Conclusion

Novel gettering and grooving procedures for buried contact rear locally-diffused (BCRL) for crystalline silicon solar, are considered. Gettering was performed by PS formation on both sides of $p$-type silicon substrates followed by photo-thermal treatments under $SiCl_4/N_2$ ambient. The porous silicon layer may create an efficient getter region for impurities localization. The improving influence of the treatments on bulk diffusion length and mobility of majority charge carriers to reach 210 $\mu$m and 1410 $cm^2V^{-1}s^{-1}$ respectively with an annealing temperature of 950°C for 90 min. However, more investigations will be required to explain the enhancement, such as deep level transitions spectroscopy (DLTS) and Hall Effect for various experimental measurement temperatures. For silicon solar cells qualitative enhancement was shown. The effect on BCRL not yet optimized, we think that more enhancement may be achieved with an adequate process, taking into account the proposed cell structure.

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