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To cite this version:

HAL Id: jpa-00249386
https://hal.archives-ouvertes.fr/jpa-00249386
Submitted on 1 Jan 1995

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Post-Diffusion Gettering Effects Induced in Polycrystalline Silicon

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(Received 19 December 1994, revised 15 March 1995, accepted 10 May 1995)

Résumé. — Nous avons effectué des “post-recuits” (900 °C/45 min) sur des échantillons de silicium multicristallin à larges grains après une diffusion de POCl₃ à différentes températures. Nous avons étudié pour la première fois l’effet de la température d’introduction des échantillons dans le four (starting température $T_s$) et la température de trempe $T_q$ sur l’efficacité de l’effet “getter” dans le silicium multicristallin. Le meilleur choix de l’optimisation des paramètres du cycle thermique tels que : la température d’introduction d’échantillons $T_s$, la vitesse de montée en température, la température et la durée du plateau, la vitesse de refroidissement en condition de trempe thermique et la température de diffusion du POCl₃ ; il en résulte une très importante amélioration de la longueur de diffusion des porteurs minoritaires dans la base de l’ordre de 275 % (35 à 160 µm). Cet accroissement de la longueur de diffusion s’accompagne d’une redistribution du profil de phosphore.

Abstract. — Large grain polycrystalline silicon wafers have been subjected to post-annealing (900 °C/45 min) after POCl₃ pre-diffusion at different temperatures. For the first time we have investigated the effect of the furnace starting and quenching temperature on the gettering efficiency. The optimisation of thermal cycle parameters include the determination of the best combination of starting temperature, of post-annealing, heating rate, cooling rate, post-annealing temperature (duration), quenching temperature and POCl₃ diffusing condition result in an increase by 275% of the minority carrier diffusion length. The second advantage of this post-annealing is the improvement of the homogeneity of activated phosphorus distribution and of the electrical properties.

1. Introduction

In polycrystalline silicon solar cells processing extra steps have to be performed in order to enhance the minority-carrier diffusion length in the bulk ($L_n$) and in order to reduce the effects of the low quality material [1-4].

Polycrystalline silicon contains a large quantity of crystalline defects and impurities so that we can have a significant degradation of the excess-carrier lifetime through the introduction of recombination centers.
The involved impurities frequently include metals as well as oxygen and/or carbon. Defects and impurities can affect also, if they are present in large concentration, the electrical properties of solar cells by increasing the shunt current or excess junction current. The manufacturing of solar cells of acceptable efficiency from such materials requires processes that take into account this particularity and which can improve defective and contaminated materials. The diffusion length in silicon substrate is small due to the large density of grain boundaries and to the presence of intergrain point and line defects, where potential cost reduction can be traded of against degradation of cell performance. Moreover, metallic impurities dissolved in the bulk or segregated at grain boundaries, may be removed by gettering steps [5]. Gettering refers to a thermal process step that removes impurities from the active regions of the device to less important regions.

Typically, gettering requires several actions to occur. First, the unwanted impurities must be placed into solid solution in the crystal, next, they must be mobile and finally, gettering sites must be provided which are in less important regions of the device and that can capture the impurities. Phosphorus gettering is an efficient mean to improve P- type silicon wafers and to get electron diffusion length greater than 150 μm, in spite of the presence of extended crystallographic defects. The heavy P- diffusion is also effective in gettering metallic impurities [6], this diffusion is accompanied by a supersaturation which can extend into the bulk far away of the normal phosphorus diffusion. In this paper we have focused our attention on thermal treatment performed after a POCl₃ diffusion and in particular on the starting temperature of post-annealing step, heating and cooling rate, in order to reach our ultimate yield of the highest attainable efficiency close to the values reported for a monocrystalline substrate. A very important additional benefit due to the starting and quenching temperature of post- annealing is observed.

2. Experiment

Our study was carried out on 2.5 × 2.5 cm² P-type low quality polycrystalline silicon (35 μm < Lₙ < 45 μm) with thickness of about 320 μm and resistivity of 0.8 Ω cm. The samples were initially pre-diffused with POCl₃ gas at low temperature (800 °C during 80 min, 825 °C during 30 min and 850 °C during 20 min). Before and after annealing, the samples were cleaned by 10% HF for 5 min. Diffusion length (Lₙ) measurement were performed on the cells before and after post-annealing by the surface photovoltage technique (SPV).

The result of the Lₙ measurement after the POCl₃ pre-diffusion confirms the poor quality of the starting material as the Lₙ values are close to 40 μm. The evolution of annealing temperature of n⁺p⁺ structures in the furnace is shown in Figure 1. Tₛ is the starting temperature at which we introduce the sample in the furnace at time t₀, Tₘ is the ambient temperature and (A.B.C.D) are the different parts of the thermal cycle. In this study we have fixed the heating rate (AB segment of the cycle ) at 10 °C/min and the temperature of the post-annealing is stabilised at 900 °C during 45 min (BC segment). The cooling rate is 2 °C/min (CD segment). All thermal treatments were carried out under an argon atmosphere.

3. Results and Discussions

Figure 2 shows the influence of the starting temperature (Tₛ) of post-annealing for n⁺p⁺ structures from Tₛ = Tₘ (Tₘ = 28 °C) to Tₛ = 900 °C. We can observe two regimes of starting temperature. (i) When the starting temperature is below 700 °C, a strong improvement of Lₙ is achieved. This improvement depends lightly on POCl₃ diffusing temperature. The improvement percentage of minority carrier diffusion length is 275%, 260% and 200% for pre-diffusing...
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**Fig. 1.** Illustration of the temperature cycle in the furnace.

**Fig. 2.** Effect of starting temperature on diffusion length of POCl₃ pre-diffused polycrystalline silicon (annealing temperature and duration 900 °C/45 min, heating rate 10 °C/min and cooling rate 2 °C/min).

Temperature of 850 °C, 825 °C and 800 °C, respectively. In this region of $T_n$ the minority-carrier diffusion length is practically constant for all the diffusing temperature. This interesting result can probably be explained by the high generation of gettering sites well adapted for most of the metallic impurities and others. The improvement percentage of $L_n$ which increases from 200% (POCl₃, 800 °C/80 min) to 275% (POCl₃, 850 °C/20 min) is explained by the increase of the phosphorus concentration during the pre-diffusing step determined by SIMS measurements from $1.2 \times 10^{21}$ At/cm² (POCl₃, 850 °C/20 min) to less than $5 \times 10^{20}$ At/cm² (POCl₃,
Our results are comparable to those found by Perichaud and Martinuzzi [7]. For a lower diffusing temperature, the phosphorus diffusion was not sufficiently heavy to produce a maximal gettering. In case of pre-diffusion temperature of 850 °C/20 min, the solubility limit is reached so that precipitates are present to enhance the gettering effect. To explain this high gettering efficiency different mechanisms have been presented, the enhanced solubility of metallic impurities, which act as acceptors, and their enhanced pairing with phosphorus within the highly P-doped layer [8, 9]. The solubility of metallic impurities such as Au and Cu is increased with dopant concentration trough enhanced metal-solid solubility by Fermi level and ion pairing. Compound formation between metal and phosphorus atoms also enhances the solubility of some metallic impurities as Au. It has been reported that a Au$_2$P$_3$ and Cu$_2$P$_3$ compound are observed in highly P-doped silicon [10, 11]. Ourmazd and Schroter [12] have found that NiSi$_2$ particles are closely associated with the SiP particles and are most frequently observed in regions containing a high density of SiP particles. They proposed that phosphorus causes SiP particles formation which, due to a volume expansion, leads to a large emission of silicon interstitials. This high improvement of $L_n$ suggests that the heavy phosphorus doping dissolves metal precipitates, in agreement with Cerofolini [13]. The post-thermal annealing of heavy phosphorus doped polycrystalline silicon is required in order to make the segregation more efficient and to move metal impurities into the phosphorus-doped $n^+$ regions. A maximum gettering efficiency results from the association of higher generation of gettering sites ($T_s < 700$ °C) and higher phosphorus concentration. (ii) When $T_s$ is above 700 °C we show a decrease of $L_n$ for all POCl$_3$ pre-diffusing temperature. The percentage of gettering efficiency decreases also more rapidly for the lower pre-diffusing temperature than for the higher one. This gettering efficiency decrease can be explained by the absence of desactivation of some trapping states when $T_s$ is above 700 °C, the nature of these trapping states are not identified at this moment. Figure 3 shows the effect of the quenching temperature ($T_q$) of post-annealing for $n^+pn^+$ structures from $T_q = 900$ °C to $T_q = T_m$.
Fig. 4. — Distribution of diffusion length in P-diffused polycrystalline silicon before and after post-annealing (starting temperature = 28 °C, heating rate 10 °C/min, post-annealing temperature and duration 900 °C/45 min, cooling rate 2 °C/min, POCl₃ diffusing temperature and duration 850 °C/20 min).

We found that minority carrier diffusion length is strongly improved when \( T_q \) is below 700 °C, this improvement depends on POCl₃ diffusion temperature, the maximal gettering efficiency is obtained for POCl₃ diffusing temperature and duration of 850 °C/20 min. When the quenching temperature is above 700 °C, gettering efficiency decreases with increasing the quenching temperature. After a high temperature step the metallic impurities are in super saturation, the fast diffusing ones (e.g., Co, Cu, Ni) have enough time to precipitate and to form inactive complexes, whereas the slow diffusing ones (e.g., Mo, Ti, V, Cr, Fe) are frozen in electrically active sites in the quenching step. The notion “slow” and “fast” depends on the quenching temperature and the speed.

One method of gettering reported in the literature uses dislocations intentionally introduced, with the assumption that impurities could be bound at the dislocations [14]. In polycrystalline silicon, gettering may be enhanced by diffusion of phosphorus down grain boundaries which will increase the effective gettering surface area. To verify this explanation pre-diffused CZ-Si (POCl₃, 850 °C/20 min) was post-annealed at 900 °C/45 min . The result shows that there is only about 40% (110 to 154 \( \mu m \)) improvement of \( L_n \) (275% for polycrystalline silicon). This result shows that a maximal gettering sites are generated in grain boundaries.

The distribution of bulk diffusion length have been studied before and after the post-thermal treatment on many samples and for many positions of the probe in order to increase the statistic. By this way, we have such a map of the evolution of the homogeneity of the electrical parameters of the material.

In figure 4 we show the effect of the post-thermal annealing on the redistribution of the bulk diffusion length. We can observe that the standard deviation (\( \delta \)) is largely reduced after the post-thermal treatment confirming that the homogeneity of doping and the distribution of diffusion length values are better in such bad polycrystalline material after this post-annealing treatment.
4. Conclusion

In this paper, we have demonstrated that high improvement of bad quality polycrystalline silicon can be achieved by a proper choice of the post-thermal annealing conditions. The high improvement of bulk diffusion length (275%) is achieved when the starting and quenching temperature of the post annealing treatment are below 700 °C, the heating rate fixed at about 10 °C/min, the post annealing temperature and duration of the cycle is chosen in the order of 900 °C/45 min for a cooling rate of 2 °C/min and a POCl₃ pre-diffusing temperature and duration of 850 °C/20 min. By this, we can transform a poor polycrystalline silicon in a better material close to monocrystalline silicon.

References