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Investigation of the dopes segregation at the grains boundaries of polycrystalline silicon films for photovoltaic application

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Abstract

The mechanism of the dopes segregation supposes the accumulation of a part the dope at the grain boundaries where it becomes electrically inactive. More over the dopes segregation induces important structural changes in the material constituent the grains boundaries, by reducing the bounding forces between the atoms, by favouring the concentrations of constraints and by preventing the vanishing of dislocations. In this work we investigate the dopes segregation at the grain boundaries in the polycrystalline silicon films. The obtained results have shown that the heat treatments before and/or after implantation reduce the number of segregation sites at the grains boundaries, and consequently they limit the structural changes that can appear and the quantity of dope atoms that can accumulate in these boundaries. In addition they are more more supplementary dope atoms that are found inside the grains when the temperature of the heat treatment increases. On the other hand, we established that arsenic atoms have a strong tendency to the segregation than the bore atoms, and we have noticed a strong migration of arsenic atoms from the boundaries towards the grains under the effect of the heat treatments. More over it was found that the concentration of arsenic atoms in the boundaries \( N_{GB} \) is more and more high when the doping increases. However the ratio \( N_{GB} / N \) relative to the dope average concentration decreases.

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1. Introduction

The polycrystalline silicon material finds numerous applications in the technologies of microelectronic components fabrication [1], in the integrated circuits and photovoltaic generators [2]. The circuit complexity and the more and the more high degree of component integration require continuous improvement and the mastery of this type of material [3-7]. In many of its applications, this material is subjected to various heat treatments in order to reduce the defects and allow the implanted ions to occupy positions where they are electrically active. The electrical

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parameters of the photovoltaic generators are limited by the grain boundaries [8,9], which possess incomplete bonds that can represent trap states to the minority carriers. The improvement of the photovoltaic parameters requires the increase of the grain size and consequently the reduction of the grain boundaries. This process can improve the photovoltaic efficiency of the solar cells produced from this material. In this work we are interested in the study of the dopes segregation at the grain boundaries in the polycrystalline silicon films doped with bore and/or arsenic and subjected to different heat treatments.

2. Experimental conditions

In order to study the influence of the heat treatments on the dopes segregation in the polycrystalline silicon, measurements of the Hall Effect and resistivity were carried out on Si-poly films whose thickness is 6880 Å. These films were doped with bore \(10^{15}\) cm\(^{-2}\) and arsenic \(10^{15}\) cm\(^{-2}\) by ionic implantation. Heat treatments were carried out before and after implantation respectively at the temperatures of 1000 to 1150 °C during 120 mn and from 1050 °C to 1200 °C during 30 mn.

3. Results and discussions

The dopes segregation mechanism supposes the accumulation of a part of the dope at the grains boundaries where it becomes electrically inactive. This mechanism lead to the reduction of dope concentration in the silicon polycrystalline films in comparison with that of a silicon monocrystal similarly doped.

The dopes segregation is a very important mechanism that should be taken into account in the interpretation of the electrical proprieties of the polycrystalline silicon, particularly for the high doping where the carriers trapping effect becomes negligible.

The dopes segregation induces important structural changes in the material constituting the grain boundary [10], by reducing the bonds forces between the atoms, by favoring the concentrations of constraints and by preventing the vanishing of dislocations [11]. If we admit, on the one hand that annealing after implantation that we have carried out allow the dope atoms in the grain to take position in the substitution sites, and on the other hand that all these atoms are ionized at 293 °K the concentration of the dope atoms at the grains boundaries will be equal to the difference between the total concentration and that of the ionized atoms (atoms in the grains)

\[N_{GB} = N - N_G = N - N_{GI}\] (1)

More over the concentration of the ionized atoms is equal to the sum of the concentrations of the free carriers and the trapped carriers

\[N_{ci} = n + n_i = n + \frac{N}{L}\] (2)

The apparent concentration of the free carriers was obtained by Hall Effect measurements for different heat treatments before and/or after implantation. Thus we have to determine the concentration of the trapped carriers for these same heat treatments.

For grains partially deserted from carriers and states traps entirely filled, the height of the barriers of potential of the deserted regions is given by [12]:

\[E_d = \frac{9}{8eN}Q^2\] (3)

While replacing \(Q\) by \(N_1\) and \(N\) by \(N_{GI}\) in the equation (3), one obtains the expression of the density of the trapped carriers:

\[N_1 = \left(\frac{8eN_{GI}E_d}{q_1^2}\right)^{\frac{1}{2}}\] (4)

If we substitute (4) in (2), one obtains a quadratic equation in \(N_{GI}\) whose resolution gives the expression of ionized atoms concentration:
By comparing (2) and (5), we deduce the expression of trapped carriers’ concentration:

$$n_t = \frac{4eE_d}{q^2L^2} + \frac{2}{qL^2} \left[ 2n\pi L^2 E_d + \frac{4e^2E_d^2}{q^2} \right]^{\frac{1}{2}}$$

The resistivity is given by the expression [13]:

$$\rho = \left( \frac{2\pi K T m_d}{q^2 N_{GI} L} \right)^{\frac{1}{2}} \exp\left( -\frac{q\Phi_g - q\Phi_d}{K T} + \frac{d_1 \exp(-b_1)}{1 - c_1 K T} a_1 \right)^{-1} \exp\left( \frac{E_d}{K T} \right) + \rho_n \left( \frac{T_1}{T} \right)^{\gamma} \frac{L - 2W_d - W_{gb}}{L}$$

The concentration of the trapped carriers for different heat treatments is obtained after the determination of the potential barrier height of the deserted regions $E_d$ from the characteristics $\log \rho = f\left( \frac{1}{T} \right)$ [14] using equation (7).

In figures 1 and 2, the diminution of the resistivity when the annealing temperature before and/or after implantation increases can be explained by the grains growth.

The strong diminution of the arsenic doped films, show that they are many more arsenic atoms which pass from the grain boundaries towards the grain when the annealing temperature before and/or after implantation increases, than in the case of the bore doping.
Figures 3 and 4 show the reduction of the dope atoms in the grain boundaries when the temperature of the heat treatments before and/or after implantation increases. Indeed the heat treatments reduce the number of segregation sites at the grains boundaries, and consequently, the quantity of the dope atoms that may accumulate in these boundaries. We have noticed that there are more and more supplementary dope atoms that are found inside the grains when the temperature of the heat treatments increases. On the other hand we established that the arsenic atoms have a strong segregation tendency at the grains boundaries than the bore atoms, and we have noticed a strong migration if arsenic atoms from the boundaries toward the grains under the effect of the heat treatments. The segregation of arsenic atoms at the grains boundaries is about 4 times higher than that of the bore atoms. For the bore doping the dopes concentration in the grains is always greater than the dopes concentration that are found at the grains boundaries, whatever the heat treatment temperature. In the case of the arsenic doping we noticed that there are many more arsenic atoms at the boundaries than inside the grains for annealing temperature before and/or after implantation respectively lower than 1100 °C and 1150 °C. The increase of the free carriers concentration with the temperature of the heat treatments before and/or after implantation is due to two effects; the reduction of the trap states and the segregation sites, leading to the freeing of some carriers and the diminution of the quantity of dope atoms at the grains boundaries.

However the increase of the dope concentration in the grains with these same temperatures can be attributed only to the reduction of dope quantity at the boundaries. We establish that the heat treatment before implantation reduce the number of dope atoms in the boundaries.

In the case of the films thermally treated after implantation, we establish a linear increase of the dope atoms proportion in the grains with the temperature, for the two kinds of the dopes (arsenic and bore). For the films thermally treated before implantation, the increase of the dope atoms proportion in the grains is low for temperatures below 1050 °C, then becomes more pronounced for the too higher temperatures. The low variation, in the range 1000-1050 °C is explained by the heat treatment effect after implantation ( 1100 °C;120 mn), which increases the size of the grains, reduces the volume of the boundaries and displaces the dope atoms from the boundaries towards the grains. On the other hand its effect on the films that were treated before implantation at T>1050 °C is negligible. Mei and Dutton [15] have shown that the dopes segregation at the grains boundaries diminishes in one hand with the thickness of the polycrystalline silicon film, and on the other hand with the increase of the grains size. Indeed, the growth of the grains, when the thickness of the film increases or under the effect of a heat treatment at high temperature [16], reduces the total volume of the boundaries, and consequently the density of the segregation sites.
Figure 4: Concentration of the dope atoms in the grains (NG) and at the grains boundaries (NGB) vs annealing temperature after implantation. Average doping Concentration: $1.54 \times 10^{19}$ cm$^{-3}$ duration of annealing after implantation: 30 mn

NG et NGB [cm$^{-3}$] vs annealing temperature after implantation [°C]

3: Concentration of dope atoms in the grains ($N_G$) and at the grains boundaries ($N_{GB}$) vs annealing temperature before implantation.

Figure 4: Concentration of the dope atoms in the grains ($N_G$) and at the grains boundaries ($N_{GB}$) vs annealing temperature after implantation.

4. Conclusion

The heat treatments before and/or after implantation reduce the number of segregation sites at the grains boundaries, and consequently, they limit the structural changes that can appear there and the quantity of dope atoms that can accumulate in these boundaries. In addition, there are more and more supplementary dope atoms that are found inside the grains when the temperature of the heat treatments increases. On the other hand, we established that
the arsenic atoms have a strong segregation tendency at the grains boundaries than the bore atoms, and we have noticed a strong migration of arsenic atoms from the boundaries towards the grains under the effect of the heat treatments. The segregation of arsenic atoms at the grains boundaries is about 4 times higher than that of the bore atoms.

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