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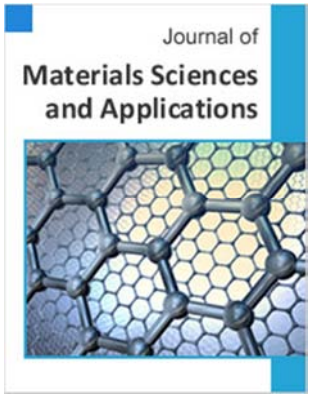

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Simulation of Multi-Plateau-Temperature Process Intended for Simultaneous Gettering of Chromium, Iron and Nickel in Silicon

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Abstract
In this paper, computational results of simultaneous gettering of chromium (Cr), iron (Fe) and nickel (Ni) in p-type silicon by phosphorus diffusion are presented. The study was carried out by a software tool "GetProg" developed in our centre CRTSE. Simulated aspect includes impurity diffusion, segregation and also precipitates dissolution phenomenon. The kinetics of dissolved impurities gettering has been described by a diffusion-segregation equation (DSE) extended by precipitates dissolution term. The input initial parameters of metals in material were mainly taken from experimental results obtained for sheet multicrystalline silicon. The simulation allowed the study of the simultaneous behaviour of Cr, Fe and Ni during an optimized multi-plateau-gettering process (MPG). Two MPG scenarios have been investigated; High-Low and Low-High temperature. The findings demonstrate that the MPG effectiveness of studied metals depends significantly on the nature of metal and its initial concentration, as well as the used MPG scenario.

1. Introduction

Both upgraded-metallurgical grade (UGM) and solar grade (SoG) silicon destined to solar cells fabrication contain various kinds of metal impurities such as Cr, Fe, Ni and Cu, with concentrations vary generally between 10^{12} cm^{-3} and 10^{17} cm^{-3}. The presence of such impurities in the material create deep level states in band gap, and generate lifetime killing recombination centers and junction leakage currents [1-4]. Consequently, an important degradation in the efficiency potential of solar cells will be seen [5, 6].

Nevertheless, most metallic impurities dissolved or precipitated can be more or less removed from the bulk of material, using extrinsic gettering technique. It refers to a thermal process step that dissolves the metallic precipitates and activates the diffusion of dissolved metals from the bulk to a high solubility surface region. This later can be generally created by phosphorus diffusion (n^+), boron diffusion (p^+), and / or by aluminium-silicon (Al-Si) alloying [7-15].

Currently, the most well studied metal contaminant in silicon is iron (Fe), and this is due to its obvious high lifetime-killing effect. Beside experimental works, different kinetics process simulation tools have been developed to engineer its distribution and investigate its behaviour in the material during gettering process [16-19]. Chromium (Cr) is also a well-known detrimental impurity in silicon, impacting silicon based solar cells performance even at concentrations as low as 10^{10} cm^{-3} [20-22]. Its acceptable total concentration in a p-type silicon wafer is around 10^{13} cm^{-3}, which is lower by one order of magnitude comparing to iron [23]. Furthermore, the harmful effect of Cr in silicon can be especially observed in its interstitial state (Cr_i), where the capture cross-sections are 1.5 and 57 times larger than iron in p- and n-type silicon, respectively [21].

Like iron and chromium, nickel is one of the more thoroughly investigated contaminant metals. It is known to be a fast diffuser with high solubility in Si. In spite of intensive research made on this metal, its electrical properties are poorly understood and the existing data on its energy levels and its recombination activity are still controversial [24]. The fraction of electrically active Ni in Si is about 1% of the respective solubility, with a mid-band gap energy level at E_c-0.4eV and $\sigma_n = 5.6 \times 10^{-17}$ cm^2 (case of p-type Si) [25]. Its majority carrier capture cross section was found to be in the range 10^{-16} - 10^{-17} cm^2 both in p- and n-type silicon [26, 27].

Despite the detrimental effects of chromium and nickel in Si, they have not sufficiently investigated as much as iron, especially, during processing steps. Moreover, the majority of published works dealing with this subject metal by metal and separately.

In this paper, we investigated by simulation, using our software tool "GetProg", the feasibility of simultaneous segregation gettering of chromium, iron and nickel in p-type silicon. The effectiveness of High-Low and Low-High multi-plateau-gettering processes (MPG) has been studied and evaluated through the fundamental electron lifetime. This study is the perspective of our work previously presented [28].

2. Simulation

The model used for the simulation describes the variation of interstitial impurity concentration C_i as a function of the depth, the time and also the gettering process temperature. It refers to a space-time differential equation that quantifies the segregation and the dissolution of precipitates phenomenon. The kinetics of gettered impurity is described by a diffusion segregation equation (DSE) [29] extended by an additional term which describes the dissolution of impurity precipitates [30], as shown in equation (1) below

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left[D\left(\frac{\partial C_i}{\partial x} - \frac{C_i}{m}\frac{\partial m}{\partial x}\right)\right] + 4\pi D N_p r_p\left(C_{eq} - C_i\right) \quad (1)$$

The first term, introduced by Tan et al. [31], gives the evolution of dissolved impurity concentration in the bulk (C_i) having the diffusivity D and the segregation coefficient m. The second term known as Ham's law [32] represents the dissolution of precipitated impurity atoms with a precipitate density N_p and a radius r_p. C_{eq} is the solid solubility of dissolved metallic impurity in silicon. The segregation coefficient used in our simulation describes the metal segregation into phosphorus diffusion region rich in phosphorus-vacancy complex (P_4V). It can be given by the following formula [8]:

$$m(P_4V) = 1 + K_{P_4V}\,[P_4V] \quad (2)$$

where K_{P4V} is an equilibrium constant related to the formation energy (E_b) of M-P_4V clusters. The values of formation energy of Cr-, Fe- and Ni-P_4V used in this study are 1.99 eV, 1.52 eV and 1.92 eV, respectively [33].

More details on the segregation coefficient, diffusivity, solid solubility and as well as the approximation done to simplify the calculation can be found in Ref. [30-36].

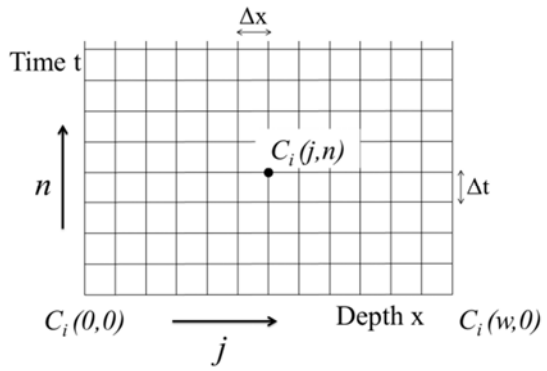

Figure 1. *Finite element mesh platform used in the simulation.*

Using the finite element mesh platform shown in Figure 1, a numerical resolution of equation (1) led to follow the variation of dissolved metal concentration $C_i(x, t)$ as a function of the depth x, time t and temperature T of the gettering process. Assuming that the initial dissolved metal concentration $C_{i0}=C_i(x, 0)$ is uniformly distributed along the silicon wafer thickness, the initial and boundary conditions used in the resolution of equation (1) can be, respectively, given as following

Initial condition:

$$C_i(x, t = 0) = C_{i0} \quad (3)$$

Boundary conditions:

$$\begin{cases} m\frac{\partial C_i(x=0,t)}{\partial t} = D\frac{\partial C_i(x=0,t)}{\partial x} \\ D\frac{\partial C_i(x=w,t)}{\partial x} = 0 \end{cases} \quad (4)$$

The approach used in this simulation is based on an explicit method, which is conditionally stable verifying equation (5). Therefore, the choice of adequate space-time parameters is indispensable to perform a stable simulation with reduced error.

$$D\frac{\Delta t}{(\Delta x)^2} \leq \frac{1}{2} \quad (5)$$

3. Results and Discussion

In our previous study [28], we have compared the influence of annealing temperature on the gettering effectiveness of Cr and Fe in silicon separately and without taking into account the effect of optimized gettering temperature (T_{opt}) of each metal on the concentration of other. In this present investigation, we assume that the material is simultaneously contaminated by Cr, Fe and Ni at different levels. The total initial chromium, iron and nickel concentrations were taken equal to 1.2 x 10^{15} cm^{-3}, 1.4 x 10^{16} cm^{-3} and 4.2 x 10^{15} cm^{-3}, with associated initial precipitate radii of 30 nm, 50 nm and 40 nm, respectively. These concentrations cover the most usual contamination level found in sheet multicrystalline silicon [37]. The as-grown interstitial concentrations are assumed to be 5 x 10^{12} cm^{-3} for all the metallic impurities.

Because each metal can be effectively gettered only at a specified optimum temperature T_{opt}, it's clear that the simultaneous presence of these three metals in material requires a multi-plateau-gettering (MPG) process of three annealing stages. The temperature T_{opt} of each plateau corresponding to a given metal can be more or less influenced by the previous one. Indeed, simulation results illustrated in figure 2 (open symbols) demonstrate that an effective gettering of Ni, Fe and Cr can be only done at temperature ranges; 200-400°C, 400-700°C and 625-775°C, respectively. So, one can note that there is various scenarios to perform a process MPG regarding the first impurity to be gettered.

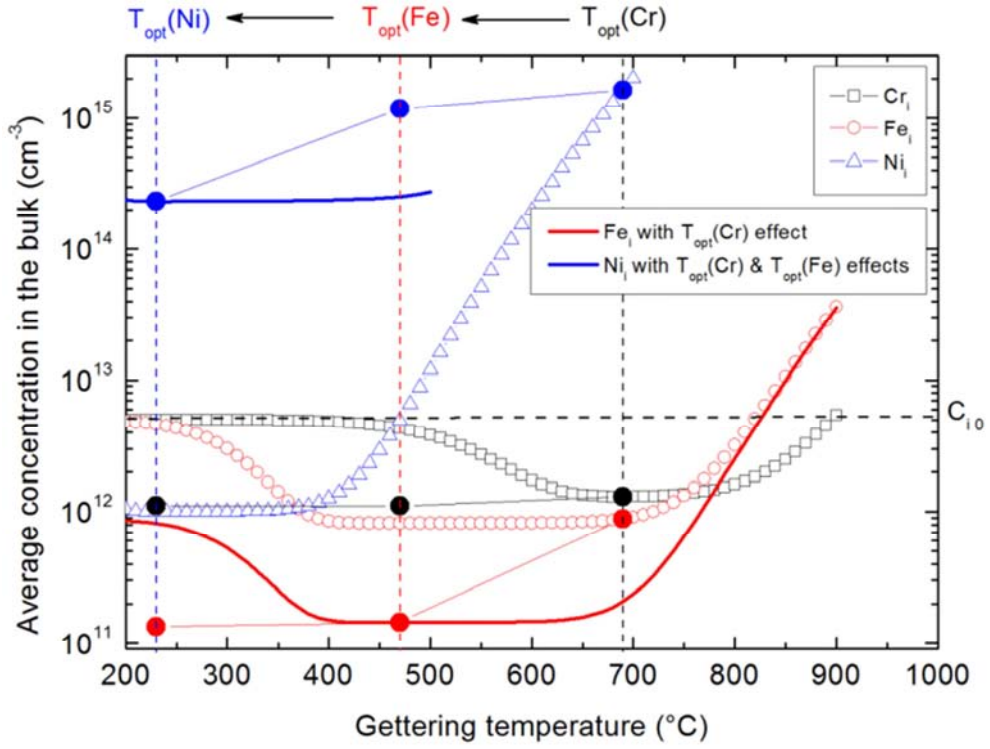

Figure 2. *Evolution of the average concentrations of chromium, iron and nickel in the bulk as function of temperature for High-Low temperature process.*

In the following, we tested by simulation the effectiveness of High-Low and Low-High MPG scenarios during an extended time of 120 minutes. The first one starts by the gettering of Cr at T_{opt}(Cr) situated around 690°C, followed by that of Fe at T_{opt}(Fe) varies typically in the range 400-600°C. This scenario finishes by low temperature ramp T_{opt}(Ni) varies between 200°C and 400°C. In the second scenario (e. g. Low-High), the simulation starts by gettering plateau of Ni and terminates by that of Cr at high temperature. It's important to note that the effect of each plateau on the concentration of the metals and their optimized gettering temperatures have been taken into account.

Figure 3 shows the evolution of average concentrations of interstitial metals in the bulk as function of temperature for High-Low scenario process. The curves in open symbols represent the independent variation of content of each metal, while the curves in lines and closed symbols represent the concentrations variation after different anneal plateaus. In this scenario, the annealing at T_{opt}(Cr)=690°C / 120 min decreases [Cr_i] from 5 x 10^{12} cm^{-3} to 1.3 x 10^{12} cm^{-3}. The effect of this process step on iron and nickel concentrations is notable. Indeed, after this annealing [Fe_i] decreases considerably from its initial value to 8.84 x 10^{11} cm^{-3} indicating a reduction of about 82% of interstitial iron in the material bulk, while [Ni_i] increases to a very high concentration (1.64 x 10^{15} cm^{-3}) which is equal to the limit solubility of nickel in Si at 690°C. This rapid increment of [Ni_i] is due to the dissolution of Ni-Si precipitates during annealing.

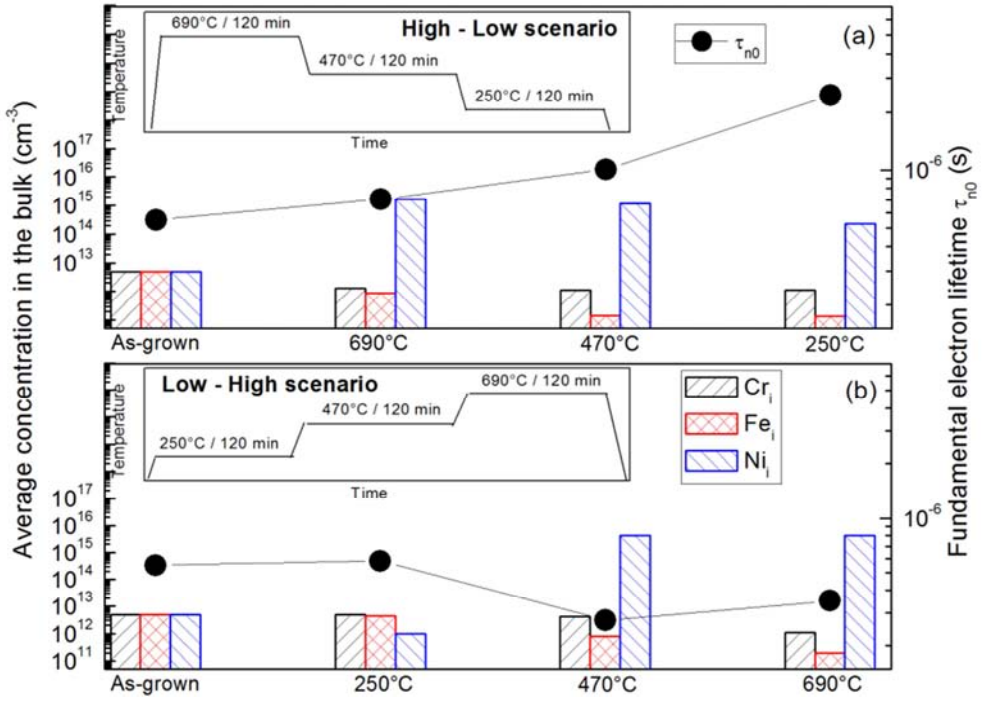

Figure 3. *Variation of the average concentrations of chromium, iron and nickel (coloured bars) and the associated fundamental electron lifetime τ_{n0} (black symbols) as function of optimized gettering temperature for High-Low (a) and Low-High (b) scenarios.*

Taking these concentrations as new initial parameters to use them in the second plateau, the optimum gettering temperature of iron is calculated to be $T_{opt}(Fe)$=470°C with $[Fe_i]$= 1.45 x 10^{11} cm^{-3} (see red line curve). $[Ni_i]$ decreases slightly and an additional decreasing of Cr content has been observed. The third annealing plateau associated to Ni impurity yields a notable diminution of $[Ni_i]$ from 1.18 x 10^{15} cm^{-3} to 2.34 x 10^{14} cm^{-3}, accompanied by a constancy of $[Cr_i]$ and $[Fe_i]$. The final concentrations of Cr_i, Fe_i and Ni_i in the bulk are respectively; 1.11 x 10^{12} cm^{-3}, 1.34 x 10^{11} cm^{-3} and 2.34 x 10^{14} cm^{-3}.

The same simulation is done for Low-High scenario and the findings were compared with those of High-Low scenario discussed above, as shown in figures 3 (a) and (b). Based on this variety of results, one can remark that there is a competition between beneficial and detrimental effects which can be, respectively, observed through the increasing and decreasing of interstitial metal concentration. For both scenarios, all annealing plateaus reduce progressively the iron and chromium content in the bulk indicating an effective gettering, while increase the concentration of interstitial nickel to high level due to the dissolution of Ni-silicide precipitates.

Because of the different carrier capture cross sections of the studied metals, the investigation of electrical propriety of material during the MPG process using only the evolution of metals concentrations is not adequate. So, the investigation can be made by the monitoring of the fundamental electron lifetime τ_{n0}. This parameter is determined throughout the wafer thickness by Shockley-Read-Hall statistics as following [38]:

$$\frac{1}{\tau_{n0}} = \nu_{th} \sum_i C_i \, \sigma_{ni} \qquad (6)$$

where ν_{th} is the thermal velocity of electron, C_i and σ_{ni} are the concentration of interstitial impurity and the electron capture cross section, respectively.

Based on equation (6) and using the metals concentrations obtained by simulation, the variation of τ_{n0} for each scenario is calculated and presented in figures 3 (a) and (b). It is clear that the first scenario yields a progressive improvement of the electron lifetime, while the second one deteriorates it especially at annealing plateaus correspond to iron and chromium gettering. These results demonstrate that a simultaneous gettering of chromium, iron and nickel can be effectively done by series of specified annealing plateaus vary from high to low temperature (e.g. High-Low scenario).

4. Conclusion

Simultaneous gettering of Cr, Fe and Ni in silicon is investigated by simulation. Two multi-plateau-gettering process (MPG) scenarios were used; High-Low and Low-High temperature. The findings demonstrate that the MPG effectiveness of the three impurities together depends significantly on the nature of metals and their initial concentrations, as well as the MPG scenario. High-Low scenario shows a notable improvement in electron lifetime due to effective gettering, while Low-High scenario yields lifetime degradation which is mainly due to the Ni silicide dissolution at high temperatures.

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