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GETTERING EFFICIENCY OF BACKSIDE ALUMINIUM LAYER AND AL-SI-EUTECTIC

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ABSTRACT: Simulations of gettering processes are presented, modelling the gettering effect of Aluminium layers on silicon wafers. Focus is set on the influence of different physical parameters like segregation coefficient, Al layer thickness and structure, and impurity concentration on the Al getter mechanism. This work is the first step towards the optimization of the gettering process of wafers made of alternative feedstock material. The simulations of gettering processes are carried out applying the Sentaurus Process simulator (Synopsis®).
Keywords: Simulation, Gettering

1 INTRODUCTION

At present solar cell production is increasing enormously worldwide. While some time ago the feedstock for solar cell industry could be provided by side branches of the electronic semiconductor industry, pure silicon is becoming a more and more demanded and as a result more and more expensive material. To ensure an ongoing growth of solar cell industry it will be essential to reduce costs of the raw material.

It is one promising approach to forgo the elaborate and high-priced cleaning processes essential for electronic industry and to use less refined silicon as raw material. This so-called Purified Metallurgical Grade (PMG) silicon is expected to be inexpensive to produce and it promises to be applicable for manufacturing solar cells with acceptable cell efficiencies [2], provided suitable processing steps are developed. PMG-silicon wafers contain concentrations of metallic impurities, which, if untreated, would reduce carrier lifetime and thus cell performance drastically. These impurities, for example iron (Fe), copper (Cu) and nickel (Ni), act as recombination centres and thus they severely reduce the minority carrier diffusion length and the cell efficiency.

Aluminium Backside Gettering is an efficient process to reduce concentrations of some of these impurity metals. The intention of the present study is to improve the aluminium getter process for use of PMG-silicon wafers. In spite of the thorough investigations for both, monocrystalline and multicrystalline wafers from usual feedstock [see e.g. 7,8], a series of open questions are to be clarified.

The values for segregation coefficients of impurities between Si and Al reported in literature, range from 10^3 to 10^7 for different impurities and temperatures [1, 6], showing the great uncertainty which is prevailing for this important parameter. A basic question is whether it is necessary to know the exact values in order to be able to effectively optimize this gettering step. The cited values of the segregation coefficient are fairly high, permitting efficient gettering for usual feedstock if the thickness of the Al layer exceeds a few µm. In PMG-silicon, metal impurities (especially Fe) can be found in much higher concentrations. For this reason gettering efficiency may be limited by the thickness of the Al layer. Keeping in mind that thickness is usually restricted to 10 – 20 µm and screen printing paste is used in the industrial solar cell process, we evaluated the Al gettering efficiency for metal concentrations typical of PMG-silicon. A one-dimensional model has been set up including diffusion of interstitially dissolved impurities, segregation at the boundary layer and dissolution of clusters.

2 SIMULATION PARAMETERS

2.1 Diffusivity and solubility

To describe a gettering process, diffusivity and interstitial solubility of transition metal impurities are crucial parameters. The faster a species diffuses, the faster it can reach the Aluminium layer; the better it is solved in the silicon lattice, the faster clusters can be dissolved. Both diffusivity and solubility can be described using Arrhenius functions:

$$D_{El}^{Si}(T) = D_{0,El}^{Si} \cdot \exp\left(-\frac{H_{M,El}^{Si}}{k_B T}\right) \quad (1)$$

$$S_{El}^{Si}(T) = S_{0,El}^{Si} \cdot \exp\left(-\frac{H_{S,El}^{Si}}{k_B T}\right) \quad (2)$$

Here, $D_{El}^{Si}(T)$ is the temperature-dependent diffusion parameter of the element El in Si, $D_{0,El}^{Si}$ is a material-specific diffusion constant, $H_{M,El}^{Si}$ is the migration enthalpy and k_B the Boltzmann constant. $S_{El}^{Si}(T)$ is the temperature-dependent solubility parameter of the element El in Si, $S_{0,El}^{Si}$ and $H_{S,El}^{Si}$ are material-specific constants.

Both quantities depend on two parameters, which are material-specific, and also strongly on the temperature. Increasing temperature means increasing diffusivity and solubility. In the range of typical gettering temperatures, i.e. about 600 °C to 1000°C, diffusivity and solubility vary over several orders of magnitude. Fig. 1 and 2 show examples for the diffusivity and solubility values from literature. [15, 3]

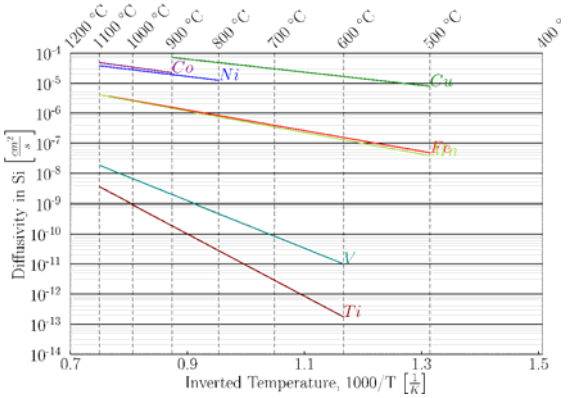

Figure 1: Diffusivity of some 3d-transition metals in silicon.Values are taken from Weber [15] and Graff [3].

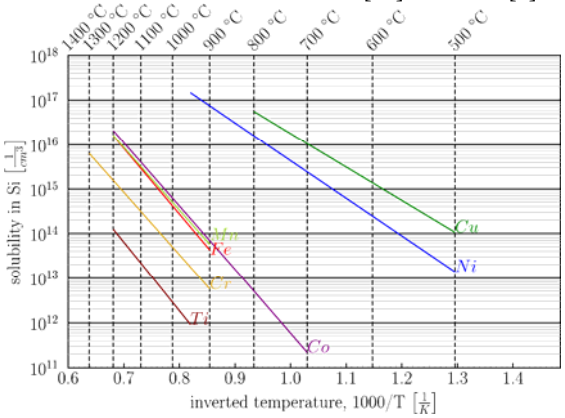

Figure 2: Solubity of some 3d-transition metals in silicon.Values are taken from Weber [15] and Graff [3].

2.2 Segregation coefficient

Another important parameter in the description of gettering processes is the segregation coefficient. It is defined as the ratio of the concentration of impurity in the Aluminium layer and the concentration in the silicon bulk, both in thermal equilibrium:

$$m^{Si-Al}_{(eq),El}(T) = \frac{c^{Al}_{eq,El}}{c^{Si}_{eq,El}} \qquad (3)$$

In recent years, several experiments have been carried out to determine the segregation coefficient quantitatively. Apel et al. [1] state as a lower limit 10^4 for Cobalt (Co) at a gettering temperature of 920 °C, deduced from lifetime measurements; Seibt et al. [14] used radioactive Co and radiotracing methods to determine the segregation coefficient for several temperatures. To their data one can fit the following Arrhenius function:

$$m^{Si}_{(eq),Co}(T) = 6.8 \cdot 10^{-6} \cdot \exp\left(\frac{2.54}{k_B T[eV]}\right) \qquad (4)$$

At 920 °C this function exceeds the value given by Apel et al. by about one order of magnitude. Luque et al. [9] used lifetime measurements to examine wafers with unknown contamination and state a much lower segregation coefficient for several temperatures. Hieslmair et al. [6] state temperature dependent segregation coefficients for Fe. They used measurements of carrier diffusion length. Their data contradicts the tendency to decrease with increasing temperatures. The authors presume that this might be a result of too short gettering times, thus impurity concentration profiles might not have reached an equilibrium state. Therefore, the authors consider their values as a lower limit. In Fig. 3 all values discussed are plotted.

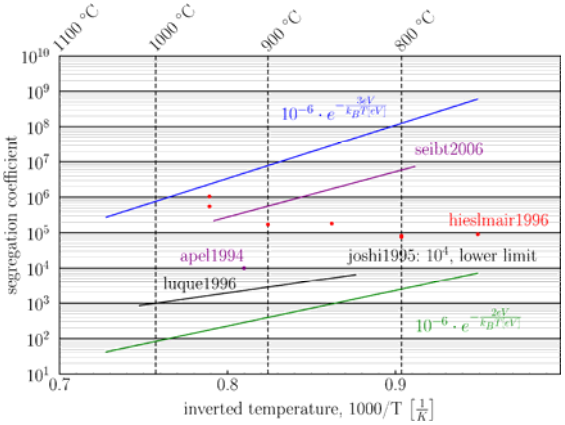

Figure 3: Different studies on segregation coefficients in recent years. References are specified in the text. Red indicates iron (Fe), purple indicates Cobalt (Co) and black an impurity metal which was not specified by Luque et al. The fictitious segregation coefficients marked in blue and green are designed as upper and lower limits of the known values and will be used later in the evaluation.

Regarding the majority of transition metals, the segregation coefficient is completely unknown. For Fe and Co there are still uncertainties.

Since data on the segregation coefficient is scarce and its measurement has proven to be difficult, one focus of this work lies on the question how much this value influences the gettering efficiency of silicon.

3 SIMULATION SOFTWARE

All the gettering simulations presented here are computed using the Sentaurus Process (SProcess) simulation tool from Synopsis®. This software offers several skills and advantages for this task. SProcess is a widespread tool in electronic semiconductor development and thus, many features, such as kinetic and thermodynamic parameters of silicon and several other elements are already implemented and tested. It is possible to implement differential equations, making it therefore easy to simulate aluminium gettering and combinations with phosphorous diffusion gettering [13]. In further steps, one can combine the gettering simulations with other modules of the solar cell process, also based on Synopsis® software. As a result it is possible to gain final solar cell parameters, such as efficiency, fill-factor etc. from simulated variations of process parameters.

4 SIMULATIONS

In the following, some examples of our simulations are shown in order to visualize our approach.

4.1 Dissolution of impurity clusters and segregation gettering

The following simulations show dissolution of Fe clusters and gettering by Aluminium segregation based on presently available parameters. For diffusivity and solubility we use the values of Fe, given by Weber [15] and Graff [3] shown in Fig. 1 and 2, as segregation coefficient we use the values for Co, given by Seibt et al. [14] shown in Fig. 3. This segregation coefficient was taken for the present simulation because it is seen as the most reliable value that can currently be found in literature. Resorting to the segregation coefficient for Co is an uncertain assumption, but it can be argued that it is reasonably correct regarding the similarity of the Co and Fe solubility in silicon (see Fig. 2). In section 5 we will check the importance of actually applying the correct value of the segregation coefficient.

To simulate the diffusion inside the silicon bulk and in the Al layer, we use the diffusion equations commonly known as Fick's law. The segregation of Fe at the Si-Al boundary layer is characterised by the following segregation equation [12]:

$$J_{Fe}^{Si\to Al} = -K_{Segr}\cdot\left(c_{Fe,Si} - \frac{c_{Fe,Al}}{m_{Fe}^{Si,Al}}\right) \qquad (7)$$

Here, $J_{Fe}^{Si\to Al}$ is the flux of Fe from the silicon bulk to the Al layer, K_{Segr} is the transport coefficient and $m_{Fe}^{Si,Al}$ the segregation coefficient of Fe in Si to Al, which depends on the gettering temperature.

As shown in Fig. 2, the solubility of interstitial impurities in the silicon lattice is limited and depends on the temperature. As a result, for higher impurity concentration there is the effect of cluster forming (precipitation). A simple, yet often used, model to describe the dissolution and growth of clusters was presented by Ham [4]:

$$\frac{\partial c_{El,Cl}(t)}{\partial t} = 4\pi\cdot D_{El}^{Si}\cdot N_{Cl}\cdot r_{Cl}\cdot(C_{El} - C_{Eq}) \qquad (8)$$

Here, $c_{El,Cl}$ is the concentration of impurity atoms trapped in precipitates, $D_{El}^{Si}(T)$ the diffusivity of the impurity, N_{Cl} the cluster density, r_{Cl} the cluster radius, c_{El} the interstitial impurity concentration and c_{Eq} the interstitial impurity concentration in equilibrium, thus the value of the solubility of interstitially dissolved impurity atoms in the silicon lattice.

Fig. 4 shows a simulation of cluster dissolution and gettering. A 240 µm wafer with an aluminium layer of 15 µm is gettered for 1 h at 850 °C. The initial concentration of clustered impurities was set to $10^{14}\,cm^{-3}$, the concentration of interstitial impurities to $10^{12}\,cm^{-3}$. After gettering, a considerable amount of impurities has diffused to the Al-layer. However, the interstitial Fe-concentration has increased due to the dissolution of precipitates.

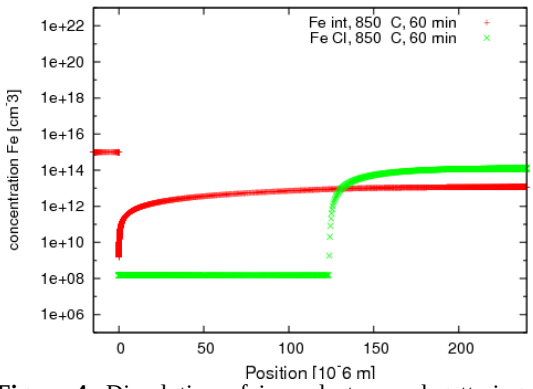

Figure 4: Dissolution of iron clusters and gettering in silicon. Interstitial Fe is marked in red, Fe clusters in green. The Al-layer is left of 0 µm.

4.2 Pre-gettering concentration

The PMG silicon is expected to contain much higher amounts of impurities than standard feedstock. We demonstrate the influence of the pre-gettering concentration on the gettering performance. In Fig. 5 the simulated concentration of clustered Fe contamination after a gettering step of 1h at 850 °C is plotted. The thickness of the Al-layer is set to 15 µm.

It is obvious that the gettering performance decreases enormously with higher impurity concentrations. While the gettering process has long been completed for a starting concentration $\mathrm{Conc}_{\mathrm{CL,Start}}$ of $10^{12}\,cm^{-3}$ and partly completed for a starting concentration of $10^{14}\,cm^{-3}$, there is nearly no wafer improvement for the other starting concentrations.

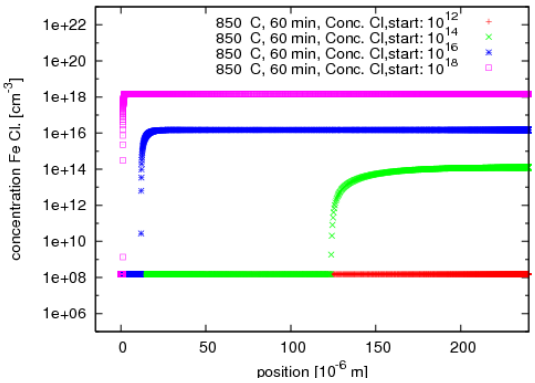

Figure 5: Gettering efficiency presuming different pre-gettering impurity concentrations in clusters [Cl,start] in the silicon bulk.

5 ASSESSMENT OF THE INFLUENCE OF SEGREGATION PARAMETERS

As a first step for the development of adapted Al-gettering processes for materials with varying impurity concentrations, we show the possibility of a fast evaluation of the influence of different parameters which determine the gettering efficiency with the help of SProcess. Of special interest is the question how important the determination of the exact value of the segregation coefficients of the relevant impurities is.

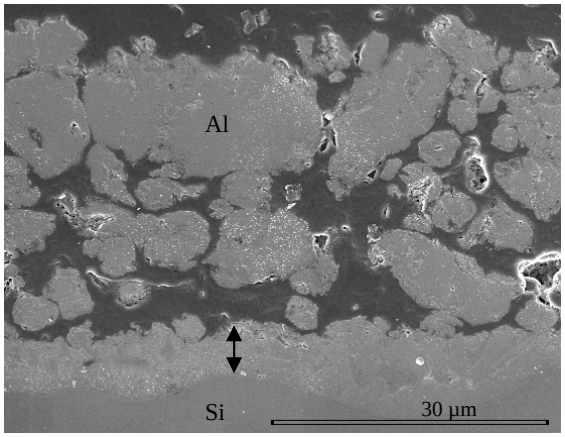

Figure 6: Cross section of Al screen printing paste after firing at 900°C. The active gettering layer is probably less than 10 µm thick (shown by the arrows), since the remaining printed layer does not constitute a coherent Al layer.

5.1 Variation of parameters

Besides the segregation coefficient, several other parameters influence the gettering behavior. The impurity concentration in the Al layer and in the Si bulk (and the fact that part of the impurity atoms are precipitated due to the solubility) have to be considered as well as the thickness of the Al:Si-eutectic layer during the gettering step. If for example screen printed Al is used, the question arises how much of the Al paste actually takes part in the gettering process Fig. 6 shows a cross section of a screen printed Al-layer with a thickness of XX µm after printing, measured following the firing step. The active gettering layer is probably less than 10 µm thick Other parameters are the transport coefficient (Eq. 7) and the diffusion coefficient of the impurities in the Al:Si eutectic. In the following, we assume that the gettering process is not limited by these two values, meaning that the transfer of the impurities from the silicon into the aluminium layer happens instantaneously once the boundary layer is reached and the atoms are redistributed by the convection in the eutectic melt. Of course, temperature and time influence the gettering performance as well.

We take again Fe as the model impurity whose solubility and diffusivity in Si are well known. Other impurities shall not be considered here. For the modelling of precipitation and dissolution of clusters, Ham's equation (Eq. 8) is applied. As in this model the precipitates are assumed to be homogeneouly distributed, and neither heterogeneous precipitation [5] nor Ostwald ripening are taken into account, results have to be evaluated with caution. Furthermore, our one-dimensional simulation cannot handle influences of grain boundaries and crystal defects. If these restrictions are kept in mind, we are however confident that important estimations about the influence of several gettering parameters can be made.

For this estimation, we do not want to investigate the effect of slow cooling ramps or additional post-gettering plateaus since this would obscure the effect of the actual high temperature step. Therefore, we apply simple high temperature plateaus and pretend that the wafers are extracted from the oven very fast. This may result in Fe_i concentrations in the bulk after gettering which are significantly above the solubility limit at room temperature.

In order to keep the simulation straightforward, we restricted the variation of the interesting parameters to two extreme values spanning the entire realistic range. Wafer thickness was fixed to 240 µm. The thickness of the Al layer was set first to 3 µm and then to 30 µm. Interestingly, we find that this thickness does not play a role in the Al gettering except for the case that the silicon bulk is very clean and the Al layer contains impurities in the percentage range, i.e. the Al is effectively contaminating the silicon (results not shown). Therefore, the structure of the Al layer – whether it is e.g. screen printed (Fig. 6) or evaporated – should not be of importance as well. In the following, we only show simulations done with d_{Al} = 3µm.

Our parameter variations then comprise the impurity content in the silicon, the contamination in the Al layer, the segregation coefficient and the gettering temperature and time. The variation ranges are denoted in Table I. Initially, the silicon contains $10^{12} cm^{-3}$ interstitial iron. Additionally, the main iron concentration of $10^{12} cm^{-3}$, $10^{15} cm^{-3}$ or $10^{18} cm^{-3}$ is found in precipitates, roughly representing standard, PMG and metallurgical grade silicon wafers. The initial iron concentration in the Al layer is varied, taking two extrema of $10^{10} cm^{-3}$ and $10^{20} cm^{-3}$. The former value marks an extreme boundary, because even clean Al contains around $10^{16} cm^{-3}$ iron atoms [11]. The latter value may come close to the actual contamination in Al screen printing paste. Usual gettering temperatures of 600°C and 1000°C were taken and the gettering time varied between 5 min. and 3 hours. For the segregation coefficient, the two fictitious Arrhenius functions of

$$m^{Si}_{(eq),fic}(T) = 1 \cdot 10^{-6} \cdot \exp\left(\frac{\Delta E_b}{k_B T[eV]}\right)$$

with ΔE_b = 2.0 and 3.0 were taken (see Fig. 3). These coefficients form upper and lower limits of the segregation values found in literature. If a great difference between the simulations was found for both coefficients, the exact value for iron would be needed in order to be able to design adapted Al gettering processes.

5.2 Results

The parameter sets we simulated are shown in Table I, column A for a segregation coefficient with ΔE_b = 2.0 and in column B for ΔE_b = 3.0. As the measurand we take the interstitial iron concentration in the silicon after the gettering step. It is evaluated at a depth of around 200 µm from the boundary layer and shown in the last columns of the table. When mentioning "gettering efficiency", which is defined as the ratio of the impurity concentration before and after the gettering step, we refer to this quantity. The resulting iron concentrations are also plotted in Fig. 7 and 8. Black bars indicate that following our simulation, the system has reached thermodynamic equilibrium and no further changes in the impurity distribution are expected. Red bars denote parameter sets in which longer gettering times would be needed for reaching equilibrium. How long this would be differs strongly from case to case.

Table I: For Al gettering following parameters have been varied: concentration of clusters in Si, temperature, time, concentration of iron in the Al layer and the segregation coefficient with 10^{-6}*exp(2.0/k_BT) (**A**) and 10^{-6}*exp(3.0/k_BT) (**B**). As a measurand the post-gettering iron concentration at the backside of the wafer is used.

Set No.	$C_{Cl(Si)}$ Start [cm^{-3}]	Temp [°C]	Time [min]	$C_{int(Al)}$ Start [cm^{-3}]	$C_{int(Si)}$ End [cm^{-3}]	
					A	**B**
1	1e12	600	5	1e10	2.6e8	1.6e8
2				1e20	2.8e14	5.1e8
3			180	1e10	2.3e8	2.5e4
4				1e20	2.8e14	4.8e8
5		1000	5	1e10	1.8e12	1.8e12
6				1e20	2.9e14	1.8e12
7			180	1e10	9.3e11	1.3e11
8				1e20	2.1e16	1.2e14
9	1e15	600	5	1e10	2.7e8	1.4e8
10				1e20	2.8e14	5.2e8
11			180	1e10	2.6e8	2.4e7
12				1e20	2.8e14	5.0e8
13		1000	5	1e10	3.7e14	3.7e14
14				1e20	3.8e14	3.7e14
15			180	1e10	4.1e14	1.5e14
16				1e20	4.1e14	3.8e14
17	1e18	600	5	1e10	1.9e9	1.9e9
18				1e20	3.6e12	1.9e9
19			180	1e10	1.9e9	1.9e9
20				1e20	2.8e12	1.9e9
21		1000	5	1e10	4.1e14	4.1e14
22				1e20	4.1e14	4.1e14
23			180	1e10	4.1e14	4.1e14
24				1e20	4.1e14	4.1e14

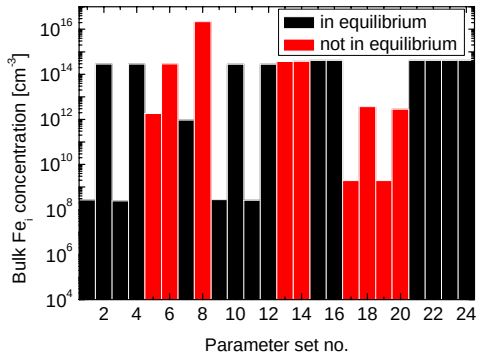

Figure 7: Variations of gettering parameters. The segregation coefficient was set to 10^{-6}*exp(2.0/k_BT). The parameters are shown in Table I.

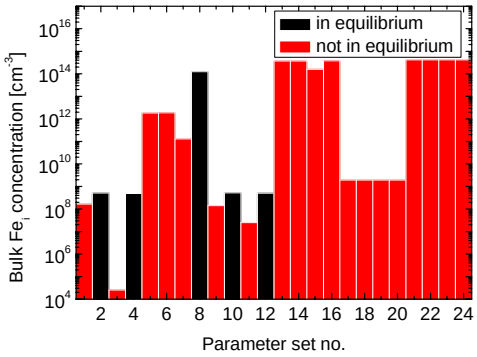

Figure 8: Variations of gettering parameters. The segregation coefficient was set to 10^{-6}*exp(3.0/k_BT). The parameters are shown in Table I.

From these calculations many interesting observations can be learnt, out of which we only discuss a few in the following. Firstly, it is obvious that reaching equilibrium takes longer the higher the segregation coefficient (compare Fig. 7 and 8). Even after a very long gettering time of 3 hours, equilibrium is reached only for the case of almost clean Si and a highly contaminated Al layer (see parameter sets 2, 4, 8, 10 and 12).

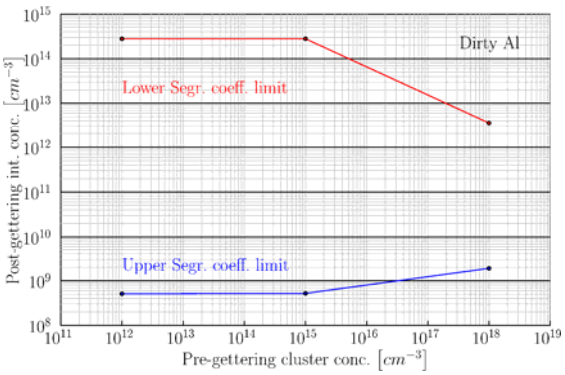

Figure 9: Influence of the segregation coefficient and pre-gettering cluster concentration on interstitial impurity concentration after gettering. Pre-gettering impurity concentration in the Al-layer is 10^{20} cm^{-3}, representing screen printed Al.

Another interesting observation is shown in Fig. 9. For a dirty Al layer it is obvious that a lower segregation coefficient results in a higher iron contamination of the bulk. This is due to the different indiffusion of contaminants from the Al layer to the bulk. For the relevant gettering times, the segregation coefficient influences the gettering efficiency maximally when the silicon wafer is standard or purified metallurgical grade and less, when the silicon itself is strongly contaminated.

On the other hand, if one has a clean Al layer, gettering efficiency is higher the cleaner the wafer is before gettering (see Fig. 10). This corresponds well with data reported by McHugo et al. [10].

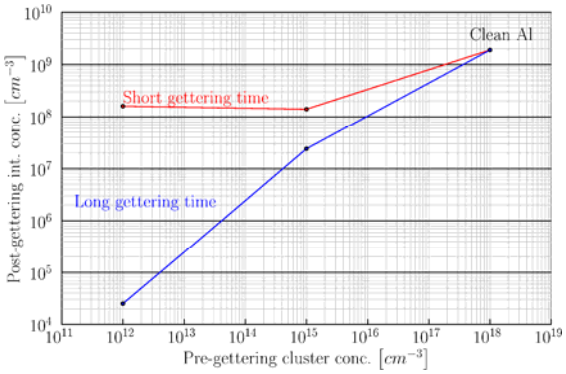

Figure 10: Influence of the gettering time and pre-gettering cluster concentration on interstitial impurity concentration after gettering. Pre-gettering impurity concentration in the Al-layer is 10^{10} cm^{-3}.

Surprisingly, for a clean Al layer, the difference in segregation coefficients results in a difference of interstitial iron concentrations of four orders of magnitude for a low gettering temperature, a long gettering time and very clean silicon (parameter set 3), but only of around one order of magnitude if a higher temperature (set 7) or a low temperature and PMG silicon (set 11) are considered. For the rest of the variations assuming clean Al, differences in segregation coefficients in the range investigated are irrelevant for interstitial iron. For this reason the exact knowledge of the segregation coefficient is of importance especially if the Al gettering is simulated for clean silicon feedstock, high temperature and long gettering times.

The differences between high and low temperature gettering are shown in Fig. 11. The gettering efficiency seems to be higher by several orders of magnitude for low temperature gettering. This is indeed the case for the interstitial impurities, but one has to remind that there is nearly no cluster dissolution at 600 °C. Thus, increasing wafer performance is only to be expected when interstitial impurities are the main lifetime reducing factor.

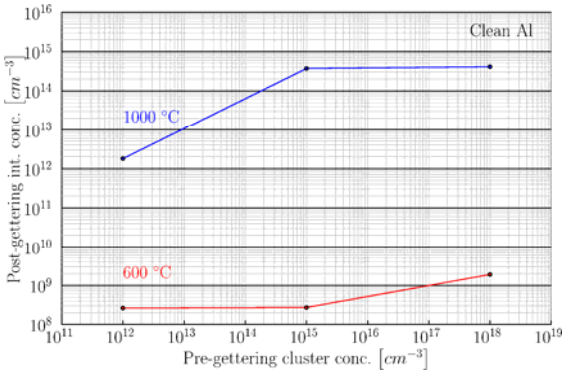

Figure 11: Influence of the temperature and pre-gettering cluster concentration on interstitial impurity concentration after gettering. Pre-gettering impurity concentration in the Al-layer is 10^{10} cm^{-3}.

One has to keep in mind that the evaluation of "gettering efficiency" presented here does not correspond directly to improvements of carrier lifetime or cell efficiency. Since we exclusively discuss the interstitial impurity concentration, the results may be linked to cell improvement only in those cases, where the impact of interstitial impurities dominates the other lifetime reducing factors. This is likely to be not the case at least for high cluster concentrations. In order to develop an optimization tool for Al-gettering processes, in a next step one has to consider all the lifetime reducing impacts.

6 CONCLUSION

In this work, Al gettering processes were investigated with the help of the simulation tool Sentaurus Process. Due to its flexibility and easy usability, this simulation program makes it possible to scan a wide parameter range in the search for optimal processing conditions. Provided the simplistic models we used give a sufficiently exact representation of the reality, our simulations show that the thickness of the Al layer is a less important parameter and that the knowledge of the exact value of the segregation coefficient for iron is only necessary if the processing of standard clean Si wafers is to be optimized, not, however, if material containing high impurity concentrations is the focus.

7 ACKNOWLEDGEMENTS

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