

4P-A8-42

A GETTERING SIMULATOR: EVALUATING CONTAMINATION AND GETTERING PROCESSES

C. del Cañizo, L.J. Caballero, R. Esteban and A. Luque
 Instituto de Energía Solar – Universidad Politécnica de Madrid
 Ciudad Universitaria s/n - 28040 Madrid. Spain. Fax: 34 1 5446341, email: canizo@ies-def.upm.es

ABSTRACT

A software tool that simulates contamination and gettering processes is presented. It is based on a quantitative model that takes into account impurity diffusion and segregation, interaction with point defects, precipitation and trapping. It also relates impurity content with lifetime. The simulator is a helpful tool to study dependence of impurity content with temperature, evolution with process duration and influence of parameters on gettering efficiency. A friendly interface facilitates the control on the choice of parameters and the obtention of values and graphics. Some examples of application are shown.

1. INTRODUCTION

Gettering steps are amply implemented in most of silicon solar cell fabrication processes to counteract unavoidable contamination. A gettering process removes lifetime-killing impurities from the bulk, transporting them to regions where their recombination activity is reduced [1].

Determining specific gettering mechanisms is rather complex. One reason is the variety of impurities to be removed, and also their different behaviour depending on their position in the silicon matrix: interstitial, substitutional, precipitated or trapped in a crystalline defect. Interaction with point defects (self-interstitials and vacancies) can also play an important role in certain cases.

We have developed a quantitative model that includes several of the mechanisms suspected or proven to occur in a gettering process. The model is described by a set of differential equations for the dynamics of a single impurity. Impurity evolution throughout the wafer depth with process duration is deduced, and impact on lifetime calculated. Details can be found in Ref [2]. We think our model can be useful for the understanding and interpretation of gettering mechanisms.

To offer a friendly interface to simulate a process and analyse results, a software tool in Visual Basic has been prepared. It solves the set of differential equations transforming them in a finite difference equation system, with main parameters defined by the user. Impurity concentrations depending on position, and their evolution during a thermal process, are presented.

The software tool, called "Gettering Simulator", is described in the paper. The different options, screens for data input and presentation of results are explained. Several specific processes have been simulated as examples, showing the kind of conclusions that can be expected from the use of the tool.

2. 'GETTERING SIMULATOR' TOOL

Figure 1 shows a picture of the main screen. Main parameters are defined: temperature and time of process, type of impurity (substitutional or interstitial) and initial concentration; options exist to define initial concentrations also for precipitated and trapped impurities, and even to establish non-uniform initial profiles for them. A "simplified model" is applied in the absence of crystalline defects and precipitates, while a "complete model" applies if they exist.

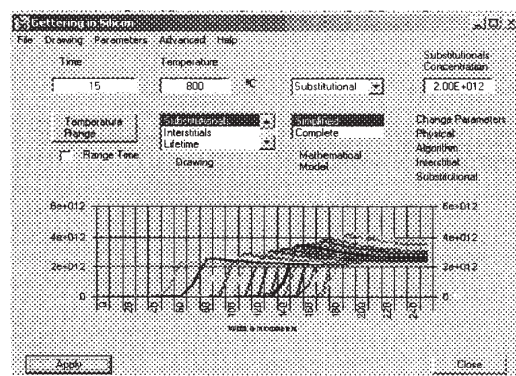


Fig. 1: Gettering simulator main screen.

There are several additional screens to define parameters:

- Physical: those regarding point and crystalline defects behaviour;
- Algorithm: mainly time and spatial interval;
- Interstitial/Substitutional: those defining impurity behaviour.

An example for a substitutional impurity is shown in Fig. 2. Diffusion coefficient, solid solubilities, velocity rate and equilibrium constants for kick-out and Frank-Turnbull reactions are defined, as well as parameters related to precipitates, segregation to the sink layer, influence in lifetime and pollution from the environment (which will be mentioned in more detail in section 3.1).

The choice of parameters to be used is of great importance. Default values based on experimental results and on those reported on literature are given. Nevertheless, the user can easily change parameter values and experience with new ones. In this way, a comparison of simulator results with experimental ones can help in determining some parameters whose values are still in controversy.

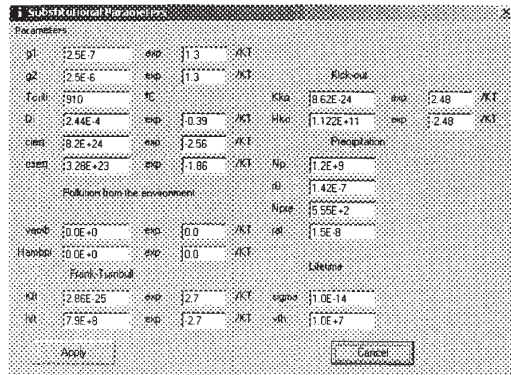


Fig. 2.: Screen for parameter definition of substitutional impurities.

Simulation results are graphically expressed, and a sheet with data which be easily exported to an Excel file produced. The possibility exists to represent substitutionals, interstitials, self-interstitials, vacancies and also lifetime, both versus wafer depth or versus process time.

To show some of the applications of Gettering Simulator, several examples are presented in next section. Iron and gold have been taken as representative of interstitial and substitutional impurities, respectively. The values chosen for the main parameters involved are shown in Table I, and they are deeply discussed in Ref. [2].

Table I. Parameters used in the calculations

Mechanisms	Symbol	Value
Diffusion (Fe)	D_i (cm^2s^{-1})	$1.30 \times 10^{-3} \exp(-0.68/kT)$
Solid solubility (Fe)	C_i^{eq} (cm^{-3})	$1.82 \times 10^{26} \exp(-2.94/kT)$
Kick-out (Au)	K_{ko}^{eq} (cm^3)	$8.62 \times 10^{-24} \exp(2.48/kT)$
	h_{ko} (s^{-1})	$8.1 \times 10^7 \exp(-2.48/kT)$
Frank-Turnbull (Au)	K_{FT}^{eq} (cm^3)	$2.86 \times 10^{-25} \exp(2.7/kT)$
	h_{FT}	$7.9 \times 10^{-5} \exp(-2.7/kT)$
Diffusion (Au)	D_s (cm^2s^{-1})	$2.44 \times 10^{-4} \exp(-0.39/kT)$
Solid solubility (Au)	C_s^{eq} (cm^{-3})	$3.28 \times 10^{-23} \exp(-1.86/kT)$
	C_i^{eq} (cm^{-3})	$8.2 \times 10^{22} \exp(-2.56/kT)$
Self-interstitials & Vacancies	I_{eq} (cm^{-3})	$2.90 \times 10^{24} \exp(-3.18/kT)$
	V_{eq} (cm^{-3})	$1.40 \times 10^{23} \exp(-2/kT)$
	D_i (cm^2s^{-1})	$51 \exp(-1.77/kT)$
	D_v (cm^2s^{-1})	$3 \times 10^{-2} \exp(-1.8/kT)$
Segregation	g (cm)	$2.5 \times 10^{-6} \exp(1.3/kT)$
Precipitation	r_0 initial (cm)	2.02×10^{-7}
	N_0 (cm^{-3})	1.2×10^{-9}
Trapping	K_{tr}^{eq} (cm^3)	$1.27 \times 10^{-29} \exp(3/kT)$
	h_{tr} (s^{-1})	$1.75 \times 10^{10} \exp(-3/kT)$
	θ (cm^{-3})	4×10^{14}

3. EXAMPLES OF APPLICATION

Three situations will be simulated: first, a process where contamination from the environment competes with Aluminium gettering; then, a study of temperature influence on Phosphorus gettering; and third, the existence of non-uniform lifetime profiles throughout a wafer due to partial gettering.

3.1 Competition between contamination and gettering

In principle, we can consider that during a thermal process a wafer is sealed from the environment (the furnace), for example with a silicon oxide on one side and a deposited Al layer on the other. But the sealing may not be enough, so that an exchange of impurities between the sample and the furnace takes place. In steady state, the impurities in the semiconductor become in equilibrium with those in the gas, where they have a partial pressure p_i , so that $C_{eq} = H p_i$ according to Henry's law. In reality, a flux F with two components is established: on one side, impurities enter the wafer at a rate proportional to $H p_i$, on the other they escape from the sample at a rate proportional to their concentration C_i .

$$F = v(H p_i - C_i) \quad (1)$$

v ($\text{cm} \cdot \text{s}^{-1}$) is a transfer coefficient dependent on the sealing conditions of the surface layer.

An example of the competition between contamination and gettering is presented in figures 3 and 4 for Al gettering of iron at 850°C , in a wafer with a silicon oxide in the left side and an Al sink layer on the right side. Initial iron concentration is $5 \times 10^{12} \text{ cm}^{-3}$.

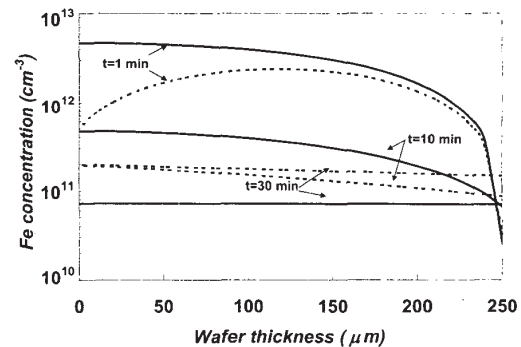


Fig. 3: Fe profile in an Al gettering process at 850°C at different instants. Solid line corresponds to a sealed wafer (no contamination from the environment) and dash line to the case of contamination from the furnace ($H p_i = 2 \times 10^{11} \text{ cm}^{-3}$, $v = 10^{-3} \text{ cm} \cdot \text{s}^{-1}$). The Al layer is in the right side.

Fig. 3 compares Fe profile at different instants in two cases: in solid line, for a perfect sealing thanks to the oxide, and in dash line for the case of contamination from the furnace with the following parameters: $H p_i = 2 \times 10^{11} \text{ cm}^{-3}$, $v = 10^{-3} \text{ cm} \cdot \text{s}^{-1}$. Tendency of impurities to diffuse towards the gettering layer is clearly shown by the Fe profile near the right side, where the Al layer is, so that total concentration diminishes by this fact. In the case of not perfect sealing, impurities escape from the wafer while

their concentration in the left side is higher than $C_{eq}=Hp_i$; when they reach this value the flux changes its direction, producing additional contamination from the furnace that "refills" the sample. Final concentration is then given by that of equilibrium C_{eq} .

Fig. 4, reproducing the same experiment in terms of average Fe concentration vs process duration, shows that although for small times the exchange of impurities with the furnace is beneficial, in the long run the concentration is higher than if perfect sealing exists: final equilibrium concentration due to gettering cannot be achieved.

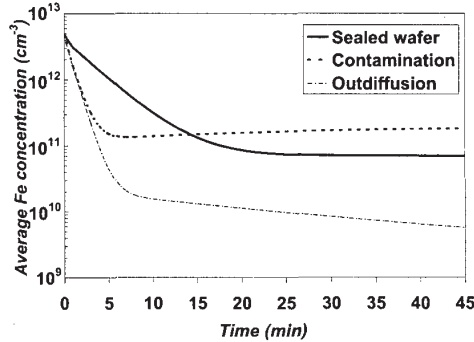


Fig. 4: Evolution of Fe concentration with time in an Al gettering process at 850°C. Comparison of three cases: a sealed wafer (no contamination from the furnace), a wafer contaminated from the furnace, and a very clean furnace that causes outdiffusion of impurities.

The figure also represents the case of a very clean furnace where the concentration of impurities in the gas is very low, described by $Hp_i=2 \times 10^9 \text{ cm}^{-3}$. The removal of iron impurities is higher than for the sealed wafer because the effect of outdiffusion to the furnace adds to the gettering effect. Outdiffusion will continue until the equilibrium value is achieved. Outdiffusion phenomenon has been experimentally shown by several authors [3].

3.2. Temperature influence on P gettering

A batch of processes at different temperatures can be easily simulated, defining the process duration and the temperatures at which the simulation should be done. A common segregation coefficient can be established for the whole set of temperatures, or different values can be given for different ranges. This last possibility can be of interest in certain cases, for example P gettering.

Supported by lifetime measurements after P gettering at different temperatures, we think that segregation to the sink layer in this case is governed by two different mechanisms, depending on temperature: at low temperatures, trapping in a solid phase and at high temperatures, segregation to a liquid phase.

To illustrate the effect, which is justified in detail in reference [4], a simulation of P gettering of iron is carried out. Under 865°C a segregation coefficient with an activation energy of 0.5 eV is defined, while another one with an activation energy of 1.7 eV is established for higher temperatures. Due to iron diffusivity, a process of 45 min is long enough to reach an equilibrium value throughout the wafer, even at the lower explored temperature of 825°C. Results are shown in Fig. 5, showing a clear discontinuity that separates two regions, each one with an increasing Fe concentration with temperature.

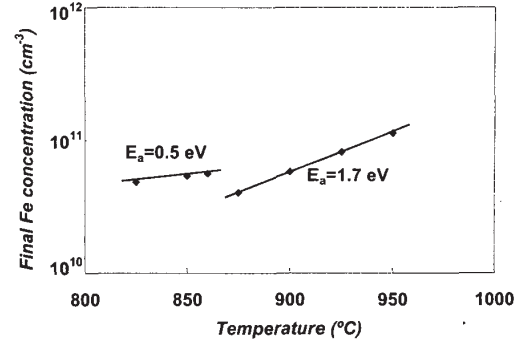


Fig. 5: Fe concentration after a P gettering of 45 min. Initial contamination of $2 \times 10^{12} \text{ cm}^{-3}$. Two segregation coefficients are defined, one for temperatures under 865°C with $E_a=0.5 \text{ eV}$, another for higher temperatures with $E_a=1.7 \text{ eV}$.

P gettering processes can benefit from this fact, because high segregation can be produced at high temperature, where impurity diffusion is also higher, and so gettering efficiency can increase.

3.3. Non-uniform lifetime profiles

It is usually assumed that bulk lifetime is constant throughout a silicon wafer. Gettering Simulator can predict the existence of steep nonhomogeneous impurity profiles, which produce nonuniform lifetime profiles.

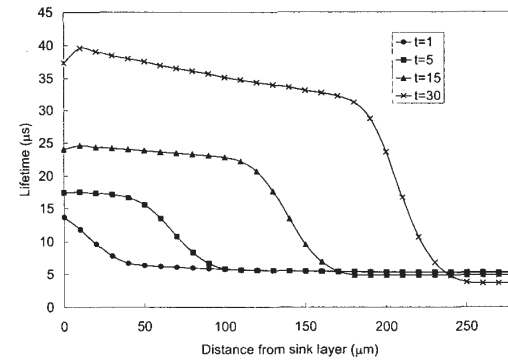


Fig. 6: Lifetime profile for several gettering times (in min) for a P gettering at 850°C. Low quality wafer, initially contaminated with $2 \times 10^{12} \text{ cm}^{-3}$ of gold, equally distributed among substitutionals, precipitated and trapped atoms.

For Shockley-Read-Hall recombination mechanisms, lifetime is associated to the impurity concentration by the expression

$$\frac{1}{\tau} = \sigma v_{th} C \quad (2)$$

where σ is the recombination cross-section and v_{th} is the carrier thermal velocity. Substitutional, interstitial, precipitated and trapped impurities follow this mechanism and their contributions should be summed up. This is done

by the program, so that lifetime after a gettering process can be easily obtained and represented.

Fig. 6 shows lifetime profiles in a low quality wafer (multicrystalline one) after a P gettering at 850°C, considering initial contamination with $2 \times 10^{12} \text{ cm}^{-3}$ of gold, equally distributed among substitutionals, precipitated and trapped atoms. An abrupt change in lifetime discriminates clearly two regions, one closer to the P layer with higher lifetime than the other. This phenomenon can have a relevant impact on the behaviour of solar cells [5].

4. CONCLUSIONS

The software tool Gettering Simulator has been developed to help in analysis of gettering and contamination processes. It solves the set of differential equations which models gettering phenomena, transforming it in a finite difference equation system, with main parameters defined by the user.

Application of the simulator can drive to interesting conclusions regarding gettering conditions, optimisation and results. Some situations are simulated to show the kind of results that Gettering Simulator can give.

An exchange of impurities with the environment during a thermal process can prevent the reduction of impurities to the levels achievable by gettering in a sealed wafer. On the other hand, outdiffusion is possible if a very clean furnace is used.

A discontinuity in lifetime measured in P gettering at several temperatures is interpreted by the existence of different segregation mechanisms depending on temperature. The phenomenon has been simulated to illustrate the effect.

After a gettering process, impurity profile throughout the wafer can be inhomogeneous, producing a nonuniform lifetime profile.

5. ACKNOWLEDGEMENTS

This work has been partially funded by the Spanish TIC2002-04561-C03-03.

REFERENCES

- [1] S. Myers, M. Seibt and W. Schröter, "Mechanisms of transition-metal gettering in silicon", *J. Appl. Phys.* **88**, 3795 (2000).
- [2] C. del Cañizo and A. Luque, "A comprehensive model for the gettering of lifetime-killing impurities in silicon", *J. Electrochem. Soc.* **147**, 2685 (2000).
- [3] S.M. Joshi, U. M. Gösele and T.Y. Tan, "Improvement of minority carrier diffusion length in Si by Al gettering", *J. Appl. Phys.* **77**, 3858 (1995).
- [4] L.J. Caballero, C. del Cañizo, A. El Moussaoui, R. Esteban and A. Luque, "Impurity segregation to sink layer during P gettering", this conference.
- [5] C. del Cañizo, I. Tobías, R. Lago-Aurrekoetxea and A. Luque, "Influence of depth-inhomogeneity of lifetime in silicon solar cells", *J. Electrochem. Soc.* **149**, G522 (2002).