

# A model for the diffusion behaviour of generation centers in CCDs.

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## Abstract

*This paper presents the characterization of additional generation centers in some pixels of an n-type buried channel CCD image sensor. Anneal experiments without a DC bias on the contacts of the sensor will give the diffusion coefficient of the center, which can be compared with literature to obtain the nature of the center. Anneal experiments with a DC bias on the contacts will show that the center is positively charged and can be removed from the active volume of the CCD.*

## Introduction

The paper will describe the characterization of white pixels in CCD image sensors. The name "white pixel" is obtained by the impression looking to a monitor which displays the image, generated by a sensor, of a dark scene. Some pixels are clearly whiter than neighbour pixels. The real cause of this is that in these pixels more charge has been generated during the integration time than in other pixels, because these white pixels contain one or more additional generation centers. The white pixels decrease the quality of the sensor and have to be avoided. In [1] it has been shown that one single generation center is responsible for a white pixel, and gold is the most probable element. In this paper the diffusion characteristics of the generation center are examined, which will lead to a proper anneal to avoid these white pixels.

## The model

A white pixel is a pixel that contains a trap filled with a generation center in the active area of the pixel. A pixel that is not a white pixel can have an empty trap, or no trap. The traps are immobile. The generation centers are considered mobile and will move randomly through the lattice, although, at room temperature their mobility is very low. In the situation at higher temperatures, the generation centers will diffuse faster, and the capture rate will increase. Even so the emission rate out of the traps will increase at higher temperatures.

### *The trap*

The reason for the introduction of the trap for metals in the model will become clear with the first experiment. It will show that white pixels can be switched "on" and "off" and "on" again, after a proper anneal step. The position of the generation center in the pixel at the first and second time that it is switched "on" is exactly the same, which can be controlled by changing some potentials on the contacts of the CCD. When a white pixel contains only a free generation center, this center can diffuse out of the active area, which means the white pixel is switched "off". When it comes back, it can be anywhere in the pixel, which means that the white pixels is switched "on", although the position of the center will in many cases not be the same as its original one.

### *Measurements*

To check the model, some anneal experiments were done by measuring the number of white pixels as a function of the anneal time for different temperatures. This means that this number is measured before and after the anneal, which is repeated multiple times.

*The number of white pixels as a function of time and temperature without a bias*

The increase of the number of filled traps  $N_t^+$  as a function of time can be expressed as:  $d N_t^+/dt = \text{Capture} - \text{Emission}$ . The Capture and Emission are given by:

$$\text{Capture}(T) = C_{\text{metal}} \cdot v_{\text{th}}(T) \cdot \sigma_{N_t}(T) \cdot N_t^- = \frac{N_t^-}{\tau_c(T)} \quad (1.a)$$

$$\text{Emission}(T) = \frac{N_t^+}{\tau_e(T)} \quad \tau_e(T) = K_b \cdot \exp(E_b/kT) \quad (1.b)$$

$C_{\text{metal}}$  is the metal concentration,  $v_{\text{th}}$  is the thermal velocity of the metal atoms,  $\sigma_{N_t}$  is the capture cross section of the trap, which is given by [2] as  $\sigma_{N_t} = \pi(q^2/(\epsilon_0 \epsilon_r kT))^2$ .  $N_t^-$  is the number of empty traps, and is equal to  $N_t^T - N_t^+$ , where  $N_t^T$  is the total number of traps.  $\tau_c$  is the capture time constant. The emission time constant  $\tau_e$  of (1.b) can be expressed with a constant  $K_b$  and a bindings energy  $E_b$ .

The number of filled traps as a function of time can now be expressed as:

$$N_t^+(t) = N_t^+(0) + (N_t^+(\infty) - N_t^+(0)) \cdot (1 - e^{-t/\tau_p}) \quad \text{with: } N_t^+(\infty) = N_t^T \cdot \frac{\tau_p}{\tau_c} \quad (2)$$

in which  $\tau_p$  is the process time constant and is given by:  $1/\tau_p = 1/\tau_c + 1/\tau_e$ .

*The number of added and removed white pixels as a function of time and temperature*

When the number of white pixels in a sensor increases after an anneal step, means that there are a certain number of pixels which were "off" before, and "on" after the anneal. This figure is called the number of Added white pixels (A). There are also pixels which were "on" before and "off" after the anneal. This figure is called the number of Removed white pixels (R). The difference of both figures represents the increase in the total number of white pixels in the sensor.

Lets consider two sample moments to measure the number of white pixels. At  $t_0$  the sample is put in the oven, and at  $t_1$  the sample is taken out of the oven. At  $t_0$ ,  $N_{t_0}^+$  traps are filled and  $N_{t_0}^-$  ( $= N_t^T - N_{t_0}^+$ ) traps are empty. During the interval  $t_0-t_1$ , a number of E traps will emit their metal atoms, resulting in  $N_{t_0}^- + E$  empty traps. During this interval, C traps will capture metal atoms, which will be divided over the empty  $N_{t_0}^-$  plus E traps. The number of pixels that will be added to the total amount of white pixels is:

$$A = \frac{N_{t_0}^-}{N_{t_0}^- + E} \cdot C \quad (3)$$

At infinite time the system is in equilibrium, and E will be equal to C. E can be expressed, by using (1.b), as:  $E = \text{Emission} \cdot (t_1 - t_0)$ , The total number of traps in the active area, calculated at infinite t, can now be determined using  $N_t^T = N_t^+ + N_t^-$  by:

$$N_t^T = N_t^+(\infty) + \frac{N_t^+(\infty) A}{N_t^+(\infty) - A \cdot \frac{\tau_e}{(t1-t0)}} \quad (4)$$

*The number of white pixels as a function of time and temperature with a bias*

In n-type buried channel CCDs the electrons are collected in a depleted n+ volumes, which are from column to column separated by p+ channels.

When this diode is reversed biased, an electric field is created. Positive elements will have a strong preference to diffuse in the direction of the negative p+ channel. To speed up this process the experiments are carried out at higher temperatures. This implies that the capture rate of the metal in the traps will decrease because the metal concentration decreases (see equation 1.a).

The bindings energy of the metal to the trap will also decrease because of the Poole-Frenkel effect [3]. The potential close to the trap is given by:  $V(r) = q/\epsilon_{si}r + E \cdot r$  in which r is the distance from the center of the trap. The reduction of the bindings energy can be expressed as  $\Delta V_b = 2(qE/\epsilon_{si})^{0.5}$ .

The number of trapped metal atoms as a function of time can now be expressed as:

$$N_t^+(t) = N_{t0}^+ * e^{-t/\tau_{eE}} \quad (5)$$

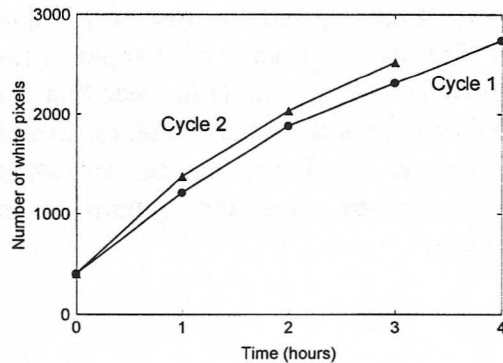
where  $\tau_{eE}$  is given by  $K_b * \exp((E_b - \Delta V_b)/kT)$ , like (1.b).

## Experiments

*Increasing and decreasing the number of white pixels*

This section shows the reason for the presence of the trap in the model.

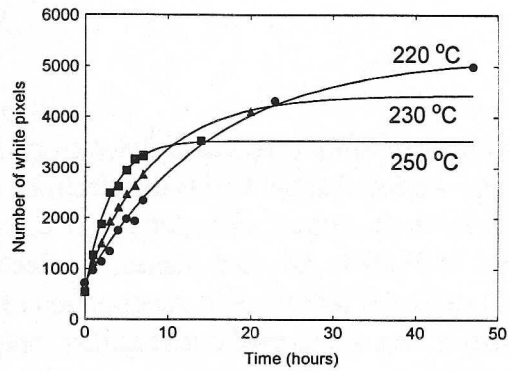
An anneal experiment, like described before, has been carried out (Figure 1, cycle 1), and after some sample times the sensor is annealed at a higher temperature to remove the white pixels (the reason of this reduction of the white pixels at higher temperatures becomes clear in a later section). When now the same experiment is repeated (cycle 2), the number of white pixels in this sensor shows almost the same increase as a function of time. From comparison with the images before and after this anneal it becomes clear that the greater part of the removed white pixels became a white pixel again. Measurements [4], which can accurately determine the place of the center in the pixel, showed that when centers come back in the white pixel it is at exactly the same place. This must be the place of the trap.



**Figure 1.** Number of white pixels versus anneal time at 250°C. After cycle 1 the number of white pixels was reset by an anneal at 280 °C. To make the graph clear, the time axis of cycle 2 starts again at t=0.

### Anneal without a bias

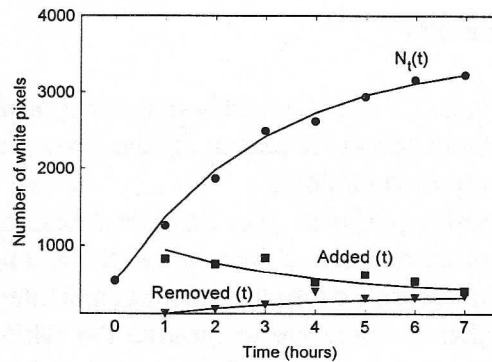
This next experiment has been carried out to determine the diffusion coefficient of the centers, the bindings energy of the trap, the total number of traps and the concentration of generation centers. A sample is put in an oven for about one hour. The number of white pixels is measured and the sensor is put in the oven again. Figure 2 shows the results, with the measured values as markers, and the fit with (2) as lines. This is done for three temperatures (with three samples). At higher temperatures the process reaches faster the equilibrium number of white pixels  $N_t(t=\infty)$ , because the generation centers walk faster through the silicon lattice at higher temperatures and so the capture rate increases. However, the value of  $N_t(t=\infty)$  decreases at higher temperature. This effect can be explained by the fact that the activation energy of the diffusion constant is smaller than the bindings energy of the trap. At higher temperatures the emission rate becomes relative larger, so that more generation centers are emitted and  $N_t(t=\infty)$  decreases.



**Figure 2.** Total number of white pixels versus anneal time for three oven temperatures.

### Added and removed white pixels

Because measuring the capture and emission rate is not possible, the number of Added and Removed white pixels is measured. Figure 3 shows an example of the measurement at 250 °C. The markers are the measured values, the lines are the fits with (2) and (3). The added white pixels are pixels that were empty at the beginning of the experiment, and are filled at the end. The inverse process has happened for the removed white pixels. It is clear that for infinite time the number of added and removed pixels become equal, the number of white pixels is constant, and the system is in equilibrium.

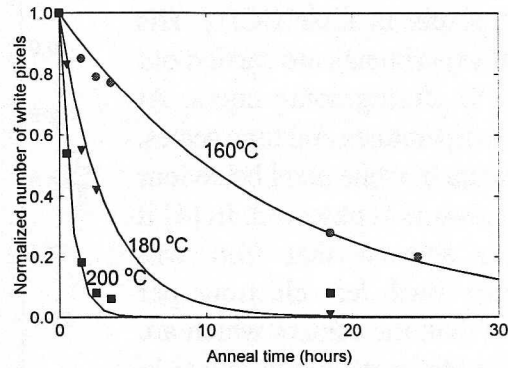


**Figure 3.** Total number of white pixels and the number of added and removed white pixels versus anneal time. Oven temperature is 250 °C.

### Anneal with electric field

Another way to remove the white pixels from the sensor is to reduce the capture rate. This can be done by applying an electric field to the sensor, so that the positively charged generation centers will drift to an unharmed place. This is done for three temperatures and the results are plotted in figure 4. Again the markers are the measurements, and the lines are the fits with (5).

It is clear that the anneal with a bias on the contacts results in a strong decrease of the white pixels. After some hours at 200 °C this number is equal to zero.



**Figure 4.** Anneal experiments under a DC bias, for three different temperatures. Because the initial number of white pixels differs slightly, the normalized number of white pixels (measured value divided by the initial value) is plotted.

### Results

Table 1 gives an overview of the obtained parameters.

The total number of traps in the active area of the sensor is 6000 (the sensor contains about 300.000 pixels).

The metal concentration is high in comparison to reported contamination levels in literature ( $10^{10} \text{ cm}^{-3}$ ). This can be explained by a getter action of the p+ channel. This means that the concentration close to the active area is higher than in other areas of the sensor. The same higher concentration next to the active area was also observed in [1].

The diffusion coefficient of the generation centers is determined by the mean free path of the metal atom multiplied with the thermal velocity obtained from (1.a)[5]. The mean free path will be close to the silicon lattice size. This diffusion coefficient comes very close to the diffusion coefficient of gold. Other elements have also been investigated, but none fit the measurements as well as gold (Figure 5).

**Table 1.** Overview of the obtained results.

|                    |  |
|--------------------|--|
| $N_t^T$            | 6000   |
| $C_{\text{metal}}$ | $10^{12} \text{ cm}^{-3}$                        |
| $D_{\text{metal}}$ | $10^{-3} \exp(-1.12/kT) \text{ cm}^2/\text{s}$ . |
| $E_b$              | 1.56 eV  |
| $\Delta V_b$       | 0.25 eV  |

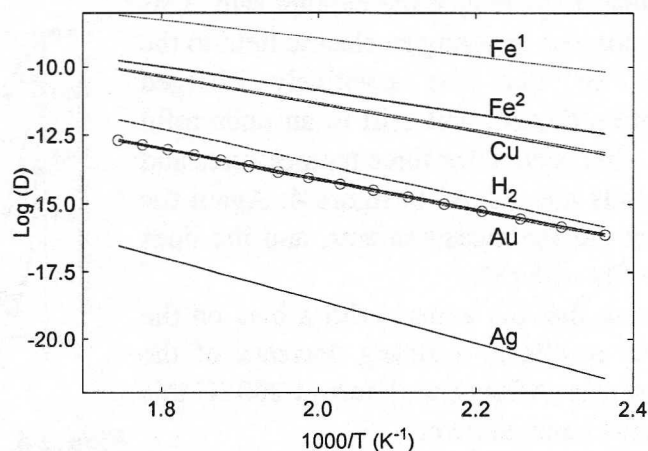


McColgin et al. [11] concludes from his work that Iron is the most probable element that causes the white pixels in their CCDs. His anneal experiments are carried out at 55 °C, during some hours. At these temperatures and time scales, no change in white pixel behaviour in our sensors is observed. In [4] it is also showed that Iron will generate much less electrons per second than the centers which are responsible in the white pixels in our sensors. This concludes that Iron is probably not causing the white pixels in our CCDs.

A comparison with literature with respect to the bindings energy is not found, what means that the nature of the trap remains unknown.

The reduction of the bindings

energy caused by the Poole-Frenckel effect is 0.25 eV which can be explained by a electric field during the anneal of  $10^5$  V/cm, which is in agreement to simulations.



**Figure 5** The diffusion coefficient versus  $1000/T$ . The markers represent the data of the diffusion coefficient, which is determined from the capture rate. The lines are the fit with diffusion coefficient from literature:

|    |           |    |            |                |     |
|----|-----------|----|------------|----------------|-----|
| Fe | [6,7,8,9] | Au | [7,8,9,10] | H <sub>2</sub> | [7] |
| Cu | [7,8]     | Ag | [9]        |                |     |

## Conclusions

It is clear to see that the model fits the data very well. From the obtained parameters the process can be optimized by removing the traps or the generation centers. A way to “repair” the sensor is found by an anneal with bias. Gold again, like in [1], seems to be the most probable element that causes the extra charge in some pixels of the sensors.

- [1] W.J. Toren and J. Bisschop, Metal contamination characterization in CCD image sensors, IEDM 1995, pp 163.
- [2] T.R. Waite, Journal of Chemical Physics, Vol. 28, January 1958, page 103.
- [3] E.M. Pell et al., J. Appl. Physics 65 (8), April 1989, page 2974.
- [4] W.J. Toren, The characterization of dark current generation centers in CCD frame transfer image sensors, Phd thesis, ISBN 90-74445-31-4.
- [5] S. M. Sze, Semiconductor devices, physics and technology, 1985, page 41.
- [6] E.R. Weber, Transition metals in silicon, Appl. Phys. A 30, page 1 (1983)
- [7] Q.R.M. for Silicon integrated circuit technology, ed. W.E. Beadle et al. John Wiley & Sons, pp 6-32, ISBN 0-471-81588-8
- [8] B.I. Bolthaks, ed. H.J. Goldsmid, Diffusion in semiconductors, Infosearch Ltd. 1963, pp 211.
- [9] Semiconductor data, Vol. 9, H. F. Wolf, ed. H. K. Henisch, Publ. Pergamon 1969, pp138.
- [10] J.S. Kang et al., Gettering in silicon, J. Appl. Phys. 65(8), April 1989, page 2974.
- [11] W. C. McColgin et al., Mat. Res. Soc. Vol. 378 (1995) page 713.