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Experimental Study of Internal Gettering Efficiency of Iron in Silicon

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Abstract

We have studied internal gettering efficiency of iron in silicon by Deep Level Transient Spectroscopy (DLTS) and standard lifetime – methods (SPV, μPCD). Conventional high–low–high anneals were performed to produce a series of wafers with varying denuded zone (DZ) width and oxygen precipitation density. The wafers were intentionally iron contaminated to a level of about $3\text{–}5 * 10^{13}\,\mathrm{cm}^{-3}$. After contamination the wafers were annealed at 900 °C and then slowly cooled to 850, 800, 750, 700 or 600 °C. After cooling the remaining interstitial iron concentration was measured by SPV, μ-PCD and DLTS. The experimental results are compared with simulations. Our results indicate that with this contamination level, the gettering is effective only at temperatures below 750 °C when iron is supersaturated over a factor of twenty. For temperatures above 750 °C the gettering is limited by iron precipitation in the bulk.

1. Introduction

In the modern semiconductor technology purity requirements of starting materials and cleanliness of processes are ever increasing. However, there are always some contaminants present. In silicon one of the most troubling ones is iron. It is one of the most common transition metals, which are fast diffusing and have deleterious effects on the device performance even when present in small concentrations. Gettering is a technique which can be used to reduce the detrimental effects of transition metals. In gettering the impurity atoms are transferred from the active surface region of a wafer to some location where they do not deteriorate the device performance.

In internal gettering one takes advantage of the oxygen atoms already present in Czochralski-grown silicon wafers. The oxygen atoms are used to form a defect free denuded zone (DZ) close to the wafer surface and to grow precipitates in the bulk. Conventionally this can be done with a three-step high–low–high anneal [1]. The cooling rate after this anneal is decisive for the gettering efficiency as the impurity atoms need to have time to diffuse to the bulk, but on the other hand, the cooling should be fast enough to maintain a high supersaturation for effective precipitation in the bulk [2].

Even though internal gettering is a widely used method, there are not enough knowledge about the process and its optimization. In this work we study experimentally how the cooling as well as DZ width and oxygen precipitate density affects the gettering efficiency of iron. Finally, we compare the experimental results to simulations and discuss how these results affect the optimization of the gettering efficiency.

2. Experimental

The silicon wafers processed were p-type (100) 10–22 Ωcm, boron-doped and 525 µm thick. The oxygen content was higher than 15.5 ppma [3]. Three different high–low–high series (A, B and C) were processed to study the effect of the denuded zone (DZ) width and the precipitation site density on the gettering efficiency of iron (Table I). Homogenous reference samples were processed for reference use (process D).

Table I. *High–low–high and homogenization processes.*

Process	Hi	Lo	Hi
A	1100 °C, 4 h	550 °C, 16 h	1100 °C, 16 h
B	1150 °C, 16 h	550 °C, 6 h	1100 °C, 16 h
C	1150 °C, 16 h	550 °C, 16 h	1100 °C, 16 h
D	1050 °C, 15 min	—	—

The DZ width of the wafers was found to be about 30 µm in process A and 60 µm in processes B–C [4]. Oxygen loss due to the out-diffusion and precipitation was about 4.8 ppma in processes A–C and the defect density is $0.2\text{–}2 * 10^{11}\,\mathrm{cm}^{-3}$ [4] in each case. There is no significant difference in the defect densities between 6 and 16 hours nucleation.

The wafers were contaminated in SC1 ($NH_4OH : H_2O_2 : H_2O$ 1 : 1 : 5) solution with added iron (30 ppb) impurities. Iron was in-diffused for 30 min at 850 °C. The surface contamination was removed by etching in $H_2O : HF : H_2O_2$ (24 : 1 : 1) solution and by cleaning in a sequence of SC1, HF-dip ($H_2O : HF$ 25 : 1) and SC2 ($HCl : H_2O_2 : H_2O$ 1 : 1 : 5). After surface cleaning the wafers were dry-oxidized for 15 min and anneal for 15 min in nitrogen ambient at 900 °C. The 30 min anneal at 900 °C allows the iron contamination to spread uniformly through the wafer so that the initial condition before cooling is known. The last cooling after annealing at 900 °C was performed in five different ways. In each case the wafers were cooled from 900 °C to 850 °C at a rate of 4 °C/min. The cooling from 900 °C to 850 °C should not be important as the contamination level is determined by the solubility at 850 °C. The initial contamination level of about $3\text{–}5 * 10^{13}\,\mathrm{cm}^{-3}$ is then approximately the same as in wafers pulled out at 850 °C at a velocity of 25 cm/min. From 850 °C the wafers were cooled at rate of 2 °C/min to 800, 750, 700 and 600 °C for the four different cooling procedures respectively. The wafers were then pulled out of the furnace at a velocity of 25 cm/min.

After cooling the remaining interstitial iron concentration was measured by SPV and μ-PCD [5, 6]. The SPV and μ-PCD measurements do not need any additional sample preparation. The iron concentration near the wafer surface was measured by DLTS [7]. Before DLTS-measurements pieces with sizes of about 1 × 1 cm were cleaved from the wafers. The dry-oxide was removed from pieces by diluted 1 : 10 HF solution and titanium Schottky-contacts of about 200 nm thickness were evaporated onto the top of the pieces. Indium/gallium alloy was used to make ohmic contacts on the backside of the pieces.

3. Results and discussion

3.1. *SPV and μ-PCD*

The iron-boron pairs were dissociated by generating high charge carrier concentration into a sample with a flashlight. Detailed

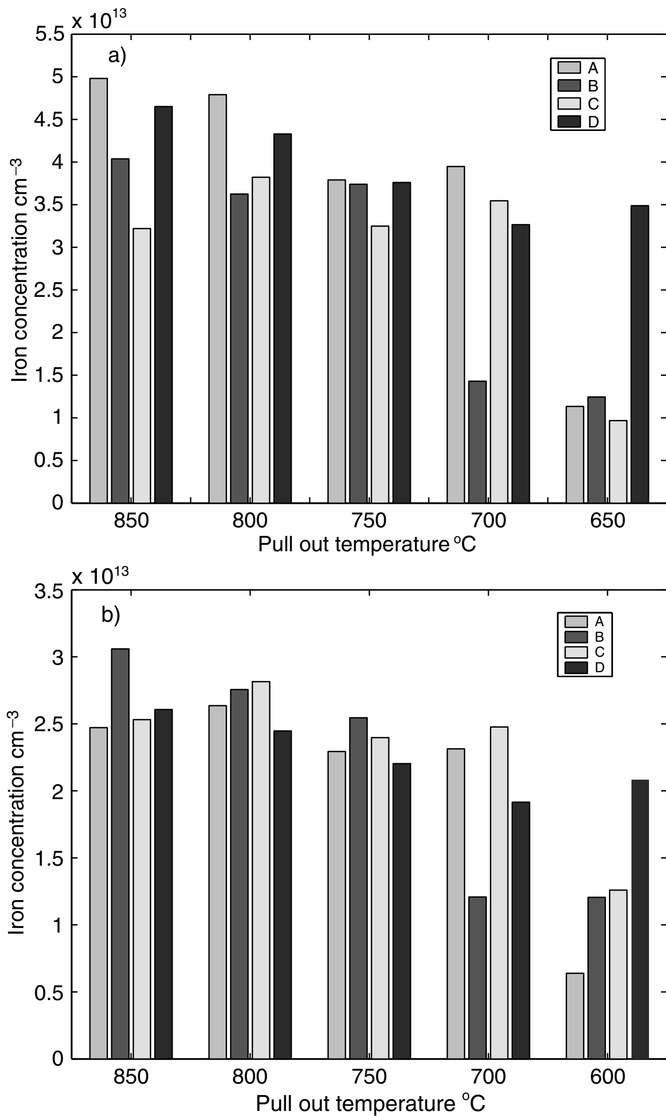

Fig. 1. The remaining interstitial iron concentration measured by SPV (a) and by μ-PCD (b) after cooling from 850 °C to pull-out temperature at a speed of 2 °C/min.

descriptions of SPV and μ-PCD systems are given in reference [5]. The iron concentration was calculated by using the same algorithm that is used for homogeneous wafers [5, 6]. Thus, in case of a DZ-wafer the effective iron concentration should be considered. The iron concentrations determined by SPV and μ-PCD are shown in Fig. 1.a–b. In the homogeneous wafers the diffusion length decreases after illumination on the average by a factor of four, which indicates that the main contamination is iron [8]. In the DZ-wafers the diffusion length decreases by a factor of 1.3 in process A and by a factor of 1.7–1.8 in processes B–C. This shows how oxygen precipitates affect the measured diffusion lengths. The effect is clearly stronger in the case of a short DZ. However, if it is assumed that a flashlight does not dissolve precipitated iron nor change the recombination properties of oxygen precipitates, the iron concentration can be estimated. In the non-contaminated DZ-samples the diffusion length (lifetime) did not change notably indicating that the background contamination level is low enough, i.e. below 10^{12} cm^3.

From Fig. 1 it can be seen that the iron concentration decreases in the process B wafers, when the pulling out temperature is 700 °C. In all DZ-wafers the iron concentration decreases to about the same level when the cooling is done to 600 °C. This clearly demonstrates that gettering occurs only at the low temperatures. In homogeneous samples the iron concentration does not decrease, which indicates that there is not enough precipitation centers for iron. By applying the effective iron diffusion constant [9] it is easy to calculate that the cooling is slow enough for iron to diffuse to the bulk during cooldown from 850 °C. Thus, the gettering above 750 °C must be limited by precipitation of iron in the bulk [10]. The iron precipitation occurs under supersaturation, therefore the decrease in precipitation may be due to enhanced solubility [11, 12] of iron in boron doped silicon. However, at this doping level the more probable reason is that only a portion of the oxygen precipitates serve as iron precipitation sites at higher temperature or lower supersaturation [13]. By comparing the contamination to the iron solubility [9] it can be concluded that the most effective gettering occurs when the degree of supersaturation was higher than two decades. Similar results are also reported in [10].

3.2. *DLTS*

The description of a DLTS method can be found from reference [7]. The DLTS results are summarized in Fig. 2. DLTS gives the iron concentration from the sample surface to a depth of about 3 µm at the reverse bias voltage used. The DLTS results of processes A–C are in agreement with SPV and μ-PCD results. However, the DLTS measurements indicate a strong decrease in iron concentration also in process D, which can be explained by the reaction of iron with the surface of the wafer [14]. The surface reaction also makes it more difficult to really conclude whether the iron is precipitated in the bulk or at the surface of the wafer. Combining the SPV, μ-PCD and DLTS measurements it can be concluded that at least some fraction of iron is captured in the bulk of the samples in processes A–C. The bulk and the surface reaction can also be separated by studying the iron dissolution, which is faster from the bulk defect region than from the surface of the wafer at temperatures 750–800 °C [14].

3.3. *Simulations*

The detailed algorithms and physical basis of the simulator can be found in reference [15]. In the simulations we use the reported

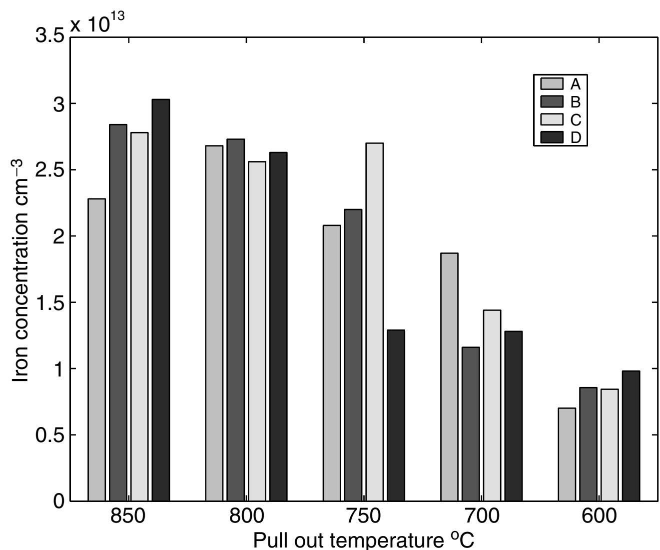

Fig. 2. The remaining interstitial iron concentration near the surface of the wafer measured by DTLS after cooling from 850 °C to pull out temperature at a speed of 2 °C/min.

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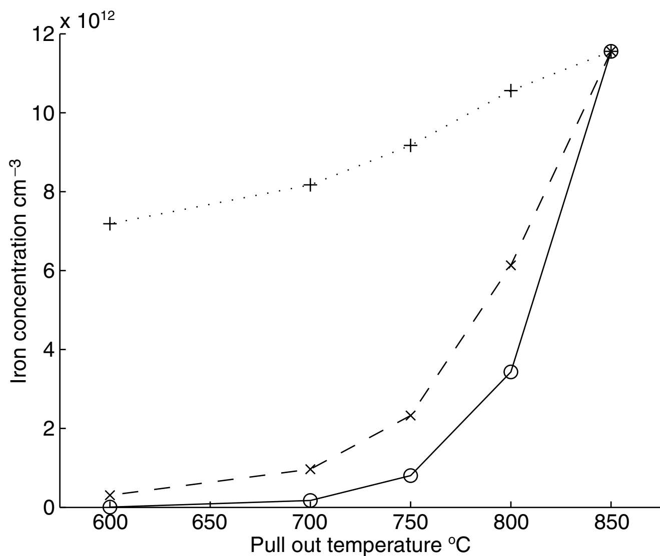

Fig. 3. The simulated iron concentration in the DZ as a function of pull-out temperature and *Nr*-product ($\circ\ Nr = 4000\,\text{cm}^{-2}$, $\times\ Nr = 400\,\text{cm}^{-2}$ and $+\ Nr = 40\,\text{cm}^{-2}$).

value for the iron solubility and diffusivity [9]. The DZ width is set to 60 μm [4]. The other material parameters needed in the simulations are the average radius (r) and the density of iron precipitation centers (N), or actually the *Nr*-product [15]. The simulations were made using three different *Nr*-products in the bulk. The precipitation in the DZ was neglected. The Neumann boundary conditions were used in the wafer surfaces i.e. no flux to wafer surfaces. The *Nr*-product was kept constant in proportion to temperature, although in reality it may depend on the temperature and/or the degree of supersaturation [13]. Thus the *Nr*-product is an effective value, which describes the precipitation strength. The initial iron contamination level was set to the iron solubility at 850 °C, so only the cooling from 850 °C was simulated. The simulation results are shown in Fig. 3.

It can be observed from the simulations that the effective *Nr*-product in our samples is between 40 and 400 cm^{-2}. This is far below the real *Nr*-product of oxygen related defects present in the samples, which can be estimated to be in the order of 10^4–$10^5\,\text{cm}^{-2}$ [16].

4. Conclusions

Our results indicate that effective gettering occurs at temperatures below 750 °C, when iron is supersaturated over a factor of twenty at a contamination level of $3–5 * 10^{13}\,\text{cm}^{-3}$. At the higher temperatures gettering is limited by precipitation of iron in the bulk. The iron precipitation above 750 °C is suppressed because only a portion of the oxygen precipitates serve as iron precipitation sites [13]. In order to perform quantitative gettering simulations this must be taken into account.

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