ENHANCEMENT OF INTERNAL GETTERING EFFICIENCY OF IRON BY LOW TEMPERATURE NUCLEATION

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In order to better understand internal gettering of iron in silicon at low supersaturation, an experimental study of iron gettering with different annealing profiles was performed. Special attention was paid to the effect of iron nucleation at low temperatures. The results reveal that gettering can be efficient even after 30 minutes anneal at 700°C if the wafers go through a low-temperature region before the actual gettering anneal. In the simplest case the low-temperature nucleation can be realized by a fast withdrawal of the wafers out of the furnace. The density of oxygen precipitates seemed to have only a minor impact on the gettering efficiency indicating that not every oxygen precipitate related gettering site is an active sink for iron.

INTRODUCTION

Internal gettering (IG), *i.e.* removal of metal impurities from the active device area by oxygen precipitates and/or associated structural defects in the bulk, is a common method used in the IC industry to improve device yields. Further understanding of IG together with predictive computer modeling is essential to improve the gettering process as current experimental optimization through device yield studies is unreasonably expensive and time consuming. There have been several publications [1,2,3,4] about the modeling of IG of transition metals in silicon, which are based on the assumption of diffusion-limited precipitation. These models, nevertheless, tend to overestimate the IG efficiency especially at low supersaturation [5, 6]. Low supersaturation is the most significant region in real IC fabrication: iron concentration is reasonably low (less than 10^{13} cm^{-3}) and front-end-of-line processing temperatures are above 600°C.

In this paper iron contaminated silicon wafers are heat-treated with different gettering profiles at low supersaturation. The gettering efficiency after a fast cooling with a room temperature step and after a traditional slow cooling is compared. These results give us a better understanding of the iron gettering behavior at low supersaturation.

EXPERIMENTAL

In the experiments we used p-type CZ-silicon with an initial oxygen level of either 14 ppma (A-samples) or 16 ppma (B-samples) as measured according to the ASTM F 121-83 standard. The wafers were first heat-treated at 1150°C for 4 hours to dissolve most of the oxygen nuclei formed during the crystal growth. Some of the oxygen out-diffused during the anneal resulting in a region of low oxygen concentration near the wafer surfaces, which act as a basis for the later denuded zone formation. The wafers were then subjected to a nucleation treatment at 550°C for 6 hours which was followed by the 1100°C, 16h growth step. The resulting drop in oxygen concentration was measured to be 6.9 ppma in A-samples and 9.3 ppma in B-samples. The denuded zone formed was about 45μm in A-samples and 25μm in B-samples measured by the scanning infrared microscopy (SIRM). The oxygen precipitate densities in both types of samples were higher than the upper detection limit of SIRM, *i.e.*, above 3×10^9 cm^{-3}. However, we can expect that the density of oxygen precipitates is higher in the B-samples than in the A-samples due to the difference in the initial oxygen level [10].

After High-Low-High anneals the wafers were intentionally iron contaminated by immersing them in the standard SC1 solution (NH_3OH:H_2O_2:H_2O 1:1:5) with added iron chloride. Iron was diffused from the surfaces into the wafers at 850°C for 50 minutes to get an initial iron concentration of $2\times10^{13}cm^{-3}$, determined by the iron solubility at 850°C. The surfaces of the wafers were then carefully cleaned and the wafers were oxidized again at 900°C to guarantee homogeneous iron distribution.

Two different kinds of gettering experiments were performed to study the effect of low temperature nucleation. The outline of the anneals is shown in Table 1. The actual gettering anneal was the same for both profiles: annealing at 700°C for varying processing times (0h, 0.5h 1h and 2h). In the first test anneal (profile 1), the wafers were slowly cooled (2°C/min) from the oxidation temperature at 900°C down to 700°C, which was directly followed by the above mentioned gettering anneal. In the second test anneal, the only difference was that after the oxidation at 900°C, the wafers were quickly pulled out of the furnace to room temperature. Then the wafers were drawn back into the furnace at a speed of 30cm/min and the gettering anneal at 700°C was performed.

Table 1. Outline of the two different annealing profiles.

Anneal profile 1	35 min @ 900°C → slow cooling → 700°C (0-2 h) → RT
Anneal profile 2	35 min @ 900°C → fast cooling → RT → 700°C (0.5-2 h) → RT

The dissolved iron concentration was measured by the microwave photoconductive decay (μPCD) technique using the well-known Fe-B light dissociation method [7]. Some of the samples were also measured by DLTS near the wafer surface to confirm the validity of μPCD measurements in case of IG wafers [8].

RESULTS AND DISCUSSION

Figure 1 shows the measured iron concentration after varying gettering anneals. Traditionally, internal gettering is activated during a slow cooling at the end of the process. However, the time consuming slow ramp is often not good enough for effective gettering [6]. This is also observed in anneal profile 1, where the wafers are slowly cooled from 900°C to 700°C. We did not observe any gettering to take place even if we kept the wafers at 700°C for two hours. The slow cooling is usually simulated by using Ham's diffusion limited precipitation theory [9], which states that the supersaturation is the driving force towards precipitation and the precipitation rate depends on the precipitate site density n and the radius of the precipitates r_0. Ham's law for the dissolved iron concentration C can be written as follows

$$C(t) = S + (C_0 - S)e^{-t/\tau}, \quad \text{where } \frac{1}{\tau} = 4\pi D n r_0 \tag{1}$$

where S is the solubility, D is the diffusivity, and C_0 is the initial dissolved iron concentration. However, if we use this formula to simulate anneal profile 1, we get a result where already after the slow cooling from 900°C to 700°C, the dissolved iron concentration reaches the value of 1×10^{11} cm^{-3}, which is the iron solubility at 700°C. The same simulation result is obtained even if we use in the bulk the value of 100 for the nr_0 product, which is not realistic in IG wafers. Obviously, the Ham's law cannot be used directly to simulate iron behavior at low supersaturation.

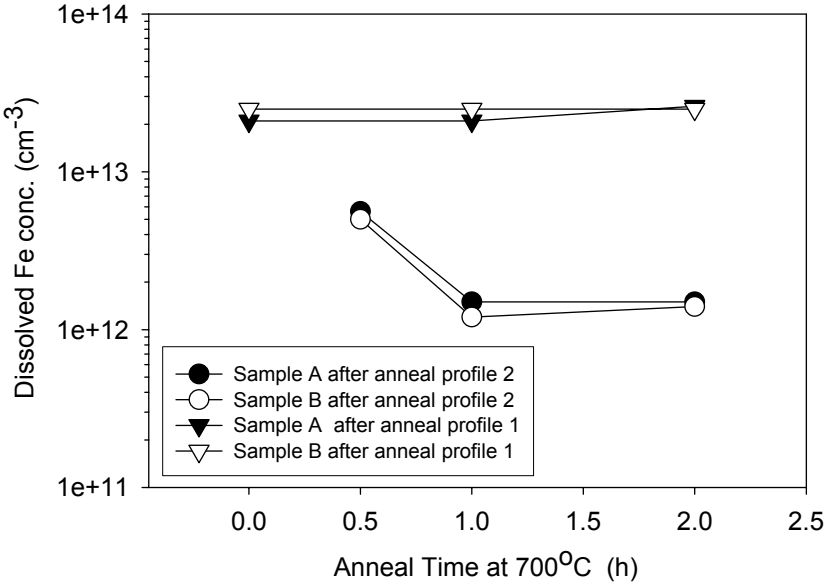

Figure 1. Measured iron concentration after gettering anneal at 700°C: i) Wafers are slowly cooled down from 900°C (triangles) ii) Wafers have been unloaded to room temperature after the oxidation and then loaded back to the 700°C gettering anneal (circles).

In the case of anneal profile 2 the gettering effect is clearly observed. Already after a 30 minute anneal at 700°C, 70% of initial dissolved iron has precipitated and after one hour 92%, respectively. A two-hour anneal does not seem to bring about any improvement in the gettering efficiency compared to the one-hour anneal. Even thought the gettering seems to be much more efficient after anneal profile 2, the dissolved iron does not reach the solubility in this case either.

We did not notice much difference in the iron gettering behavior between samples with different oxygen precipitate densities (A and B samples). This implies that not all oxygen precipitates are active gettering sites for iron. In homogeneous reference wafers that underwent the same gettering anneals (both profile 1 and 2), we hardly observe any iron precipitation to take place, which suggests that iron does not precipitate homogeneously nor out-diffuse to the oxidized surfaces.

The enhanced gettering efficiency after anneal profile 2 can be explained by the formation of iron nuclei to some of the oxygen precipitation related defects at low temperature. After nucleation iron has a low barrier for precipitation at higher temperature while its diffusivity is increased. This results in strong gettering and the dissolved iron concentration begins to decrease. The phenomenon is analogous to oxygen precipitation in silicon [10]. High enough supersaturation is needed before nucleation and precipitation take place. For iron the required supersaturation level may be lower compared to oxygen as iron precipitates heterogeneously to the existing defects while oxygen may need to precipitate homogeneously.

CONCLUSIONS

Our experiments show that the gettering efficiency of iron can be drastically improved if the wafers are exposed to a short low temperature step to form iron nuclei before the actual gettering anneal. The results indicate that instead of concentrating on a slow cooling at the end of the device processing, one can improve the gettering efficiency by making a “low-high” anneal to activate the gettering. The optimum nucleation temperature is yet to be determined. However, our experiments show that the nucleation time required for effective gettering is not excessive. In order to optimize the furnace time consumed on gettering, the best option is most likely to pull the wafers out of the furnace (the pull-out temperature is insignificant) and then draw them back into the furnace at constant temperature. One has to keep in mind that competitive gettering [11] by the areas of heavily doped real devices probably reduces the overall gettering efficiency.

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