

Experimental evidence for the presence of segregation and relaxation gettering of iron in polycrystalline silicon layers on silicon

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Experimental evidence is provided that gettering of iron by polycrystalline silicon (polysilicon) is driven by a combination of two gettering mechanisms, segregation and relaxation. The segregation coefficient of iron in polysilicon in samples annealed at temperatures between 1020 and 1175 °C varied from approximately 16 to 2. The efficiency of relaxation gettering by polysilicon was characterized using Ham's model of diffusion-limited gettering. The product nr_0 for the 11- μm -thick polysilicon layer was estimated as 10^6 cm^{-2} . © 2004 American Institute of Physics. [DOI: 10.1063/1.1819512]

Gettering of transition metals by a layer of polycrystalline silicon (polysilicon) deposited on the back side of silicon wafers has been widely used by the silicon industry as a means to remove transition metals from the wafer and improve the minority carrier lifetime. One of the advantages of polysilicon gettering which found applications in silicon on insulator wafer manufacturing is that a poly-Si layer can withstand very high annealing temperatures (over 1200–1300 °C) without losing its gettering properties.

It has been debated for years whether polysilicon gettering is driven by relaxation or segregation mechanisms or by their combination (see, e.g., Ref. 1, and references therein). This letter provides direct experimental evidence that gettering of iron by polysilicon contains relaxation and segregation components, suggests experimental procedures to separate segregation and relaxation components, and provides some quantitative characteristics for both mechanisms.

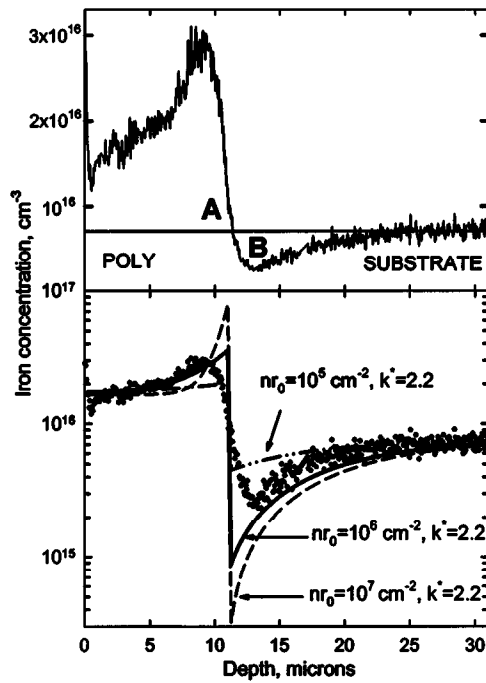
The difference between the relaxation and segregation gettering is that segregation is an equilibrium process which takes place at the processing/annealing temperatures, whereas relaxation takes place only during cooling as the impurity gets supersaturated.¹ In theory, one could distinguish segregation from relaxation by quenching a sample from the annealing temperature to room temperature sufficiently fast to freeze-in the high-temperature distribution of metals. However, it is not always possible to achieve the required quenching rate. Since the diffusion coefficients of impurities in silicon depend exponentially on temperature, the quenching rate required to freeze-in the metal distribution also exponentially increases with the annealing temperature. The most commonly used quenching solutions are silicone oil (estimated average quenching rate 100–250 K/s), ethylene glycol (1000 K/s), and 10% NaOH solution (2000 K/s).² The experiments presented in the following demonstrate that even quench in the NaOH solution is not sufficiently fast to freeze-in the iron distribution at temperatures above approximately 1000 °C.

In our recent conference report³ we used silicone oil quench of poly-Si/Si samples to characterize the efficiency of iron gettering. However, since it can be easily estimated that iron can diffuse as much as 10 μm during silicone oil quench, more sophisticated experimental procedures are needed to fully separate segregation from relaxation.

This study suggests two such experimental procedures to separate segregation from relaxation. The first procedure illustrated in Fig. 1 requires that SIMS depth profile of Fe in quenched poly-Si/Si structure be taken to a sufficiently large depth where iron concentration reaches its equilibrium solubility. The structure presented in Fig. 1 consists of 11 μm of undoped polysilicon deposited by chemical vapor deposition using standard process parameters used at Sumitomo Mitsubishi on top of a *p*-type 4 in. (100) Czochralski- (CZ)-grown (525- μm -thick) silicon substrate. The polysilicon grain size was typically from 0.3 to 0.6 μm . The sample was contaminated from the back side by scratching it with an iron wire, annealed in a vertical furnace at 1150 °C in $\text{N}_2 + 5\% \text{H}_2$ ambient for 90 min, and quenched in silicone oil. The transition area between the polysilicon and the substrate (at a depth of 11 μm) appears to be rather broad presumably due to an uneven surface of the poly-Si, which was observed by scanning electron microscopy in a cross-sectional image taken on a cleaved sample.

The important features of the profile in Fig. 1 are transients in the iron concentration in the polysilicon layer and in the substrate. These transients originate from relaxation gettering of iron during the silicone oil quench, whereby supersaturated iron diffuses from the substrate to the polysilicon layer and precipitates there, primarily in the areas close to the poly-Si/substrate boundary. The total amount of iron that was gettering due to a combination of segregation and relaxation mechanisms in the poly-Si layer can be determined, in units of Fe atoms per cm^2 of the sample surface, by integrating the area “A” of the plot in Fig. 1(a) between the SIMS data in poly-Si and the equilibrium iron solubility. The total amount of iron that diffused into the polysilicon layer due to relaxation gettering during cooling can be calculated by integrating the area “B” in the substrate. By performing the

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FIG. 1. Secondary ion mass spectroscopy depth profile of iron diffused in 11 μm polySi/Si structure at 1150 $^{\circ}\text{C}$ and quenched in silicone oil. (a) Depth profile plotted using a linear concentration scale. The solid horizontal line is the equilibrium iron solubility at the diffusion temperature. (b) The same depth profile plotted on a logarithmical scale together with the results of numerical modeling. The solid line represents the best fit, the dashed lines are variations of the nr_0 product.

integration, one obtains $A = 1.44 \times 10^{13} \text{ cm}^{-2}$ and $B = 2.52 \times 10^{12} \text{ cm}^{-2}$. Since the area A is 6.4 times greater than the area B , the relaxation gettering alone cannot account for all iron accumulated in poly-Si. Hence, both relaxation and segregation mechanisms are present. The segregation coefficient k can be determined as follows

$$k = \frac{S(\text{poly})}{S(\text{substrate})} = \frac{\text{Fe}_{\text{eq}} + (A - B)/d}{\text{Fe}_{\text{eq}}} \approx 2.6, \quad (1)$$

where Fe_{eq} is the equilibrium Fe solubility in silicon at the anneal temperature, d is the thickness of the poly-Si layer, and $S(\text{poly})$ and $S(\text{substrate})$ are the solubilities of iron in polysilicon and in the substrate.

In order to obtain a quantitative measure of the relaxation gettering efficiency of the polysilicon layer (which is characterized in Ham's theory⁴ by the product of the precipitation sites density n times their radius r_0), we performed computer modeling of gettering of iron during cooling. The algorithm of the gettering simulator used for this analysis is described in detail elsewhere.⁵ The parameters of the model were varied to obtain the best fit, shown in Fig. 1(b). Although there are some small discrepancies between the experimental and modeled curves, most notably in the transition area between the substrate and the poly-Si layer, all features of the experimental spectra are well reproduced. To demonstrate the sensitivity of the fit to the nr_0 product, two additional curves (dashed lines) with the nr_0 ten times greater and smaller than the fitted value are also shown. The segregation coefficient obtained from the fit is $k = 2.2$. The nr_0 product⁴ for the polysilicon layer was estimated from the

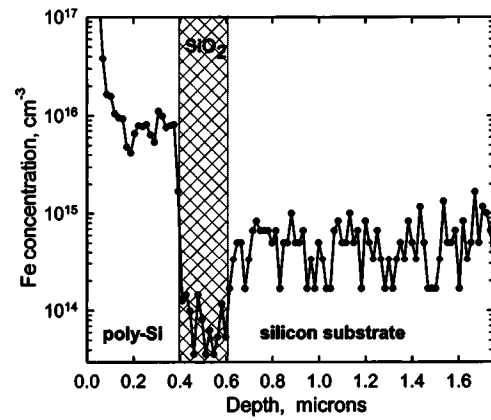


FIG. 2. SIMS depth profile of iron diffused in 0.37 μm poly-Si/197 nm thermal SiO_2 / p -Si substrate. Iron was diffused from the back side of the wafer at 1020 $^{\circ}\text{C}$, diffusion time 8 h, silicone oil quench.

fit as 10^6 cm^{-2} . This value should be compared to a range of values of nr_0 for internal gettering sites in CZ-silicon (see Ref. 6) of $10^3 - 5 \times 10^5 \text{ cm}^{-2}$.

Another 11 μm poly-Si sample was quenched from a temperature of 1175 $^{\circ}\text{C}$ in 10% NaOH. The depth profile (not shown) was similar in shape to that in Fig. 1. This indicates that NaOH solution was not sufficiently fast to freeze-in the distribution of interstitial iron. Integration of the areas A and B using the same procedure as used in Fig. 1 gave the segregation coefficient of $k \approx 1.6$ at 1175 $^{\circ}\text{C}$.

The second experimental procedure which we used to separate the segregation gettering consists in using a thin diffusion barrier between the polySi and the substrate. Figure 2 is a SIMS profile taken on a structure consisting of 0.37 μm of polysilicon and 200 nm of SiO_2 on top of a silicon substrate. The sample was annealed for 8 h at 1020 $^{\circ}\text{C}$, which was sufficient for iron to diffuse through silicon dioxide and establish its equilibrium distribution at the annealing temperature. On the other hand, the diffusivity of iron in silicon dioxide is too slow to allow iron to diffuse through it during the quench. Therefore, even at relatively slow cooling rates, the concentration of iron in polysilicon represents its concentration established at the annealing temperature. The segregation coefficient in this sample was determined as $k \approx 16$.

The probable cause for segregation of iron in polysilicon is a difference in its free energy in a perfect silicon lattice and in a distorted lattice near the defects such as dislocations or grain boundaries. This model was used to explain the effects of segregation of arsenic,⁷ boron,⁸ and phosphorus^{9,10} to grain boundaries in silicon. Since the lattice is substantially distorted only within very short distances (typically, several lattice constants) from the dislocation cores, one can expect that segregated metals would thinly and homogeneously decorate grain boundaries and dislocations.

Since polysilicon is very inhomogeneous and contains both grain boundaries where the impurities can segregate and relatively unstressed silicon within the grains which has no segregation effect, the macroscopic segregation coefficient and nr_0 product observed in the experiments should depend on the microscopic structure of the polysilicon layer (such as grain size and relative orientation of the adjacent grains) and are likely to vary depending on the thickness and growth conditions of the layer. Since the polySi layers used in Figs. 1 and 2 and those studied in Ref. 3 have different thickness,

they may have different segregation properties at the same annealing temperature and should not be directly compared.

The presence of the segregation component in polysilicon gettering is advantageous for gettering of low iron contamination levels in integrated circuit industry since it expands the temperature region in which gettering is efficient and increases the overall gettering efficiency. On the other hand, the segregation effect may have negative effect on multicrystalline silicon (mc-Si) wafers used for solar cells. These materials are known to contain high transition metal concentrations¹¹ which are notoriously difficult to remove from mc-Si.¹² Segregation of metals at grain boundaries could be a mechanism responsible for the resistance of mc-Si to gettering.

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