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Modeling of heterogeneous precipitation of iron in silicon

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A model is presented for the growth and dissolution of iron precipitates at oxygen-related defects in silicon during thermal processing. The heterogeneous nucleation of iron is taken into account by special growth and dissolution rates, which are inserted into a set of modified chemical rate equations. This approach allows us to calculate the size distribution of iron precipitates and the residual iron concentration. By comparing the simulated results with experimental ones, it is proven that this model can be used to estimate the internal gettering efficiency of iron under a variety of processing conditions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2099531]

The capability of oxide precipitate-related defects to capture impurities is widely utilized in the integrated circuit industry to remove harmful metal contaminants from the device area. As experimental process optimization for the impurity gettering is expensive and time consuming, several theoretical papers[1–4] discuss modeling of gettering of impurities, especially iron. In these papers, the change in the interstitial iron concentration due to heterogeneous precipitation of iron is calculated as suggested by Tan *et al.*[4]

$$\frac{\partial C_{\mathrm{Fe}}}{\partial t} = -4\pi r_{\mathrm{ox}} N_{\mathrm{ox}} D (C_{\mathrm{Fe}} - C_S), \tag{1}$$

where N_{ox} is the total density of oxide precipitates, r_{ox} is the average radius of the oxide precipitates, D is the diffusion constant of iron, C_{Fe} is the interstitial iron concentration, and C_S is the solid solubility of iron in silicon. Equation (1) can be obtained from Ham's diffusion limited precipitation law for fixed radius,[2,5] thus, we refer to the Eq. (1) as Ham's law.

Experiments show that Eq. (1) is approximately valid for iron at very high supersaturation,[1,6] for example, as the temperature is around 200 °C and the iron contamination level is around 1×10^{13} cm^{-3}. However, the universal validity of Eq. (1) may be questioned as other experimental results indicate that iron precipitation occurs only above a certain critical supersaturation level.[7–13] In addition, Takahashi *et al.*[14] found out that, for a fixed amount of precipitated oxygen, the gettering efficiency of large oxide precipitates was higher than the gettering efficiency of small oxide precipitates in the case of cooling at the rate of 25 K/s. In the case of isothermal annealing at 190 °C, the result was opposite: The gettering efficiency of small oxide precipitates was higher.[14] These experimental observations[7–14] clearly confirm that Eq. (1) is not valid at low supersaturation as the nucleation of iron precipitates is ignored. In this letter, we present a model for heterogeneous precipitation of iron in silicon which is valid under any saturation level. The model includes the nucleation of iron precipitates, although iron reactions with the possible nucleation sites are treated in a very simplified manner for the time being.

Classical nucleation theory is based on the assumption that a precipitate can grow or dissolve only by one atom at a time. Such a cluster evolution is described by chemical rate equations (CREs):

$$\frac{\partial f_n}{\partial t} = I_n - I_{n+1} \quad n = 0, 1, \ldots, \tag{2}$$

where n is the number of iron atoms and f_n is the density of heterogeneous precipitation sites containing n atoms of precipitated iron. The flux from size $n-1$ to size n is

$$I_n = g_{n-1} f_{n-1} - d_n f_n, \tag{3}$$

where g_n and d_n are growth and dissolution rates, respectively. Conventionally, the CREs are used to model homogeneous nucleation. In our model, the idea is that we simulate how the heterogeneous precipitation sites attract the iron atoms. That also justifies the use of Eq. (2) to model the precipitates of all sizes. In addition, in our model, the index n starts from zero in contrast with the modeling of the homogeneous nucleation, and f_0 refers to the density of gettering sites, which do not contain iron, i.e., they have not yet become effective precipitation sites for iron. The density of effective precipitation sites and the concentration of precipitated iron can be calculated from the simulated size distribution function. The rate of change in the interstitial iron concentration can be calculated from

$$\frac{\partial C_{\mathrm{Fe}}}{\partial t} = -\sum_{n=0} I_n. \tag{4}$$

It is reasonable to assume that iron concentration at the interface of gettering site is in thermodynamical equilibrium with the iron precipitate, i.e., the growth of iron precipitates is a diffusion-limited process. Equation (1) assumes that this equilibrium interface concentration is equal to the solid solubility of iron. We presume that the equilibrium iron concentration at the interface depends on the number of iron atoms precipitated to the gettering site. This assumption can be jus-

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tified using general nucleation theory, in which the equilibrium concentration depends on the size of the nucleus.[15]

The model can be applied to the internal gettering of iron. The experiments[1,6] suggest that iron is apparently captured by a surface, which is larger than the surface of iron precipitate itself. However, we do not know for sure whether it is the oxide precipitates or secondary defects associated with oxide precipitates that act as the gettering sites for iron. When modeling the internal gettering, we choose the total density and the average radius of the oxide precipitates to characterize gettering sites as these seem to have correct magnitudes. Consequently, we obtain the growth and dissolution rates for heterogeneous iron precipitation from Eq. (1) by replacing the solid solubility of iron by size dependent equilibrium concentration C_{eq}:[16]

$$g_n = 4\pi r_{\mathrm{ox}} D C_{\mathrm{Fe}} \text{ and } d_n = 4\pi r_{\mathrm{ox}} D C_{\mathrm{eq}}. \tag{5}$$

At this point, it is important to note that our model reproduces the experimental observation[14] that a large oxide precipitate more easily becomes an effective iron precipitation site than a small precipitate. This experimentally confirmed behavior may be due to the larger surface of the precipitate, or it may be caused by extended defects, which are often associated with large precipitates.[14,17,18]

For simplicity, we assume that the local equilibrium concentration has the form

$$C_{\mathrm{eq}} = C_{\mathrm{eff}} \exp\left(\frac{E_a}{kTn^{1/2}}\right), \tag{6}$$

where $E_a/n^{1/2}$ describes the fact that iron has a higher chemical potential in a small cluster than in a large cluster. C_{eff} is the equilibrium concentration at the interface of a very large iron precipitate. The surface energy and the strain[14,17,18] and the morphology[1] of oxide precipitates, as well as the charge state of iron, can all have their own contributions to the iron precipitation behavior. However, in our model, the iron precipitation is described simply by one fitting parameter, E_a, where the above-mentioned effects are included implicitly. Using the Eqs. (4)–(6), it can be easily shown that our model reduces to Eq. (1) at high supersaturation, i.e., when $C_{\mathrm{Fe}} \gg C_{\mathrm{eq}}$ at all n. Generally, after nucleation, our model reduces to Eq. (1) with a small revision: N_{ox} is replaced by the density of effective precipitation sites.

We test the model by analyzing the experimental results, which we have reported in Refs. 8, 10, and 11. The experimental details can be found in these references and only essential parts are repeated here. In these references, we studied the gettering of iron using nearly identical starting material and oxygen precipitation anneals. Thus, in the following simulations, we use the oxide precipitate density of 2×10^{10} cm^{-3} and radius of 76 nm.[8] The denuded zone is neglected in the simulations as, at temperatures higher than 600 °C, gettering is limited by the precipitation of iron rather than by the diffusion of iron to oxide precipitates in the bulk. In our simulations, we use $1\times10^{-3}\times\exp(-0.67\ \mathrm{eV}/kT)\ \mathrm{cm}^2/\mathrm{s}$ (Ref. 19) as the effective iron diffusion constant and $C_{\mathrm{eff}}=4.3\times10^{22}\exp(-2.10\ \mathrm{eV}/kT)$ cm^{-3} (Ref. 7). The C_{eff} value determined by Aoki *et al.*,[7] after high-temperature indiffusion and precipitation of excess iron at lower temperatures, is larger than the generally used high-temperature solid solubility of iron.[19] This may indicate that iron precipitates to a different chemical or structural phase than the source phase during iron indiffusion. We solve the CREs using the selected grid point method.[16]

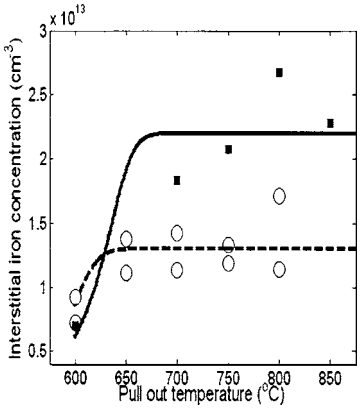

FIG. 1. Experimental results of slow cooling (2 °C/min) from 850 °C to pull out temperature are taken from Ref. 8 (squares) and 11 (open circles). In the simulated results, the fitting parameter E_a is 0.88 eV and the initial iron concentration is 2.2×10^{13} cm^{-3} (solid line) or 1.3×10^{13} cm^{-3} (dashed line).

Figure 1 shows the experimental results of slow cooling (2 °C/min) from 850 °C to different pull out temperatures with initial iron concentrations 1.3×10^{13} and 2.2×10^{13} cm^{-3}. Also shown are the simulated results with E_a=0.88 eV, and they are in reasonably good agreement with the experimental results. Both experiments and simulations indicate that gettering (iron precipitation) starts only as the wafer is cooled to about 650 °C, i.e., as the supersaturation reaches the critical level, which is $kT\ln(C_{\mathrm{Fe}}/C_{\mathrm{eff}})\approx 0.34$ eV. Hieslmair *et al.*[1] have observed experimentally that only some of the oxide precipitates serve as iron gettering sites at high temperatures. We can actually calculate the so-called effective iron precipitation site density. The simulated iron precipitation site density is about 7.7×10^7 cm^{-3} after cooling the wafer to 600 °C, i.e., more than three orders of magnitude smaller than the reported oxide precipitate density.

An appropriate temperature window for the gettering of iron depends on the contamination level. Gettering takes place at higher temperatures if the contamination level is higher. Experimental results[9,13] indicate that the gettering of iron at the contamination level of 10^{11} cm^{-3} is not possible even by extremely slow cooling to 500 °C or long isothermal anneal at 300 °C. This is because a sufficiently high supersaturation level and diffusivity are not reached simultaneously under these processing conditions. The results imply that gettering at low iron concentration requires low temperature and impractically long annealing times. This problem might be overcome by using a low-temperature nucleation anneal.[10] The nucleation anneal can just be a fast ramp to close to room temperature (RT), followed by a ramp back to the gettering temperature.[10]

In our experiments,[10] the wafers were divided into two different gettering treatments: (i) In the first treatment, the wafers were annealed at 900 °C, and then slowly cooled to 700 °C where the isothermal gettering anneal was performed. (ii) In the second treatment, the wafers were pulled out directly from 900 °C, air cooled to RT, loaded again to 700 °C and annealed further for different times. As shown in Fig. 2, the ramp to RT has a drastic effect on the iron precipitation behavior at 700 °C. The simulation agrees with

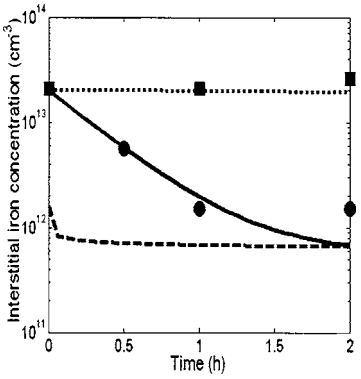

FIG. 2. The interstitial iron concentration dependence on annealing time for 700 °C annealing. The squares are our experimental results (see Ref. 10) without a RT step and circles are experimental results when the RT step is included in the process. The simulated results without the RT step (dotted line is the fitting parameter E_a=0.88 eV) and with the RT step E_a= 0.88 eV (dashed line), E_a=1.37 eV (solid line).

experiments such that no gettering occurs when wafers are annealed at 700 °C after cooling from 900 °C. In the RT step simulation, we assume a ramp rate of 25 °C/s during air cooling to RT and ramp up to 700 °C. If E_a is set to 0.88 eV, the simulation shows too rapid iron precipitation during the ramps and therefore overestimates the gettering. Better agreement with the experimental results is acquired if E_a is set to 1.37 eV. It seems that the value of E_a may be temperature dependent, but constant E_a value of 0.88 eV can be used at temperatures above 600 °C. However, it must be pointed out that the simulated results are very sensitive to variations in the value of E_a. The assumption of diffusion-limited precipitation leads also to overestimation of growth, which has a significant effect for small clusters during fast ramps. Further studies are needed to determine the temperature dependency of E_a as well as the possibility of surface reaction-limited growth of the iron precipitates.

In conclusion, we propose an improved model for the heterogeneous precipitation of iron in silicon. The model assumes that the heterogeneous precipitation sites that have already gettered some iron are more attractive gettering sites than the ones with no iron. Basically, this assumption, together with the use of CRE to simulate the cluster evolution, leads to the model which includes the nucleation of iron precipitates. The simulation results show that the model can be used to explain results of internal gettering experiments, which cannot be explained using the Ham's law alone.

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