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Diffusion of Iron in Silicon Dioxide

Deepak A. Ramappa*^z and Worth B. Henley

Center for Microelectronics, University of South Florida, Tampa, Florida 33620, USA

A quantitative analysis of diffusion of iron in silicon dioxide is presented. A source of iron deposited on the surface of thermally oxidized silicon wafers was diffused at temperatures ranging from 700–1100°C in an inert (nitrogen) ambient. The iron concentration in SiO₂ and Si was measured using total reflection X-ray fluorescence, deep level transient spectroscopy, and surface photovoltage techniques. A two-boundary diffusion model was applied to the experimental data to determine the diffusivity and segregation coefficient of iron in SiO₂. It is observed that iron diffusivity in SiO₂ follows the Arrhenius relationship and has a thermal activation energy of 1.51 eV. Iron exhibits a strong tendency to segregate into silicon dioxide and has a value of $k = 1.1 \times 10^{-7}$ at 1000°C, where $k = N_{Si}/N_{oxide}$.

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Atomic level purity and physical uniformity are required in silicon dioxide (SiO₂) films to prevent oxide weak spots and resulting premature dielectric breakdown. Unintentional low-level chemical contaminants cause defects which reduce oxide quality.¹ Foremost among oxide defect generators are transition metal impurities introduced into silicon during wafer processing through contaminated chemicals or processing equipment.² Metallic contamination is often introduced through the wafer surface or the dielectric layers grown thereon. Metallic surface contamination diffuses and becomes distributed throughout the wafer even after minimal thermal processing. Therefore the masking properties of silicon dioxide against surface metallic contamination diffusion is a matter of general concern to the silicon industry.

Iron is a common heavy metal contaminant in silicon integrated circuit (IC) processing. Iron diffusion through passivation and isolation structures into the device region can be very deleterious to silicon devices. Iron exhibits very high diffusivity (10^{-6} cm²/s at 900°C) and solubility (2×10^{13} cm⁻³ at 900°C) in silicon.³ Iron also plays an important role in the decoration of defects in silicon. This can be detrimental to the device region of the wafer, as strain fields and process-induced defects can localize and supersaturate the iron impurities in this sensitive area. This supersaturation is responsible for localized precipitation, which is known to cause premature dielectric breakdown.⁴

Despite the significance of iron contamination on metal-SiO₂-Si (metal-oxide-semiconductor, MOS) devices, there is very little published data on iron diffusion in SiO₂. Diffusion in SiO₂ of other metallic contaminants like Na, Au, Cu, Ni, Ag, Pd, and Ti have been studied previously.⁵⁻⁹ Iron diffusion coefficients measured by radio active tracer diffusion in several other types of oxides¹⁰⁻¹² like aluminum oxide (Al₂O₃), chromium oxide (Cr₂O₃), magnesium oxide (MgO), titanium oxide (TiO₂), silicate glass (30%Na₂O·3.7%Fe₂O₃·6.3%Al₂O₃·60%SiO₂), synthetic silica glass, and ferrous and ferric oxides have been reported; but none in pure electronic grade SiO₂. Further, though the effects of iron decorating the Si/SiO₂ interface have been extensively investigated, segregation properties of iron have been only studied qualitatively.¹³⁻¹⁵

In this paper we present results on diffusion of iron in SiO₂ films grown on Si. Fe concentration profiles in SiO₂ and Si are measured using total reflection X-ray fluorescence (TXRF), deep level transient spectroscopy (DLTS), and surface photovoltage (SPV) characterization techniques. A solution of Fick's one-dimensional diffusion equation is used to derive the diffusivity of iron in SiO₂ from the measured concentration profile of iron. Further, a two-boundary diffusion model is applied to interpret the segregation properties of iron at the SiO₂-Si interface. The probable mechanism of iron diffusion in SiO₂ is discussed.

Experimental

The experimentation was performed using 3 in. 1-2 Ω cm, float-zone (FZ) grown Si<100> wafers. The samples were cleaned in the order HF--SC1--HF--SC2--HF. SC1 was a 1:2:10 solution mixture of ammonium hydroxide, hydrogen peroxide, and water heated to a temperature 65°C. SC2 was a 1:1:5 solution mixture of hydrochloric acid, hydrogen peroxide, and water maintained at 65°C. Using the technique of surface photovoltage, the background level of iron contamination from the starting wafers, cleaning procedure, and subsequent furnace processing was established to be about 7×10^{10} atoms/cm³ at 1100°C.

Selected wafers were oxidized at 850°C in an oxygen ambient to grow dry thermal oxides 120 nm thick. The oxide thicknesses were measured by ellipsometry. Wafer to wafer oxide variation was found to be less than 2 nm. Iron contamination was performed by spin doping the surface of the oxide with a 100 ppm ferric chloride (FeCl₃) solution. Iron at the surface of the SiO₂ was then diffused by thermal annealing in a nitrogen ambient for a duration of 90 min at several temperatures over the range of 700–1100°C.

Following the in-diffusion, the iron concentration profile within the SiO₂ was measured by TXRF. Successively etching down the oxide to different oxide thicknesses (using dilute HF solution) followed by quantitative assessment of iron using TXRF provided the iron concentration profile. Each measurement performed by the Rigaku 3750TXRF spectrometer was a five point wafer map for 500 s using an X-ray power setting of 30 kV and 300 mA. The energy of the X-ray source beam was 9.67 keV (W-Lβ) and the detection limit of system was about 10^9 atoms/cm². The detector was calibrated prior to the measurement of each wafer to avoid saturation of the detector.

Following TXRF measurements, the SiO₂ on the samples was completely etched off with a dilute HF solution. Interstitial iron concentration (Fe_i) in the silicon bulk was measured using the SPV technique. The SPV method provides measurement of minority carrier diffusion length and is relevant to the bulk properties of the silicon. Interstitial iron concentration within the bulk was determined from the lifetime measurements using well-known Fe-B pairing relationships.^{16,17} Full wafer maps and 25 point line scan measurements were performed on each wafer using SPV.

DLTS was used to measure iron concentrations in the surface silicon layer at the Si/SiO₂ interface. Aluminum Schottky diodes were fabricated on several samples followed by single shot capacitance transient measurements under reverse bias conditions. An optical activation procedure¹⁶ was used to dissociate the Fe-B pairs in the sample. The interstitial iron DLTS peak at 0.4 eV was identified and quantitative measurement of iron was extracted from the measured peak height of the capacitive transient. Measurements were performed at a reverse bias of +5 V and sampled at a rate window of 200 s⁻¹. Since the technique measures iron concentrations in the depletion region of the diode, iron concentrations in the Si layers adjacent to the Si/SiO₂ interface were determined.

* Electrochemical Society Student Member.

^z E-mail: ramappa@eng.usf.edu

Results and Discussion

The spin-on iron deposition procedure using 100 ppm FeCl_3 solution routinely yielded a oxide surface iron concentration of 10^{15} atoms/cm². This was confirmed by TXRF measurements on wafers prior to the diffusion process. TXRF mapping data indicated the iron concentration uniformity to be $\pm 10\%$.

Diffused iron concentration profiles in SiO_2 following in-diffusion at temperatures of 900, 1000, and 1100°C for 90 min are shown in Fig. 1. The iron concentrations were measured by TXRF after successive etching of oxide to thickness of approximately 60 and 10 nm as indicated in Fig. 1. Iron concentration uniformity for each measurement was found to be $\pm 10\%$. The SiO_2 surface iron concentration prior to diffusion is also shown in the figure.

Considering the surface source of iron to be an infinite source of iron compared to the initial (prediffusion) oxide iron concentration, a one-dimensional solution to Fick's law of diffusion can be applied. Thus, if the surface concentration of iron is N_0 atoms/cm² and remains relatively constant for the duration of diffusion, then the concentration profile follows the solution

$$N(x, t) = N_0 \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right) \quad [1]$$

where the $N(x, t)$ is the iron concentration in the oxide at a distance of x after a diffusion time t . The diffusivity D of iron in SiO_2 can thus be calculated at every diffusion temperature using the TXRF measured iron concentrations in the oxide at oxide thicknesses of 60 and 10 nm.

Diffusion constants for iron in SiO_2 at various temperatures are plotted as a function of reciprocal of absolute temperature in Fig. 2. It is observed that the diffusivity of iron in SiO_2 follows the Arrhenius relationship and can be represented as

$$D = 4 \times 10^{-8} \exp \left(\frac{-1.51 \text{ [eV]}}{kT} \right) \quad [\text{cm}^2/\text{s}] \quad [2]$$

obtained by a least square fit of the data. An activation energy of 1.51 eV is thus derived. Table I shows a review of previously published activation energies of different metallic impurities in SiO_2 and Fe in other glasses.

Amorphous materials, being in a thermodynamically nonequilibrium state can hardly be expected to follow atomistic diffusion

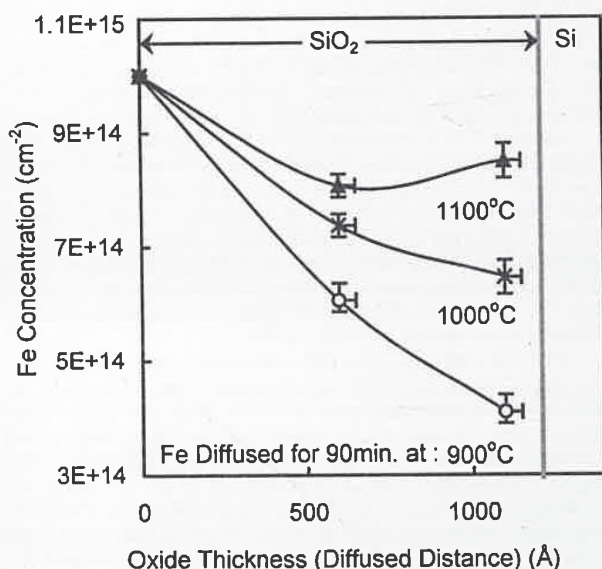


Figure 1. Iron concentration profile in SiO_2 following in-diffusion at temperatures of 900, 1000, and 1100°C for 90 min. Iron concentrations were measured by TXRF.

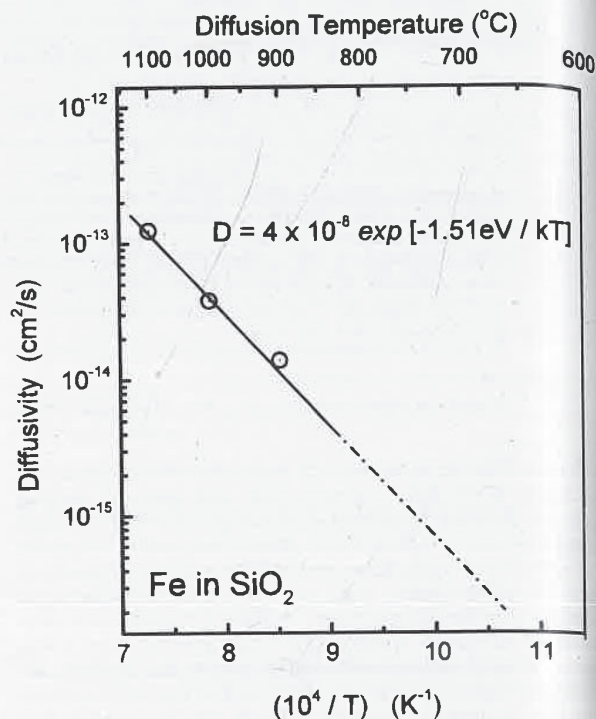


Figure 2. Temperature dependence of Fe diffusivity in SiO_2 .

mechanisms established for well ordered crystalline materials. Thus the interpretation of the chemical diffusion coefficient of Fe in SiO_2 measured here depends on details of the solution of Fe in SiO_2 and its electrical properties. According to Atkinson¹² iron can be only be assumed to be associated with point defects in SiO_2 and the diffusion of Fe will then depend on the density of these defects and their thermal diffusivity. One such interaction would be the substitution of Si^{4+} by Fe^{3+} in tetrahedrally coordinated positions. These negatively charged defects would then be compensated by positively charged oxygen vacancies.^{12,20} Thus, the introduction of iron into SiO_2 would result in the production of positively charged oxygen vacancies and, hence, the diffusion of these electrostatically interacting defects (ambipolar diffusion)²¹ would determine the diffusion coefficient of iron.

It is observed from Table I that the diffusion of Fe in soda-lime-glass and silicate glass is considerably higher than the value obtained for Fe diffusion in pure SiO_2 in this paper. Since these glasses are known¹⁰ to contain a significantly higher amount of oxygen and other cation vacancies the higher diffusivity of Fe can thus be accounted for. In addition, other studies have noted the increase in diffusivity of several dopant impurities in SiO_2 when the impurities are ion-implanted as opposed to thermally diffused.²² This again is attributed to a higher concentration of oxygen vacancies in SiO_2 .

It is also observed from Table I that the activation energy E_a of other metals in SiO_2 , which is related to the potential barrier for diffusion in SiO_2 , decreases with decrease in atomic size of the diffusing species. The value of $E_a = 1.51$ eV obtained in this research for iron is less than that of copper, nickel, and gold but higher than that of sodium. This suggests that the diffusion mechanism of these metal ions in SiO_2 is not only vacancy enhanced diffusion as discussed earlier but also interstitial. Thus it is conjectured that the mechanism of iron diffusion in SiO_2 is by a combination of the vacancy and interstitial modes of diffusion.

To evaluate the segregation properties of iron at the interface the Si bulk iron concentrations are determined. The Si bulk iron concentrations following iron in-diffusion through a SiO_2 layer of 120 nm thickness at various temperatures for an annealing duration

Table I. Typical diffusivities and activation energies and of different metallic impurities in SiO₂ and other glasses.

Metallic impurity	Oxide/glass	D_0 (cm ² /s)	E_a (eV)	D (@ T°C) (cm ² /s)	Ref.
Au	SiO ₂	1.52×10^{-7}	2.14	4.6×10^{-16} (1000)	18
Cu	SiO ₂		1.82	1.2×10^{-11} (450)	8
Ni	SiO ₂	7.2×10^{-10}	1.61	2.5×10^{-16} (1000)	6
Na	SiO ₂	6.9	1.3	5.2×10^{-5} (1000)	18
Fe	SiO ₂ ·Fe ₂ O ₃	6×10^{-3}	3.0	5×10^{-15} (1000)	12
Fe	(Na ₂ O·Al ₂ O ₃ ·SiO ₂)			3.5×10^{-15} (450)	19
Fe	(Na ₂ O·CaO·SiO ₂)			1.3×10^{-6} (1200)	10
Fe	Al ₂ O ₃	9.2×10^{-8}	1.17		11
Fe ^a	SiO ₂	4×10^{-8}	1.51	3.8×10^{-14} (1000)	

^a This work.

of 90 min is shown in Fig. 3. Iron concentrations measured in the top 1 μm of the Si wafer and in the Si bulk were measured by the DLTS and SPV techniques, respectively. Figure 3 also shows iron solubility³ curve and iron concentrations measured on reference wafers for which iron indiffusion was performed with no initial oxide.

From Fig. 3 it is observed that the iron concentrations measured on reference wafers follow closely the solubility curve for temperatures up to 1000°C. This validates the effectiveness of the contamination procedure. Comparing the iron concentrations measured by DLTS and SPV it is observed that the Si surface iron concentration (DLTS) is consistently of the same magnitude as the bulk iron concentration (SPV). This suggests that there is no significant segregation of iron from the Si wafer bulk to the silicon adjacent to the interface.

The masking effect of the silicon dioxide film against iron impurity incorporation into silicon is also evident from Fig. 3. The data indicates that if and when the SiO₂ layer is present the amount of iron diffused into the silicon at lower temperatures (<900°C) is relatively small. At temperatures above 900°C, there is a significant increase in the amount of iron that is transported to the Si bulk. This suggests that for a given SiO₂ thickness, there exists a diffusion temperature beyond which the oxide fails to mask the silicon bulk from iron impurity incorporation.

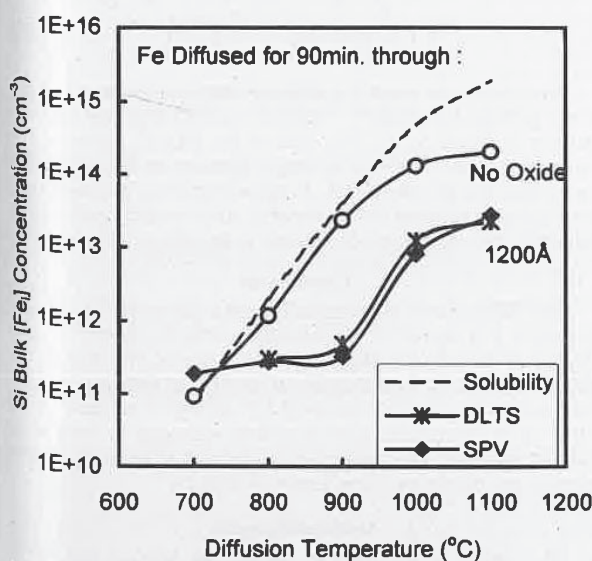


Figure 3. The masking effect of an oxide layer against the diffusion of surface iron contamination into Si. The presence of SiO₂ on the wafer reduces the amount of iron transported into silicon.

Following thermal annealing iron diffuses through the silicon dioxide layer into the SiO₂-Si interface before being transported into the underlying silicon bulk. The SiO₂-Si interface is known to act as a sink for impurities.²³ Normally, an impurity tends to segregate or remain at the interface if it reduces the interfacial free energy or stress. Metallic impurities including iron have been reported to have a tendency to accumulate in the oxide near the interface.^{13,14} This "pileup" characteristic introduces a discontinuity in the concentration profile of iron from the oxide into silicon.

To interpret the experimentally observed distribution of iron at the SiO₂-Si interface a two-boundary diffusion model is applied to the iron concentration profile at the Si-SiO₂ interface. This model developed by Sah *et al.*,²⁴ estimates the ratio of the equilibrium impurity concentrations at the interface between two media as a function of the diffusivities of the impurity in the two media. It is described here briefly for the sake of completeness. The diffusion of an impurity into a semi-infinite region [Si] through a layer of finite width [SiO₂] is given by

$$D_1 \frac{\partial^2 N_1}{\partial x^2} = \frac{\partial N_1}{\partial t} \quad \text{for } -a < x < 0 \quad [3]$$

$$D_2 \frac{\partial^2 N_2}{\partial x^2} = \frac{\partial N_2}{\partial t} \quad \text{for } x > 0$$

As illustrated in Figure 4, a is the oxide thickness, D_1 and D_2 are the diffusivities of iron in SiO₂ and Si, and N_1 and N_2 denote the iron concentration in the corresponding media. Following the discontinuity of iron concentration at the interface, the boundary conditions are given by

$$N_1(-a, t) = N_0 \quad \text{for } t > 0 \quad [4]$$

$$N_2(x, t) \rightarrow 0 \quad \text{as } x \rightarrow \infty, t > 0 \quad [5]$$

$$D_1 \frac{\partial N_1}{\partial x} = D_2 \frac{\partial N_2}{\partial x} \quad \text{at } x = 0, t > 0 \quad [6]$$

$$\frac{N_2(0, t)}{N_1(0, t)} = k \quad \text{for } t > 0 \quad [7]$$

Here, N_0 denotes the constant concentration of iron at the surface of the oxide and k is the thermodynamic segregation coefficient of iron at the SiO₂-Si interface. k is defined as the ratio of the equilibrium concentration of iron in SiO₂ adjacent to the interface to the concentration of iron in the silicon near the interface.

Equation 3 subject to the boundary conditions gives a solution in the form of summation for both N_1 and N_2 , which has been derived in detail elsewhere.^{25,26} A good approximation would be the first term of the summation given by

$$N_1(x, t) = N_0 \left(\operatorname{erfc} \frac{a+x}{L_1} - \frac{k-\mu}{k+\mu} \operatorname{erfc} \frac{a-x}{L_1} \right) \quad [8]$$

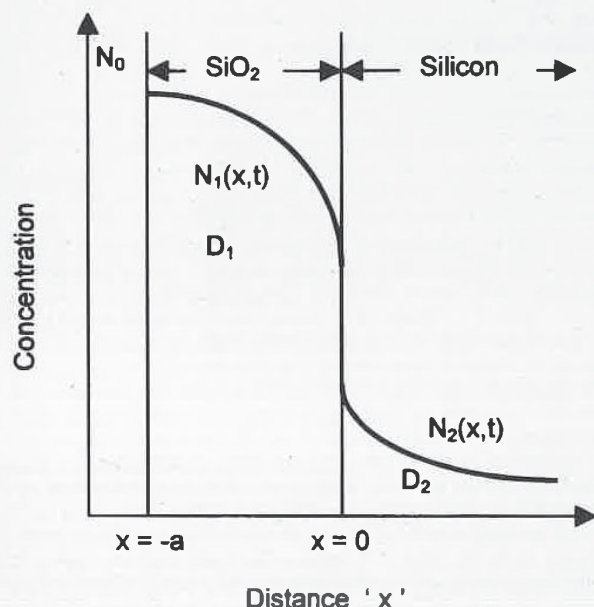


Figure 4. Diffusant concentration distribution in SiO₂ and in Si for the two-boundary diffusion model.

$$N_2(x, t) = \frac{2k\mu}{k + \mu} N_0 \operatorname{erfc}\left(\frac{a}{L_1} + \frac{x}{L_2}\right) \quad [9]$$

where

$$\mu = \sqrt{\frac{D_1}{D_2}} \quad L_1 = 2\sqrt{D_1 t} \quad L_2 = 2\sqrt{D_2 t} \quad [10]$$

Using Eq. 8 and 9 with the experimental data, the iron impurity diffusion profile in SiO₂ and Si is calculated and plotted for diffusion temperatures of 900, 1000, and 1100°C in Fig. 5.

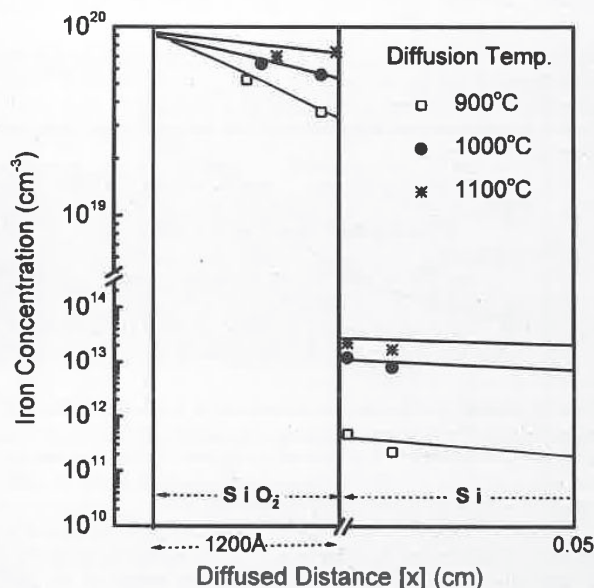


Figure 5. Iron impurity diffusion profile in SiO₂ and Si at temperatures of 900, 1000, and 1100°C. The solid lines represent the concentration profile as predicted by the two-boundary diffusion model. Iron concentrations in SiO₂ was measured by TXRF and in the Si bulk by DLTS and SPV.

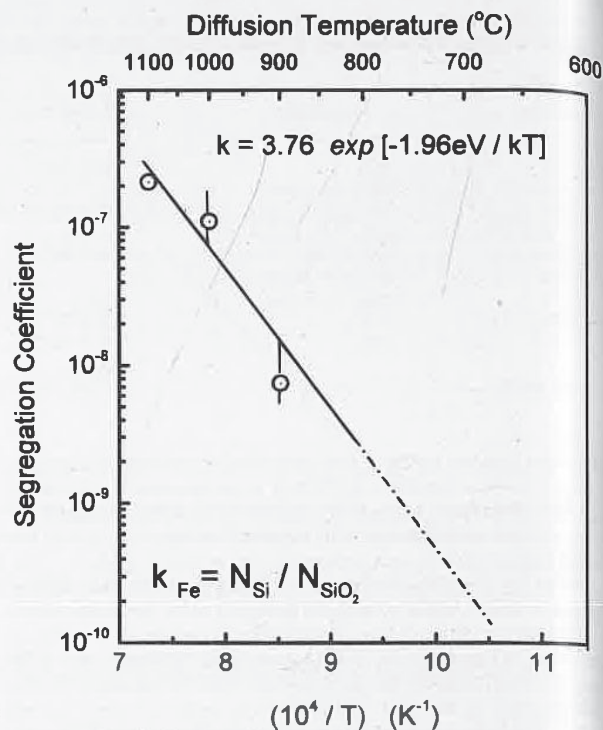


Figure 6. Temperature dependence of iron impurity segregation coefficients at the SiO₂-Si interface.

The iron impurity segregation coefficients at the SiO₂-Si interface at the various diffusion temperatures are estimated using the above model and are plotted in Fig. 6. To establish that the segregation of iron is indeed an equilibrium effect, the coefficients are plotted as a function of temperature. Experimentally measured segregation coefficients defined as the ratio of the Fe measured by DLTS and TXRF methods are also shown in Fig. 6. The segregation coefficient k is observed to obey Arrhenius law and can be described by the equation

$$k = 3.76 \exp\left(\frac{-1.96 \text{ [eV]}}{kT}\right) \quad [11]$$

From the above result it is observed that in agreement with previous published literature¹³⁻¹⁵ iron has a strong tendency to preferentially segregate to the SiO₂ side of the SiO₂-Si interface. This strong segregation tendency seemingly impedes the diffusion of iron from SiO₂ into the silicon bulk. In the process the segregation could lead to supersaturation of iron impurity and eventually precipitation which in turn could prove detrimental to the gate oxide integrity.

Conclusions

The diffusion of iron in thermally grown silicon dioxide is experimentally investigated. A two-boundary diffusion model has been applied to describe the diffusion profile of iron in SiO₂ and Si. Iron diffusivity in SiO₂ is an exponential function of diffusion temperature and has an activation energy of 1.51 eV with a prefactor of 4×10^{-8} cm²/s. Iron tends to preferentially segregate in SiO₂ at the SiO₂-Si interface. The segregation is observed to be an equilibrium process and has an activation energy of 1.96 eV.

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References

1. A. Goetzberger and W. Shockley, *J. Appl. Phys.*, **31**, 1821 (1960).
2. L. Jastrzebski, in *Semiconductor Silicon*, H. R. Huff, K. G. Barraclough, and J.-i. Chikawa, Editors, PV 90-7, p. 614, The Electrochemical Society Proceedings Series, Pennington, NJ (1990).
3. E. R. Weber, *Appl. Phys. A*, **30**, 1 (1983).
4. W. B. Henley, L. Jastrzebski, and N. F. Haddad, *J. Non-Cryst. Solids*, **187**, 134 (1995).
5. E. Yon, W. H. Ko, and A. B. Kuper, *IEEE Trans. Electron. Devices*, **13**, 276 (1966).
6. R. N. Ghoshtagore, *J. Appl. Phys.*, **40**, 4374 (1969).
7. Y. S. Diamand, A. Dedhia, D. Hoffsetter, and W. G. Oldham, *J. Electrochem. Soc.*, **140**, 2427 (1993).
8. J. D. McBrayer, R. M. Swanson, and T. W. Sigmon, *J. Electrochem. Soc.*, **133**, 1243 (1986).
9. D. R. Collins, D. K. Schroder, and C. T. Sah, *Appl. Phys. Lett.*, **8**, 323 (1966).
10. C. Russel, *J. Non-Cryst. Solids*, **134**, 169 (1991).
11. J. Askill, in *Tracer Diffusion Data for Metals, Alloys, and Simple Oxides*, p. 7,IFI/Plenum, New York (1970).
12. A. Atkinson and J. W. Gardner, *Corros. Sci.*, **21**, 49 (1981).
13. A. Ohsawa, K. Honda, and N. Toyokura, *J. Electrochem. Soc.*, **131**, 2965 (1984).
14. Y. Kamiura and F. Hashimoto, *Appl. Phys. Lett.*, **53**, 1711 (1988).
15. C. D. Thurmond, in *Properties of Elemental and Compound Semiconductors*, H. C. Gatos, Editor, p. 1221, Interscience, New York (1960).
16. J. Lagowski, P. Edelman, A. M. Kontkiewicz, O. Milic, W. Henley, M. Dexter, L. Jastrzebski, and A. M. Hoff, *Appl. Phys. Lett.*, **63**, 3043 (1993).
17. G. Zoth and W. Bergholz, *J. Appl. Phys.*, **67**, 6764 (1990).
18. W. E. Beadle, J. C. C. Tsai, and R. D. Plummer, in *Silicon Processing Quick Reference Manual*, p. 6, John Wiley & Sons, New York (1985).
19. G. H. Frischat, in *Ionic Diffusion in Oxide Glasses*, Trans. Tech. S. A., p. 447, (1975).
20. K. S. Seal, T. Futami, and Y. Ohki, *J. Appl. Phys.*, **83**, 2357 (1998).
21. F. A. Kroger, in *The Chemistry of Imperfect Crystals*, Chap. 20-3, North Holland, Amsterdam (1964).
22. J. L. Prince and F. N. Schwetmann, *J. Electrochem. Soc.*, **121**, 705 (1974).
23. C. R. Helms, in *The Si-SiO₂ System*, P. Balk, Editor, p. 119, Elsevier, Amsterdam (1988).
24. C. T. Sah, H. Sello, and D. A. Tremere, *J. Phys. Chem. Solids*, **11**, 288 (1959).
25. H. S. Carslaw and J. C. Jaeger, in *Conduction of Heat in Solids*, Clarendon, Oxford (1959).
26. J. Crank, in *The Mathematics of Diffusion*, Clarendon, Oxford (1975).