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Precipitation and denuded zone formation in silicon single crystal during high temperature anneal

Dasharath Patel
San Jose State University

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crystal during high temperature anneal**

Patel, Dasharath Revabhai, M.S.

San Jose State University, 1994

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PRECIPITATION AND DENUDED ZONE FORMATION IN
SILICON SINGLE CRYSTAL DURING HIGH TEMPERATURE ANNEAL

A Thesis Presented to
The Faculty of the Department of Materials Engineering
San Jose State University

In Partial Fulfillment of
the Requirements for the Degree
Master of Science

by

Dasharath Patel

May, 1994

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APPROVED FOR THE DEPARTMENT OF MATERIALS ENGINEERING

Thesis Advisor: Dr. Peter S. Gwozdz

Committee Chairman: Dr. Sree Harsha

Committee Member: Dr. Jowei Dun

APPROVED FOR THE UNIVERSITY

ABSTRACT

PRECIPITATION AND DENUDED ZONE FORMATION IN SILICON SINGLE CRYSTAL DURING HIGH TEMPERATURE ANNEALING

by Dasharath Patel

The effect of anneal temperature and oxygen content on nucleation rate of oxygen precipitates in silicon was studied. The dependence of denuded zone thickness on temperature and time of anneal and on oxygen content were investigated.

The results in n-type silicon fits the model proposed by Inoue et al.^[1] for temperatures between 550°C to 850°C. No significant difference in nucleation rate was seen between lightly doped n-type and p-type silicon. The denuded zone widths were determined at 1000°, 1100°, and 1200°C for n-type silicon adapting the model derived by Wijaranakula et al.^[2] for p-type silicon. The results agreed with the model for annealing times from 0.5 to 10 hours; for large annealing times the measured zone widths were greater than the calculated widths from the model.

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1.0 INTRODUCTION

Precipitation in Czochralski silicon supersaturated with oxygen is widely studied because of its beneficial as well as detrimental effects on silicon devices. Intrinsic gettering, which is trapping of metallic impurities away from the active devices during device processing by precipitates, has shown beneficial effect on device performance.[16,17,20] However, too many precipitates are known to cause slip and warpage in the wafer.[34] Degradation of devices has been observed if the metal associated precipitates and the stacking faults initiated by the decomposition of oxygen supersaturated solution are too close to the active devices.[20,35] Because of the necessity of a defect-free region where devices are fabricated, denuding of oxygen from top surface is an important step of the intrinsic gettering sequence. In short, a precipitate-free zone near the surface and precipitates in the bulk of silicon are required for effective intrinsic gettering.

Precipitation and denuded zone formation for n-type single crystal silicon were investigated in this study. Previous in-depth work by Inoue et al. on precipitation^[1] and Wijaranakula et. al on denuded zone formation^[2,3] were done on p-type (boron doped) silicon. A study of precipitation and denuded zone formation for n-type wafers supersaturated with oxygen is not available in the literature. Even though p-type

silicon accounts for approximately 75% of the starting material consumed today, n-type starting material is increasingly used in the semiconductor industry today^[33] because of its application in fabrication of high-speed devices. Therefore, there is a need to study the precipitation and denuded zone formation for n-type silicon.

The Czochralski single crystal growth technique and the characteristics of oxygen in silicon are covered in Chapter-2. Oxygen is incorporated into silicon as an impurity in Czochralski grown silicon. Oxygen solubility and diffusivity in silicon are two key parameters affecting the denudation and precipitation processes, which are also briefly covered in Chapter 2.

The denudation and nucleation models of precipitation are reviewed in Chapter 3. General comments on nucleation and growth of precipitates are given in the beginning of Chapter-3. The homogeneous nucleation model for precipitation as proposed for p-type silicon by Inoue et al. and a slightly modified version of the denuded zone formation model by Wijaranakula et al. are described in Chapter 3.

Doping levels affect precipitation kinetics by altering the charge state of oxygen reacting species in silicon. This subject is reviewed in Chapter 3, section 3.4.

The objective of this thesis is to revisit the previous work done by Inoue et al. on precipitate nucleation and Wijaranakula et al. on denuded zone formation for n-type silicon and to study the effect of oxygen content on nucleation and denuded zone formation.

2.0 BACKGROUND ON SINGLE CRYSTAL SILICON AND OXYGEN SILICON

2.1 Semiconductor Industry and Silicon^[4]

Silicon in single crystal form is the material of choice for 95% of the semiconductor devices fabricated at present. Some of the reasons for silicon's popularity as the starting material for the semiconductor industry are:

1. The stability of thermally grown silicon dioxide makes planar process possible.
2. The higher band gap of silicon compared to Germanium, for example, allows devices to be built with high operating temperatures (up to 150°C).
3. The intrinsic resistivity of silicon is about 230,000 Ω -cm. Therefore, high-voltage rectifying devices can be made using silicon.
4. Infrared sensing devices can be made with silicon.
5. Silicon is cheap and abundant; silicon comprises about a quarter of the earth's crust.

2.2 Single Crystal Silicon^[6,8]

The fabrication of very large scale integration (VLSI) devices requires silicon substrates having very high crystalline perfection. G.K. Teal was one of the first to develop single crystal growth process using polycrystalline

silicon.^[5] There are two primary methods of growing single crystal silicon- Float-Zone (FZ) and Czochralski (CZ). The float-zone method is used to obtain impurity-free single crystal silicon used for power devices. The Czochralski grown silicon contains the intentional dopant impurities as well as unintentional impurities such as oxygen and carbon.

2.2.1 Czochralski (CZ) Method for Single Crystal Silicon

A substantial percentage (80 to 90%) of silicon crystals used for the semiconductor industry are prepared by the CZ technique. Czochralski growth method is based on controlled solidification from a silicon melt. The standard production process currently in use is the same as it was pioneered by Dash and others in the late 1950s to grow dislocation-free single crystal. Figure 1 shows a schematic diagram of a typical CZ crystal grower. The sequence of events that occurs during the crystal growth is listed below:

1. The quartz crucible is loaded with polycrystalline silicon charge and precise amount of dopants,
2. The chamber is pumped down and backfilled with an inert gas; then the charge is melted,

Figure 1. Czochralski Crystal Grower^[8]

(S.W.Wolf and R.N.Tauber, Silicon Processing for VLSI)

3. The seed crystal of silicon with known orientation is dipped in the melt and withdrawn with a controlled rate to obtain dislocation-free ingot,
4. The ingot of desired diameter (shouldering) is achieved by adjusting melt temperature, pull rate and crucible and ingot rotation rates. These factors are controlled precisely during the entire crystal growth.

The crystal is rounded and marked with the desired orientation marks (flats or notches). The silicon wafers are then formed by slicing the rounded ingot into thin slices which are lapped, polished and cleaned. The wafers are then annealed at 550-650°C to remove oxygen thermal donors formed during cooling of the crystal. At temperatures of approximately 450°C, SiO₄ structures are formed which increase resistivity for n-type material and reduce resistivity of p-type material, hence called thermal donors.^[10,36,37] A short anneal (30 minutes) at 600°C, is sufficient to annihilate these donors.^[10]

2.3 Oxygen in Silicon^[11]

Other than the doping species (phosphorous or boron), oxygen is the most abundant impurity in CZ silicon, with concentrations ranging from 5×10^{17} atoms/cm³ to 1.5×10^{18} atoms/cm³ (ASTM Designation F-121). Oxygen is incorporated

in silicon during the growth of the crystal as a result of slow dissolution (approximately 8×10^{-7} gms/cm².sec) of the quartz crucible into the melt.^[9] Most of the dissolved oxygen in the melt escapes in the form of SiO vapor; a fraction of the remaining oxygen is incorporated in the solid crystal as it solidifies. The amount of oxygen which can be incorporated in the solid depends on the segregation coefficient of oxygen, which is the ratio of the solubility of oxygen in solid phase to that in liquid phase. The segregation coefficient of oxygen in silicon is estimated to be 0.5-1.25 depending on the method of measurement.^[11]

2.3.1 Oxygen Solubility in Silicon.

Kaiser and Keck were among the pioneers to analyze oxygen in silicon.^[12] They used an infra-red (IR) absorption technique and suggested that nearly all of the dissolved oxygen occupies dispersed, isolated interstitial sites in silicon. They proposed that each oxygen atom is bonded to two neighboring silicon atoms of the crystal thus satisfying the valency requirements for both silicon and oxygen. Based on the intensity of the absorption by the Si-O-Si anti-symmetric vibration mode at 9 μ m wavelength in the IR spectra, a method to determine the interstitial oxygen concentration in silicon was proposed. The vacuum fusion analysis was used for calibration. In this method, a sample is melted in a graphite

crucible in vacuum. The oxygen from the sample reacts with carbon from the crucible to form carbon monoxide which is quantitatively measured by gas phase IR absorption. The IR absorption method, being simple and quick, is widely used in the semiconductor materials industry to determine interstitial oxygen content in silicon.

Hrostowski and Kaiser^[13], who used the liquid helium temperature IR spectroscopy analysis on samples annealed at 1000°C-1250°C, were among the first to determine oxygen solubility in silicon. More recent work by J. C. Mikkelsen^[14], who employed Secondary Ion Mass Spectroscopy (SIMS) to determine oxygen concentration for the temperature range of 600°C-1240°C, revealed solubility shown in Figure 2. The equilibrium oxygen content is expressed in the following form (from Figure 2):

$$C_{O}^{eq} = 9.3 \times 10^{22} \cdot \exp (-1.52\text{eV}/k T)$$

where, C_{O}^{eq} = equilibrium oxygen concentration, atoms/cm³

k = Boltzman constant in eV/°K units

T = absolute temperature, °K

Figure 2. Oxygen Solubility in Silicon^[14]

2.3.2 Oxygen Diffusivity in Silicon

Oxygen is a fast diffuser in silicon compared to impurity dopants commonly used in device manufacturing such as phosphorous and boron. Figure 3 shows a typical Arrhenius plot of diffusivity of oxygen in silicon.^[14] The data represented on this plot have been extracted by various techniques including fitting to out-diffusion profiles measured by SIMS, charge particle activation, and IR absorption.^[11] From the plot of diffusivity vs. $1/T$ of Figure 3, the diffusivity of oxygen in silicon is expressed by the following^[14]:

$$D = 0.13 \exp \left[\frac{-2.53 \text{ eV}}{kT} \right] \text{ cm}^2/\text{sec},$$

where, k = Boltzman constant in eV/°K units

T = absolute temperature, °K

Figure 3. Oxygen Diffusivity in Silicon^[14]

2.3.3 Effect of Oxygen in Silicon

Oxygen is incorporated in Czochralski silicon at a super-saturated level when the crystal is solidified from the melt. When silicon wafers are annealed between 650°C to 1000°C, the excess oxygen in the silicon precipitates out as silicon oxide.^[15] These "oxygen precipitates" as well as the strain-field regions such as dislocation loops and stacking faults trap the metallic impurities such as iron and copper away from the active device area.^[16] The effectiveness of intrinsic gettering by "oxygen precipitates" to improve CMOS device yield was demonstrated by L. Jastrzebski et al.^[17] As shown in Figure 4, during a period of high heavy metal contamination in the process, the yield, given in arbitrary units, was demonstrated to be higher for intrinsic gettered wafers than for standard wafers which did not receive the intrinsic gettering.

When a silicon wafer is heated to 1000°C-1200°C for four to twelve hours, and then processed through two successive anneals, one in the range of 650°C-750°C for four to twelve hours and the other at 1100°C-1200°C for sixteen to twenty-four hours, a denuded zone (DNZ), nearly free of oxygen-induced defects is observed near the top and bottom surfaces of the wafer.^[19,20] The precipitates and stacking faults are confined to the bulk region of the wafer. Active devices are fabricated in the top 10µm-30µm denuded region of silicon.

Proper denuded zone together with "oxygen" precipitates in the bulk are required for improved yield and performance of devices. Figure 5 shows an example of a good denuded zone and bulk defects (precipitates and stacking faults) on a processed silicon wafer.

Figure 4. Effect of Gettering on CMOS Device Yield [17]

Figure 5. Example of Good Intrinsic Gettering^[38]

3.0 PRECIPITATION AND DENUDATION THEORY

This chapter contains a background literature review on precipitation and denudation. The specific models for oxygen precipitation and denudation are reviewed in Sections 3.2 and 3.3, respectively.

3.1 General Comments on Precipitation Theory

This section is a qualitative summary describing "oxygen precipitate" formation in silicon.^[43] The purpose is to familiarize the reader with the concept of precipitate formation and dissolution required to understand the mathematical models of Section 3.2 and 3.3.

3.1.1 General Situation for High Temperature

Consider silicon which is supersaturated with oxygen. The free energy for associated oxygen atoms with silicon atoms is lower than the energy for isolated oxygen atoms. So there is a tendency for oxygen atoms to form silicon-oxygen clusters. But the clusters are statistically unstable, they form and dissolve continually. Given sufficient time, an equilibrium size distribution of the clusters will be achieved, which is schematically shown in Figure 6 using arbitrary units on a log-log scale. As can be seen from this figure, there is a

large number of very small clusters and the number of clusters decreases drastically as the size increases.

The size and shape of the distribution is dependent on the anneal temperature and the amount of the supersaturation (oxygen content). For a given oxygen content, as annealing temperature increases, the curvature of the equilibrium curve changes (as shown in Figure 6) such that at very high temperatures, very few large size clusters will be present. At a given annealing temperature, higher the oxygen content, higher the cluster density will be; therefore, the equilibrium curve will move outwards.

Even though there may be a sizable distribution of unstable clusters, none of the clusters grow into a stable precipitate because of their size being less than the critical size for the precipitate nuclei at high temperatures of annealing. Therefore, after long time anneal at high temperature, a statistical equilibrium distribution of unstable clusters will be present, but very little precipitation (nucleation) is observed.

Figure 6. Equilibrium Size Distribution of Oxygen Clusters in Silicon after Annealing

3.1.2 General Situation for Low Temperature Nucleation

Consider the situation of anneal at low temperature of a sample which is supersaturated with oxygen. The equilibrium cluster distribution after long time anneal at low temperature is schemetically shown in Figure 7. All clusters are continuously in process of growth and dissolution. Very large clusters will now reach a size where they can form stable nuclei by adding available isolated oxygen atoms.

A characteristic radius, called critical radius (r_c) is defined as the radius where the free energy of cluster formation is a maximum and therefore represents an unstable equilibrium. Clusters smaller than r_c will shrink and decrease the free energy. Clusters larger than r_c grow because this leads to decrease in free energy. The clusters of radius r_c are unstable, having equal chances of shrinking or growing. In Figure 7, r_c is arbitrarily shown to be a cluster containing seven oxygen atoms. The actual magnitude of r_c is a complex function of the silicon crystal-precipitate interface, temperature and oxygen concentration. The critical nucleus radius increases as temperature increases for a given oxygen content and it decreases as oxygen content increases at a given temperature.

Figure 7. Low Temperature Nucleation and Precipitate Growth
at Intermediate Temperature

3.1.3 Intermediate Temperature after Nucleation

Once a stable nucleus is formed, its growth (increase in size) is achieved by addition of oxygen atoms. The oxygen availability is determined by the net diffusion of oxygen to the nucleus. Oxygen diffusion, as all other diffusion processes, is an exponential function of temperature.

Therefore, at higher temperature, the diffusion of oxygen atom will be higher than at low temperature. Consequently, the rate of growth of nuclei will be higher at high temperature. The precipitates thus formed are now large enough to be detected by the stain and microscope inspection technique[31]. Figure 7 shows schemetically the distribution of precipitates thus formed.

Precipitate dissolution, which is briefly described in the following section, also takes place at very high temperatures. Therefore, the intermediate temperature should be high enough for adequate oxygen diffusion but low enough to avoid precipitate dissolution.

3.1.4 High Temperature Dissolution

Starting (conceptually) with a sample containing a distribution of oxygen clusters, at high temperature, the clusters will dissolve and oxygen atoms thus released will go into solid solution. The precipitate shrinkage may occur by one or both of the following:

1. The precipitate size is smaller than the critical radius.
 2. The oxygen content is undersaturated around the precipitates.
-

Given a long enough anneal time, the arbitrary initial size distribution will approach the statistical equilibrium distribution of unstable clusters. At very high temperature the critical radius is large, therefore the number of nuclei which will survive is small. Also the diffusion of oxygen away from the precipitates will be higher, maintaining the under-saturation of oxygen near the precipitates. As a result, the precipitate dissolution may occur very fast at very high temperature.

Along with the homogeneous nucleation as described above, heterogeneous nucleation in which nucleation is initiated at a defect or impurity in the crystal can also occur. The energy barrier for heterogeneous nucleation is lower than that for homogeneous nucleation. During the crystal growth, thermal defects like vacancies, interstitials, dislocations as well as impurities like carbon can be incorporated in the silicon. Heterogeneous nucleation can be significant if considerable numbers of these defects are present in the silicon.

During crystal growth, the top (seed end) of the crystal will be at low temperature longer than the tail end. This variation in time at low temperature results in different amounts of grown-in nuclei in the wafers, depending on the location on the ingot the wafers are obtained from.^[39] Furthermore, the thermal donor anneal (as briefly mentioned

in Chapter 2) may cause nucleation in the wafers. However, during this anneal, the wafers do not stay at temperatures above 650°C for longer than 30 minutes, and so the contribution of this anneal to the nuclei formation is usually not significant. These homogeneously grown nuclei during crystal growth and wafer processing will add to the density of nuclei in subsequent nucleation annealing. In the worst case, they may behave like "heterogeneous" seeds.[1]

3.2 Oxygen Precipitation

Starting with the pioneering work of Kaiser^[25] and Patel^[26], oxygen precipitate formation in silicon has been studied over the last thirty-five years. Experimentally, it has been shown that oxygen precipitates have been noticed in a nucleation anneal temperature range of 550°C-800°C, and that very few precipitates have been observed in defect-free silicon at nucleation temperatures above 1000°C.[1,28] It has also been shown, from these studies, that the initial oxygen content is the most critical parameter for the precipitate formation, and there is a threshold oxygen content value below which no precipitation is achieved.[1,27-30]

3.2.1 Nucleation Model^[1]

The homogeneous nucleation model presented by Inoue et al.^[1] which is one of the most complete models on oxygen precipitate formation is described below. Other studies on oxygen precipitate formation have also implied that homogeneous nucleation may be the primary precipitate formation mechanism for defect-free silicon wafers at temperatures below 900°C.^[30] Only for the wafers with low oxygen content (below 25ppm -ASTM Standard F-120) and with high carbon content (above 5×10^{16} atoms/cm³), the precipitate formation was predominantly heterogeneous at temperatures above 950°C.^[30]

Inoue et al. proposed, based on the classical nucleation theory (Appendix 2), that the nucleation rate of oxygen precipitates is expressed by

$$J = n^* Z w^* \text{-----} (1)$$

where, n^* = equilibrium critical nucleus density

Z = Zeldowich factor for non-equilibrium distribution
 $= 0.001$ ^[1]

w^* = oxygen impingement frequency on to a critical nucleus

With the assumption that the embryo is spherical and the strain effect in nucleation is negligible, n^* and w^* are given by

$$n^* = n_1 \exp(-\Delta G(r^*)/kT) \text{ ----- (2)}$$

$$w^* = [4\pi(r^*)^2/d^2] n_1 d P \exp(-E/kT) \\ = 4\pi(r^*)^2 n_1 D/d \text{ ----- (3)}$$

$$\text{with } \Delta G(r^*) = 4/3 \pi(r^*)^3 \Delta G_V + 4\pi(r^*)^2 \beta \text{ ----- (4)}$$

$$r^* = - 2\beta/\Delta G_V \text{ ----- (5)}$$

$$\Delta G_V = \Delta H_V(T_E - T)/T_E \text{ ----- (6)}$$

where,

n_1 = nucleation site density, or oxygen content in
case of homogeneous nucleation, $\#/\text{cm}^3$

ΔG = free energy of critical nucleus formation

k = Boltzman constant, $\text{eV}/^\circ\text{K}$

T = annealing temperature, $^\circ\text{K}$

β = interfacial energy between precipitate and matrix
 $= 430 \text{ erg}/\text{cm}^2$ [1]

ΔG_V = volume-free energy for precipitation

ΔH_V = dissolution enthalpy $= 6.67 \times 10^{10} \text{ erg}/\text{cm}^3$ [1]

T_E = oxygen saturation temperature $= 11973 / \ln [1.63 \times 10^{21}/C_i], ^\circ\text{K}$

r^* = critical radius

d = typical atomic distance $= 2.35 \text{ \AA}$

P = probability of oxygen atom impinging to a critical
nucleus which is equal to the oxygen vibration frequency

E = oxygen diffusion barrier height (2.4eV)

D = oxygen diffusion coefficient, cm^2/sec

Substituting Eqs.(2) to (6) in Eq.(1), nucleation rate is expressed by

$$J = Zn_1^2 \cdot 4\pi \cdot A^2 (D/d) \cdot \exp[-4/3 (\pi \beta A^2 / kT)] \quad \text{----- (7)}$$

where $A = 2\beta T_E / \Delta H_v (T_E - T)$

The theoretical plots based on equ. (7) as well as experimental results by Inoue et al. on p-type CZ silicon wafers with (100) orientation are shown in Figure 8 and Figure 9. As can be seen from these two figures, the data-fit to the model is excellent. These results support the claim by Inoue et al. that homogeneous nucleation was the primary mode of the nucleation of the oxygen precipitates for nucleation temperatures below 900°C.

Figure 8. Effect of Anneal Temperature on Nucleation Rate^[1]

Figure 9. Effect of Oxygen Content on Nucleation Rate^[1]

3.3 Denudation

The depletion of oxygen from the surface at high temperature is the primary mechanism of denuded zone formation.[18-22] However, other mechanisms, namely, precipitate formation and dissolution rates, also affect the denuded zone formation. Craven and Korb[20] showed that for low temperature anneals (up to 900°C), the precipitate formation had large effect on denuded zone formation and for high temperatures (1000°C and above), oxygen out-diffusion predominated the denuded zone formation.

The denuded-zone formation model described below is based on the methodology described by Wijaranakula and Metlock for their study of denuded zone formation. Homogeneous nucleation, in which the presence of grown-in precipitates is neglected, will be assumed in the present model. Because the oxygen concentration of the denuded zone is close to the equilibrium level after the denudation anneal, the number of oxygen clusters will be negligible in the denuded zone. Therefore, the homogeneous nucleation assumption is valid.

3.3.1 Denuded Zone Formation Model.[2,3]

The model summarized below is based on a typical high-low-high temperature anneal sequence which was briefly described in section 2.3.3. During the first high temperature

anneal, oxygen diffuses out towards the surface due to oxygen concentration gradient from bulk to the surface. During the low temperature anneal following the high temperature anneal, the oxygen precipitate nuclei will be formed; the rate of nuclei formation is mainly dependent on the oxygen concentration. Finally, at the high temperature anneal following nucleation anneal, some of the nuclei will grow to form stable precipitates while the others will dissolve back to solution depending on the critical radius (r_c).

(a) During the first anneal at a high temperature T_D , the oxygen profile is given by the solution of Fick's second law of diffusion (Appendix-1):

$$C(x,t) = C_S + (C_i - C_S) \operatorname{erf} U \quad \text{-----} (8)$$

where, $C(x,t)$ = oxygen concentration at distance x and time t

C_S = oxygen concentration at the surface which is

assumed to be the equilibrium concentration

C_i = initial bulk oxygen concentration

$$U = x / [2 \sqrt{Dt_D}]$$

D = oxygen diffusivity at denudation temperature T_D

$$= 0.13 \exp[-2.53 \text{ eV}/kT_D] \text{ cm}^2/\text{sec}$$

t_D = Denudation time

k = Boltzman constant

The value of C_S can be safely assumed to be the equilibrium concentration corresponding to the (first) anneal temperature.

(b) During the low-temperature nucleation anneal the precipitate radius can be expressed, according to Zener theory^[23], as a function of nucleation time t_N and is given by ,

$$r_p^N = \alpha_3^* \sqrt{D_N t_N} \quad \text{----- (9)}$$

Where D_N is oxygen diffusivity at nucleation temperature, and α_3^* is the three-dimensional growth coefficient which can be expressed by the following relationship:^[43]

$$\alpha_3^* = \sqrt{\Omega_{Ox} C(x,t)} = \sqrt{\Omega_{Ox} C_{eq}^D [1 + (S_D - 1) \operatorname{erf} U]} \quad \text{----- (10)}$$

where, $S_D = C_i / C_{eq}^D$ = super-saturation ratio between initial bulk oxygen concentration C_i and oxygen solubility C_{eq}^D at the denudation temperature.

$$\Omega_{Ox} = \text{volume of SiO}_2 \text{ molecule} = 4.76 \times 10^{-23} \text{ cm}^3$$

(c) Finally, the critical radius r_C^G during the growth anneal in terms of the depth x (or U) is given by the following expression:^[24]

$$r_C^G = \beta \Omega_{Ox} / kT^G \ln[1 + (S_G - 1) \operatorname{erf} U] \quad \text{----- (11)}$$

where, β = surface-free energy = 430 erg/cm² (1)

T^G = growth temperature

S_G = super-saturation ratio between bulk oxygen concentration and the oxygen solubility at the growth temperature.

The growth of the precipitate will occur if the r_p^N is larger than the critical radius at growth temperature (r_c^G). Thus the denuded zone depth (x_{DNZ}) is defined as the value of x , where, $r_p^N = r_c^G$.

Therefore,

$$\sqrt{\Omega_{OX} D^N C_{eq}^D t_N [1 + (S_D - 1) \operatorname{erf} U]} = \beta \Omega_{OX} / \{k T^G \ln[1 + (S_G - 1) \operatorname{erf} U]\} \quad -- (12)$$

The value of x_{DNZ} can be calculated for each denudation time (t_N) or initial oxygen content (O_i) by trial-and-error iterations using Eqn.(12). Figure 10 and Figure 11 show the theoretical as well as experimental plots of denuded-zone depth dependence on denudation time and temperature and initial oxygen content, respectively as obtained by Wijanarakula et al.[2]

Figure 10. Plots of DNZ width as a Function of Denudation Time[2]

Note: After denudation, all samples received anneal at 750°C for 16 hours followed by anneal at 1000°C for 16 hours.

Figure 11. The Dependence of DNZ on Initial Oxygen Content^[2]

3.4 General Comments on Effect of Dopant Level on Oxygen Precipitation in Silicon

In the intrinsic silicon, which is very pure and contains negligible amount of dopant impurities, each silicon atom shares its four valence electrons with the four neighboring atoms. However, for n-type silicon, the substitutional phosphorous atom with five valence electrons replaces one silicon atom and "donates" one electron to the conduction band. Inversely, for a p-type silicon, boron with three valence electrons substitutes for one silicon and accepts one electron to form four valence bonds. In effect, a positively charged carrier ("hole") is created in the valence band for a p-type semiconductor.

3.4.1 Effect of Temperature on Intrinsic Carrier Concentration^[41]

At most temperatures of interest to us, there is sufficient thermal energy to excite some electrons from the valence band to the conduction band. Equal numbers of holes are left behind in the valence band. At equilibrium,

$$n = p = n_i, \text{ where } n_i \text{ is the intrinsic carrier concentration.}$$

The intrinsic carrier concentration is given by the following expression, which is called the mass-action law:

$$n \cdot p = n_i^2 = N_C N_V \exp (-E_g/kT),$$

where, N_C and N_V are the allowed density of states near the edges of conduction band and valence band, respectively. Although, N_C and N_V vary somewhat with temperature, n_i is much more temperature dependent because of the exponential term in the above expression. Figure 12 shows the intrinsic carrier concentration as a function of temperature for silicon, germanium and gallium arsenide.

3.4.2 Resistivity vs. Carrier Concentration

Intrinsic silicon (containing no dopants) is an insulator. Conductivity is the term generally used to characterize how conductive a material is. As dopants are introduced in the silicon, it becomes more conductive and its resistivity decreases. Experimentally, resistivity of a silicon can be determined using four-point probe method.^[42] Figure 13 shows a plot of resistivity of silicon with different dopant concentration obtained by such a technique.^[45]

Figure 12, Intrinsic Carrier Concentration Dependence on Temperature for Silicon, Germanium and Gallium Arsenide^[44]

Figure 13. Dopant Density vs. Resistivity for Silicon^[45]

3.4.3 Effect of Temperature and Dopant Level on Carrier Concentration (Charge State) for Silicon

Whether a semiconductor will behave like an intrinsic material at a certain temperature depends on the (initial) doping level, its energy band gap, and the temperature. The majority extrinsic carrier concentration of a semiconductor at low temperature (above the ionization temperature) is equal to the dopant concentration. As the temperature increases the intrinsic carrier concentration increases exponentially. At some high temperature, the contribution to the total carrier concentration from the intrinsic carriers approaches the original extrinsic carrier concentration. Above this temperature, the material behaves just like an intrinsic semiconductor.

The effect of impurity level and temperature on the carrier concentration for silicon is schematically shown in Figure 14. These plots are based on the intrinsic carrier dependence on temperature (Figure 12) and the assumption that all dopants will be ionized above about 200°K. From these plots, for low dopant concentration (below 10^{15} atoms/cm³), the silicon will behave like an intrinsic material at temperatures as low as 200°C and therefore, the dopant concentration will not have any effect on the charge states at temperatures higher than 200°C. However, if the dopant level is high enough (above 10^{18} atoms/cm³) the major contribution

for the carrier concentration will be from the dopants even at temperatures as high as 500°C. In this case, the charge state is affected by the dopant concentration even at high temperatures.

Figure 14. Schematic Plot of Carrier Concentration as a Function of Temperature and Dopant Level for Silicon

3.4.4 Effect of Dopant Level on Oxygen Precipitation

The precipitation kinetics can be affected by the dopant level for a highly doped silicon. The effect of dopant level on precipitation is schematically shown in Figure 17.^[45] It can be seen from this plot that the precipitate density decreases drastically for n-type silicon at dopant level of 1×10^{18} atoms/cm³ and for p-type silicon at dopant level of 5×10^{19} atoms/cm³. The explanation of this dopant effect is based on the assumption that the point defects (vacancies and interstitials) play a key role in precipitate nucleation. When silicon is heavily doped, the ionized dopant species tie up the vacancies. Therefore there are fewer vacancies to nucleate the precipitates and so the nucleation rate is lowered. For a lightly doped silicon, there are fewer ionized dopant species to reduce the vacancy concentration, and so the nucleation rate is not affected.

Figure 15. Precipitate Density Versus Doping Level for n and p Type Silicon^[45]

4.0 OBJECTIVE

The objective of this thesis is to reproduce previous work done by Inoue et al. on oxygen nucleation rate study and by Wijaranakula et al. on denuded zone formation in silicon. The previous studies both by Inoue and Wijaranakula were done on p-type silicon. The purpose of the present study was to apply the nucleation model proposed by Inoue et. al and the denudation model proposed by Wijaranakula et al. on n-type silicon. A secondary objective was to see if there was any difference between lightly doped n-type and lightly doped p-type silicon for nucleation rate and denuded zone formation.

5.0 EXPERIMENT

Six-inch n-type (100) phosphorous doped CZ silicon wafers with resistivity range of 10-30 Ω -cm were used for this study. Sets of 10-30 Ω -cm p-type (boron doped) (100) samples were included as a control group during one part of denudation as well as nucleation experiments. The annealing sequence for denudation experiment is described in section 5.2 and that for the nucleation experiment is described in section 5.3.

All annealing was done in a temperature and ambient controlled horizontal quartz furnace at the Integrated Circuit Laboratory (I.C.Lab) at San Jose State University. The schematic diagram of the furnace used for this study is given in Figure 16. The oxygen content measurements for each sample before the first anneal and after the final anneal were done at Integrated Device Technology (IDT), Inc., San Jose. The denuded zone measurements were done using the angle lap and stain technique^[2] and the precipitate density measurements were done using cleave and stain technique^[1] both done also at IDT.

Figure 16. Schematic Diagram of Annealing Furnace

5.1 Experimental Procedural Steps.

The following is the list of steps followed for this experiment. The angle polish was only applicable to the denudation samples.

Wafer Requirements. The wafers used for this study were obtained from MEMC Corporation. The wafers were processed at the vendor as per the standard production process. The sample wafers required for different oxygen content were obtained by selecting different portions of the same ingot (seed end of ingot is generally higher in oxygen content than the tail end). The thermal donor kill anneal at 600-650°C for 30 minutes was done in the wafer form by the manufacturer before the polishing step.^[46]

Furnace Profiling. Type-K thermocouple (TC) (Nickel-Chromium vs. Nickel-Aluminum) enclosed in quartz sheath was used to profile the furnace. The potentiometer (pot) setting on the analog controller for the center zone on the temperature control board was determined for each target temperature to obtain desired temperature as measured by the TC placed in the center of the furnace tube. Fluke model 2190A was used for temperature read out. The repeatability of the actual furnace temperature obtained from the pot setting was within $\pm 5^\circ\text{C}$ for all temperatures. These pot settings were used during the experiment to obtain required temperatures.

Oxygen Content Measurement. Nicolet ECO-DX system based on Fourier Transform IR measurement was used to measure the interstitial oxygen content at the center of the sample. The system was calibrated with a known reference calibration set before measuring the samples.

Sample Preparation. The six-inch wafers were cleaved using a diamond scribe such that four quadrants were obtained from each wafer. One quadrant was used as a sample with characteristics of the experiment scribed on it (e.g. 1000°C-1 hr).

Wafer Processing. Samples were processed in the furnace by first bringing the furnace temperature to the desired value using the profile set-points. The ambient gas or gases were selected by switching the toggle switches to ON or OFF on the gas panel. The samples were then loaded in a quartz boat and then inserted in the furnace using 50-75 cm/min push rate. The samples were left in the furnace at the desired temperature for duration of the cycle time. The temperature set points and the ambient gases were changed when the first anneal time expired; and the samples were left at the temperature and the ambient of the second anneal cycle. The same was repeated for the third cycle if needed, for the denuded zone experiments. The samples were pulled out of the furnace after the end of the last cycle at the pull rate of

50-75 cm/min. The samples were air cooled for five to ten minutes and then unloaded from the quartz boat.

Oxide Strip. The grown oxide on all the samples was striped using 10:1 HF solution (10 parts de-ionized water and one part 49% hydrofluoric acid) until the solution de-wetted the sample surface when the samples were lifted from the solution. The wafers were rinsed with deionized water (DI) and blow dried with an air gun.

Angle Lap. A small rectangular piece from each sample for the denudation group was angle lapped using a 3° angle block on an Ecomet-3 polisher with a glass disc. The sample to be angle lapped was mounted on the block such that the polished (shiny) surface of the sample was to come in contact with the polishing wheel. The samples were checked periodically (every 10 minutes) after the first 30 minutes of polish for sample integrity and width of the polished area. The angle lap was stopped when the width was over 100 μm . The samples were rinsed in DI water and blow dried using a nitrogen gun.

Wright Etch. The angle lapped pieces for the denuded zone group and cleaved pieces from the nucleation group were etched in a small plastic beaker using Wright etch solution^[31] for two minutes to decorate the defects. The beaker was constantly agitated during the entire two minutes to prevent etch artifacts. The samples were rinsed in DI

water and then blow dried. The etch rate of the Wright etch was determined (previously) to be one micron per minute by measuring the thickness difference of a wafer measured before and after a five minute Wright etch (the thickness was measured using ADE Thickness Measurement Tool).

Photomicrographs. Polaroid photographs for all samples were obtained at the magnification which gave the complete and clear hard copy of the viewed sample. For the denudation samples, the angle lapped surface was photographed such that the edge of the top surface and the bulk of the silicon where the denuded zone ended were clearly visible. In the case of the nucleation group, the (110) plane (the cleaved plane) of the sample was photographed.

Defect Density and Denuded Zone Determination. A structure with known dimensions was photographed at the magnifications to be used for the sample photographs to calibrate the measurement technique. This calibration factor was used to determine the defect density per cm^2 and the denuded zone in microns.

5.2 Denuded Zone Formation Experiment.

5.2.1 Denuded Zone vs Denudation Time and Temperature

Samples with oxygen content of 7.5×10^{17} atoms/cm³ were used for this group. The denudation time and temperatures investigated are listed in Table 1. The nucleation treatment at 650°C in nitrogen ambient for sixteen hours was done following the denudation anneal. This was followed by the precipitate growth anneal at 1000°C in 97% N₂/3% O₂ ambient for sixteen hours.

Table 1. Denudation Temperature and Time Matrix

<u>Temperature</u>	<u>Denudation Time, hours</u>
1000°C	0.5,1,3,16
1100°C*	0.5,1,3,16
1200°C	0.5,1,3,16

*Note: p-type samples as a control group were processed with this group.

All four samples corresponding to four denudation times for each temperature were processed together such that the samples received the required denudation times. The sixteen

hour sample was entered in the furnace first; the three-hour sample was loaded when three hours were left for the sixteen hour sample. Similarly, the one-hour and the half-hour samples were loaded when one hour and half hour were remaining, respectively, on the sixteen-hour timer.

5.2.2 Effect of Oxygen Content on Denuded Zone

Samples with the oxygen contents of 6.5×10^{17} atoms/cm³, 7.5×10^{17} atoms/cm³, 8.1×10^{17} atoms/cm³ and 9.1×10^{17} atoms/cm³ were used for this experiment. As explained before, different portions of the same ingot were used to obtain the range of the oxygen content for this group. The denudation, the nucleation and the precipitate growth anneals used for this part are as follows:

Denudation- 1100°C for seven hours in 97% N₂ /3% O₂ ambient.

Nucleation - 750°C for 16 hours in N₂ ambient.

Precipitate Growth - 1000°C for 16 hours in 97% N₂ /3% O₂ ambient.

This part was combined with the 1100°C part of the first group (5.2.1) such that these samples were inserted in the furnace while seven hours were left in the denudation cycle.

5.3 Oxygen Precipitate Nucleation Rate Experiment

5.3.1 Nucleation Temperature vs. Nucleation Rate

Samples with oxygen content of 7.5×10^{17} atoms/cm³ were used for this part. The nucleation temperatures used for this part are: 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, and 850°C. High-temperature denudation anneal was not done for this group. The sample for each corresponding nucleation temperature was processed separately through the entire nucleation and growth anneal. After each nucleation anneal all samples received 1000°C growth anneal. A sample of p-type silicon of similar oxygen content was processed with the n-type sample as a control for each temperature. The nucleation and growth cycles used for this part are listed below:

Nucleation- sixteen hours at temperature "x" in N₂ ambient.

Precipitate Growth- sixteen hours at 1000°C in 97% N₂/ 3% O₂ ambient.

5.3.2 Nucleation Rate vs. Oxygen Content

Sixteen hours of nucleation anneal at 750°C in N₂ ambient and 16 hours of precipitate growth anneal at 1000°C in 97% N₂/ 3% O₂ ambient were used for this part. The oxygen content studied were 6.7×10^{17} atoms/cm³, 7.5×10^{17} atoms/cm³, 8.1×10^{17} atoms/cm³, and 9.1×10^{17} atoms/cm³.

After all the samples received the anneal treatments, they were processed through oxide strip and oxygen content measurement. The denuded zone samples were angle lapped separately and then Wright etched in one batch. The nucleation rate samples were Wright etched also in one batch. After Wright etch, the photographs were taken for all the samples and the defect density and denuded zones were determined. The nucleation rate was calculated by dividing the defect density by the nucleation anneal time and the amount of silicon etched (2 microns).

5.4 Precipitate Dissolution Experiment

Wafers with 30ppm oxygen content were used for this experiment. This experiment was done to test an assumption that the as-received wafers did not contain any precipitates. The procedure described below was used for both 1000°C and 1200°C dissolution temperatures.

Three quadrants, which were obtained by cleaving one wafer into four quadrants, were scribed with "xxxx-yy" where, "xxxx" represented temperature and "yy" represented anneal times (six, twelve and twentyfour hours). The interstitial oxygen content of each sample was measured before anneal using Nicolet FTIR. All four samples were loaded in a quartz boat and inserted in the furnace profiled to 1000°C using 50 cm/min push rate. The six hour, the twelve hour and the

twentyfour hour samples were removed from the furnace after six, twelve and twenryfour hour anneal times, respectively. The pull rate used was also at 50 cm/min. All samples were dipped in 10:1 HF solution then rinsed in DI water and blow dried with air gun. The final oxygen contents were measured for all the samples using Nicolet FTIR.

6.0 RESULTS/DISCUSSION

6.1 Change in Interstitial Oxygen Content

The interstitial oxygen content before the first anneal and after the final anneal temperatures for each sample is given in Appendix 3. From these data, it can be seen that the ΔO_i (the difference between the final interstitial oxygen content and the initial oxygen content) increases as the denudation time increases for denudation temperature of 1000°C and 1100°C. This is as expected from the denudation model (more out-diffusion as denudation time is increased). However, at 1200°C, the ΔO_i does not increase from 0.5 hr denudation time to 16 hrs of denudation time, instead there is a slight decrease as the time increases. The explanation of this observation is as follows.

The ΔO_i for the denudation samples comprises of two components. The first one is due to the out-diffusion of oxygen, and the remaining is from the precipitate growth part of the cycle. The reduction in oxygen from the nucleation part is assumed to be negligible (which was also experimentally confirmed.^[40]) It is also assumed, as described in the theory section, that there are no pre-existing precipitates in as received wafers (homogeneous case). This assumption was confirmed by the results of a precipitate

dissolution experiment, as part of this study, the results of which are shown in Appendix 4.

From the dissolution study, it was observed that there was no observable increase in oxygen content after long anneal at both 1000°C and 1200°C. On the contrary, there was a decrease in the oxygen content after the anneal, which was a result of out-diffusion of oxygen from the silicon. The out-diffusion for sixteen hours at 1000°C and 1200°C can be estimated from these results to be one ppm and 4ppm, respectively. Subtracting the ΔO_i contribution of the out-diffusion part from the total ΔO_i of the denudation experiment for sixteen hour denudation at 1000°C and 1200°C (Appendix 3), the ΔO_i from the precipitate growth can be estimated to be 16.7 ppm and 12 ppm for 1000°C and 1200°C, respectively.

As the denuded zone is formed, the thickness of the silicon which contains appreciable oxygen content for precipitate nucleation and growth is reduced. The reduction of the thickness for sixteen hour denudation at 1000°C is 52 μ (twice the denuded zone width), while that for the sixteen-hour denudation at 1200°C is 170 μ . Subtracting the reduction in thickness from an assumed original thickness of 675 μ of the wafer, the effective thickness for precipitate formation (nucleation and growth) can be calculated to be 623 μ and 505 μ for the denudation temperatures of 1000°C and 1200°C, respectively.

The precipitate density of the samples for the denudation group is assumed to be independent of the denuded temperature (which was also observed from the photographs of the Wright etched samples which received denudation anneal of three hours at 1000°C and 1200°C as shown in Appendix 5). Therefore, there are fewer total precipitates in a sample which received sixteen hour denudation anneal at 1200°C (less cross-section area which contained precipitates) than the one which received sixteen hour anneal at 1000°C. As a result, the ΔO_i from the precipitate growth is lower for a sample which received sixteen-hour denudation anneal at 1200°C than the one which received 1000°C denudation anneal for sixteen hours. It turns out that the percent reduction in effective wafer thickness between the sample which received 1200°C anneal and the one which received 1000°C anneal (which is 24%) is almost the same as the percent reduction in the ΔO_i from precipitate growth between the 1200°C sample and the 1000°C sample (which is 28%).

The ΔO_i for the nucleation part of the experiment are as predicted by the nucleation theory. Figure 17 shows the plot of ΔO_i vs. the nucleation temperature. The ΔO_i is very small at temperature of 500°C and it increases as nucleation temperature is increased. The maximum in ΔO_i is reached at around 700°C and then it decreases again reaching insignificance at 850°C. It is worthwhile noting that the reduction in interstitial oxygen content

after nucleation and growth anneals can be safely used to predict the temperature at which the highest precipitate density will be achieved.

Figure 17. Reduction in Oxygen Content vs. Nucleation Temperature

The delta O_i as a function of starting Oxygen content is shown in Figure 18. The delta O_i for low oxygen content sample (27ppm) was insignificant but it increased as the oxygen content increased. This finding agrees with the

previous work by Inoue et. al^[1] which showed that there was a threshold value for interstitial oxygen content below which the precipitated oxygen (the difference between the starting and final oxygen content) was very low.

Figure 18. Reduction in Oxygen Content vs. Starting Oxygen Content

6.2 Denuded Zone Formation

The photomicrographs of the polished and Wright etched samples for 1000°C denudation group is shown in Figure 19. As can be seen qualitatively from these photomicrographs, the

Figure 19. Photomicrographs of the $11^{\circ}30''$ polished surface for 1000°C denudation anneal (with 16 hrs nucleation anneal at 750°C and 16 hrs growth anneal at 1100°C)

denuded zone increases with denudation time as expected. Figure 20 shows the plots of denuded zone vs. denudation time for three different denudation temperatures. It can be seen from these plots that, the experimental results match closely to the theory for denudation time close to three hours. At longer denudation times however, especially for 1100°C and 1200°C, the model underestimates the denuded zone width. This can be explained by higher apparent diffusivity at higher temperature compared to the one predicted by the model.

Figure 21 shows the plot of denuded zone vs. starting oxygen content. The experimental results follow the trend predicted by the model; however, the model underestimates the denuded zone. This trend of higher actual denuded zone compared to the model is also explained by higher apparent diffusivity than the theoretical value used in the model.

Figure 20. Denuded Zone vs Denudation time at 1000°, 1100°, and 1200°C Denudation Temperatures.

Figure 21. Denuded Zone vs. Starting Oxygen Content

6.3 Nucleation Rate

The plot of nucleation rate vs. nucleation temperature is given in Figure 22. As can be seen from this figure, the experimental results agree well with the ones predicted by the theory. The shape of the curve is identical to the one from Inoue et al. (Figure 8). Note that the temperature range studied by Inoue et. al was from 650°C to 850°C, while the range for the current work was from 550°C to 850°C. However, the nucleation rate obtained in this study is one to two order of magnitude lower than the one from the work of Inoue et. al. This discrepancy is explained in the following paragraph.

The precipitate measurement technique employed by Inoue et. al was transmission electron microscope (TEM) while the method used for the current study was Wright etch and microscope inspection. TEM is generally capable of detecting a smaller defect than the microscope inspection, resulting in higher precipitate counts with TEM compared to microscope inspection. There was no comparison done during this work between the TEM technique and the microscope method. Another reason for the difference in the results could be that the crystals used by Inoue et. al may have received different thermal history than the one used for this study. This could result in different number of embryos (not nuclei) being frozen in from the crystal growth and consequently the final

precipitate nucleation rate will most likely be different^[1]. And finally, there is the effect of the heterogeneous centers in the wafer on the observed nucleation rate. It is possible that the wafers used by Inoue et. al may have more numbers of heterogeneous centers than the wafers used in the current work (note that the Inoue et. al work was done using wafers from different suppliers, while the current work was done using wafers received from only one supplier).

The nucleation rate results also show that there seems to be no difference in the nucleation rate between n-type and p-type silicon we studied. This result agrees with the previous prediction that for lightly doped silicon, the type of dopant does not affect the nucleation rate (Figure 15).

Figure 22. Nucleation Rate vs. Nucleation Temperature

The nucleation rate vs oxygen content results are shown in Figure 23. As can be seen, the nucleation rate vs. oxygen content also shows similar trend as seen by Inoue et. al (Figure 9). The results also show close correlation with the model. The nucleation rate for this group is also one to two order of magnitude lower than the one obtained by Inoue et. al.

Figure 23. Nucleation Rate vs. Starting Oxygen Content

7.0 CONCLUSION

The objective of repeating the work on oxygen precipitate nucleation by Inoue et. al and on denuded zone formation in silicon by Wijaranakula et. al was met. The stain and microscope inspection method of determining nucleation rate for oxygen precipitates is applicable for the oxygen content looked at in this study. For lower oxygen content samples in which sufficient amount of precipitation may not occur, this technique may not be applicable. Transmission electron microscopy (TEM) might be required for studying precipitation in lower oxygen content samples.

The accuracy of the method used for this work was not compared with any other known methods because of unavailability of other methods. Transmission electron microscopy (TEM) method could be used for this purpose. The precision of this technique also was not determined because there are no known reference standards available with known number of oxygen precipitates. The repeatability of the stain and microscope inspection was done by etching three samples which received the same heat treatment. The results are shown in Appendix 6. The repeatability of this technique is found to be $\pm 5\%$ which shows the merits of this technique.

The secondary objective of comparing the nucleation rate and denuded zone results of lightly- doped n-type silicon with lightly-doped p-type silicon was also met. A study of effect of dopant species on oxygen precipitation using the stain and microscope inspection technique is recommended as a future thesis subject.

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APPENDIX-1

Solution to the Fick's Second Law of Diffusion

Fick's second law for one dimensional case is given by the following general format:

$$dC(x,t)/dt = D \, d^2C(x,t)/dx^2$$

where, $C(x,t)$ = Concentration

t = time

D = Diffusivity

x = distance

The solution of this equation is dependent upon the initial and boundary conditions. The denudation of oxygen from silicon surface is a constant source problem, so the initial and boundary conditions are as follows:

The initial condition: At $t=0$, $C(x,t) = C_s$ = Oxygen concentration at the surface which is assumed to be the equilibrium concentration.

The boundary Condition: $C(\infty,t) = C_i$ = Background oxygen concentration

Using these two conditions, the solution of the Fick's Second law is given by,

$$C(x,t) = (C_s - C_i) \operatorname{erf} U$$

$$\text{where, } U = x/[2\sqrt{Dt}]$$

APPENDIX-2

The Classical Homogeneous Nucleation Theory

The classical nucleation model as applied to the phenomenon of oxygen precipitation in silicon is briefly described in the following paragraph. Homogeneous nucleation where there are no preferred sites for nuclei to form is assumed in this case.

Assuming there is no chemical or volume change, the total Gibb's free energy for the nucleation process is given by,
$$\Delta G_{\text{Total}} = \Delta G_{\text{volume}} + \Delta G_{\text{surface}} \text{ ----- (1)}$$

where, ΔG_{volume} is the volume free energy, which is negative and $\Delta G_{\text{surface}}$ is the surface free energy.

$$\Delta G_{\text{Total}} = 4\pi r^2 \beta + 4/3\pi r^3 \Delta G_v \text{ ----- (2)}$$

where, β = surface free energy per area, and

ΔG_v = volume free energy per unit volume which can be expressed by,

$$\Delta G_v = \Delta H_v (T_{\text{tr}} - T) / T_{\text{tr}}$$

where, ΔH_v = dissolution enthalpy, and T_{tr} is the

Equilibrium Transformation Temperature

The critical radius at which the precipitate is stable is reached when $\partial \Delta G_v / \partial r = 0$,

$$\text{Therefore, } 8\pi r \beta + 4\pi r^2 \Delta G_v = 0 \text{ at } r = r^*$$

$$\text{and, } r^* = -2\beta / \Delta G_v$$

$$\text{or } r^* = -2\beta T_{\text{tr}} / \Delta H_v (T_{\text{tr}} - T) \text{ ----- (3)}$$

Therefore, $\Delta G^* = 16\pi\beta^3 (T_{tr} - T) / 3 \cdot [\Delta H_v(T_{tr} - T)]^2$ ----- (4)

The cluster formation in homogeneous nucleation case is a statistically random process and the size distribution obeys the Boltzman's distribution function. Once a cluster has reached the critical radius, it either can grow to be a stable nucleus by incorporating additional oxygen atom, or it can dissolve by losing one oxygen atom.

From equation (3), the critical radius is dependent on the extent of super cooling ($T_{tr} - T$). The larger the supercooling, smaller the critical radius, therefore, more number of nuclei (larger the area under the distribution curve). And from eq. (4), larger the supercooling, lower the energy barrier for phase transformation, and so, higher the number of precipitates.

Nucleation Rate. In classical nucleation theory, nucleation is the process in which one oxygen atom impinges upon a critical nucleus and is absorbed to form a stable nucleus. The nucleation rate(J) is comprised of the number of atoms that can be fit on a nucleus, the frequency at which atoms jump successfully, and the number of sites in the matrix. It is given by the following:

$$J = (4\pi r^{*2}/d^2) \cdot [n_1 d p v \exp(-\Delta G_1/kT)] \cdot [n_1 \exp(-\Delta G^*/kT)]$$

where, r^* = critical radius

d = atomic distance

ΔG_1 = oxygen diffusion barrier

n_1 = nucleation site density

p = probability of oxygen impinging on nucleus

v = oxygen vibration frequency

k = Boltzman constant

T = annealing temperature

ΔG^* = free energy for critical nucleus formation

In the above expression, $p.v.\exp(-\Delta G_1/kT)$ can be replaced with the diffusivity of oxygen (D) for simplicity.

Appendix-3

Interstitial Oxygen Content Before the First Anneal and
After the Final Anneal

NUCLEATION GROUP				DZ GROUP			
	START	FINAL	DELTA		START	FINAL	DELTA
SPLIT	Oi, ppm	Oi, ppm	Oi, ppm	SPLIT	Oi, ppm	Oi, ppm	Oi, ppm
n-550°C	30.1	27.9	2.2	n-1000-.5	30.2	18.9	11.3
n-600°C	30.1	17.9	12.2	n-1000-1	30.2	16.2	14.0
n-650°C	30.1	7.1	23.0	n-1000-3	30.2	14.6	15.6
n-700°C	30.1	5.8	24.3	n-1000-16	30.2	12.5	17.7
n-750°C	30.3	10.3	20.0	n-1100-.5	30.1	23.1	7.0
n-800°C	30.3	23.2	7.1	n-1100-1	30.1	21.0	9.1
n-850°C	30.3	28.1	2.2	n-1100-3	30.1	20.2	9.9
p-550°C	30.0	27.5	2.5	n-1100-16	30.1	17.2	12.9
p-600°C	30.0	19.4	10.6	p-1100-.5	29.7	23.8	5.9
p-650°C	30.0	8.5	21.5	p-1100-1	29.7	18.6	11.1
p-700°C	30.0	5.2	24.8	p-1100-3	29.7	15.9	13.8
p-750°C	29.5	6.1	23.4	p-1100-16	29.7	12.8	16.9
p-800°C	29.5	16.6	12.9	n-1200-.5	30.3	11.9	18.4
p-850°C	29.5	27.4	2.1	n-1200-1	30.3	12.3	18.0
27ppm	26.9	25.2	1.7	n-1200-3	30.3	12.5	17.8
30ppm	30.0	19.6	10.4	n-1200-16	30.3	13.9	16.4
32ppm	32.4	16.3	16.1	27ppm	26.9	23.9	3.0
36ppm	36.4	1.9	34.5	30ppm	30.0	10.7	19.3
				32ppm	32.4	9.6	22.8
				36ppm	36.4	4.2	32.2

Appendix-4

Precipitate Dissolution Experiment

WAFER ID	SPLIT	START Oi, ppm	FINAL Oi, ppm	DELTA Oi, ppm	COMENTS
1	1000°C, 3 hrs	31.2	30.8	0.4	
2	1000°C, 6hrs	31.4	30.8	0.6	
3	1000°C, 12hrs	31.2	30.4	0.8	
4	1000°C, 24hrs	31.2	30.2	1.0	
5	1200°C, 3hrs	30.2	29.0	1.2	
6	1200°C, 6hrs	30.2	28.4	1.8	
7	1200°C, 12hrs	30.0	27.8	2.2	(repeatability of Oi)
8	1200°C, 24hrs	31.0	24.9	6.1	(24.9,24.8,24.8)

Appendix-5

Precipitate Density vs. Denudation Temperature

1000°C Denudation

1100°C Denudation

1200°C Denudation

Appendix-6

Repeatability Study of The Stain and Inspection Method

Nucleation Temperature = 750C

<u>Sample #</u>	<u># of Defects</u>	<u>Area, cm²</u>	<u>Defect Density</u> <u>#Def. /cm²</u>
1	79	2.3×10^{-5}	3.4×10^6
2	84	2.3×10^{-5}	3.6×10^6
3	88	2.3×10^{-5}	3.8×10^6

Average Defect Density = 3.6×10^6 #/cm²

Standar Deviation = 2.0×10^5

Percent Std. Dev. = + 5%