

## THE ENGINEERING OF INTRINSIC POINT DEFECTS IN SILICON WAFERS AND CRYSTALS

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### Abstract

Using new techniques which manage intrinsic point defect concentrations during the growth of silicon crystals *and* subsequent processing of silicon wafers, it is possible to achieve two highly desirable results. First, using techniques which maintain crystals sufficiently close to equilibrium during growth such that it is possible to grow *large diameter CZ* silicon crystals which are *completely free* of agglomerates of vacancies (voids) or self interstitials (dislocation loops). Secondly, through the control of quenched-in vacancy concentration profiles in thin silicon *wafers* during Rapid Thermal Annealing processes, it is possible to obtain *ideal* oxygen precipitation behavior in silicon wafers. Such vacancy concentration engineered wafers are effectively *programmed* to produce robust defect distributions suitable for Internal Gettering (IG) applications. The performance of such wafers is independent of all parameters previously important to engineering of IG structures: oxygen concentration, crystal growth method and even the application in which the wafer is used. These two new types of material represent important simplifications to the successful defect engineering of silicon wafers in advanced IC applications. It is shown that, taken together, results from both crystal growth and wafer processing studies place a large number of constraints on the parameter set used to describe the properties of the vacancies and self-interstitials in silicon. A model for the oxygen precipitation enhancement in the MDZ process is given.

### Keywords

Vacancies, Self-interstitials, Microdefects, Oxygen precipitation, Internal Gettering

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## Introduction

If the polished CZ silicon wafer - as opposed to epitaxial substrates - is to survive as a suitable electronic material for new generations of advanced IC devices, then it appears that new, cost effective, approaches to the engineering of defects in CZ grown silicon must be implemented. The problem is two-fold: (1) two classes of defects *intrinsic* to melt-grown silicon, vacancy- and interstitial-type agglomerated defects and (2) the control of the precipitation of oxygen. Intrinsic point defect related agglomerates or *microdefects* are formed during the crystal growth process. The precipitation of oxygen occurs during processing of silicon wafers into ICs, but with a strong connection to crystal growth and wafer heat treatments preceding device processing. These defect types are not new to silicon technology but the demands on their control have increased dramatically in recent years. Furthermore, as the silicon industry matures, there is a need to simplify material selection processes. Uncertainty of performance must be eliminated and with it the need to highly *tailor* silicon products to specific applications. The complications which arise out of the complex interactions of defects from initial solidification of the silicon crystal ingot through device processing add undesirable costs and rigidity to the use of silicon as an electronic material. Native point defects play the key role in these problems.

### *Vacancy-type defects*

The first challenge lies with a defect unique to silicon grown from the melt, an agglomeration of excess vacancies into a rather low-density (typically ca.  $10^6 \text{ cm}^{-3}$  for the case of CZ silicon) void-type microdefect [1]. If present, this type of defect can result in the failure of gate oxides and are of increasing importance in device geometries on the order of the void sizes (on the order of 100-150 nm), isolation failures and other topological faults [2]. Depending on the mode of detection, void-type defects are also referred to as D-defects, COPs, Flow Pattern Defects, Light Scattering Tomography Defects and GOI-defects.

### *Silicon self-interstitial-type defects*

There exists another and, if anything, even more harmful defect type unique to silicon grown from a melt: agglomerates of excess silicon self-interstitials into large dislocation loops. These defects are sometimes referred as A-defects or Large Etch Pit defects. Their density is generally far lower than that of the void microdefects but their size usually orders of magnitude larger – hence their importance.

### *The precipitation of oxygen*

The control of the behavior of oxygen in silicon is undeniably one of the most important challenges in semiconductor materials engineering. In the 20 or so years since the discovery of the internal gettering effect in silicon wafers, many scientists and engineers have struggled with the problem of precisely and reliably controlling the precipitation of oxygen in silicon which occurs during the processing of wafers into integrated circuits (ICs). This has been met with only partial success in the sense that the “defect engineering” of conventional silicon wafers is still, by in large an *empirical* exercise. It consists largely of careful, empirical *tailoring* of wafer type (oxygen concentration, crystal growth method, and details

of any additional pre-heat treatments, for example) to match the *specific* process details of the application to which they are submitted in order to achieve a good *and* reliable Internal Gettering (IG) performance. Reliable and efficient IG requires the robust formation of oxygen precipitate free surface regions (denuded zones) and a bulk defective layer consisting of a minimum density (at least about  $10^8 \text{ cm}^{-3}$  [3]) oxygen precipitates during the processing of the silicon wafer. Uncontrolled precipitation of oxygen in the near surface region of the wafer represents a risk to device yield.

### The control of the agglomeration of intrinsic point defects during crystal growth

It is important to keep in mind that the root causes of the two types of intrinsic microdefects, vacancy and interstitial, lie in the local conditions under which the silicon solidified and that these conditions do not overlap one another. The two types of microdefects thus are never found together in the same part of a crystal. This is a result of the manner in which the reactants, the excess intrinsic point defects, are incorporated into the growing crystal. Rapid recombination between vacancies and self-interstitials at high temperatures result in a supersaturation of one species and an undersaturation of the other depending on the value of the ratio  $v/G$ , where  $v$  is the pull rate and  $G$  the local axial temperature gradient in the crystal near the melt-solid interface. A critical value of  $v/G$  separates crystals or regions of crystals grown with excess vacancies from those with excess self-interstitials. The model for this fundamental feature of silicon crystal growth was developed by Voronkov in 1982. [4]. The vast majority of silicon produced today is grown under conditions that result in vacancy-type void defects only. Also possible are fully interstitial-type crystals and, due largely to radial variation in  $G$ , crystals of a mixed type. These usually consist of axially symmetric regions of vacancy-type material surrounded by interstitial-type material [5-7]. Most ring-like crystal non-uniformities can be traced to a boundary between vacancy and interstitial type growth and to the adjoining boundary regions or bands [7]. An image of a copper decorated axial section of a crystal and a schematic diagram of the resulting distribution of agglomerated defects in a crystal grown with decreasing pull rate such that the critical value of  $v/G$  is crossed is shown in Figure 1.

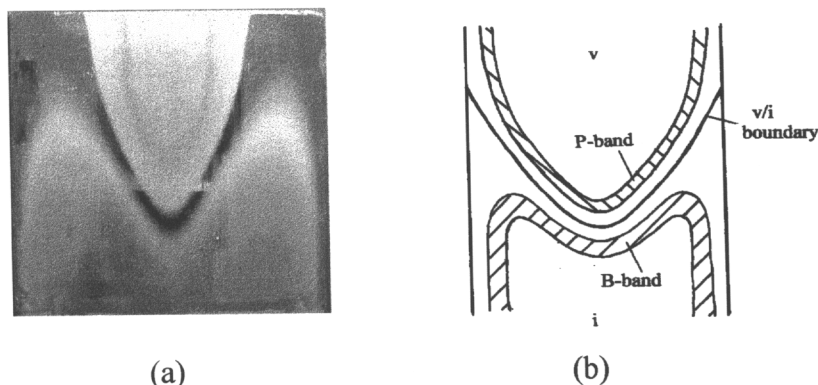


Fig. 1. (a) An axial cross section of an etched Cu-decorated CZ crystal section at the transition from vacancy-type defect growth conditions (the upper “U-shaped” section) and interstitial-type defect conditions (the lower “M-shaped” structure). (b) A schematic diagram of the structure.

The region inside the p-band (large vacancy concentrations) contains voids. The p-band (lower vacancy concentrations) contains oxide particle which are responsible for the subsequent nucleation of stacking faults during oxidation at high temperatures. The region between the p-band and the V/I boundary at

still lower vacancy concentrations, contains neither void nor particles but exhibits an enhanced oxygen precipitation upon subsequent heat treatments. This region is called the “L-band”. A similar marginal band (the “H-band”) of enhanced oxygen precipitation in the void region just inside the p-band is also observed. Just outside the L-band in the interstitial region is another microdefect-free region, but without enhanced oxygen precipitation. Deeper into the interstitial region one finds a marginal band of B-defects [5,7,9], still deeper A-defects, the large dislocation loops.

### *Void reaction control*

One approach to the improvement of the microdefect problem is to grow crystals in the vacancy mode but to engineer the reactions which produce voids. It is found that the resultant density of voids is proportional to the factor  $q^{3/2}C_v^{-1/2}$  [6], where  $q$  is the cooling rate at the temperature at which the reaction occurs and  $C_v$  the local concentration of vacancies. The v/G model [4], although only a one dimensional model, usually gives  $C_v$  accurately at distances greater than a about a centimeter or so from the crystal surface. For more complete and detailed picture, numerical simulation must be performed. The void reaction occurs over a very narrow temperature range (about 5K) at a temperature which depends on  $C_v$  [6]. The range of typical reaction temperatures lies between about 1000 and 1100 °C [7, 9, 10]. The problem of reducing void defect density is thus a coupled engineering problem. A growing silicon ingot is a rigid object. One must engineer simultaneously the coupled problems of the incorporation of vacancies near the growth interface ( $v$  and  $G$  at about the melt temperature) and the cooling rate at the reaction temperature ( $v$  and  $G$  at a temperature which depends on  $C_v$ ). This can be done, but for largely practical reasons, only about a factor of 10 reduction in void density is possible. For some applications, this is not enough improvement to insure device yields which are not limited by the starting substrate defectivity.

### *Perfect Silicon*

A more robust solution to the microdefect problem and one which circumvents the question and resultant complications of whether or not the material is *sufficiently* improved to meet the needs of an arbitrary IC process is not to *control* the microdefect reaction, but to *suppress* it. As described above, there exist two marginal bands straddling the transition from vacancy to interstitial type silicon in which the reactions which produce microdefects do not occur. In these regions, the concentrations of either vacancies or self-interstitials are too low to drive the reactions during the cooling of the crystal. They differ in character due to the differing effects of unreacted vacancies or interstitials on the subsequent nucleation of oxygen clusters at lower temperatures. Excess vacancies enhance the clustering, while excess interstitials suppress it. In terms of process control, the width in v/G space around the critical value which produces sufficiently low concentrations of both vacancies or interstitials is on the order of 10%. Growth processes which can control v/G to within 10% around the critical value both axially and radially are capable of producing microdefect-free silicon. This is not an easy task. Methods exist which result in the partial relaxation of this requirement such that the production of such “Perfect Silicon” is practically possible along nearly the entire crystal length. In general, three types of Perfect Silicon are possible: 1) entirely vacancy type, exhibiting a generally enhanced oxygen precipitation, 2) entirely interstitial type perfect material in which oxygen precipitation is suppressed and 3) a mixed type. Figure 2 illustrates the difference between sections of vacancy defective, interstitial defective and interstitial-perfect silicon when decorated by copper.

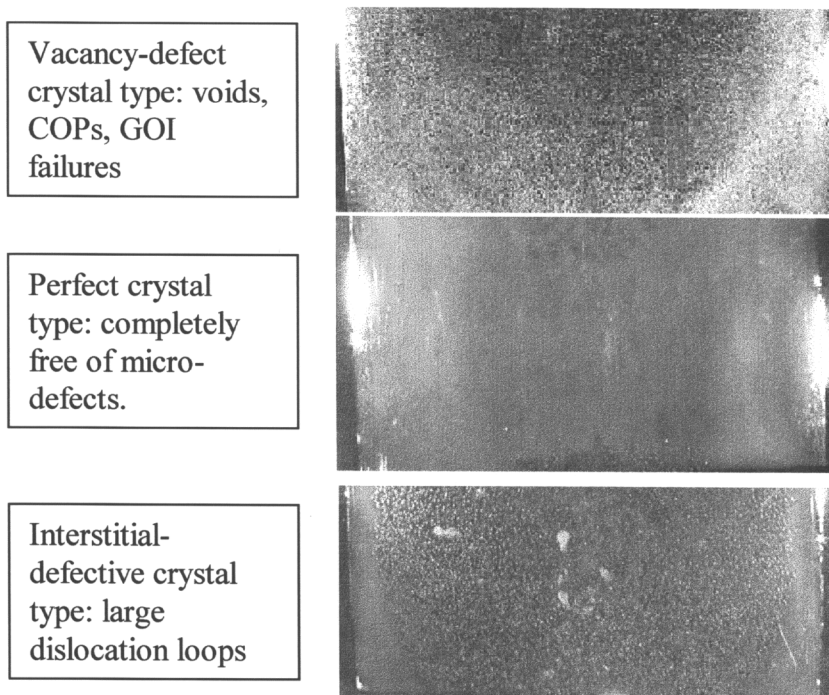


Fig. 2. Images of silicon crystal cross-sections after copper decoration and etching.

### The control of oxygen precipitation through the engineering of vacancy concentration in silicon wafers: “Magic Denuded Zones”

In the discussion above, it was noted that there exists a region of vacancy concentration accessible through crystal growth in which no microdefects are formed but in which the clustering of oxygen is significantly enhanced. It is also possible to achieve such levels of vacancy concentration in thin wafers through the proper control of their heating and cooling. By doing so, it is possible to strongly affect the subsequent precipitation behaviour of the wafer. In fact, it is possible, through the judicious control of point defect generation, injection, diffusion and recombination to install vacancy concentration profiles into silicon wafers which result in the ideal precipitation performance for Internal Gettering (IG) purposes. Such a wafer is said to have a “Magic Denuded Zone”(MDZ) [11].

While high concentration of vacancies enhance oxygen clustering, it is found that there is a lower bound on vacancy concentration for which clustering is “normal”. It is quite a sharp transition around about  $5 \times 10^{11} \text{ cm}^{-3}$ . Installing a vacancy concentration profile which rises from the wafer surface into the bulk of the wafer crossing the critical concentration at some desired depth from the surface results in a wafer with a surface region of “normal” silicon and a bulk of vacancy enhanced precipitation. This is the core the MDZ concept. In modern low vacancy silicon, oxygen precipitation is suppressed if grown-in pre-existing clusters are dissolved by simple high temperature heat treatments. Such material is known as “Tabula Rasa” silicon. [12]. The dissolution of grown-in clusters is an integral part of the thermal treatments necessary to install the required vacancy concentration profile. From the “Tabula Rasa” state, re-nucleation of stable oxygen clusters at low temperatures (ca. 450-700°C) is inhibited in almost all practical cases by the requirement of relatively long incubation times, even though the oxygen

concentration remains high. In the high vacancy regions, the incubation times are reduced over a wide temperature range to very small values [11]. The very large difference in incubation times between high and low vacancy concentrations is primarily responsible for the creation of the denuded zone effect. An example of the precipitate profiles achieved from two different installed vacancy concentration profiles is shown in Figure 3. Vacancy concentration profiles were measured by a Pt diffusion technique [13]. In low vacancy concentration surface regions, the Pt technique is not very accurate due to competition with the kick-out mechanism for platinum incorporation. The estimated value of the vacancy threshold concentration for precipitation enhancement comes from observations of bulk vacancy concentration and precipitation rates.

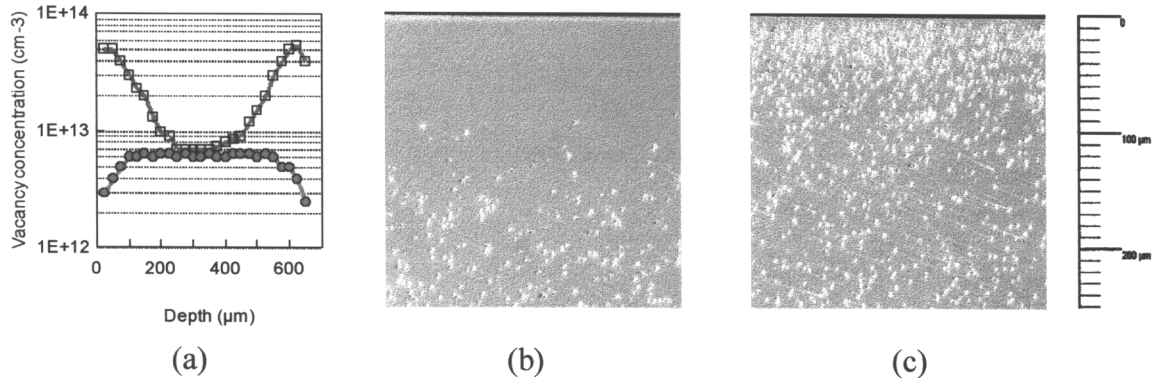


Fig. 3. Vacancy concentration profiles (a) from Pt diffusion results on two samples heat treated at 1250°C for 30 s in a nitrogen (squares) and argon (circles) ambient. Following this the wafers were given a precipitation test treatment (4 hrs, 800°C + 16 hrs 1000°C). (b) Argon treatment (MDZ). (c) Nitrogen treatment. The bulk precipitate densities in both cases is approximately  $5 \times 10^{10} \text{ cm}^{-3}$ .

#### *The installation of vacancy concentration profiles in thin silicon wafers*

The installation of MDZ vacancy concentration profiles in a thin silicon wafers is a three step process, all of which occur in a single Rapid Thermal Processing (RTP) step [12]. 1) When silicon is raised to high temperatures, vacancies and interstitials are spontaneously produced in equal amounts through Frenkel pair generation, a very fast reaction. At distances far removed from crystal surfaces we thus have  $C_I = C_V = \{C_{Ieq}(T)C_{Veq}(T)\}^{1/2}$ , where T is the process temperature. Were the sample to be cooled at this point the vacancies and interstitials would merely mutually annihilate each other in the reverse process of their generation. 2) In thin wafers however the surfaces are not far away and this situation changes very rapidly. Assuming equilibrium boundary conditions (*not oxidizing or nitriding*) leads to coupled fluxes of interstitials to the surface and vacancies from the surface ( $C_{Ieq}(T) < C_{Veq}(T)$  for the temperature ranges of interest (see below)) and the rapid establishment of equilibrium conditions throughout the thickness of the wafer. Experiments suggest that this occurs very rapidly – in a matter of seconds or even less. This equilibration is primarily controlled by the diffusivity of the fastest component, the self-interstitials, since the concentrations are roughly equal. 3) Upon cooling, two processes are important: direct recombination of vacancies and interstitials, and surface recombination and the resulting fluxes toward the surfaces. The slower vacancies are now the dominant species of the coupled diffusion ( $C_V \gg C_I$ ) and hence the equilibration processes toward the equilibrium state at the surface is not as fast as the interstitial dominated initial equilibration. It is thus possible to freeze in excess vacancies at not unreasonable cooling rates. For samples cooled rapidly, the residual bulk concentration of vacancies following recombination with interstitials,  $C_V$ , is the initial difference ( $C_V$

$-C_{1e}$  (at the process temperature, T). Closer to the surfaces  $C_V$  is lower due to diffusion (again now primarily controlled by the dominate vacancies) toward the decreasing equilibrium values at the wafer surface. The relatively rapid cooling rates achievable (50-100 °C/s) in RTP systems insure that sufficiently high concentrations of vacancies can be frozen in the bulk of the wafer to achieve the MDZ effect. In general the level of bulk precipitation is controlled by the value  $C_V$  (determined by the process temperature) while the depth of the denuded zone is controlled by the diffusion of vacancies during cooling. Such information, coupled with numerical simulation of the coupled diffusion process, can be very important points of reference in analysing the parameters of the native point defects in silicon. For example, critical vacancy concentrations ( $=C_{Ve}(T)-C_{1e}(T)$ ) for precipitation enhancement (ca.  $5-8 \times 10^{11} \text{ cm}^{-3}$ ), is achieved at about 1175 °C while at about 1250 °C much higher vacancy concentration is found, to be between about  $2-5 \times 10^{12} \text{ cm}^{-3}$ . The uncertainty in these numbers reflect our uncertainty in the platinum diffusion technique. Further experiments with various cooling rates and subsequent relaxation rates of an installed profile during a second RTP process at a different temperature give insight into the diffusivity of vacancies at various temperatures. Such information gained from MDZ experiments is coupled with information gleaned from crystal growth experiments to compile a unified picture of the point defect parameters. This is discussed below.

#### *Advantages of the use of vacancies to control oxygen precipitation in wafers*

MDZ is a very powerful tool for the resolution of the problem of oxygen precipitation control in silicon wafers. The installation of an MDZ vacancy concentration profile effectively programs a silicon wafer to behave in a well-defined and ideal way. Essentially all the difficulties associated with the robust engineering of IG structures are removed at a stroke. At MDZ vacancy concentration levels the control of the nucleation reactions is de-coupled from the oxygen concentration over the entire practical CZ range ( $4-10 \times 10^{17} \text{ cm}^{-3}$ ) thus eliminating the need for tight oxygen control in CZ crystal growth. The “tabula rasa” character of MDZ heat treatments erases the all details of oxygen clustering during crystal growth. Finally the extraordinarily rapid incubation of clusters at low temperatures insures that the installed vacancy “template” is “fixed” essentially as wafers are loaded into their first high temperature heat treatment. The vacancies are consumed in this process and only the clusters in their well-defined distribution are left behind to grow. No further nucleation takes place, except in extraordinary circumstances. In short, an MDZ wafer is a generic high-performance IG wafer de-coupled from the need to tailor a specific material to a specific process. Our goal of simplicity is thus achieved.

#### *The mechanism of the vacancy effect on oxygen precipitation*

At low T oxygen clusters are nucleated to high density even without vacancies but there is a long incubation (several hours at 650°C) before subsequent high-temperature anneal results in an appreciable precipitate density,  $10^9 \text{ cm}^{-3}$  or higher. This incubation, most likely, is not related to a lag in the time-dependent nucleation rate but rather to the problem of subsequent survival of nucleated oxygen clusters. The clusters formed without volume accommodation (without assistance of vacancies) would inevitably dissolve at higher T since the strain energy per oxygen atom becomes larger than the oxygen chemical potential. The only way to survive is to relieve the strain energy by emitting enough self-interstitials, to acquire some space in lattice. The emission rate is expected to be of strong size dependence. It becomes appreciable only if the cluster size is over some critical limit. To achieve this size, some incubation time is required. However, with vacancies present, the clusters will relieve the strain simply by absorbing

vacancies. The vacancy species at low T exist predominantly as  $O_2V$  complexes (bound vacancies – see below). The  $O_2V$  species may be of high enough mobility even at low T, to be absorbed by the clusters at the nucleation stage. Even if this is not the case, vacancies will be absorbed during the subsequent ramp-up of the temperature since the effective vacancy diffusivity (averaged over  $O_2V$  and V species) is a fast increasing function of T. Either way, at the beginning of the precipitation stage (for example at  $1000^\circ\text{C}$ ) each cluster will contain m vacancies ( $m=C_v/N$  where N is the cluster density). The critical vacancy number  $m^*$  - for clusters in equilibrium with the equilibrium solution of point defects – is estimated to be about 100 at  $1000^\circ\text{C}$  (it is slightly dependent on the oxygen concentration). This important estimate comes from the oxide/silicon interfacial energy fitted to account for the microdefect formation [16]. If the actual value of m exceeds  $m^*$  then the cluster-controlled point defect concentrations correspond to interstitial supersaturation (and vacancy undersaturation). Under such condition, all the clusters can grow simultaneously since self-interstitials are removed to the sample surface thus providing more space for the clusters. This means that m will increase, and the number of oxygen atoms in each cluster (n) will follow the increase in m. However if the starting value of m is below  $m^*$  (a much more likely situation), the point defect solution in equilibrium with clusters corresponds to interstitial undersaturation; then the interstitials diffuse from the sample surface into the bulk decreasing m – and thus inducing the cluster dissolution. Along with this (presumably slow) process there will be fast coalescence with respect to the size m: the clusters of smaller m will lose vacancies while the clusters of larger m will get those vacancies. In this way the total cluster density N will decrease while the average size m will increase, until it becomes larger than  $m^*$ . After that, all the remaining clusters can grow simultaneously. This consideration results in a simple rule for the final precipitate density  $N_p$ . It is on the order of  $C_v/m^*$  (about  $10^{10}\text{ cm}^{-3}$  for  $C_v=10^{12}\text{ cm}^{-3}$ ). It is remarkable that though the initial (nucleated) cluster density N may strongly depend on the oxygen content, the final precipitate density  $N_p$  is almost independent of the oxygen content: it is controlled by the vacancy concentration  $C_v$ . When the vacancy concentration is low, the starting size  $m=C_v/N$  will be accordingly small. The clusters of small m would simultaneously lose the vacancies to the vacancy solution, and will be completely dissolved.

Another mechanism of vacancy-enhanced precipitation is direct agglomeration of the vacancy species ( $O_2V$ ) during the nucleation stage. The production of this new cluster population – by agglomeration not of oxygen but of  $O_2V$  - goes in parallel with the nucleation of oxygen-only clusters considered above. Attachment of the  $O_2V$  species to a cluster may proceed either by direct migration of these species or by the dissociation with subsequent fast migration of a released free vacancy to a cluster followed by attachment of oxygen atoms. For both ways the nucleation rate is not very sensitive to the oxygen content but controlled primarily by the species concentration,  $C_v$ . If the vacancy size of clusters,  $m=C_v/N$ , is below  $m^*$ , the precipitation anneal will result in a coalescence process (described above), and the cluster density N will be reduced to the final value on the order of  $C_v/m^*$ . At low  $C_v$  the nucleation rate of  $O_2V$ -clusters would be negligible.

The two mechanisms of vacancy-enhanced oxygen precipitation share some common features: (a) the basic effect of vacancies is to supply the oxygen clusters with space necessary for the cluster survival during the precipitation anneal; (b) the vacancy concentration must be over some limit to enhance the precipitation. (c) the produced precipitate density is controlled by the vacancy concentration rather than by oxygen content. It is likely that the first mechanism is important at low T (at  $650^\circ\text{C}$  or below). The second mechanism certainly operates at higher T (like  $800^\circ\text{C}$ ) – when the effective vacancy mobility is



enough for vacancy-assisted nucleation of oxygen clusters. The first mechanism is not operative at all at such T since the nucleation rate of oxygen-only clusters becomes negligible.

### **Conclusions drawn regarding the intrinsic point defect parameters taken from the combination of crystal growth and MDZ experiments**

Both the problems of microdefect formation in crystal growth and MDZ involve the properties of point defects at high temperatures. At high temperatures in lightly doped material, the analysis of the problem should be free of the complications of complexes and charged species. This section discusses conclusions drawn from the analyses of both problems taken together to present a coherent view of the properties of free, neutral point defects in silicon and the nature of complexing at lower temperatures.

Recombination rate. The v/G rule for grown-in microdefect type (the type of incorporated intrinsic defect) implies that the balance between defect recombination and pair generation is achieved very rapidly. The characteristic equilibration time  $\tau_r$  must be much shorter than the time spent within the near-interface region where major defect annihilation occurs (for float-zoned crystals this dwell time may be as short as 20s). This conclusion is in line with the extremely short equilibration time observed in MDZ experiments in wafers at 1250°C (on the order of 1s). This result means that both equilibration processes (pair generation/recombination and diffusion) occurs within this short time. The characteristic time  $\tau_r$  is therefore in the order of 1s (or less) at 1250°C. Since  $\tau_r$  is a fast decreasing function of T, it will be still much lower (several milliseconds or less) at the melting point.

Self-interstitial diffusivity. The short equilibration at 1250°C also means that the characteristic diffusion time,  $(d/\pi)^2/D_i$  – where d is the wafer thickness (0.07cm) – is on the order of 1s. Accordingly, the interstitial diffusivity,  $D_i$ , is on the order of  $5 \times 10^{-4} \text{ cm}^2/\text{s}$ . The estimate for  $D_i$  at the melting point (resulting from quenched-in microdefect patterns) is the same number [4]. This coincidence implies that (a) the interstitial diffusivity is very high, (b) the temperature dependence of  $D_i$  is not significant (at least over 1250°C). The interstitial migration energy  $E_{mi}$  is thus rather low. We adopt  $E_{mi} = 0.2 \text{ eV}$  following the data of Watkins [14].

Vacancy diffusivity. This value was deduced [15] from the observed density and size of voids:  $D_v$  is about  $2 \times 10^{-5} \text{ cm}^2/\text{s}$  at the void formation temperature (around 1100°C); a slightly higher number follows from the cavitation model of void production [16]. Since the vacancy is mobile even at the room temperature [15], the vacancy migration energy  $E_{mv}$  can be then deduced to be about 0.35eV [6]. This is close to the number obtained by Watkins, 0.45 eV. On the other hand, the vacancy diffusivity is the parameter that largely controls the width of a denuded zone in the MDZ process: that zone is basically formed due to vacancy out-diffusion during fast cooling of wafers after RTP anneal. Accordingly a good estimate for  $D_v$  (assuming the above low migration energy) can be deduced from the observed quenched-in vacancy profiles under a variety of cooling rate conditions. The deduced diffusivity at the reference temperature of 1100°C is about  $2 \times 10^{-5} \text{ cm}^2/\text{s}$ , in excellent accord with the microdefect-based number for  $D_v$ .

The difference of equilibrium vacancy and interstitial concentrations. Both the world of grown-in microdefects and the world of MDZ are based on the inequality  $C_{ve} > C_{ie}$ . This inequality (at the melting

point) insures the change-over from interstitial incorporation (at  $v/G$  below the critical ratio) to vacancy incorporation (at higher  $v/G$ ). Incorporation of vacancies in the MDZ process is based on a similar inequality at the process temperature: the quenched-in vacancy concentration in the wafer bulk is equal to  $C_{ve}-C_{ie}$  at the process temperature. This difference – for the two temperatures, 1250 and 1175°C - was measured by Pt technique with some uncertainty. The melting point difference can be deduced from the amount of vacancies stored in voids [10] calculated from the LST data on the void density on size, in dependence of  $v/G$ . This difference lies within rather narrow limits,  $(2-3)\times 10^{14}\text{cm}^{-3}$ . The ranges for  $C_{ve}-C_{ie}$  are thus available for the three temperatures; these are shown in Fig. 4.

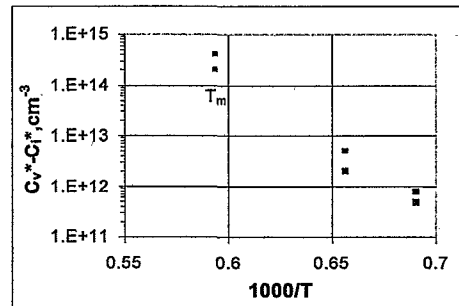


Fig. 4. The range of the solubility difference for vacancy and self-interstitial. The melting point ( $T_m$ ) range is based on the measured amount of vacancies in voids. The range for the two other temperatures (1250 and 1175 °C) comes from MDZ data.

**Formation energies.** The plot of Fig. 4 imposes strong constraints on the values of formation energies,  $E_v$  for vacancy and  $E_i$  for self-interstitial. The melting point value for the equilibrium interstitial concentration,  $C_{im}$ , is fixed by the estimated diffusivity  $D_i$  and the value of the  $D_i C_{ie}$  product ( $2.3 \cdot 10^{11}\text{cm}^2/\text{s}$  at the melting point) known from self-diffusion and zinc diffusion data [17]. Making allowance for some uncertainty in both  $D_i$  and  $D_i C_{ie}$ , a reasonable range for  $C_{im}$  is  $(5-15) \times 10^{14}\text{cm}^{-3}$ . If one specifies the formation energies, then the temperature dependence of  $C_{ve}-C_{ie}$  can be plotted for various  $C_{vm}$  and  $C_{im}$  within the fixed ranges for  $C_{im}$  and  $C_{vm}-C_{im}$ . If none of these curves falls within the ranges of Fig. 4, the chosen energies  $E_v$  and  $E_i$  are rejected. Otherwise they are considered as consistent with the data of Fig. 4. This procedure shows that acceptable energies are very close one to the other. The acceptable range for the average energy  $E=(E_i+E_v)/2$  and for (very small and negative) energy difference  $E_i-E_v$  is shown in Fig. 5. Both formation energies are over 4.3eV. To be consistent with self-diffusion

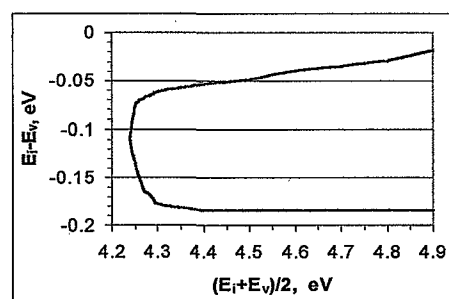


Fig. 5. The values of average formation energy and the energy difference consistent with the data shown in Fig. 4. These values are in the area inside the curve.

data,  $E_i$  must be lower than the activation energy for the  $D_iC_{ic}$  product, 4.9eV [17]. Since the interstitial migration energy is thought to be 0.2eV (or perhaps somewhat larger), the actual estimate for the interstitial formation energy is  $E_i \leq 4.7\text{eV}$ . The final range for  $E_i$  is then from 4.3 to 4.7eV. The vacancy formation energy  $E_v$  is within the same range. An important implication of these estimates is that the activation energy for the vacancy contribution into the self-diffusivity,  $E_v+E_{vm}$ , lies within the range 4.7-5eV. It is thus comparable to that for the interstitial contribution,  $E_i+E_{im}=4.9\text{eV}$ . The interstitial contribution to self-diffusivity prevails at high T [17]. It will then prevail over the whole temperature range, with no cross-over to vacancy-dominated self-diffusivity at lower T. A presumed cross-over point is indeed refuted by recent data [17].

Critical  $v/G$  ratio. This is expressed [4] through the average formation energy  $E$ , the  $D_iC_{im}$  product and the concentration difference  $C_{vm}-C_{im}$  – same parameters that are relevant in the above analysis of the formation energies. On substituting the numerical values of these parameters one gets for  $(v/G)_{cr}$  a rather narrow range consistent with the value found experimentally [7,18] ( about  $2 \times 10^{-5} \text{ cm}^2/\text{s}$  or  $0.12 \text{ mm}^2/\text{minK}$ ). This result shows the self-consistency of the present approach to the estimation of the point defect parameters.

Vacancy binding by oxygen. The reaction of vacancies with oxygen, to form a  $O_2V$  complex (a bound vacancy) must be invoked [7] to account for non-zero residual concentration of vacancies in as-grown crystals. The residual vacancies are manifested in subsequent oxygen precipitation which is strongly banded spatially, due to a banded distribution of residual vacancies [7,8]. The binding (complexing) reaction is strongly dependent on temperature: there is some characteristic binding temperature,  $T_b$ , separating the higher-temperature region (where the free vacancies dominate) from the lower-temperature region (where the vacancies exist predominantly as  $O_2V$ , with only a small fraction of free vacancies). The binding temperature was estimated to be somewhat over  $1000^\circ\text{C}$  ( $1020^\circ\text{C}$  or perhaps slightly higher). The basic implication of the binding reaction is that the effective vacancy mobility is rapidly reduced below  $T_b$ , and the vacancy loss to microdefects is thus strongly suppressed, giving an opportunity for some vacancies to survive – as  $O_2V$  complexes. The suppression of vacancy mobility below  $T_b$  is also of great importance in the MDZ process. If the quenched-in depth profile of vacancies is simulated without the binding reaction, the computed vacancy concentration is far lower than the measured value (for some cooling rates). Even if the computed concentration at the wafer centre is not low (at higher cooling rates) the profile shape is strongly different from that observed. When the vacancy binding is taken into account, the computed profiles are in accord with the experiment. The vacancy binding is also clearly manifested if the MDZ wafers are subjected to the second RTP process at a temperature  $T_2$  lower than that of the first RTP anneal (at  $T_1=1250^\circ\text{C}$ ). At  $T_2=1100^\circ\text{C}$  (well above the binding temperature) the initially installed vacancy profile disappears within 20s. At  $T_2=1000^\circ\text{C}$  a similar relaxation occurs but within a much longer time scale (at 60 s it is not yet fully relaxed) indicating to a considerably reduced effective vacancy diffusivity. At  $T_2=900^\circ\text{C}$  the vacancy profile does not change at all within 15 min indicating to a strongly reduced effective vacancy mobility; therefore the temperature of  $900^\circ\text{C}$  is already well below  $T_b$ .

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## References

- [1] T.Ueki, M.Itsumi and T.Takeda, *Appl.Phys.Letters* 70 (1997) 1248.
- [2] J.G. Park, G.S. Lee, J.M. Park, S.M. Chon and H.K. Chung, *ECS Proc*, vol. 99-1, (1999) 324.
- [3] R. Falster, GR Fisher and G Ferrero *Appl. Phys. Lett.* 59, (1991) 809.
- [4] V.V.Voronkov, *J. Crystal Growth* 59 (1982) 625.
- [5] A.J.R. de Kock, *Philips Res. Repts Suppl.* 1 (1973) 1.
- [6] V.V.Voronkov and R. Falster, *J Crystal Growth*, 194 (1998) 76.
- [7] R Falster, VV Voronkov, JC Holzer, S Markgraf, S McQuaid , L MuleStagno, in *ECS Proc.*, vol 98-1, (1998) p. 468.
- [8] V.V.Voronkov and R. Falster, accepted for publication in *Journal of Crystal Growth*.
- [9] N.I. Puzanov, A.M. Eidenzon, *Semicond. Sci. Techol.* 7 (1992) 406.
- [10] T. Saishoji, K. Nakamura, H. Nakajima, T. Yokoyama, T. Ishikawa, J. Tomioka, in *ECS Proc.*vol. 98-13, 1998, p. 28.
- [11] R.Falster, D Gambaro, M Olmo, M Cornara, H Korb, *Mat. Res. Soc. Syp. Proc.* Vol. 510 (1998) p.27.
- [12] R Falster, M Cornara, D Gambaro, M Olmo, M Pagani, *Solid State Phenom.* 57-58 (1997) 123.
- [13] M. Jacob, P. Pichler, H. Ryssel and R. Falster, *J. Appl. Phys.*, **82**, 182 (1997).
- [14] G.D. Watkins, in *ECS Proc.*vol. 99-1, 1999, p. 38.
- [15] V.V. Voronkov, R. Falster, *J. Crystal Growth*, 198/199 (1999) 399.
- [16] V.V. Voronkov, this volume.
- [17] H. Bracht, in *ECS Proc.*vol. 99-1, 1999, p. 357.
- [18] E. Dornberger, W. von Ammon, *J. Electrochem. Soc.* 143 (1996) 1648.