Clustering of oxygen atoms around carbon in silicon

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Transmission electron microscope studies of carbon-doped Czochralski silicon, when combined with previous infrared data on the same specimens, reveal a double peak in the carbon-sited oxygen-cluster size distribution after 64 h at 750 °C. The first peak, which represents most of the carbon and oxygen in the specimen, is comprised of clusters with an average of two oxygens per carbon atom. These clusters can survive 64 h at 1000 °C although they are not created by such an anneal, suggesting that carbon atoms have difficulty trapping a first oxygen atom at 1000 °C. The second peak in the distribution near $10^4$ oxygen atoms in size is populated with regular (111)-octahedral precipitates having large dilatational strain fields. The two peaks in the size distribution, and their dependences on heat treatment, indicate roles for both seeding (creation of metastable clusters below critical size) and nucleation (achievement of energetic stability) in the formation of carbon-sited precipitates. The observations confirm a trend toward octahedral precipitate morphologies in carbon-doped specimens. However, the trend may result not from site differences but from effects of carbon or point defects on strain energy during precritical cluster growth. Finally, differences between secondary defects associated with precipitation in low- and high-carbon specimens suggest that substitutional carbon atoms at 1000 °C act as sites for silicon self-interstitial condensation near precipitates.

I. INTRODUCTION

Oxygen is the major impurity in commercial Czochralski silicon. With abundances on the order of 20 ppmv, it plays a key role as a site and potential defect during integrated circuit device manufacture. As a result, processes involved in the formation of oxygen precipitates have become the subject of intensive study. In particular, recent experimental work has suggested the existence of precursor phases for both the rodlike defects associated with 450 °C thermal donors, and the polyhedral (often platelet) precipitates which usually dominate final stages of oxygen precipitation in silicon. Recent work has also implicated possible roles for both carbon and silicon point defects in the sintering of these latter precipitates.

There are many carbon-related sites in silicon which are candidates for precipitate growth. The focus in this paper is on the particular site to which most substitutional carbon atoms go after a long heat treatment of high-carbon material at 750 °C. We present details of the structure and abundance of precipitates in low- and high-carbon silicon as correlated with previously published IR absorption data. This data suggests that the site may be a "perturbed" version of the C(3) site reported earlier in radiation-damaged silicon. The observations here provide evidence that carbon-sited clusters can act as metastable "seeds" for the subsequent nucleation of polyhedral oxygen precipitates. A second role for carbon atoms, as sites for the condensation of silicon point defects, is suggested by observed secondary defect structures. Finally, the results of Tsai et al. which indicate a tendency toward octahedral (three-dimensional) instead of platelet (two-dimensional) precipitate morphologies in heavily carbon-doped silicon are confirmed.

Because of varied uses in the literature of words describing early precipitation stages, the usages adopted here are described below. Cluster is a term applied to any impurity aggregate. At a given temperature, a precipitate is any cluster which is larger than the critical size for energetic stability (the size above which addition of impurity atoms to the cluster decreases total system energy). Nucleation is the addition of an oxygen atom to clusters one atom shy of the critical size. Seeds at a given temperature are clusters below the critical size embryos which are kinetically stable specifically in the sense that the odds for their capture of an impurity atom are at least as high as the odds for their loss of one.

II. EXPERIMENT

The silicon used in this study was n-type (3 Ω cm phosphorous doped) silicon obtained from 100-mm-diam (100) ingots grown by the Czochralski method with and without added carbon. Growth conditions were the same for both ingots. Wafers and slugs were cut from the middle portion of the crystals, and subjected to the following heat treatments in dry oxygen: no heat treatment, 64 h at 750 °C, 64 h at 1000 °C, and 64 h at 750 °C followed by 64 h at 1000 °C.

Infrared (IR) absorption measurements were made from a subset of these specimens, and have been reported by Shimura et al. Substitutional carbon and interstitial oxygen concentrations were determined using conversion constants from the ASTM F121-80 ([O$_i$] = 2.45a$_{cm}$) and F123-81 procedures, and are summarized in Table I. Shimura et al. also proposed that broad bands at 850 and 1100 cm$^{-1}$ observed in some of these specimens are associated with bonds in a single-carbon atom/SiO$_4$ (C-SiO$_4$) agglomerate. If the carbon atoms lost from substitutional (C) sites during the 64 h at 750 °C heat treatment are transferred to such C-SiO$_4$ sites, then published spectral peak areas indicate that the mass absorption coefficient for C-SiO$_4$ in the 850-cm$^{-1}$ band is approximately 0.7 that of C in the 607-cm$^{-1}$ substitutional carbon band. This value is also consistent with conservation of carbon atoms (within detectability limits) between C and C-SiO$_4$ sites during the other heat treatments. Hence, we have estimated C-SiO$_4$ abundances on
TABLE I. Estimated number densities and sizes.

<table>
<thead>
<tr>
<th>Thermal treatment (h•°C)</th>
<th>C_&lt;sub&gt;4&lt;/sub&gt; conc. (cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>C-SiO/sub&gt;4 conc. (cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Precipitate abundance (cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Precipitate image size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-carbon silicon:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-grown</td>
<td>9 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>&lt;5 × 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>&lt;1 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>--</td>
</tr>
<tr>
<td>64:750</td>
<td>9 × 10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>&lt;5 × 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>&lt;1 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>1 × 10&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>64:750 + 64:1000</td>
<td>2 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>&lt;3 × 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>&lt;1 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>150-400</td>
</tr>
<tr>
<td>64:1000</td>
<td>4 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>&lt;5 × 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>&lt;1 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>100-500</td>
</tr>
<tr>
<td>High-carbon silicon:</td>
<td></td>
<td></td>
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<tr>
<td>as-grown</td>
<td>9 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>3 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>&lt;1 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
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<tr>
<td>64:750</td>
<td>2 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>&lt;3 × 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>3 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>1 × 10&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>64:750 + 64:1000</td>
<td>6 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>9 × 10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>2 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>4 × 10&lt;sup&gt;13&lt;/sup&gt;</td>
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<td></td>
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<td>7/300</td>
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</tbody>
</table>

<sup>a</sup> Data from Ref. 10.
<sup>b</sup> Calculations using data from Ref. 10 (see text).
<sup>c</sup> Number densities estimated on the basis of typically 30-40 cm<sup>3</sup> of silicon examined in the TEM.
<sup>d</sup> Two distinct precipitate populations are listed for this material.

this basis, and these are listed in Table I as well.

Specimens for the transmission electron microscope (TEM) study were cut, usually in (100) section, into 3-mm disks and thinned to perforation either chemically via jet thinning or mechanically by ion milling. Precipitates were detected in conventional TEM images, frequently using a small, objective aperture under [022] dark-field conditions with the specimen tilted just off the Bragg condition. Defect searches were generally conducted at both 30 and 100 K magnifications. The method is useful for detecting and counting volume defects between 5 and 500 nm in size, when they are present in sufficient abundance. Precipitate number densities and size ranges reported in Table I are average values for four or more TEM specimens, determined by counting typically several hundred precipitates in each and inferring specimen thickness (hence volume surveyed) using wedge or stacking fault interference fringes. Values of number density measured on different specimens from the same group always agreed within a factor of 2 or 3.

III. RESULTS

A. TEM observations

TEM observations of precipitate structure will be summarized briefly. As indicated in the rows of Table I labeled “as-grown,” no defects (precipitates or otherwise) were observed in either the high- or low-carbon specimens before heat treatment.

Figure 1 illustrates typical defect types seen in heat treated low-carbon material. After the 64 h at 750 °C heat treatment, a moderate density (1 × 10<sup>17</sup> cm<sup>-3</sup>) of [100] platelet precipitates with long dimensions of typically 60 nm, and significant dilatational strain fields, were observed [Fig. 1(a)]. A subsequent 64 h at 1000 °C treatment of this material results in creation of a higher density (5 × 10<sup>11</sup> cm<sup>-3</sup>) of square [100] platelet oxygen precipitates [Fig. 1(b)]. These larger precipitates (major dimensions between 150 and 400 nm) exhibited the usual [010] and [001] diagonal seams in [100] projection (suggesting the edge structure of a flattened octahedron), and were accompanied by a range of secondary defects such as dislocation tangles, punched out dislocation loops, and hexagonal loops. Similar precipitates and defects were observed in material given only a 64 h at 1000 °C treatment [Fig. 1(c)], although the density of precipitates was much lower (1 × 10<sup>10</sup> cm<sup>-3</sup>). Loss of interstitial oxygen in these low-carbon materials appeared to be correlated with an SiO<sub>2</sub> line near 1225 cm<sup>-1</sup>,<sup>10</sup> and no evidence of carbon-related IR features were seen (Table I).

Figure 2 illustrates the defect types seen in heat treated high-carbon material. The high-carbon silicon after 64 h at 750 °C [Fig. 2(a)] contained a much higher density of micro-

FIG. 1. Typical defects in low C material after (a) 64 h at 750 °C, a [100] platelet; precipitate; (b) 64 h at 750 °C followed by 64 h at 1000 °C: a square [100] platelet with associated punched-out dislocations; (c) 64 h at 1000 °C: a large square [100] platelet. Punched-out dislocation loops and precipitate-dislocation complexes were common in both specimen b and c.

FIG. 2. Typical defects in high C material after (a) 64 h at 750 °C: small [111] octahedra and a dislocation dipole; (b) 64 h at 750 °C followed by 64 h at 1000 °C: small equant precipitates and a hexagonal dislocation loop; (c) 64 h at 1000 °C: a square [100] platelet precipitate and its characteristic colony of associated loops.

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precipitates \((1 \times 10^{13} \text{ cm}^{-3})\) than did its low-carbon counterpart. Although maximum dark-field image dimensions (including strainfield) under [220] reflection for these precipitates were typically 25 nm, precipitate widths themselves were more like 1/3 of that distance. Figure 3 shows a single microprecipitate imaged using a variety of dark-field reflections. The fourfold mirror symmetry illustrated here was honored for all precipitates. This indicates equant, as opposed to planar or rodlike, precipitate morphologies. The (400) dark-field image in [001] projection [Fig. 3(b)], however, shows that the strain field does not have full circular symmetry. There is instead significant strain near [110] and [110] edges of the precipitate body, which are weakly visible in some micrographs as a square with [110] edges. But there is less strain along precipitate diagonals (silicon [100] and [010] axes). These observations indicate that the precipitates are regular octahedra with silicon [111] faces.

Contrast analyses following Ashby and Brown\(^{15}\) are consistent with interstitial-type strains orthogonal to the octahedral faces, and with a fractional misfit of 2% in linear dimension between the strained precipitate and its cavity in the silicon lattice. The relative absence of shear strain components (which might, for example, result in a more spherically symmetric strain field) suggests that the precipitate/silicon interface is not coherent. These results support the Tsai et al.\(^{12}\) report of octahedra, identified to consist of poorly crystallized \(\text{SiO}_2\) via electron-energy loss and diffraction experiments, in carbon-doped silicon after 750°C anneal.

Because of the regular octahedral shape, the volume of a given precipitate in this material can be expressed simply as \(0.47a^3\), where \(a\) is the octahedron side. To determine the size distribution as well as the total volume of precipitated phases, we measured precipitate abundances \(N_p\) in logarithmic size intervals which span the range of observed sizes. For intervals centered at \(a = 6.0, 8.0, 9.2,\) and 10.7 nm, we found \(N_p = <3 \times 10^{11}, 2 \times 10^{11}, 4 \times 10^{11}, 4 \times 10^{11}\), and \(<3 \times 10^{11}\) per cm\(^3\), respectively. The shape of the distribution, centered about the volume-averaged size of \(a = 8.4\) nm, makes it unlikely that appreciable volume lies in precipitates outside of the observed range. Since the density of oxygen atoms in silica phases is on the order of \(5 \times 10^{27} \text{ O/cm}^3\),\(^{16}\) this means that about \(1 \times 10^{17}\) O atoms/cm\(^3\) are tied up in precipitates.

A 64 h at 1000°C anneal of high-carbon wafers already subjected to the 64 h at 750°C treatment resulted in (i) a moderate increase in the number density and size of precipitates, (ii) some relaxation of the strong precipitate strain fields, and (iii) creation of some extended secondary defects. These latter consisted of micron-sized stacking faults, dislocation dipoles, and dislocation loops [Fig. 2(b)], generally not associated with a specific precipitate. The octahedral habit of the precipitates, although possibly intact, appeared to be somewhat less regular.

In material subjected to the 64 h at 1000°C treatment without a prior 64 h at 750°C anneal, two populations of defects (distinct in both size and number density) were observed. The largest defects included submicron platelet precipitates \((1 \times 10^{13} \text{ cm}^{-3})\) surrounded by loop colonies [Fig. 2(c)], crossed dislocations with some evidence of decoration, and punched-out dislocation loops. Superimposed on this was a background \((1 \times 10^{13} \text{ cm}^{-3})\) of extremely tiny microprecipitates (image width on the order of 7 nm) which were too small for detailed characterization, but also too small to contain an appreciable fraction of the total oxygen (i.e., less than 10% by the calculation above).

**B. Distribution of cluster sizes after 64 h at 750°C**

The IR and TEM observations, when considered together, allow us to examine in some detail the distribution of carbon-sited clusters in high-carbon material after 64 h at 750°C. Results are summarized in Fig. 4. The abundance peak near \(10^9\) oxygen atoms is obtained by plotting the TEM precipitate size data reported above. Upper and lower limits are based on counting uncertainties in determining the size distribution shape.

The abundance peak (Fig. 4) centered on clusters with only two oxygen atoms is determined as follows: Of the \(9 \times 10^{17}\) interstitial oxygen atoms per cm\(^3\) found in the specimen before heat treatment, \(2 \times 10^{17}\) remain in interstitial sites and \(1 \times 10^{17}\) are found in the larger precipitate.

![FIG. 3. Dark-field micrographs, using 100-kV electron and an acceptance halffield near a 4 m rad. a) In [220] carbon-doped Czochralski silicon after 64 h at 750°C heat treatment. b) [220] operating reflection. c) [220] operating reflection.](image)

![FIG. 4. Abundances of carbon-seeded oxygen clusters per unit oxygen-atom interval vs cluster size (number of oxygen atoms) in carbon-doped silica after 64 h at 750°C. Upper and lower limits for clusters with fewer than 10 oxygen atoms assume a single-carbon atom per cluster, and show cluster size per carbon atom based on IR and TEM measurements. The dotted curve shows the maximum-width power-law size distribution for that case. Upper and lower limits near 10 oxygen atoms per cluster are based on TEM precipitate size measurements, and the solid curve outlines the shape of the inferred peak.](image)
clusters. This leaves only $6 \times 10^{17}$ oxygen atoms to be distributed at the $3 \times 10^{17}$ carbon sites in the specimen, or an average of 2 oxygens per carbon. The primary uncertainties in this average probably lie not with the small terms subtracted from $9 \times 10^{17}$, but with the ASTM IR calibrations themselves. Thus, TEM and IR measurements together argue that most of the oxygen resides in clusters which are much smaller than the precipitates seen in the TEM.

We can further constrain the shape of the peak at small cluster sizes if we assume that the clusters form around individual carbon atoms, as suggested by the correlated C-SiO$_2$ bands in the IR. Then the (relative) absence of clusters in the specimen with a single 64 h at 1000 °C heat treatment implies that capture and retention of a single-oxygen atom (the first step in forming a C-SiO$_2$ cluster) is kinetically unlikely at that temperature. This is especially so since enhanced mobilities at 1000 °C make the number of opportunities for such capture in 64 h much larger than the number of opportunities at 750 °C. On the other hand, 2/3 of the C-SiO$_2$ clusters formed at 750 °C survive a subsequent treatment of 1000 °C (Table I), indicating that at least $2 \times 10^{17}$ cm$^{-3}$ of the clusters have thermal stability not possessed by the single-oxygen cluster.

The width of C-SiO$_2$ absorbance bands in these specimens suggests that the clusters may derive this high-temperature stability from the presence of more than one oxygen atom. If this is the case, constraints on the total amount of carbon ($\sum n_i$) and oxygen ($\sum \omega_i$) in clusters with multiple oxygens take the form

\[
2 \times 10^{17} \leq \sum n_i < 3 \times 10^{17},
\]

\[
5 \times 10^{17} \leq \sum \omega_i < 6 \times 10^{17},
\]

where $n_i$ is the number of $i$-oxygen clusters per cm$^3$. These conservation rules provide upper limits on the abundance of clusters with more than one atom, and a lower bound on the abundance of two-oxygen clusters as well (Fig. 4).

Because of the uncertainties in IR calibration constants, and the possible existence of carbon sites not visible in the IR, it is possible that the average number of oxygens per carbon atom at these small cluster sizes is actually higher than two. In this case, the observations still limit the width of the lower distribution peak. This is illustrated by the curves in Fig. 4. The continuous curve at large cluster sizes (solid line) was obtained by simply drawing a line between observed upper and lower limits. For small cluster sizes, the curve (dotted line) plots the maximum-width power-law distribution for clusters with more than one oxygen atom. The calculation takes advantage of the fact that the conservation rules [Eq. (1)] for a power-law distribution can be simply expressed in terms of the Riemann zeta function. The minimum-width distribution consistent with the observations is a spike centered at the average number (2) of oxygens per cluster.

Thus, measurements of high-carbon specimens confirm the existence of two peaks in the size distribution of oxygen clusters. Most of the oxygen and carbon after 64 h at 750 °C is found in clusters with only a few oxygen atoms per carbon. These clusters are kinetically stable to 1000 °C, although their formation at that temperature (but not at 750 °C) is inhibited. The first peak occurs near $10^6$ oxygen atoms in the cluster abundance distribution. It is likely that the first peak represents a population of clusters smaller than the critical size, and the second represents energetically stable precipitates. The two peaks are otherwise difficult to explain, especially since they may straddle critical size estimates in the literature (e.g., near 20 oxygen/cluster) for incoherent, equidimensional SiO$_2$ clusters at 750 °C in silicon with $2 \times 10^{17}$ O/cm$^3$. It the first abundance peak represents subcritical clusters, then the existence and behavior of the second abundance peak can be explained as the result of a thermodynamic nucleation and growth process "fed" by the first.

IV. DISCUSSION

A. Role of carbon sites in oxygen precipitation

The foregoing observations suggest a role for individual carbon atoms as sites for polyhedral oxygen precipitates. They therefore reinforce previous reports of high precipitate number densities associated with carbon doping. Their correlation with data on vibrational structures in the IR suggest that the particular carbon site involved may be related to the C(3) site seen in irradiated material. The site appears to actively trap oxygens at 750 °C, but not at 1000 °C. To the extent that loss of substitutional carbon after a heat treatment reflects this trapping process, then this site is probably the same one whose effect on oxygen precipitation has been reported by Leroueil and others in high-carbon silicon. Interpreted in this way, these earlier studies imply that at 750 °C carbon is incorporated into clusters at a rate near $3 \times 10^{-5}$ s$^{-1}$ per carbon atom in the specimen, and that there is an upper temperature limit on carbon's seeding activity near 800 °C.

Surprisingly, the observations here are also consistent with the report by Livingston et al. that precipitate number density is unrelated to the number of carbon atoms at non-substitutional sites in as-grown material with $5 \times 10^{16}$ C/cm$^3$. This is because prior exposure below 700 °C in the crystal puller is likely to have overwhelmed the carbon effect. Earlier precipitation studies have provided evidence of a site for polyhedral precipitates which is seeded only at temperatures below 700 °C. That site acts as the primary site for polyhedral precipitates nucleated below 700 °C in low-carbon silicon with an "induction" history (e.g., of 1 h) in the 500-650 °C range. Such material exhibits nucleation rates near $10^{12}$ precipitates cm$^{-3}$h$^{-1}$ at 750 °C in silicon with $5 \times 10^{15}$ C/cm$^3$. Since $3 \times 10^{17}$ C/cm$^3$ in high-carbon specimens of this study support nucleation of only $2 \times 10^{11}$ precipitates cm$^{-3}$h$^{-1}$ at 750 °C, it is likely that the primary precipitation sites in the two materials are different. Given that tens of hours in the 700-800 °C range cannot makeup for the lack of a few hours at lower temperature in low-carbon silicon, the rapid 750 °C seeding activity reported...
here further suggests that the site observed in low-carbon material is kinetically distinct from the one observed here. Thus an induction preanneal below 700 °C to create seeds for nucleation in the 700–800 °C range should be unnecessary in the presence of sufficient carbon, which appears capable of siting metastable seeds in its own at temperatures up to 800 °C. By comparison, the relative effectiveness of a 600 °C site for enabling precipitate formation in low-carbon silicon suggests that this low-temperature site may involve only silicon and oxygen.

B. Seeding as prerequisite to nucleation

The strong effects of prior thermal history on nucleation rate in low-carbon material have prompted suggestions that a metastable reservoir of subcritical oxygen clusters feeds the nucleation process in that material. Results above (Table I) indicate that carbon-sited clusters created at 750 °C with as few as two oxygen atoms are kinetically stable and able to grow into new precipitates (i.e., nucleate) at 1000 °C. This constitutes direct evidence that a metastable reservoir of subcritical clusters exists, and is correlated with the formation of carbon-sited precipitates. For sites in both low- and high-carbon material, the reservoir is characterized experimentally by a “seeding cutoff” temperature $T_c$, above which seeds are not formed, and by a “memory loss” temperature $T_m$ (greater than $T_c$) above which previously created seeds are destroyed. A physical explanation for these effects is suggested by this work, as follows.

The existence of subcritical seeds, whose abundance depends on prior thermal history, conflicts directly with the steady-state assumption commonly invoked to describe the distribution of subcritical clusters in classical nucleation theory. $^{23}$ This steady-state assumption considers only absolute formation energies in predicting the subcritical distribution. If impurity migration barrier energies (often several eV) for small clusters are considered as well as absolute formation energies, then failure of the steady-state assumption is understandable. In particular, low-temperature IR data on the kinetics of thermal donor cluster growth near 450 °C suggests the existence of a local maximum in oxygen desorption barrier energy as a function of cluster size for rodlike precipitates with only a few oxygen atoms. $^{23}$ Such a local maximum may also be expected during subcritical growth at polyhedral precipitate sites, especially if a crystalline phase with significant lattice mismatch is present during the early phases of cluster growth. Interface discontinuities to accommodate the mismatch could then cause the required decrease in desorption energy with increasing cluster size for sizes past the peak. Such mismatch is suggested by TEM observations of a possible precursor with octahedral habit and 0.203-nm reflections (compare silicon’s 0.192 nm) along silicon [220]. $^{24}$

Since a captured oxygen is unlikely to remain long enough for a second oxygen to come along at temperatures above the seeding cutoff temperature ($T_c$), $T_c$ defines an effective desorption barrier for the first oxygen atom captured by a site. At temperatures low enough to capture a first oxygen, addition of more oxygens is kinetically feasible. As long as interstitial oxygen is available, this addition of atoms will continue for all cluster sizes within the desorption barrier peak. Clusters with sizes beyond the peak would again find it easy to lose an oxygen atom. Hence the abundance of clusters between the peak in kinetic stability and critical size may still be modeled with a steady-state expression. $^{22}$ The only difference between a traditional steady-state model, and this one, is that here a population of kinetically stable clusters (reflecting prior thermal history) provides seeds for the nucleation process $^4$ at temperatures well above the thermal cutoff for oxygen capture by an unoccupied site.

The above model suggests that IR measurements of subcritical cluster formation rate at temperatures below 750 °C may allow virtually direct measurements of the product of oxygen flux and the cross section for initial oxygen capture, and hence, relative measurements of oxygen mobility. Thus, properties of the carbon site confirm the importance of a subcritical reservoir in the modeling of oxygen precipitation, and may provide a useful probe of precipitation physics as well.

C. Effect of carbon on precipitate shape

Differences between precipitate number densities in high- and low-carbon material appear to reflect differences between oxygen clustering sites, but observed differences in precipitate morphology do not. Octahedral morphologies may in fact be a possible endpoint in the evolution of any oxygen cluster. Although early-stage oxygen precipitates in the shape of regular octahedra are rare in the literature, images of late-stage oxygen precipitates (e.g., Fig. 1[a]) commonly suggest the edge structure of a flattened [111] octahedron. Moreover, an octahedral habit seems to be preferred by precipitates generated at temperatures above 100 °C even in material which grows platelets at lower temperatures. $^{11}$ Therefore, there are reasons to expect that the initial packing of oxygen atoms into clusters may occur similarly for octahedral and platelet precipitates, regardless of site, and that shape differences reflect external and not internal constraints on cluster growth.

The minimization of surface plus strain energies provides a well-known mechanism for deciding the balance between two-dimensional (low-strain) and three-dimensional (high-strain) modes of precipitate growth. $^{25}$ For oxygen precipitates in silicon, the amount of strain energy for a given precipitate depends on the ability of the silicon lattice to accommodate displaced silicon interstitials. Yasutake et al. $^{26}$ have shown that the tendency of interstitials to form perfect loops may lessen effective strain energies, and thereby explain the preference toward octahedral growth at high temperatures. The tendency toward octahedral growth in high-carbon silicon at 750 °C may also be explained by this minimization process, if carbon can be shown to lessen strain energy or its effects.

IR studies $^{77}$ and the observations of secondary defect formation reported here and by Yasutake et al. $^{26}$ suggest that substitutional carbon atoms can trap silicon self-interstitials. Although this might reduce strain energies, the existence of platelet and octahedral precipitates (without inter-
mediate shapes) in the same specimen is difficult to explain with this mechanism unless silicon lattice anisotropy permits only two growth modes. A different possibility is that oxygen clusters in high-carbon silicon avoid strain effects which flatten clusters in low-carbon silicon while the clusters are subcritical, and presumably most vulnerable. In particular, a dense equant or octahedrally shaped crystalline precursor would have better chance of surviving to critical size if the phase transition to an incoherent final precipitate phase occurs at larger cluster sizes in high-carbon silicon. This is possible if surface forces dominate volume forces to larger cluster sizes, although it requires that carbon-doped silicon exhibit higher (not lower) strain energies for a given precipitate (e.g., as a result of high interstitial content and/or oxygen precipitation). A set of stable precipitates with geometries similar to that of their precursor phase might then follow from heavy carbon doping. If the phase change occurs below critical size for only some of the precipitates (e.g., with intermediate levels of carbon doping), then intermixed platelets and octahedra like those reported by Tsai et al. would be expected.

D. Effect of carbon on secondary defects

There are striking differences in secondary defects generated after the 64 h at 1000 °C treatment between high- and low-carbon material [Figs. 1(c) and 2(c)]. These differences appear unrelated to the ability of carbon atoms to site oxygen clusters since precipitate sizes are essentially the same, and most of the carbon remains in substitutional sites before and after the heat treatment. Although self-interstitial condensation appears in both cases to occur in the neighborhood of large precipitates, the preferred mode in high-carbon material appears to be the formation of many small loops. One explanation is that substitutional carbon atoms at 1000 °C provide sites for condensation of interstitials and interstitial clusters during oxygen precipitate growth. These sites tend to cluster around precipitates either because the solubility of interstitials is lower in the compressed silicon surrounding precipitates, or because precipitate strain fields attract substitutional carbon impurities because of their small covalent radius. The former possibility is consistent with the observations of Yasutake et al. concerning a role for carbon in suppressing formation of extended point defect clusters, and the latter is consistent with recent evidence for the coaggregation of carbon and oxygen in silicon.

V. SUMMARY

We report here TEM observations of precipitates and associated defects in heat-treated wafers of high- and low-carbon silicon. The observations confirm previous reports that heavy carbon doping increases precipitate number densities, and creates precipitates with highly regular octahedral shapes at 750 °C. The main conclusions are that: (i) carbon atoms can provide sites at 750 °C for the formation of polycrystalline oxygen precipitates; (ii) most of the oxygen and carbon in high-carbon specimens after a 64 h at 750 °C heat treatment is found in subcritical clusters with as few as two oxygen atoms per carbon; (iii) such clusters are kinetically stable and able to grow into precipitates at temperatures as high as 1000 °C, although these clusters are not efficiently created at that temperature; (iv) the foregoing conclusions, along with correlation between subcritical cluster abundances and the number of precipitates created at other heat treatment steps, confirm that a seeding process is prerequisite to the nucleation of precipitates at carbon atom sites; (v) the primary sites for polyhedral precipitate formation in low- and high-carbon silicon exhibit very different seeding kinetics in the 700–800 °C range, suggesting that different sites dominate precipitation in these limiting cases, and that literature studies which disagree on the role of carbon may be reconciled by this fact; (vi) the tendency toward octahedral morphologies in high-carbon silicon is likely related to effects of carbon or point defects on matrix strain energies, possibly during precritical cluster growth; and (vii) the secondary defects generated by precipitation in high-carbon silicon are strikingly different from those in low-carbon silicon, and suggest that substitutional carbon atoms at 1000 °C may act as sites for point defect clusters near large precipitates.

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17. E.g., S. I. Tsuchiya, J. M. Gurney, and T. Arai, M. Naege, N. Inoue,


17e.g. J. Burke, *The Kinetics of Phase Transformations in Metals* [Pergamon, London, 1965], Chap. 5.


