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Finding unstrained 10-nm lattice defects in silicon, given 10^{11} per cubic centimeter

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Our ability to image individual atoms and atom-columns only brings the practical problem of finding a *statistically-useful* number of nanoscale structures into sharper focus. In crystalline materials like metals and semiconductors, a key tool for locating lattice defects has been diffraction contrast from defect strain fields. For example, the lattice can be oriented just off the diffracting condition in darkfield, at which point defect strain fields (even at low magnification) light up like stars in the night sky.

An important challenge in the gigascale silicon-device industry is the management of oxygen-related defects as allies (e.g. for "impurity gettering") in the device-making process. However, nucleation and growth of oxygen clusters from ~10-20 ppma of dissolved interstitial oxygen O_i is a complex process, predicated on thermal history in the 600^{o}C range, and involving electrically active thermal donors, lattice vacancies early on [1], a variety of precipitate "shape changes" [2,3] e.g. from unstrained mono-layer plates to (111) octahedra to platelets on (100), and expansion-related silicon self-interstitial dislocation loops and stacking faults as more and more oxygen comes out of solution. The population of oxygen clusters with fewer than 10^5 oxygen atoms, often associated with thermal history during crystal growth, is of special importance. However it has been resistant to quantitative characterization because of unstrained-configurations and surface O-intrusions [4] in that size range.

Because silicon's diamond lattice naturally cleaves on (111), the preference for strained platelet formation on (100) is a mystery. This *unexpected* break in symmetry might be explained by anecdotal evidence [5] that unstrained monolayer oxygen-molecule or "ninja-plates" naturally form on (100) because of lattice potential considerations, but are very hard to find given their lack of strain. At some point these "decloak" [6] to form strained octahedra (cf. Fig. 4). As size increases and surface energies become less important, these octahedral clusters return to the original (100) plate for 2D growth above say 10-nm in size, as depicted in Fig. 1. What TEM images of the strained octahedral won't reveal are the broken bonds left by the O_i as the puddle drains to form the octahedral defect. Figure 2 shows the three stage model for the ninja defect uncloaking in plot form.

The problem is that systematic study of oxygen clusters below 10 nm in one or more dimensions has been hampered by number densities e.g. in the 10^9/cc range, and by 10 nm (weakly strained) oxide intrusions which form (even during TEM observation!) on freshly ion-milled silicon surfaces exposed (even briefly) to air on their way into the TEM. As discussed previously [7], high-oxygen and high-vacancy silicon results in more like 10^{11} instead of 10^9 oxygen precipitates per cubic centimeter, with their panoply of extended defects (cf. Fig. 3) for impurity gettering. This means that the "sub-10 nm" cluster population is at least that abundant.

We are thus exploring ways in high-oxygen and high-vacancy silicon to (i) suppress the formation of surface intrusions [4] e.g. by tripod-polishing instead of ion-milling, and to (ii) find contrast mechanisms that might let us find and gain reasonable statistics on unstrained oxygen clusters in as-grown material. As you can see from Fig. 2, these may be over 100[nm] in length even in they are only a monolayer in

thickness. Ideas for highlighting such defects in the TEM are invited in this context. This might help the photovoltaic and device industries better characterize their "frozen-in" oxygen-cluster distributions prior to device manufacture, and help us clarify the mysteries surrounding a case where the decisions of individual oxygen molecules play an important role in the shape of much larger precipitates [8].

References:

[1] V.V. Voronkov, ECS Transactions **vol 18** (2009) 945-957.
[2] G. Fraundorf et al , JECS Solid State Science and Technology **vol 132** no. 7 (1985) 1701-1704.
[3] R. Falster et al., Solid State Phenomena **vol 108-109** (2005) 97-102.
[4] Shu-han Lin et al., *Electrochemical and Solid-State Letters*, **5**:9, G83-G85.
[5] W.Bergholz et al., Philos. Mag. B **vol 59**, N5, (1989) 499-522.
[6] J.D. Murphy et al., ECS Transactions, **vol 33** N11 (2010) 121-132.
[7] Roberts et al., *Microscopy and Microanalysis* **22**:S3, (2016) 942-943.
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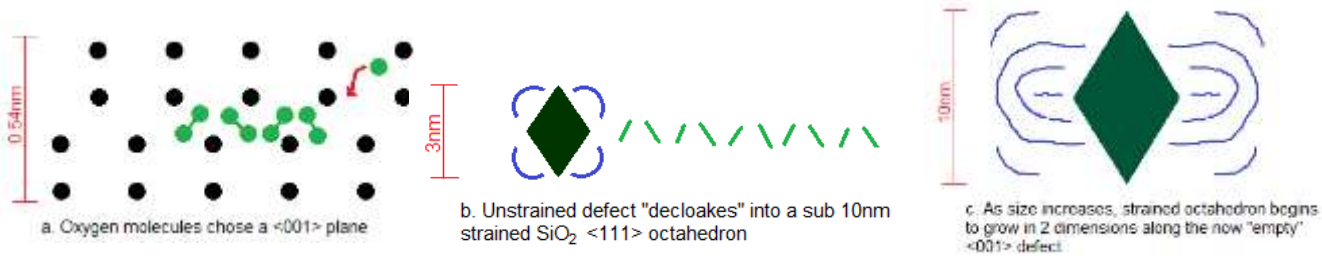

Figure 1. The stages of platelet formation in high vacancy Czochralski Silicon. The graphic goes from oxygen interstitials in puddles to small octahedrals. The transition back to a two dimensional growth is abetted by a buildup of pressure in the lattice, shown by the prismatic loop dislocation mechanism. The residual broken bonds from the oxygen monolayer becomes the Achilles' heel of the lattice, giving precedence for the transition back to two dimensions along the weakened plane.

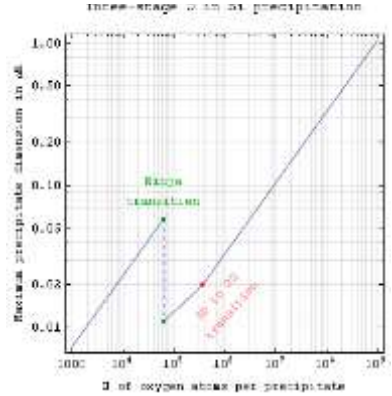

Figure 2. Transition point representation of the three stage model of oxygen precipitation. The number of oxygen atoms per precipitate at transitions (green and red dots on the plot) have been inferred from previous observations in the literature.

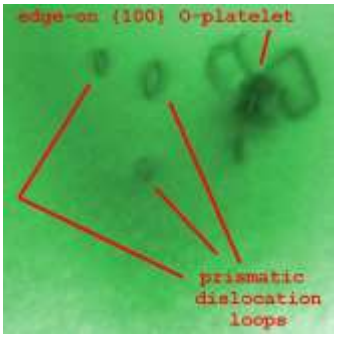

Figure 3. Close up of TEM image showing an oxygen precipitate platelet lying edge-on on a Si-001 plane. Around it are interstitial dislocation loops created by the volume-excess associated with interstitial oxygen precipitation. Field width is about 1.16μm [6]

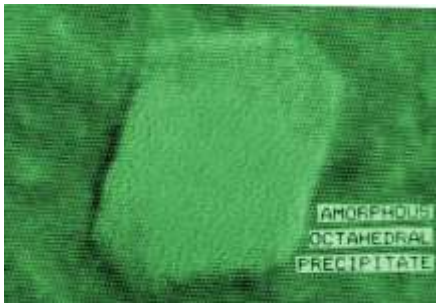

Figure 4. Closeup of a TEM image of a SiOx octahedron with {111} lattice fringes along the facets. Field width is about 35.8nm.

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