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STUDIES OF OXYGEN-RELATED AND CARBON-RELATED DEFECTS IN HIGH-EFFICIENCY SOLAR CELLS

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We are studying oxygen- and carbon-related defects in silicon, particularly as related to high-efficiency silicon solar cells. We are carrying out a survey of these process-induced defects, of life-time measurement techniques, and of defect aggregates in general. We are carrying out coordinated experimental and theoretical studies of process-induced defects, and have initiated a new series of annealing experiments, including flash-lamp heating of "as-received," pre-heat-treated and homogenized samples, using DLTS, IR, TEM, positron annihilation, and, as needed, EPR and x-ray scattering studies.

Isolated oxygen is an interstitial (O_i) in a puckered bond-centered position as shown in Fig. 1. This defect is NOT electrical active. It has several infra-red bands, the one

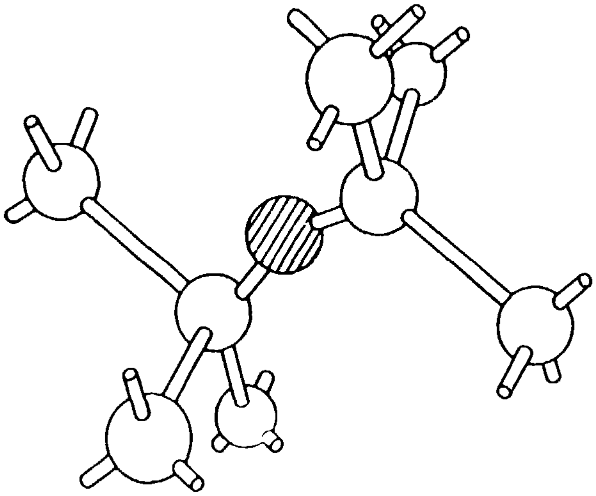

Figure 1. Configuration of interstitial oxygen in the silicon lattice.

that will concern us being at ca. 1100 cm^{-1}. But oxygen in Czochralski-grown silicon is supersaturated with oxygen at all practical temperatures for processing and use, and oxygen does a number of strange and wonderous things. These are outlined in Fig. 2. There appear now to be (at least) two lines of precipitation for oxygen. One line progresses through the original thermal donors (found first by Fuller et al. in 1955, before it was known that oxygen is in the lattice), to the <110> rods (shown by Bourret to be coesite, a high pressure phase of silica - SiO_2) with their associated extrinsic/interstitial dislocation dipoles. It is presumed that interstitials are emitted in this precipitation process; we have shown that the emission of Si=O is energetically favorable vs a silicon interstitial, and that this option may be operative at high temperatures and in oxidation processes. Note that this line of precipitation does not persist to high temperatures, i.e., the rods (and dislocations dipoles) dissolve in favor of the second line of precipitation.

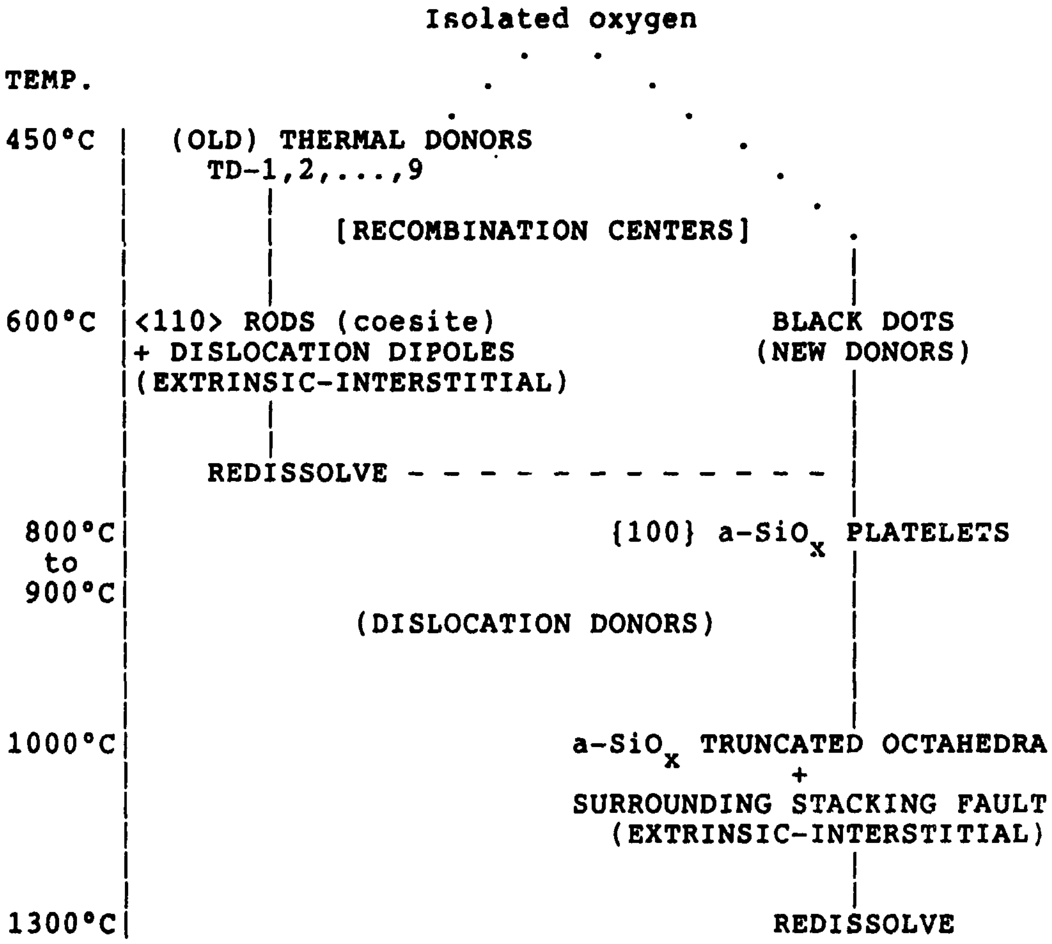

Figure 2. Summary of oxygen processes in silicon.

The second line of precipitation is first evident with "black dots" in transmission electron microscopy experiments. These grow into amorphous SiO_x defects, {100} platelets at higher temperatures and into truncated octahedra at even higher temperatures. Then at temperatures approaching the melting point of silicon (e.g., 1300°C) the precipitated oxygen dissolves into the isolated interstitials that we started with. Depending on the thermal cycling that the samples experience, the precipitates can give rise to prismatic dislocation loops, and other dislocation networks.

At 450°C recombinations centers appear along with the thermal donors. It is not clear which of the lines of precipitation they belongs to, or if either, but these centers are oxygen dependent.

Thus oxygen introduces shallow donors and centers deep in the forbidden gap. But the defects produced by oxygen precipitation also provide gettering centers for recombination centers, e.g., the iron-group transitions elements, which tend to be fast diffusers. It is not exactly clear how this gettering works, but it is known that iron and copper precipitate at different sites.

And the means by which oxygen precipitates is still not certain. Kaiser, Frisch and Reiss argued that the main features of the formation of the (old) thermal donors could be explained as the sequential agglomeration of oxygen atoms. The difficulty was that the mobility of the oxygen is not sufficient to account for the rate of thermal donor formation. In verifying our earlier measurements of the diffusion coefficient of oxygen with an activation energy of 2.54 eV, Stavola et al. found that in "as-received" samples the oxygen motion occurs with an activation energy of 1.9 eV. This anomalous diffusion has been presumed to be defect-assisted.

In irradiated silicon we had earlier established the (vacancy+oxygen) center, (V·O), as shown in Fig. 3. [We also found $(V_2 \cdot O)$, $(V_2 \cdot O_2)$, $(V_3 \cdot O)$, $(V_3 \cdot O_2)$, and $(V_3 \cdot O_3)$ centers but they will not concern us here.] When the (V·O) center disappears on annealing, the $(V \cdot O_2)$ center is created (see

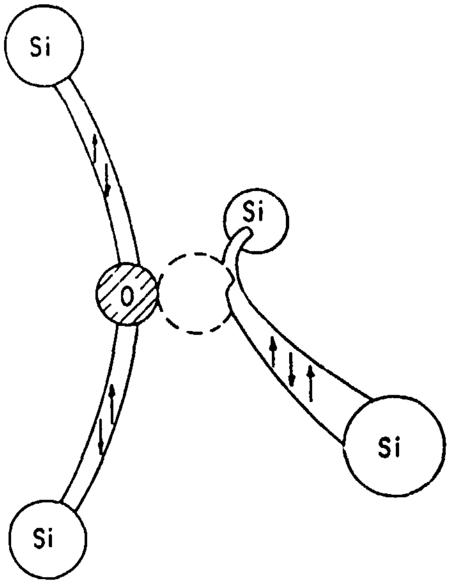

Fig. 3. The (vacancy + oxygen) center in silicon.

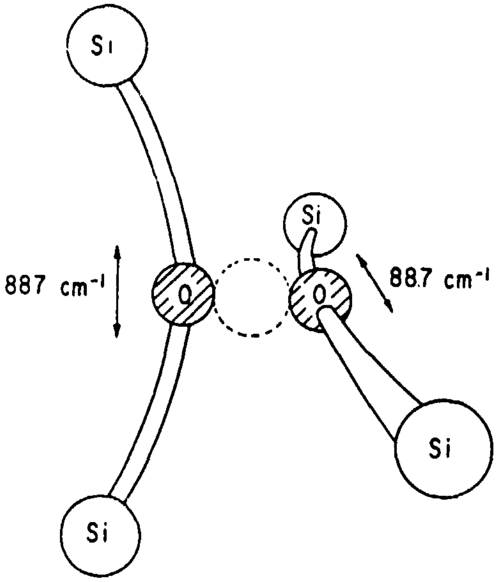

Fig. 4. The (vacancy + two-oxygen) center in silicon.

Fig. 4), as we have recently verified by studying the dependence of the formation of this defect on the oxygen concentration. Subsequent annealing of this center leads to a $(V \cdot O_3)$ center, or what might be called a $(V \cdot O_2)+O_i$ center, as shown in Fig. 5.

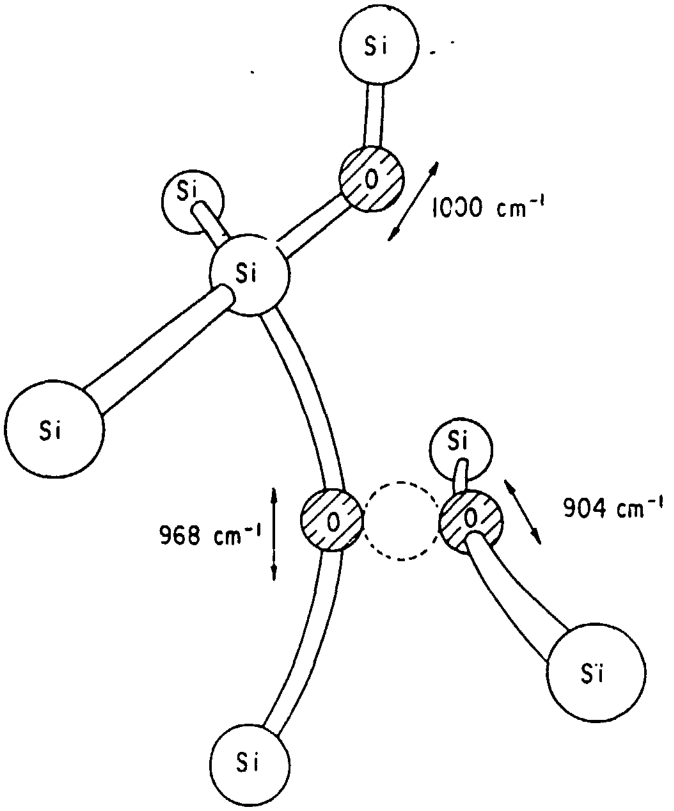

Fig. 5. $(V \cdot O_2) + O_i$ center in silicon.

In recent studies we have found that the growth of the $(V \cdot O_2)$ band is characterized by a ~ 1.9 eV activation energy, i.e., essentially the same as the anomalous diffusion of Stavola et al. (See Fig. 6) This argues that the anomalous diffusion occurs by the dissociation of the $(V \cdot O)$ center,

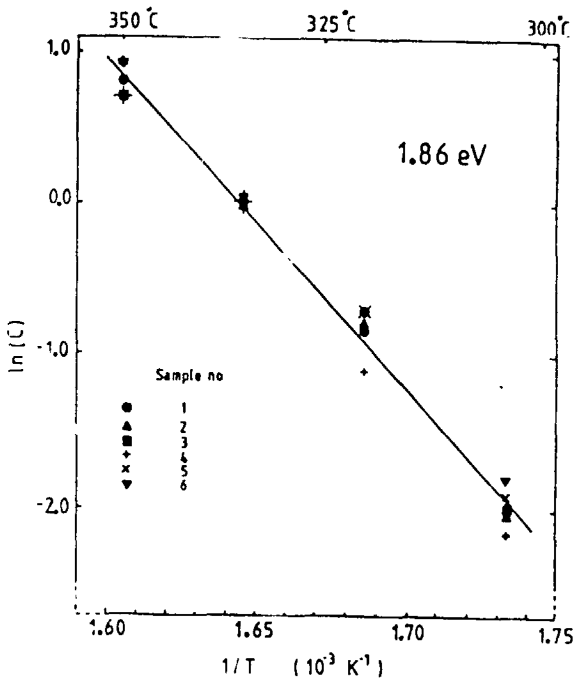

Fig. 6. Arrhenius plot for the growth of the $(V{\cdot}O_2)$ defect.

with that process causing the O_i to move through the lattice, e.g.,

$$(O_i) + (V) \rightarrow (V{\cdot}O) \rightarrow (O_i) + (V)$$

and the growth of the $(V{\cdot}O_2)$ by the free vacancy encountering two adjacent oxygens, e.g.,

$$(V) + (Si\text{-}O\text{-}Si\text{-}O\text{-}Si) \rightarrow (V{\cdot}O_2).$$

This important advance needs further experiments to test its several implications, and these experiments are being done.

In related studies we have found that infra-red bands associated with thermal donors can be found in floating-zone silicon (i.e., low-oxygen) silicon that has been neutron-irradiated in transmutation doping. Thus the vacancies created in that process can substantially accelerate defects agglomeration, a point that also is important in ion-implantation.

As is seen in Fig. 2, there are nine different thermal donors which have been resolved by infra-red studies, where they have Rydberg transitions characteristic of double donors. What then are these thermal donors? The consensus is that they consist of a core (or perhaps there are several such cores) which has a double plus charge state, that the Rydberg states arise from the attraction of electrons to this double plus center, and that successive donors occur as additional oxygens are added to, or adjacent to, this core. We have developed a theory that describes the electrical behavior of this hierarchy of thermally-induced double donors, including a core and an electronically repulsive oxygen-rich region, which repulsive region grows in size as oxygens are added to the defect. We have succeeded in fitting the perturbation to the ground state energies all nine double donors as shown in Fig. 7.

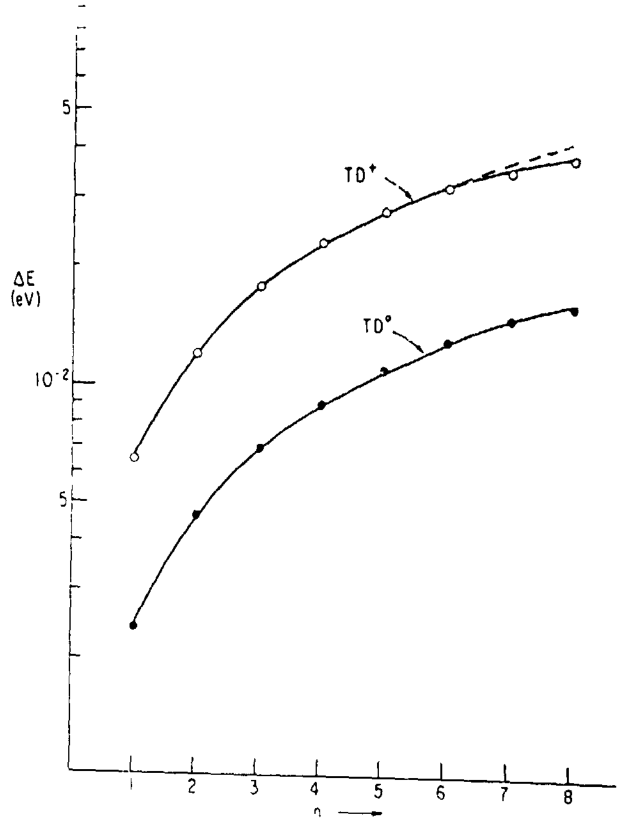

Fig. 7. Perturbation energy for the thermal donor ground states versus added oxygens.

What then is the core (or are the cores)? We have identified the most likely core for the homogeneously-nucleated oxygen precipitate as the "ylid," the saddle-point for oxygen diffusion, stablized by the presence of two or more additional oxygens. We conclude as well that the precipitation strain-energy can also cause the emission of an interstitial leaving the core as the $(V \cdot O_2)$ center. These processes are consistent with precipitation processes which yield coesite plus interstitial dislocation dipoles. They also provide a mechanism for the loss of thermal donor activity, as is observed, and for the creation of recombination centers. But a number of lines of investigation need to be pursued to be certain of these models.

Why then the two line of precipitation? Our working hypothesis is that the "black dot" line involves carbon. Since carbon contracts the lattice, it will relieve the strain associated with oxygen agglomeration, delaying the formation of the strain-induced formation of the thermal donors which we employed for the "old" thermal donors. This permits the "new" thermal donors to be associated with carbon, as is observed, and to be more stable. But these matters must be pursued further to achieve certainty.

What about the recombination centers? As we indicated the processes that we have discussed can create recombination centers, e.g. the $(V_2 \cdot O)$, $(V_2 \cdot O_2)$, etc. centers, which we passed over. But the experimental results are becoming quite incisive. Suezawa and Sumino have argued persuasively that one of the thermal donors involves eight oxygens. But just as persuasively Glinchuk _et_ _al_. have observed a recombination center that contains eight oxygens!

Clearly the agglomeration can follow several paths, and much needs to be done to sort out these matters. Still we have made great progress.