

The oxygen dimer in Si: Its relationship to the light-induced degradation of Si solar cells?

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It is widely believed that the light induced degradation of crystalline silicon solar cells is due to the formation of a B_sO_{2i} recombination center created by the optically excited migration of the oxygen dimer (charge-state-driven motion). In this letter the concentration dependence of the neutral state of O_{2i} on $[O_i]$ in p- and n-type Cz-Si has been determined using infrared absorption. A systematic search for the absorption signature of the dimer in the doubly positively charged state has been unsuccessful. These data strongly suggest that charge-state-driven motion (Bourgoin–Corbett mechanism) of the oxygen dimer cannot occur in typical solar silicon and hence bring into question the accepted degradation mechanism. © 2011 American Institute of Physics.

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The belief that the well characterized oxygen dimer (O_{2i}) (Refs. 1–4) plays a key role in the formation of the recombination center responsible for the light-induced degradation of n⁺p solar cells is widely published.^{5–11} The materials used in these studies have been boron-doped Czochralski-grown (Cz) monocrystalline Si and solar-grade multicrystalline Si. The assignment was based on the experimentally observed quadratic dependence of the concentration of the recombination center (inferred from lifetime measurements) on the interstitial oxygen content ($[O_i]$) in the Si crystals studied and calculations of the defect energies of boron–oxygen complexes.^{5–9} In a broader context, the dependence of the O_{2i} concentration on $[O_i]$ is not always quadratic but can depend on the thermal history and the presence of some impurities, particularly, carbon and hydrogen.^{1,2,12} However as will be seen later, the set of as-grown carbon-lean samples studied here, typical of solar cell Si materials, displays a near quadratic dependence.

The key issue is the formation mechanism which is proposed to occur by diffusion of the oxygen dimer in p-type Si at room temperature (RT) upon minority carrier injection and its subsequent interaction with substitutional boron (B_s) atoms forming a B_sO_{2i} complex.^{5–9} The B_sO_{2i} complex was argued to be a powerful recombination center responsible for the degradation of n⁺p solar cells.^{5,6} The enhanced O_{2i} diffusion at RT in Si was suggested to occur under minority carrier injection via the Bourgoin–Corbett mechanism, which requires the existence of two stable configurations of O_{2i} in different charge states. This is calculated to reduce the energy required for diffusion of the dimer from 0.86 eV (low mobility at RT) to 0.3 eV.^{7–9} Results of *ab initio* modeling studies suggested the existence of two alternative structures of the dimer in silicon crystals with different doping.^{4,7,9} In n-type or intrinsic Si the dimer is in the neutral charge state

with the so-called “staggered” (ST) configuration. This is an energetically favorable configuration for O_{2i} ,^{3,4,7,9,13} while in p-type Si the center has been calculated to be in the doubly positively charged state (O_{2i}^{2+}). The minimum energy configuration for this charge state is expected to be “ring” or “square” (SQ).^{7,9} The transition between the two configurations is predicted to occur when the Fermi level is at about $E_v + 0.40$ eV.⁷

In the present study we have carried out infrared (IR) absorption measurements on a number of n- and p-type Cz-Si crystals with different doping levels and oxygen content including materials with identical doping and oxygen content to those in which light induced degradation attributed to B_sO_{2i} has been observed. The focus of the work was on the search for experimental evidence of the existence of O_{2i} in the doubly positive charge state in the SQ configuration, an essential prerequisite for the Bourgoin–Corbett enhanced diffusion mechanism and hence central to the proposed degradation process. We have also determined a dependence of the O_{2i} concentration on interstitial oxygen content for as-grown Cz-Si crystals. The IR absorption spectra have been measured at 300 K and at ~15 K in the frequency range 400–4000 cm^{-1} with the use of Bruker IFS113v spectrometer. The O_i concentration was determined from measurements of intensity of absorption band at 1107 cm^{-1} using the calibration coefficient $3.14 \times 10^{17} \text{ cm}^{-2}$.

The oxygen dimer in the SQ configuration in Si has not been detected previously, and therefore we have performed *ab initio* calculations to get a clue as to the possible location and intensity of local vibrational modes (LVMs) due to O_{2i}^{2+} . The ST and SQ forms of O_{2i} were calculated in 64 Si-atom cubic supercells using the AIMPRO local density functional code¹⁴ under similar conditions to those reported in Ref. 7 (the minimum energy configurations obtained by us are similar to those shown in Fig. 2 in Ref. 9). The LVMS were

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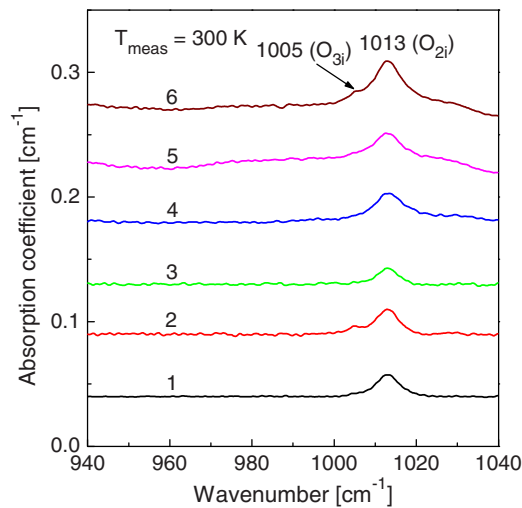


FIG. 1. (Color online) Infrared absorption spectra measured at 300 K with the resolution of 1 cm^{-1} for as-grown Cz-Si crystals with the following values of doping impurities and interstitial oxygen concentrations: 1-[B] = $1.5 \times 10^{14} \text{ cm}^{-3}$, $[\text{O}_i] = 1.2 \times 10^{18} \text{ cm}^{-3}$; 2-[B] = $7 \times 10^{15} \text{ cm}^{-3}$, $[\text{O}_i] = 1.05 \times 10^{18} \text{ cm}^{-3}$; 3-[B] = $8 \times 10^{14} \text{ cm}^{-3}$, $[\text{O}_i] = 9.5 \times 10^{17} \text{ cm}^{-3}$; 4-[P] = $2 \times 10^{14} \text{ cm}^{-3}$, $[\text{O}_i] = 1.1 \times 10^{18} \text{ cm}^{-3}$; 5-[P] = $7 \times 10^{14} \text{ cm}^{-3}$, $[\text{O}_i] = 1.0 \times 10^{18} \text{ cm}^{-3}$; 6-[P] = $7 \times 10^{13} \text{ cm}^{-3}$, $[\text{O}_i] = 1.3 \times 10^{18} \text{ cm}^{-3}$. The spectra are shifted on the vertical axis for clarity.

calculated for neutral O_{2i}^0 -ST and doubly positively charged O_{2i}^{2+} -SQ structures by diagonalizing the dynamical matrix.⁴ To estimate their relative LVM intensities, effective charges q of O atoms and first and second neighboring Si atoms were obtained from their Mulliken bond populations. The intensity of the mode is then related to the squared change in the dipole moment of the defect when the atoms are displaced according to their mass weighted normal coordinates.

In agreement with previous calculations,⁴ O_{2i}^0 -ST gives rise to two pairs of O-related LVMs. Of particular relevance for this letter is the high frequency pair with modes calculated at 992 cm^{-1} and 954 cm^{-1} with relative intensity 1.0 and 0.66, respectively. Their splitting arises both from vibrational coupling and from a small difference between the two Si-O-Si units. Although we underestimate the experimentally observed LVM frequencies of O_{2i}^0 -ST by $\sim 60 \text{ cm}^{-1}$, they are consistent with a 55 cm^{-1} underestimation for the asymmetric mode of O_i in Si. For O_{2i}^{2+} -SQ, two pairs of O-related modes are also anticipated. The ones with the highest frequency lie at 787 cm^{-1} and 702 cm^{-1} with relative intensity 0.00 and 2.16, respectively. O_{2i}^{2+} -SQ is centrosymmetric (both O atoms are equivalent), i.e., the frequency separation arises from vibrational coupling alone, where the 787 and 702-cm^{-1} modes are symmetric and asymmetric stretch modes with respect to the inversion symmetry center. We note that although the 787 cm^{-1} mode is IR-inactive, the 702 cm^{-1} mode is predicted to be at least twice more intense than the high-frequency modes of O_{2i}^0 -ST which we observe with ease.

Figure 1 shows IR absorption spectra in the frequency range $940\text{--}1040 \text{ cm}^{-1}$ measured at 300 K for a number of phosphorus- and boron-doped Si crystals with different oxygen content. The spectra recorded on n- and p-type samples are very similar. The absorption line at 1013 cm^{-1} due to the neutral ST oxygen dimer is the dominant one in all the spectra. An inspection of the spectra in the whole frequency range shows that except weak LVM lines due to substitu-

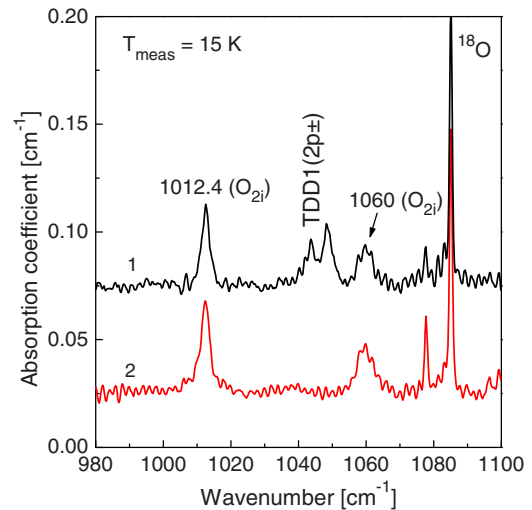


FIG. 2. (Color online) Infrared absorption spectra measured at 15 K with the resolution of 0.5 cm^{-1} for as-grown Cz-Si crystals with the following values of doping impurities and interstitial oxygen concentrations: 1-[B] = $1.5 \times 10^{15} \text{ cm}^{-3}$, $[\text{O}_i] = 9.5 \times 10^{17} \text{ cm}^{-3}$; 2-[P] = $2 \times 10^{14} \text{ cm}^{-3}$, $[\text{O}_i] = 1.1 \times 10^{18} \text{ cm}^{-3}$. The spectra are shifted on the vertical axis for clarity.

tional boron atoms there are no additional absorption lines in the spectra of p-type Si samples compared to those for n-type Si samples. Particularly, no LVM lines have been detected in the frequency range $650\text{--}800 \text{ cm}^{-1}$ in either n- or p-type Si samples. According to an analysis based on resistivity measurements on the samples, the equilibrium Fermi level position at the measurement temperature (300 K) was in the range of $E_c - (0.27\text{--}0.33) \text{ eV}$ and $E_v + (0.22\text{--}0.32) \text{ eV}$ in all n- and p-type Si samples, respectively. In p-type material this would satisfy the condition that the Fermi level is closer to the valence band than $E_v + 0.40 \text{ eV}$ (the calculated transition energy)⁷ and hence, in the studied material and in the more heavily doped p-Si, if this calculation is correct, it would be expected that the majority of the dimers would be in the doubly positively charged state (O_{2i}^{2+}). Irrespective of the calculated population of O_{2i}^{2+} the absorption measurements have been done on material identical to that in which the boron oxygen degradation has been observed experimentally. In these circumstances the existence of O_{2i}^{2+} is essential if the Bourgoin-Corbett enhanced diffusion mechanism occurs. The results obtained indicate that the doubly positively charged O_{2i} complex is undetectable in our sample set and hence raise doubts as to its existence.

Figure 2 shows IR absorption spectra in the frequency range $980\text{--}1100 \text{ cm}^{-1}$ measured at 15 K for two as-grown Cz-Si samples doped with either phosphorus or boron. The interstitial oxygen concentration was nearly equal in these samples, and the equilibrium Fermi level position at 15 K was calculated to be at about $E_c - 0.05 \text{ eV}$ and $E_v + 0.05 \text{ eV}$ in n- and p-type Si samples, respectively. An analysis shows that the intensities of absorption lines at 1012 cm^{-1} and 1060 cm^{-1} due to ST oxygen dimer are essentially the same in the samples studied. In attempts to transform the O_{2i} center into the doubly positively charged state and to detect LVMs due to the dimer in this charge state we have measured IR absorption spectra at 15 K with and without the use of a Ge filter and after different cooling conditions (cooling in the dark or with white light illumination). After slow cooling in the dark the O_{2i} center is expected to be in the energetically favorable O_{2i}^{2+} -SQ state in

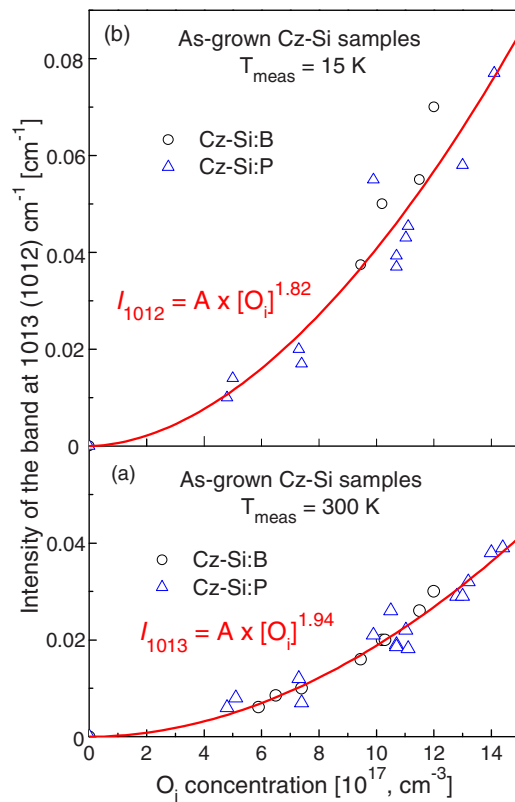


FIG. 3. (Color online) Intensity of IR absorption band at 1013 (1012) cm⁻¹ due to ST oxygen dimer measured at (a) 300 K and (b) 15 K vs interstitial oxygen concentration in as-grown Cz-Si samples.

p-type silicon, while white light illumination will generate both holes and electrons moving the Fermi level toward middle of the gap and freezing the structure energetically favorable for the mid-gap position of the Fermi level. The above attempts have not resulted in noticeable changes in the intensity of the line at 1012 (1060) cm⁻¹ in either n- or p-type samples.

Figure 3 shows dependencies of intensities of the O_{2i}-related absorption line at 1012 (1013) cm⁻¹ on interstitial oxygen content measured at 15 (300) K for a number of as-grown Cz-Si n- and p-type samples with low carbon content. The data at both measurement temperatures for n- and p-type samples can be described by the same power law dependence. The solid lines in Fig. 3 represent least squares fits of all the experimental data by a power law dependence $I_{O_{2i}} = A \times [O_i]^n$ with pre-factor A and n values as fitting parameters. The n values were found to be 1.82 ± 0.25 and 1.94 ± 0.13 for the data obtained from the spectra measured at 15 K and 300 K, respectively.

The data obtained show that in the temperature range 15–300 K in both n- and p-type Si the O_{2i} complex is only seen in the neutral charge state (ST configuration). There is no indication of the existence of the oxygen dimer in the

doubly positively charged state. Without O_{2i}²⁺ the charge-state-change driven motion of the oxygen dimer at RT cannot occur. This throws considerable doubt on the accepted model of the formation of a B_sO_{2i} recombination center via Bourgoin–Corbett diffusion of O_{2i} for the optically induced degradation of boron and oxygen doped silicon for photovoltaics. It adds to the concerns resulting from difficulties in explaining the degradation behavior of compensated material^{15,16} and makes alternative mechanisms recently proposed more likely.¹¹

Finally, the existence of O_{2i}²⁺ in the SQ configuration in Si has been predicted by theoretical modeling in Refs. 7 and 9. We have also calculated the electronic properties of the dimer using supercell and cluster boundary conditions, with cells and clusters containing up to 216 and 293 Si atoms, respectively, and with several basis functions for the Kohn–Sham levels and charge density. The results obtained are consistent with the previously reported double donor character of O_{2i} with a (0/++) level in the lower half of the gap. This could arise from a fundamental insufficiency of the calculation methods used and further work for solving the problem is necessary.

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