

Experimental Evidence of the Oxygen Dimer in Silicon

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Optical characterization of the oxygen dimer in silicon has been performed for the first time. The vibrational IR absorption bands at 1012, 1060, and 1105 cm^{-1} are shown to arise from this complex. Using heat-treatment studies, the dimer binding energy is determined to be about 0.3 eV. Indications of the high migration ability of the dimer predicted earlier are found as well. [S0031-9007(97)04994-6]

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It is well known that silicon wafers used for integrated circuits require the presence of oxygen, due to its beneficial effects such as wafer hardening and intrinsic gettering [1]. Czochralski grown silicon (Cz-Si) typically contains $\sim 10^{18} \text{ cm}^{-3}$ of interstitial oxygen (O_i) which in a very large temperature range remains highly supersaturated. The clustering of oxygen atoms in Cz-Si has been widely studied [1,2]. At high temperature treatments ($>700 \text{ }^\circ\text{C}$), different quartz precipitates have been observed to form. The processes of their formation are now rather well understood and found to be governed by the diffusion of O_i atoms.

At lower temperatures ($<700 \text{ }^\circ\text{C}$) and especially in the range of about 350–550 $^\circ\text{C}$, oxygen agglomeration in Cz-Si gives rise to different families of electrically active clusters, so-called thermal donors (TDs). In spite of intensive studies for more than 40 years, their structure and formation mechanisms are still not known. The main reason is that the kinetics of TD formation cannot be described within the framework of oxygen clustering limited by the normal diffusion rate of O_i atoms [3]. In fact, all of the modern TD kinetic models assume the existence of a fast diffusing oxygen-related species (FDS). However, the origin of such a species remains to be one of the main puzzles in the problem of TD formation or, in general, in the problem of oxygen diffusion and precipitation in Cz-Si at elevated temperatures ($<700 \text{ }^\circ\text{C}$).

Various kinds of FDS have been suggested [4] including complexes of oxygen with an intrinsic defect or impurity, self-interstitials created by oxygen pair formation, quasifree O_i atoms, and oxygen molecules or dimers. At present, the latter suggestion seems to be the most attractive because it allows consistent explanation of a number of facts concerning enhanced oxygen in- and outdiffusion as well as kinetics of O_i loss and TD formation [5,6]. However, little is known about the properties of the dioxygen complex. Theoretical studies [7–11] have shown that an oxygen molecule is not stable in the Si lattice and only the dioxygen complex formed from two O_i atoms with a common silicon neighbor (oxygen dimer, O_{2i}) can be stable in certain configuration. It has been found that the binding energy of such a complex lies in the range of 0.1–

1.0 eV and that the formation of it does not result in an ejection of a Si self-interstitial. Besides, it was revealed [7,11] that the activation energy for migration of the O_{2i} complex could be appreciably lower than that of a single oxygen atom.

In accordance with *ab initio* calculations, the O_{2i} complex is electrically inactive, but it should give rise to local vibrational modes (LVMs) in the neighborhood of the main LVMs of O_i . However, until recently such modes have not been detected experimentally, probably because of their low intensity. Only recently in the paper of Stein and Medernach [12], a LVM band at 1005 cm^{-1} introduced effectively in Cz-Si by plasma hydrogenation at 275 $^\circ\text{C}$ was attributed to the oxygen dimer. Earlier, some satellite lines near the 29.3 cm^{-1} O_i band were observed by means of high sensitive acoustic phonon spectroscopy [13]. These lines were assigned to the oxygen pairs because of the quadratic dependence of their intensity on the O_i concentration. However, these assignments [12,13] are very tentative and, in fact, none of the oxygen dimer characteristics is known exactly.

Recently the vibrational infrared (IR) absorption bands related to small oxygen clusters (TDs and their precursors) were discovered [14–16]. It has been argued [17,18] that one of these bands (located at 1012 cm^{-1}) is related to the oxygen dimer. This assignment was based mainly on some similarities between the expected annealing behavior of the oxygen dimer and that of the complex giving rise to the 1012 cm^{-1} band. In the present paper, an experimental evidence for this suggestion is given and two other IR absorption bands associated with the oxygen dimer are revealed.

In this study, the IR absorption analysis was carried out using a Bruker IFS 113v Fourier Transform Infrared Spectrometer. The measurements were performed at room temperature and at 10 K. We used as-grown phosphorus and boron doped Cz-Si samples of 2–60 $\Omega \text{ cm}$ with an O_i concentration in the range $(4\text{--}15) \times 10^{17} \text{ cm}^{-3}$ and a substitutional carbon (C_s) concentration $\leq 2 \times 10^{16} \text{ cm}^{-3}$. We also included a few samples with a high carbon concentration as well as samples doped with the isotope ^{18}O (99% enrichment). The concentration of O_i

and C_s was monitored by measuring the absorption bands at 1107 [19] and 605 cm^{-1} [20], respectively. The heat treatment (HT) was performed in nitrogen ambient or in air and followed by quenching in isopropyl alcohol.

Our study was focused on some weak IR absorption bands related to oxygen complexes which can remain after high-temperature HTs. It is well known that at temperatures above about 550 °C small oxygen clusters (like TDs) are not stable and that their quasiequilibrium concentration is very low. But this is not the case for the oxygen dimer. A unique feature of this complex is the ability to exist in noticeable concentration at high temperatures. This may be clarified in the following manner. It is evident that at $T > 550$ °C the dynamical equilibrium between the O_i atoms and their pairs should occur. The capture of dimers (clustering) cannot be a dominant process as compared with dimer dissociation. Otherwise a rapid loss of interstitial oxygen should occur which has never been observed in perfect and carbon-lean crystals [4]. Thus, if the equilibrium between O_i and O_{2i} is reached, then it is easy to estimate the concentration of oxygen dimers (N_2^{eq}) using the standard principles of statistical mechanics. Since the typical concentration of oxygen atoms in Cz-Si crystals ($N_1 \sim 10^{18} \text{ cm}^{-3}$) is much less than the density of possible sites for them in the Si lattice ($N_{\text{SO}} = 10^{23} \text{ cm}^{-3}$), the N_2^{eq} value can be found as [21]

$$N_2^{\text{eq}} = \frac{N_1^2 g_2}{N_{\text{SO}} g_1} \exp\left(\frac{E_{b2}}{kT}\right), \quad (1)$$

where g_1 and g_2 are the numbers of possible O_i and O_{2i} sites per unit cell (it is easy to show that $g_1 = 4$ and $g_2 = 12$) and E_{b2} is the dimer binding energy. So, even if E_{b2} is low (~ 0.1 eV), the oxygen dimer can exist in Cz-Si crystals in noticeable concentrations ($\geq 10^{14} \text{ cm}^{-3}$) at high temperatures up to the Si melting point and, accordingly, can be detected in heat-treated samples.

Figure 1 shows typical IR absorption spectra in the range 1000–1120 cm^{-1} for Cz-Si samples, as grown and annealed for 30 min at 550 and 700 °C. In all of the spectra besides the well-known bands related to the natural oxygen isotopes ^{18}O and ^{17}O , three other LVM bands located at 1012.4, 1059.8, and 1105.3 cm^{-1} are observed. In samples doped with isotope ^{18}O , the bands were shifted to 969.2, 1011.8, and 1057.1 cm^{-1} , respectively. So, evidently, they are related to oxygen. However, isolated O_i atoms cannot give rise to these bands. Their intensity was found to vary noticeably with the HT temperature (see Fig. 1), while the O_i concentration remained constant during these short-time anneals. Therefore, these bands should originate from some oxygen-related complex. Since the bands were observed earlier even after dispersion treatments at 1100 [16] and 1350 °C [22], it appears likely that this complex is an oxygen dimer. Larger and more stable oxygen

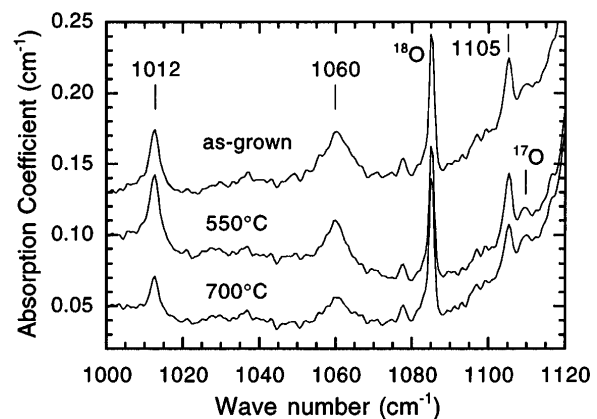


FIG. 1. Absorption spectra measured at 10 K of Cz-Si samples with O_i and C_s concentrations of about 1.1×10^{18} and $3 \times 10^{15} \text{ cm}^{-3}$, respectively.

clusters will not be formed during such a short (≤ 1 s) cooling down process.

To check such an assignment, we have investigated the dependence of the integrated absorption (IA) coefficient of the bands at 1012, 1060, and 1105 cm^{-1} on the oxygen content in the samples. To reach an equilibrium level of the bands, all of the samples were annealed for 30 min at 600 °C. The experimental data obtained are presented in Fig. 2. For different oxygen concentrations ranging from 4×10^{17} to $1.5 \times 10^{18} \text{ cm}^{-3}$, the IA of the 1012, 1060, and 1105 cm^{-1} bands clearly display a square dependence on the O_i concentration. The similar dependencies were also obtained after HTs at other temperatures in the range 500–1000 °C. These results unambiguously show that the bands studied are arising from a complex involving two O_i atoms, i.e., from the oxygen dimer.

One of the most important characteristics of the dimer is the binding energy. To determine the E_{b2} value, we have studied the temperature dependence of the IA

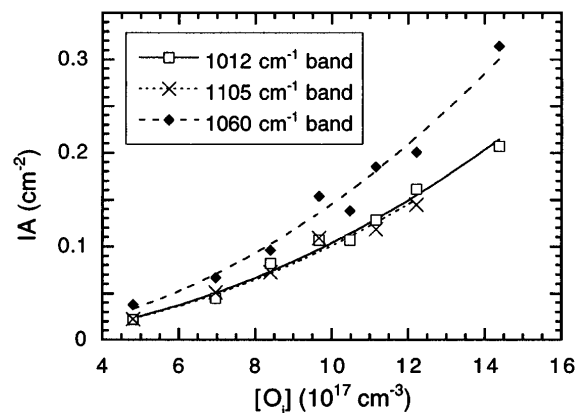


FIG. 2. The IA of the bands at 1012, 1060, and 1105 cm^{-1} measured at 10 K and plotted versus the O_i concentration. The curves in the figure are quadratic functions fitted to the experimental data.

equilibrium level for all three bands in the range 500–1000 °C. Figure 3 shows the corresponding experimental results. In this figure, the IA values were normalized to the square of the O_i concentration, in accordance with Eq. (1), in order to take into account small deviations of the O_i concentration among the different samples. It is clearly seen that the plots obtained cannot be described by a simple exponential function according to Eq. (1). There is a flat region in the range of 800–1000 °C and, only in the range of 500–700 °C, an exponential increase in IA with a decrease in temperature is observed. But this result can be expected since according to estimations [18] the lifetime of the dimer, or, in other words, the characteristic time required to reach N_2^{eq} , is rather short at high temperatures (<10 ms at $T > 800$ °C). Apparently the cooling rate used in the present study was insufficient to freeze an equilibrium state of dimers at $T \geq 800$ °C. So, in further analysis, we have concentrated on the temperature region 500–700 °C.

It was deduced that the temperature dependencies of IA of the bands at 1012 and 1060 cm^{-1} are characterized by the same slope of 0.3 eV [23]. The corresponding slope for the band at 1105 cm^{-1} was found to be about 0.2 eV. However, the data for this band are not so definitive as for the bands at 1012 and 1060 cm^{-1} . This band is not observable at room temperatures since it falls into the region of the strong 1107 cm^{-1} band of O_i . Besides, at low temperatures its position practically coincides with that of bands related to the C_s - O_i complex [24] and electronic transitions of singly ionized TD2($3p \pm$) [25]. So, it was rather difficult to determine properly the IA of the band at 1105 cm^{-1} in samples containing TDs (after HT at 500 °C) or carbon in high concentrations. Nevertheless, it appears that this band could arise from some dimer configuration ($E_{b2} \sim 0.2$ eV) slightly different from the main one ($E_{b2} = 0.3$ eV) giving rise to the bands at 1012

and 1060 cm^{-1} . The latter value of the dimer binding energy should be considered as the most reliable one. It is worth noting that the most recent calculations [10] gave the close value of $E_{b2} = 0.4$ eV.

Assuming that the oscillator strength for the dimer-related 1012 and 1060 cm^{-1} bands and the O_i -related band at 1107 cm^{-1} are similar, we have estimated the preexponential factor in the expression describing the temperature dependence of the ratio N_2^{eq}/N_1^2 . It was found to be equal to about $(1-3) \times 10^{-23} \text{ cm}^3$. The value obtained is surprisingly close to $g_2/g_1 N_{SO} = 3 \times 10^{-23} \text{ cm}^{-1}$ given by Eq. (1). Such a coincidence can serve as an additional support for the assignment of these bands to the oxygen dimer.

An identification of the band at 1012 cm^{-1} as arising from the oxygen dimer allowed us to reinterpret some previous data concerning the annealing behavior of this band at the TD formation temperatures [14–16]. It is now evident that there are two different kinds of oxygen complexes giving rise to the IR bands positioned at about 1012 cm^{-1} : (a) oxygen dimers that exist in as-grown crystals and can be rapidly transformed into TDs during the initial stages of HT at 350–450 °C, and (b) higher order complexes formed after more prolonged anneals. In Ref. [16], the temperature dependence (350–470 °C) of the equilibrium level (IA) of the 1012 cm^{-1} band related to the first kind of complexes was obtained. Those data, together with the new ones obtained after high temperature HTs, are plotted in Fig. 4. The maximum achievable equilibrium level of the 1012 cm^{-1} band corresponds to a temperature around 450–500 °C. At lower HT temperatures, a significant decrease occurs. This fact, together with the observed rapid transformation of “as-grown” dimers into the first TD species [15], manifest clearly that at $T < 450$ °C the capture processes of mobile dimers dominate.

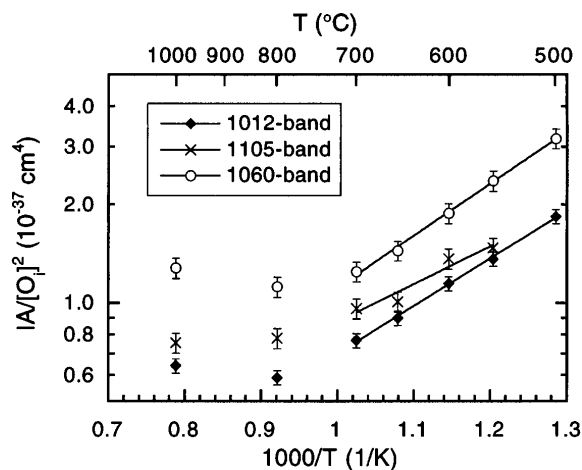


FIG. 3. Annealing temperature dependencies of the IA of the dimer-related bands measured at 10 K, normalized to the square of the O_i concentration.

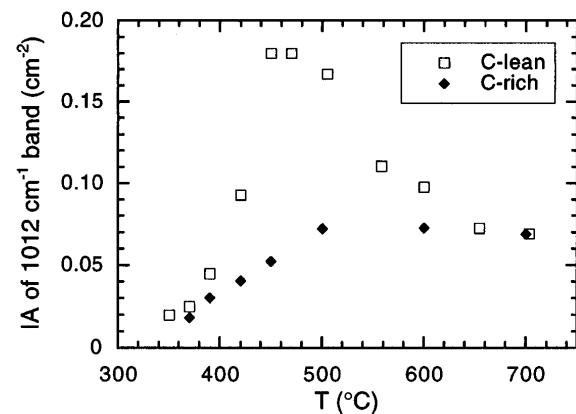


FIG. 4. The quasiequilibrium of the IA of the 1012 cm^{-1} band measured at 293 K versus annealing temperature, for carbon-lean ($[O_i] \approx 1.0 \times 10^{18} \text{ cm}^{-3}$, $[C_S] \leq 10^{16} \text{ cm}^{-3}$) and carbon-rich ($[O_i] \approx 1.1 \times 10^{18} \text{ cm}^{-3}$, $[C_S] \approx 3 \times 10^{17} \text{ cm}^{-3}$) samples.

It is well known that the presence of carbon in a high concentration suppresses the TD generation in Cz-Si crystals. This phenomenon has recently been associated with the capture of dimers by carbon [5,6,17]. In the present study, we have found that, indeed, the equilibrium level of the 1012 cm^{-1} band in the carbon-rich samples is essentially lower as compared with the carbon-lean ones at the TD formation temperatures (see Fig. 4). The similarity in O_{2i} concentration for C-lean and C-rich samples for $T > 600\text{ }^\circ\text{C}$ is because C_s-O_n complexes ($n \geq 2$ [24]) are not stable while dissociation of O_{2i} becomes more and more effective.

In summary, we have assigned three vibrational IR absorption bands related to the oxygen dimer in Si. An experimental characterization of this abundant oxygen cluster is performed for the first time. The dimer binding energy is determined to be about 0.3 eV. Experimental support of the high migration ability of this complex predicted earlier is found as well. There are strong grounds for believing that further studies will lead to the determination of the main diffusion characteristics of this complex and to further insight into the problem of oxygen clustering at elevated temperatures.

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