

Clustering of Oxygen Atoms in Silicon at 450 °C: A New Approach to Thermal Donor Formation

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Clustering of oxygen atoms in silicon at 450 °C has been correlated with a group of infrared vibrational absorption bands observable at room temperature. The bands are related to the formation of thermal donors and show a good correlation with results from different experimental techniques. It is suggested that three categories of thermal donors are developing corresponding to absorption bands at about 975, 988, 1000, 1006, and 1012 cm^{-1} .

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Oxygen is an important impurity in silicon materials used for integrated circuits due to its beneficial effects such as wafer hardening and intrinsic gettering. However, in a very large temperature range (up to 1200 °C) the solution of interstitial oxygen in silicon remains highly supersaturated. At temperatures where oxygen becomes mobile ($> 350^\circ\text{C}$) aggregation of oxygen atoms starts, which can cause harmful effects in circuit performance. Future processing (high complexity, low temperature processing) requires a deeper knowledge about the nature of these defects.

The clustering of oxygen atoms in Czochralski grown (Cz) silicon has been widely studied [1]. At high temperature treatments (800–1000 °C) different quartz precipitates have been observed to form and at lower temperatures smaller clusters are developing, giving rise to the new donors (ND) (550–750 °C), the thermal donors (TD), and the shallow thermal donors (STD) (350–500 °C).

The TDs in silicon are probably among the most studied defects in semiconductors [2,3]. The experimental studies have included techniques such as resistivity measurements, infrared absorption spectroscopy, photoluminescence, electron paramagnetic resonance, electron nuclear double resonance, Hall effect, deep level transient spectroscopy, and photothermal ionization spectroscopy.

The structure of these defects is suggested to be a core to which oxygen atoms aggregate to form a series of closely related donor structures. Several core models have been presented [1–3] but so far no model has been experimentally verified. Very detailed information about these defects comes from electron paramagnetic resonance (EPR) and infrared (IR) spectroscopy at low temperatures. IR spectroscopy results show many absorption bands related to electronic transitions which have been systematically studied and ordered into an effective mass-like series corresponding to at least nine different double donors, TD1–TD9 [1]. Several models have been presented on the growth kinetics of TDs [1–3] trying to tie the clustering of oxygen to the TD formation kinetics. Most models use a serial formation process instead of parallel processes [4].

Oxygen in silicon is known to give rise to several vibra-

tional IR absorption bands both as an interstitial atom and in combination with vacancies [5] or with impurity atoms [6]. Also the formation of oxygen precipitates in the range 800–1000 °C is known to give rise to different IR absorption bands [7,8]. However, no oxygen related vibrational absorption band has so far been correlated with the formation of TDs. One reason is probably that the low concentration of these defects that is achieved is about 2 orders of magnitude lower than the interstitial oxygen concentration.

In this study we formed thermal donors in Cz-silicon materials by heat treatment for different times at 450 °C. We used as-grown phosphorus and boron doped Cz-silicon samples with an interstitial oxygen concentration in the range $(5\text{--}9) \times 10^{17}$ at/cm^3 and a carbon concentration below detection limit. Sample dimensions were $10 \times 5 \times 5$ mm. We also included a few samples with a high carbon concentration in the range $(5\text{--}50) \times 10^{16}$ at/cm^3 . The concentration of interstitial oxygen and substitutional carbon was monitored by measuring the well-known absorption bands at 1107 [9] and 605 cm^{-1} [10], respectively. The spectrometer used for the IR studies was a Bruker Fourier transform IR 113v. The heat treatment was performed in nitrogen atmosphere and was followed by a HF dip.

Our study was focused on some weak absorption bands in the range 975–1013 cm^{-1} which were affected by a 450 °C treatment. The position of the bands can shift a little ($\approx 1 \text{ cm}^{-1}$) with heat treatment time. Our numbers for the peak positions should therefore be considered as approximate.

We followed the development of TDs by resistivity measurements using a four-point probe taking into account the double donor character of the TDs. From low-temperature IR absorption spectra we measured the electronic transition bands of the TDs in the range 350–1200 cm^{-1} .

Several vibrational bands are related to interstitial oxygen in Cz silicon at room temperature [11]. The strongest band is positioned at 1107 cm^{-1} . A band at 1013 cm^{-1} has sometimes been included in this group but we could not find such a correlation. For the oxygen atom in an almost substitutional position (*A* center) a vibrational

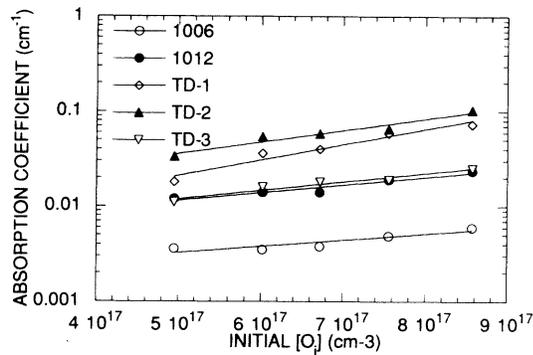


FIG. 1. The strength of TD IR absorption bands at 10 K for TD1, TD2, and TD3 together with the room temperature bands at 1006 and 1012 cm^{-1} , for as-grown samples of different interstitial oxygen concentration.

band at 830 cm^{-1} has been reported [5]. Oxygen precipitates formed in the temperature range $800\text{--}1000^\circ\text{C}$ [8] give rise to IR absorption bands in the range $1050\text{--}1250 \text{ cm}^{-1}$. Broad IR bands related to different forms of SiO_x can be observed in the range $980\text{--}1100 \text{ cm}^{-1}$ [12]. It is therefore reasonable to expect that oxygen in a TD should have vibrational absorption bands in the spectral range of $800\text{--}1250 \text{ cm}^{-1}$.

IR absorption bands at 1006 and 1013 cm^{-1} have previously been reported [11,13,14]. One suggestion presented is that a band observed at 1012 cm^{-1} is related to a nuclei for thermal donors [14]. Another interpretation is that a band at 1013 cm^{-1} is an overtone of an IR band at 514 cm^{-1} related to interstitial oxygen [11]. However, no systematic study of these bands has been presented so far.

The as-grown samples used in this study were all investigated both at room temperature and at 10 K before heat treatment. We always found traces of absorption bands at low temperatures corresponding to the well-known electronic transitions for TD1–TD3 and the bands at 1006 and 1012 cm^{-1} . In some cases there was an indication of a band at $987\text{--}988 \text{ cm}^{-1}$. In Fig. 1 we can see that the strength of these bands correlates well with the initial interstitial oxygen concentration. Results from low temperature measurements of TD1–TD3 bands are also included. TD3 correlates well with the 1000 and 1006 cm^{-1} bands while TD1 and TD2 do not.

We present the structure of bands around 1012 cm^{-1} observed after different heat treatment times at 450°C in Fig. 2. The complex structure can be deconvoluted into three different symmetric bands at 1000, 1006, and 1012 cm^{-1} . The behavior of these bands shows similarities with a group of oxygen precipitate related bands observed in the range $1075\text{--}1225 \text{ cm}^{-1}$ after treatment at 900°C [8]. Within a broad structure we can resolve individual bands which grow up at different rates. A band at the high energy side dominates after long heat treatment times.

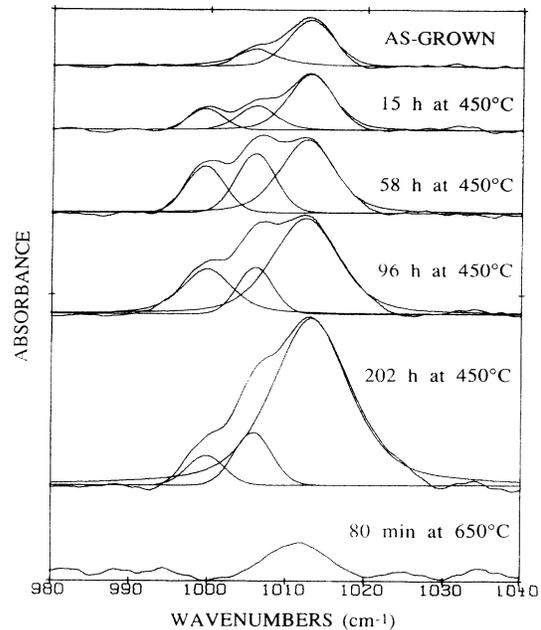


FIG. 2. Room temperature absorption spectra for samples heat treated at 450°C for different times. A reference spectrum and a spectrum for a sample post-treated at 650°C for 80 min is included.

In Fig. 2 is also presented the effect of a donor removal treatment at 650°C followed by rapid cooling which is widely used to destroy thermal donors. The bands which grew up with heat treatment at 450°C disappear and a small broad band at 1012 cm^{-1} is left together with a new band at 968 cm^{-1} . After this treatment the interstitial oxygen concentration was almost back to its initial value. It is reasonable to assume that more stable structures like the NDs [15] are developing during such a treatment which could explain a small loss of interstitial oxygen. The broad structure of the band preserved probably means that some extended clusters are not dissolved after 80 min.

We determined the total concentration of TDs from resistivity measurements after every heat treatment. This is plotted in Fig. 3 together with the sum of the strength of the bands at 1000, 1006, and 1012 cm^{-1} . We can see a good correlation between the two curves, which supports our suggestion that we have found the oxygen clusters where TDs are developing.

Looking at the individual bands (Fig. 4) we see that the 1000 and 1006 cm^{-1} bands grow up, saturate, and decrease slowly with increasing time, while the 1012 cm^{-1} band grows monotonously. These results indicate a serial formation process where one type of cluster is transformed to another. When comparing the rapid growth of the electronic bands for TD1 and TD2 as observed at 10 K [16] we can see that they do not correlate with the time scale of any of these bands. If we instead take the sum of the electronic bands related to TD3–TD6

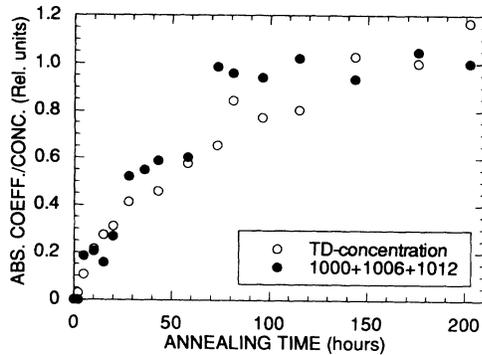


FIG. 3. The sum of the strength of the IR bands at 1000, 1006, and 1012 cm^{-1} together with the TD concentration from resistivity measurements after different annealing times at 450°C.

we get a good correlation during the growth.

The 1012 cm^{-1} band grows up more slowly, broadens, and continues to grow during long heat treatment times. The low temperature double donor bands cannot be correlated to this curve. We therefore conclude that a different type of TD is related to these clusters. After about 200 h a small decrease of the 1012 cm^{-1} band occurs simultaneously with a loss of TDs as observed by resistivity measurements. This is probably related to a transfer of the clusters to more extended neutral defects.

To explore the early clustering process and to look for TD1 and TD2 related bands we heat treated some samples at 390°C. Two new bands grew up at 975 and 988 cm^{-1} and reached a maximum about 3 and 20 h, respectively. The band at 988 cm^{-1} appeared after some treatments also at 450°C but not in a regular way. More results are under way to clarify this. Our tentative assignment of these bands is that the 975 band is related to TD1 and the 988 band to TD2.

The vibrational IR absorption bands related to interstitial oxygen and different point defects including oxygen in combination with vacancies or carbon typically increase in vibrational frequency between 300 and 10 K with about 5–30 cm^{-1} . For the oxygen precipitate bands, however, no significant change with temperature can be observed [8]. The bands reported in this study show a small ($\leq 1 \text{ cm}^{-1}$) or a nonsignificant shift from 300 to 10 K. In other words the clusters related to these bands behave like precipitates or SiO_x complexes.

Concerning the atomic composition of the clusters, IR absorption of different Si_xO_y materials has been extensively studied. In one report [12] evaporated silicon oxides were investigated after different heat treatments and the position of a broad IR absorption band was related to the ratio of Si/O as measured by other techniques. A comparison with our results suggests that the composition of our clusters should be close to SiO .

Several atomic models for the TDs have been presented [3]. One configuration for oxygen clustering that has

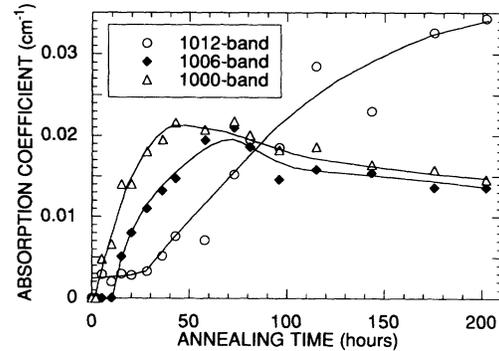


FIG. 4. The strength of the absorption bands at 1000, 1006, and 1012 cm^{-1} after different annealing times at 450°C.

been suggested is a chain of Si-O molecules developing at 450°C with a core in the compressed center giving rise to TDs [17]. Referring to the results above on vibrational frequencies of SiO , the Si-O-Si-O chain could be the configuration giving rise to the bands in the range 975–1012 cm^{-1} . This can, however, not explain the electrical activity observed. During the formation process of a SiO chain the chain will probably collapse at some point due to stress and silicon atoms will be punched out into interstitial positions and form complexes which could be the electrically active TDs. One such possible model has been theoretically studied [18] and suggested to have vibrational frequencies at 984 and 901 cm^{-1} which is close to our findings. In the same model the core of the TD is proposed to be a divalent silicon interstitial with a pair of adjacent interstitial oxygen atoms. The formation of this core forces two electrons into a lone pair p -like orbital on the divalent silicon atom. This could explain the double donor character for TDs. The loss of the double TDs as observed with low temperature IR spectroscopy for long heat treatment times could be caused by another oxygen atom bonding to the divalent silicon interstitial resulting in a single donor which finally is neutralized by yet another oxygen atom. There is a systematic change in the peak position of the oxygen vibration in these different structures of approximately 6 and 12 cm^{-1} which could be caused by the addition of more and more oxygen atoms to the cluster.

EPR has been used to study TDs [19]. Spectra like $NL8$, $NL9$, and $NL10$ have been suggested to originate from different TDs or from different charge states of a TD [20]. Because of differences in Fermi level position the relative strength of these spectra varies. In a phosphorous-doped material a good correlation between the growth of TDs as determined by resistivity measurements and the growth of the $NL10$ spectrum was observed [21]. In boron-doped samples the situation is more complex and initially $NL8$, $NL9$, and $NL10$ all grow up while at longer times $NL8$ and $NL9$ decrease and $NL10$ continues to grow [21].

From results using deep level transient spectroscopy it

has been suggested that there are different TDs related to *NL8* and *NL10* [22]. The TDs related to *NL10* have a smaller generation rate and a higher thermal stability than the TDs corresponding to *NL8*.

There are clearly similarities in the kinetic behavior of these spectra and the bands we have studied at 1000, 1006, and 1012 cm^{-1} . The initial increase of the 1000 and 1006 cm^{-1} bands is followed by a decrease which occurs on a time scale similar to the behavior of *NL8* and *NL9*. The continuous growth of the 1012 cm^{-1} band is similar to the behavior of the *NL10* spectrum. This spectrum can be observed already in as-grown materials [19] which is also the case of the 1012 cm^{-1} band.

Our conclusions would then be the following: *NL10* is originating from clusters corresponding to the 1012 cm^{-1} band. *NL8* and *NL9* are related to defects in other types of clusters like the ones corresponding to the 1000 and 1006 cm^{-1} bands.

A high concentration of carbon in silicon is known to strongly suppress the formation of TDs [13]. We included in this study samples with a concentration of both oxygen and carbon of about 5×10^{17} atoms/ cm^3 . There was no observable TD concentration even after 180 h at 450°C neither from resistivity measurements nor from low-temperature IR spectroscopy. Room temperature IR results showed no sign of the bands around 1012 cm^{-1} . Instead a new band at 1026 cm^{-1} appeared which has previously been suggested to be related to a carbon-oxygen complex with probably two oxygen atoms involved [10].

Apparently oxygen is clustering with carbon in this case, giving rise to a structure which does not affect the resistivity. For samples with an oxygen concentration of 6×10^{17} atoms/ cm^3 and carbon concentration of 6×10^{16} atoms/ cm^3 we observed both thermal donor formation and up-growing bands around 1012 and 1026 cm^{-1} after 450°C treatments. Carbon is known to eliminate mobile self-interstitials in silicon through the $\text{C}_s + \text{Si}_i \rightarrow \text{C}_i + \text{Si}_s$ reaction. If the TD core model discussed above (18) with a silicon interstitial giving rise to the double donor character is modified with a carbon atom replacing the silicon atom the core would become an electrically neutral defect. Because of the lower mass of the carbon atom as compared to the silicon this would result in a higher vibrational frequency for the involved oxygen atoms which is also observed.

In summary we have studied clustering of oxygen atoms in different configurations in silicon giving rise to vibrational bands in the range 975–1013 cm^{-1} . A kinetic study of the growth of these bands at 450°C and at 390°C reveals that three categories appear. The clusters corresponding to the 975 and 988 cm^{-1} bands develop rapidly followed by the next category, the 1000 and 1006 cm^{-1} bands. The band at 1012 cm^{-1} grows up with a slower rate and corresponds to a more temperature stable

configuration. These three categories correspond well to three different types of TDs as reported by several investigators using different techniques.

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