

## Substitutional Oxygen in Silicon

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Oxygen is present in silicon single crystals used for integrated circuit manufacturing, and has an important impact on fabrication yields and material properties. This paper suggests that oxygen is incorporated in two independent sites in the lattice. The first is termed "interstitial", and is characterized by an infrared absorption at  $9\mu\text{m}$ . The second species is inferred from an infrared absorption at  $19\mu\text{m}$ , which was originally assigned to interstitial oxygen. Comparison to carbon and boron lines indicates that the  $19\mu\text{m}$  line may be due to a fully substitutional oxygen atom.

Silicon crystals grown from the melt contain oxygen at a level of  $10^{17}$ - $10^{18}$  atoms/cm<sup>3</sup> due to the dissolution of the quartz crucible which contains the molten material. Many of the properties of silicon are strongly influenced by the presence of this element, including its mechanical strength, the formation of SiO<sub>x</sub> precipitates during device processing, and the formation of thermal donors on heating at 450°C. Many of these phenomena are difficult to understand, and experiments to determine oxygen solubility, diffusivity and other properties often show very different results, depending on the thermal history of the material. In order to better understand the behavior of oxygen in silicon, it is useful to determine how the atom is incorporated into the lattice during crystal growth.

Oxygen in silicon gives rise to infrared absorption bands at  $1106\text{ cm}^{-1}$  ( $9\mu\text{m}$ ) and  $513\text{ cm}^{-1}$  ( $\sim 19\mu\text{m}$ ) at room temperature. These are shown in Figure 1 together with the absorption from carbon. The original interpretation of Kaiser and Keck<sup>1)</sup> was that both absorptions are due to an interstitial species. However, Bosomworth and co-workers<sup>2)</sup> showed that the  $19\mu\text{m}$  line is not an absorption of interstitial oxygen, but left it unassigned. This absorption must be due to oxygen, since it shows an isotope shift when  $\text{O}^{18}$  is substituted for  $\text{O}^{16}$ , as determined by Hrostowski and Kaiser.<sup>3)</sup>

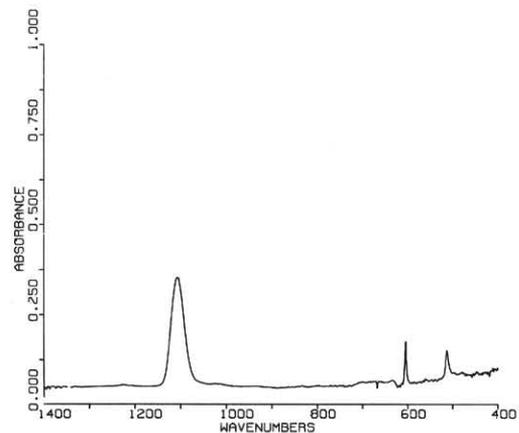


Figure 1. Room-temperature infrared spectrum of silicon containing oxygen and carbon. The differential absorbance spectrum was obtained with a Fourier Transform instrument. Peaks are seen at  $1106\text{ cm}^{-1}$  ( $9\mu\text{m}$ ) for "interstitial" oxygen, at  $607\text{ cm}^{-1}$  ( $\sim 16\mu\text{m}$ ) for carbon and  $513\text{ cm}^{-1}$  ( $19\mu\text{m}$ ) for oxygen.

An examination of the absorption frequencies of light elements in silicon shows that the  $19\mu\text{m}$  absorption is related to that of isolated carbon and boron atoms. Table I shows the absorption frequencies at low temperatures, to allow direct comparison of carbon and oxygen to boron. Figure 2 is a plot of these frequencies versus inverse square root of isotopic mass. The straight line relation indicates simple harmonic oscillator

behavior, which means that all three impurities occupy the same site in the lattice, having the full symmetry of the silicon crystal. This means either a substitutional or fully interstitial site. Evidence indicates that boron and carbon are substitutional, implying that the 19 $\mu$ m absorption corresponds to substitutional oxygen. The existence of this second oxygen species can help to explain some puzzling aspects of its behavior in silicon. The intensity of the absorption suggests that the concentration of this species is about five percent of the interstitial species in commercial silicon samples where the 9 $\mu$ m absorption coefficient is 3-4 cm<sup>-1</sup>.

TABLE I

Low Temperature Absorption Frequencies for Light Elements in Silicon

ISOTOPE	FREQUENCY (cm <sup>-1</sup> )	REFERENCE
O <sup>18</sup>	506.4	3
O <sup>16</sup>	517.3	3
C <sup>14</sup>	572.8	4
C <sup>13</sup>	589.1	4
C <sup>12</sup>	607.5	4
B <sup>11</sup>	622.8	5
B <sup>10</sup>	645.8	5

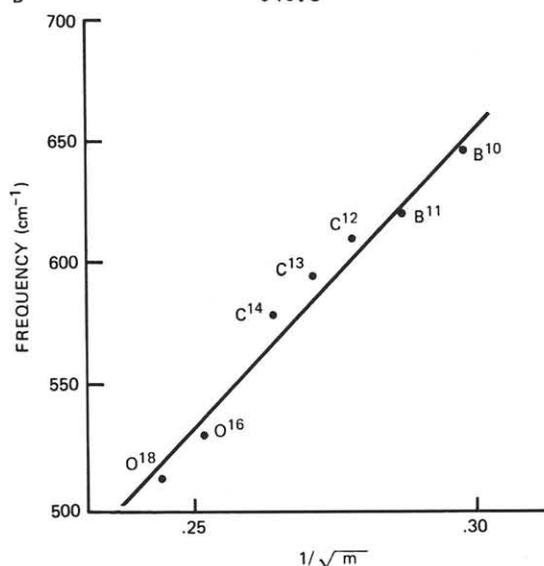


Figure 2. Infrared absorption frequencies of impurities in silicon plotted versus  $1/\sqrt{m}$ . The straight-line relation suggests that all the impurity absorptions are due to the same center, and that this center has the full symmetry of the silicon lattice. This implies either a substitutional or interstitial site for all the impurity species.

Although there is much controversy concerning the segregation coefficient of oxygen in silicon, the only direct determination by Yatsurugi and co-workers<sup>6)</sup> gave a value of  $k = 1.25$ . It is suggested here<sup>7)</sup> that such a value can be due to individual segregation coefficients for interstitial oxygen ( $k = 1.0$ ) and substitutional oxygen ( $k = 0.25$ ). This can explain inhomogeneous oxygen precipitation, anomalous diffusion coefficients, and the fluctuation of oxygen donor formation on a microscale. Substitutional oxygen should be a double donor, and a recent model<sup>8)</sup> for the donor complex suggests both substitutional and interstitial species are combined in such a way that the substitutional atom's two extra valence electrons are released on heating at 450°C.

REFERENCES

1. W. Kaiser and P.H. Keck, J. Appl. Phys. 28, 882 (1957).
2. D.R. Bosomworth, W. Hayes, A.R.L. Spray, and G.D. Watkins, Proc. Roy. Soc. A 317, 133 (1970).
3. H.J. Hrostowski and R.H. Kaiser, Phys. Rev. 107, 966 (1957).
4. R.C. Newman and J.B. Willis, J. Phys. Chem. Solids 26, 373 (1965).
5. S.D. Smith and J.F. Angress, Phys. Lett. 6, 131 (1963).
6. Y. Yatsurugi, N. Akiyama, Y. Endo, and T. Nozaki, J. Electrochem. Soc., 120, 975 (1973).
7. W.C. O'Mara in "Defects in Silicon", W.M. Bullis and L.C. Kimerling ed., Electrochem. Soc. Princeton, N.J., 1983, p. 120.
8. W.W. Keller, J. Appl. Phys. 55, 3471 (1984).