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Infrared absorption by interstitial oxygen in germanium-doped silicon crystals

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The effects of germanium doping on the 30-, 1100-, and 1200-cm^{-1} bands of Si-O-Si were investigated. The Si-O-Si centers, perturbed by the nearby Ge atoms, caused absorptions at largely shifted positions in each band. The oscillator strengths of the 1200-cm^{-1} absorptions and the peak separations between the 1100-cm^{-1} absorptions were largely reduced from the corresponding unperturbed ones. Our previously obtained model consistently explains both of the peak energies and the oscillator strengths of these absorptions. The oscillator-strength and peak-separation reduction are both ascribed to the weakening of the anharmonic coupling between the 30- and the 1100-cm^{-1} impurity modes which causes the 1200-cm^{-1} band to be their combination band.

I. INTRODUCTION

The interstitial oxygen in silicon, forming the $\langle 111 \rangle$ Si-O-Si center, causes absorption bands in the 30-, 1100-, and 1200-cm^{-1} regions.[1-4] Each band consists of a cold peak due to a transition from the ground state and hot peaks due to transitions from the thermally populated excited states. The peak energies in these bands are listed at the top of Table I ([Ge]=0 ppm). Many papers have been presented on the origin of these absorptions.[1-9] Our model,[8,9] which was an extension of the model of Bosomworth *et al.*,[1] explained them as follows: The 30-cm^{-1} band is caused by the two-dimensional (2D) anharmonic motion of oxygen in the plane perpendicular to the $\langle 111 \rangle$ axis [Fig. 1 of Ref. 9]. The 1100-cm^{-1} band is caused by the A_{2u} local mode in which the oxygen vibrates along the $\langle 111 \rangle$ axis. The anharmonic coupling of these two excitations causes the 1200-cm^{-1} band as their combination band whose *oscillator strength* (intensity per one Si-O-Si center) reflects the strength of the coupling.[8,9] The combination-band nature had been indicated previously.[1] Our calculated energy levels and optical transitions[9] explained these absorptions well.

We have pointed out that without the coupling the

TABLE I. Absorption peak energies of the Si-O-Si centers measured for [Ge] =0 and 13 400 ppm. The dashes indicate that the corresponding absorption was not observed as a clear peak. The superscript to each value indicates the measurement temperature: a, 4.5 K; b, 15 K; c, 35 K; and d, 55 K. All absorptions for [Ge]=0 ppm have already been reported in Refs. 1–6, although the peak energies are slightly different.

Types Si-O-Si center	Measured absorption peak energies						(cm^{-1})
			[Ge] = 0 ppm				
Oi-I	29.2^{a}	37.7^{c}	43.3^{d}	49^{c}	1136.4^{a}	1128.2^{b}	1121.9^{c}
					1205.7^{a}	1216.4^{c}	
			[Ge] = 13 400 ppm				
Oi-I	30.1^{a}	38.3^{c}	——	——	1135.9^{a}	1128.1^{b}	1121.2^{c}
					1206.4^{a}	1217.2^{c}	
Oi-II	33^{a}	——	——	——	1130.1^{a}	1126.2^{d}	1123^{d}
					1213^{a}	——	
Oi-III	36^{a}	——	——	——	1118.5^{a}	1115.5^{d}	——
					——	——	

three transitions corresponding to the cold and hot peaks in the 1100-cm^{-1} band [Fig. 4(a) of Ref. 9] were reduced to a pure one-phonon transition in the A_{2u} mode.[9] Hence, the separation between the cold and hot peaks in this band, which we refer to as the hot-peak separation, is a barometer of the coupling strength. If the coupling is weakened, the oscillator strength of the 1200-cm^{-1} band and the hot-peak separation of the 1100-cm^{-1} band should be decreased.

In this study, we heavily dope the crystal with germanium impurities so that a large number of the Si-O-Si centers neighbor the Ge atoms. It is expected that the presence of the Ge atoms changes the coupling strength at the nearby Si-O-Si centers. For these Ge-neighboring Si-O-Si centers, the oscillator strength for the 1200-cm^{-1} band and the hot-peak separation of the 1100-cm^{-1} band will be changed from the unperturbed ones. In addition, since the Ge atoms may affect the electronic state of the nearby Si-O-Si centers, peak-shift behavior for the Ge doping will differ from that for the elastic strains. For the elastic strains, the peak shifts in the 1100-cm^{-1} band are one order of magnitude smaller than those in the other two bands.[1] This may not be true for the present case of Ge doping. Application of our model to these Ge-perturbed Si-O-Si centers is a test of the model, since both of the peak energies and the intensities must be explained consistently. The above prediction for the nature of the coupling is also examined.

The paper has two purposes. One is to investigate how the Ge doping perturbs the absorptions in the three bands. The other is to demonstrate that our previous model[8,9] also well describes these perturbed absorptions. In Sec. II, we show that the Si-O-Si centers neighboring the Ge atoms cause the largely shifted absorptions. In Secs. III and IV, reviewing our model,[8,9] we quantitatively explain the oscillator strengths of the absorptions, and confirm that weakening of the coupling is essential for their characteristic behavior. In Sec. V, we discuss the location of the Si-O-Si centers neighboring the Ge atom. The anomalous peak-shift behavior is pointed out and discussed. The paper details our previous publication,[10] clarifying the effects of the coupling.

II. EXPERIMENT AND RESULTS

Several crystal ingots with germanium concentrations [Ge] up to 13 400 ppm were grown by the Czochralski method. We measured [Ge] by the inductively coupled plasma analysis. The position and the shape of the room-temperature oxygen peak at 1107 cm^{-1} were almost unchanged by the Ge doping, from which the interstitial oxygen concentrations [Oi] were determined according to the American Standard for Testing and Materials F121-79 procedure. The [Oi] were in the range 30.7–34.2 ppm. All samples were p type with specific resistivities 8–11 Ω cm. The carbon concentrations were below 0.1 ppm. The infrared and far-infrared absorption measurements were carried out with the Fourier transform spectrophotometers JEOL JIR-100 and BRUKER IFS-120HR, respectively. The maximum resolution was 0.1 cm^{-1} for both infrared and far-infrared measurements.

The ordinate of the spectra shown in this paper, "normalized absorbance," is the absorbance divided by the sample thickness t and [Oi], i.e., $[\log_{10}(I_0/I)]/t[\mathrm{Oi}]$. This is proportional to the absorption coefficient per unit [Oi].

A. 1100-cm^{-1} band

Figure 1 shows the [Ge] dependence of the absorption spectra in the 1100-cm^{-1} region measured at 4.5 K. New peaks grow up at 1130.1 and 1118.5 cm^{-1} as [Ge] increases. The shifts of these peaks from the original 1136.4-cm^{-1} peak are too small to be ascribed to formation of the direct Ge-O-Si or Ge-O-Ge bonds. The area intensity of each new peak was in proportion to [Ge]. Thus it would be reasonable to attribute these new peaks to two types of the Si-O-Si centers each perturbed by a nearby Ge atom. Hereafter, we refer to these Ge-neighboring Si-O-Si centers causing the new peaks at 1130.1 and 1118.5 cm^{-1} as Oi-II and Oi-III, respectively. We also refer to the Si-O-Si centers causing the original absorption at ~1136 cm^{-1} as Oi-I.

For all spectra in Fig. 1, the total area of the spectrum (total band area) for the range 1100–1150 cm^{-1} was almost constant (1.58±0.03 cm^{-2}ppm^{-1}), with growth of the new peaks canceling reduction of the original 1136-cm^{-1} peak. This suggests the following: (i) The oscillator strengths (area intensity of absorption per one Si-O-Si center) of Oi-I, -II, and -III are almost the same as each other, and almost independent of [Ge]. (ii) Only the per-

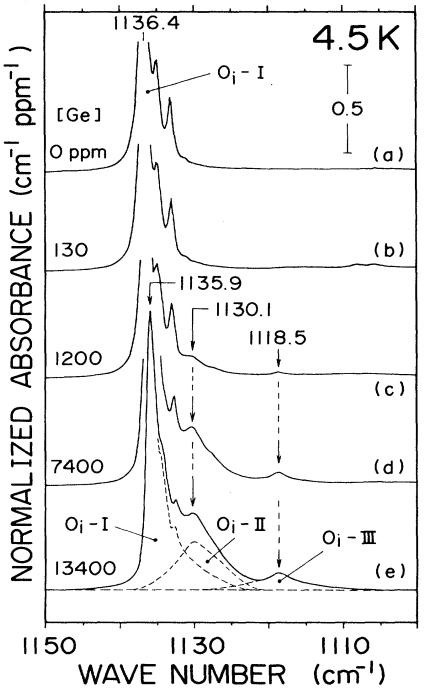

FIG. 1. Germanium concentration dependence of the 1100-cm^{-1} band measured at 4.5 K. Whole feature of the band is shown only for [Ge]=13 400 ppm. The spectra (c), (d), and (e) consist of the overlapping three components due to Oi-I, -II, and -III centers. Decomposition of the spectrum is shown for (e), where each component peak is described with a dotted line.

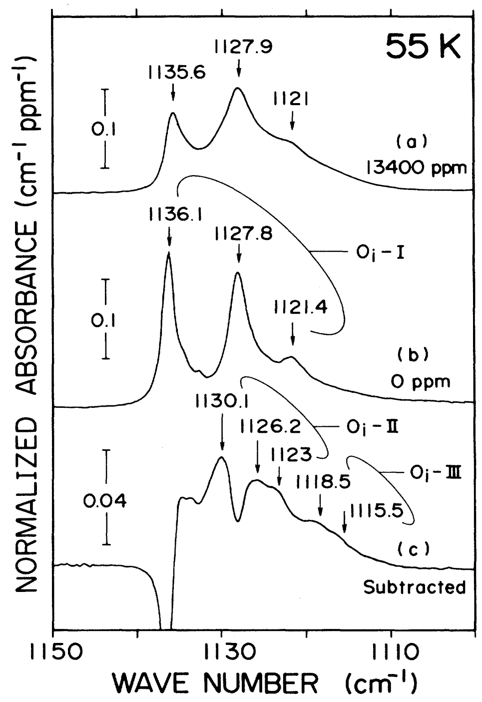

FIG. 2. The 1100-cm^{-1} bands measured at 55 K for [Ge]=13 400 ppm (*a*), and 0 ppm (*b*). The spectrum (*c*) was obtained by subtracting 70% of the spectrum (*b*) from the spectrum (*a*).

centages of Oi-I, -II, and -III centers vary with [Ge]. (iii) Accordingly, the ratio of the area of each component peak [spectrum (*e*) in Fig. 1] to the total band area is nearly equal to these percentages. (iv) For [Ge]=13 400 ppm, for example, (70±8)% of the total Si-O-Si centers exist as Oi-I, (22±8)% as Oi-II, and (8±2)% as Oi-III. The symbol ± indicates the uncertainty in determining the area of each overlapping peak.

The spectra (*a*) and (*b*) in Fig. 2 were obtained at 55 K for [Ge]=13 400 ppm and 0 ppm. Subtracting 70% (the percentage for Oi-I) of the spectrum (*b*) from (*a*), we obtain the spectrum (*c*) for the contribution from Oi-II and -III. It has the peaks at 1130.1, 1126.2, 1123, 1118.5, and 1115.5 cm^{-1}. From the similar procedures for various temperatures, we found that the temperature dependence of the peaks at 1130.1, 1126.2, and 1123 cm^{-1} was analogous to that of the cold and the hot peaks due to Oi-I [spectrum (*b*)]. Therefore, these peaks belong to Oi-II, and are assigned to the transitions similar to those for Oi-I [Fig. 4(a) of Ref. 9]. The peaks at 1118.5 and 1115.5 cm^{-1} are considered to be the set of the cold and hot peaks due to Oi-III.

In the light of our model,[8,9] the above assignments also mean that Oi-II and -III have the similar low-energy 2D excitation coupled to the A_{2u} local mode. In Fig. 2, the hot-peak separations of Oi-II and -III, ~4 and 3 cm^{-1} [spectrum (*c*)], are much smaller than that of Oi-I, ~8 cm^{-1} [spectrum (*b*)], suggesting much weaker couplings at Oi-II and -III. Accordingly, the oscillator strengths of Oi-II and -III for the 1200-cm^{-1} band are expected to be much smaller than that of Oi-I. For [Ge]=0 ppm and 13 400 ppm, Table I summarizes the peak energies.

B. 30-cm^{-1} band

Figure 3 shows the spectra of the 30-cm^{-1} band measured at 4.5 K. The plateaulike absorption in the range 32–37 cm^{-1} becomes clear as [Ge] exceeds 1200 ppm. This behavior coincides with that of the new peaks due to Oi-II and -III in the 1100-cm^{-1} band. As seen above, Oi-II and -III, having the low-energy excitation, may cause absorptions in the far-infrared region. Thus we attribute the plateau to Oi-II and -III. As in the case of the 1100-cm^{-1} band, the total band area for the range 28–38 cm^{-1} was nearly constant (0.026±0.004 cm^{-2}ppm^{-1}) for all cases of [Ge], suggesting the similar situation: the oscillator strengths of Oi-I, -II, and -III are almost the same as each other and almost independent of [Ge]. Using the determined percentages for Oi-I, -II, and -III (Sec. II A), we can well decompose the plateau into the peak at ~33 cm^{-1} due to Oi-II and the peak at ~36 cm^{-1} due to Oi-III [spectrum (*c*) in Fig. 3]. The measured hot-peak energies are given in Table I.

C. 1200-cm^{-1} band

In contrast to the preceding two bands, the total band area for the range 1193–1220 cm^{-1} greatly decreases with increasing [Ge], as shown in Fig. 4. The total band area for [Ge]=13 400 ppm is 70% of that for the 0 ppm case (0.0598 cm^{-2}ppm^{-1}). The band in the heavily doped cases consists of only two structures: the Oi-I peak

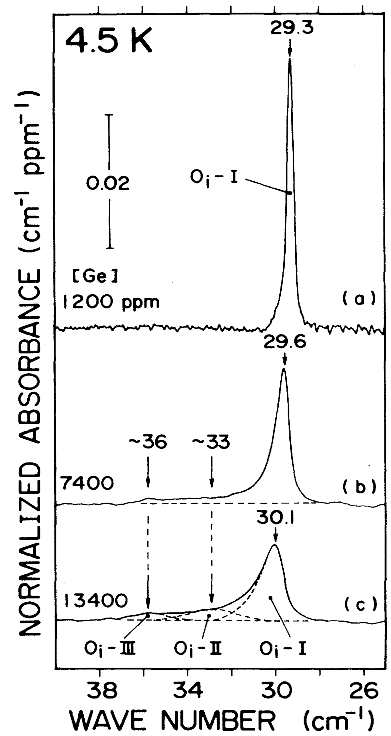

FIG. 3. Germanium concentration dependence of the 30-cm^{-1} band measured at 4.5 K.

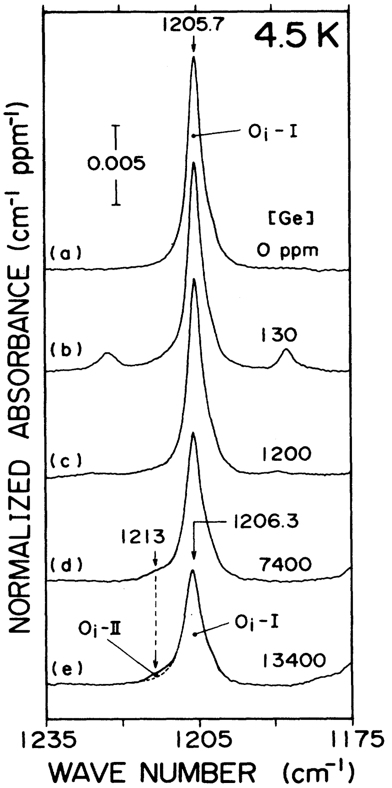

FIG. 4. Germanium concentration dependence of the 1200-cm^{-1} band measured at 4.5 K. Two small peaks in (*b*) are irrelevant, which were sometimes observed even for [Ge]=0 ppm.

at ~1206 cm^{-1} and the weak absorption at 1213 cm^{-1} assigned to Oi-II. The area intensity of the 1213-cm^{-1} absorption for [Ge]=13 400 ppm is (3±1)% of that of the 1205.7-cm^{-1} peak for [Ge]=0 ppm. On the other hand, for [Ge]=13 400 ppm, the percentage of Oi-II centers was as much as (22±8)% (Sec. II A). Thus, the oscillator strength of Oi-II is only 7–29 % of that of Oi-I ([Ge]=0 ppm), in agreement with the expected reduction of the oscillator strength (Sec. II A). The absorption by Oi-III was not observed. The hot-peak separation of Oi-III in the 1100-cm^{-1} band was smaller than that of Oi-II [spectrum (*c*) in Fig. 2], suggesting a still smaller oscillator strength at Oi-III. This would be why the absorption by Oi-III centers of small percentage [(8±2)%] was absent. The hot-peak energies are given in Table I.

III. MODEL AND CALCULATION OF THE OSCILLATOR STRENGTHS

Our model Hamiltonian[8,9] consists of three parts: the 2D anharmonic motion of oxygen in the static host-lattice potential $\alpha r^2+\beta r^4$ ($\beta>0$), the A_{2u} local phonon of the bare frequency ω, and the anharmonic interaction with the coupling constant g. Here, r is the radial displacement of oxygen from the $\langle 111\rangle$ axis. The Schrödinger equation for the total Hamiltonian is reduced to that for the 2D motion in the renormalized potential $\alpha_N r^2+\beta r^4$, which involves the effects of the coupling and depends on the A_{2u} phonon state $|N\rangle$ (phonon number N), where $\alpha_N \equiv \alpha+(\hbar g/\omega)(N+1/2)$. The eigenenergies $E_{kl,N}$ and the radial apart of the eigenfunctions $\xi_{k|l|,N}(r)\cdot[e^{il\phi}/\sqrt{(2\pi)}]\cdot|N\rangle$ are calculated, for each N, from the following reduced equation for the renormalized 2D motion:

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{d}{dr}\left[r\frac{d}{dr}\right]-\frac{l^2}{r^2}\right]+\alpha_N r^2+\beta r^4+\hbar\omega(N+\tfrac{1}{2})\right\}\xi_{k|l|,N}(r)=E_{kl,N}\xi_{k|l|,N}(r) , \tag{1}$$

where l is the $\langle 111\rangle$-axial angular momentum, and k labels the eigenstates with the same (l,N) as $|k,l,N\rangle$. For every (l,N), let k take $0,1,2,\ldots$ from the lowest energy state. For each N, Eq. (1) determines an energy-level ladder (multiplets) of the 2D motion. We solve Eq. (1) by a numerical method.[8,9]

For low enough temperatures, the oscillator strengths of the transitions $|0,0,0\rangle\rightarrow|k,0,1\rangle$ ($k=0$ for the 1100-cm^{-1} band, and $k=1$ for the 1200-cm^{-1} band) are written as[9]

$$I(0,0,0\rightarrow k,0,1)=\frac{(\hbar M^*)^2}{2}\frac{E_{k0,1}-E_{00,0}}{\hbar\omega}O_{k0,00} , \tag{2}$$

$$O_{k0,00}\equiv\left[\int_0^\infty dr\, r\xi_{k0,1}(r)\xi_{00,0}(r)\right]^2 , \quad k=0,1 . \tag{3}$$

When $g=0$, $O_{10,00}$ and the 1200-cm^{-1} transition vanish because of the orthonormality of the radial eigenfunctions. Hence for the relevant range of g, $O_{10,00}$ and the 1200-cm^{-1} oscillator strength decrease with decreasing $|g|$. From our electric dipole interaction,[9] the oscillator strength of the transition $|0,0,0\rangle\rightarrow|0,\pm1,0\rangle$ for the 30-cm^{-1} band is written as

$$I(0,0,0\rightarrow 0,\pm1,0)=\frac{(e^*)^2}{2}(E_{01,0}-E_{00,0})\times\left[\frac{\hbar^2}{2m\beta}\right]^{1/3}T_{01,00} , \tag{4}$$

$$T_{01,00}\equiv\left[\int_0^\infty dr\, r^2\xi_{01,0}(r)\xi_{00,0}(r)\right]^2 . \tag{5}$$

$O_{k0,00}$ ($k=0,1$) and $T_{01,00}$ are calculated by using the radial eigenfunctions expressed as Eq. (10) of Ref. 9.

IV. RESULTS OF CALCULATION

The parameters (α,β,ω,g) were fitted to the observed peak energies listed in Table I. For the case of [Ge]=0 ppm, which we dealt with previously,[9] we again performed parameter fitting for consistency and precision.[11] The fixed parameter values are given in Table II. As seen from the table, the value of $|g|$ of Oi-II has been largely reduced from that of Oi-I, confirming our suggestion for the weakened coupling at Oi-II (Sec. II A). For [Ge] = 13 400 ppm, Fig. 5 shows the calculated potentials and the energy levels of Oi-I and -II, together with assignment of the peaks to the transitions. We see that the calculation has well described the observed peak energies. Also for [Ge] = 0 ppm (Oi-I), disagreement between the calculated transition energies and the observed peak energies was less than 1 cm^{-1} for nearly all peaks. The peak assignment and the energy-level scheme for this case are the same as the previous ones [Fig. 4(a) of Ref. 9].

As seen from Fig. 5(b), the calculation has well described the reduced hot-peak separations of Oi-II in the 1100-cm^1 band [spectrum (*c*) in Fig. 2]. This is a result of the above-mentioned reduction of $|g|$ at Oi-II: Due to the $|g|$ reduction, the shape of the upper and the lower potentials [Fig. 5(b)] became similar to each other, which made the upper and the lower energy-level ladders similar to each other. This reduced the transition-energy differences (the hot-peak separations) for the 1100-cm^{-1} band.

TABLE II. Values of the parameters ($\alpha,\beta,\hbar\omega,\hbar g/\omega$) of the Si-O-Si centers determined for [Ge] = 0 and 13 400 ppm. The values for Oi-III were indeterminable for lack of the measured peak energies.

Types of Si-O-Si center	α (meV/Å^2)	β (meV/Å^4)	$\hbar\omega$ (meV)	$\hbar g/\omega$ (meV/Å^2)
		[Ge] = 0 ppm		
Oi-I	−15.948	241.95	143.18	−27.364
		[Ge] = 13 400 ppm		
Oi-I	−13.464	239.45	142.93	−25.899
Oi-II	−36.122	372.43	141.12	−15.730

Table III shows the calculated values for the relevant factors in the oscillator strengths (2) and (4). These values well explain the present observation that only for the 1200-cm^{-1} band, the oscillator strength of Oi-II was largely reduced from that of Oi-I. The calculated value in Table III, 17%, is in good agreement with the experimental value 7–29% (Sec. II C). The dominant factor for this reduction of the 1200-cm^{-1} oscillator strength is the reduction of $O_{10,00}$ in (2): $O_{10,00}=0.0392$ for Oi-I ([Ge] = 0 ppm) and 0.0065 for Oi-II ([Ge] = 13 400 ppm). Furthermore, this reduction of $O_{10,00}$ is also a result of the above-mentioned reduction of $|g|$ at Oi-II. This is

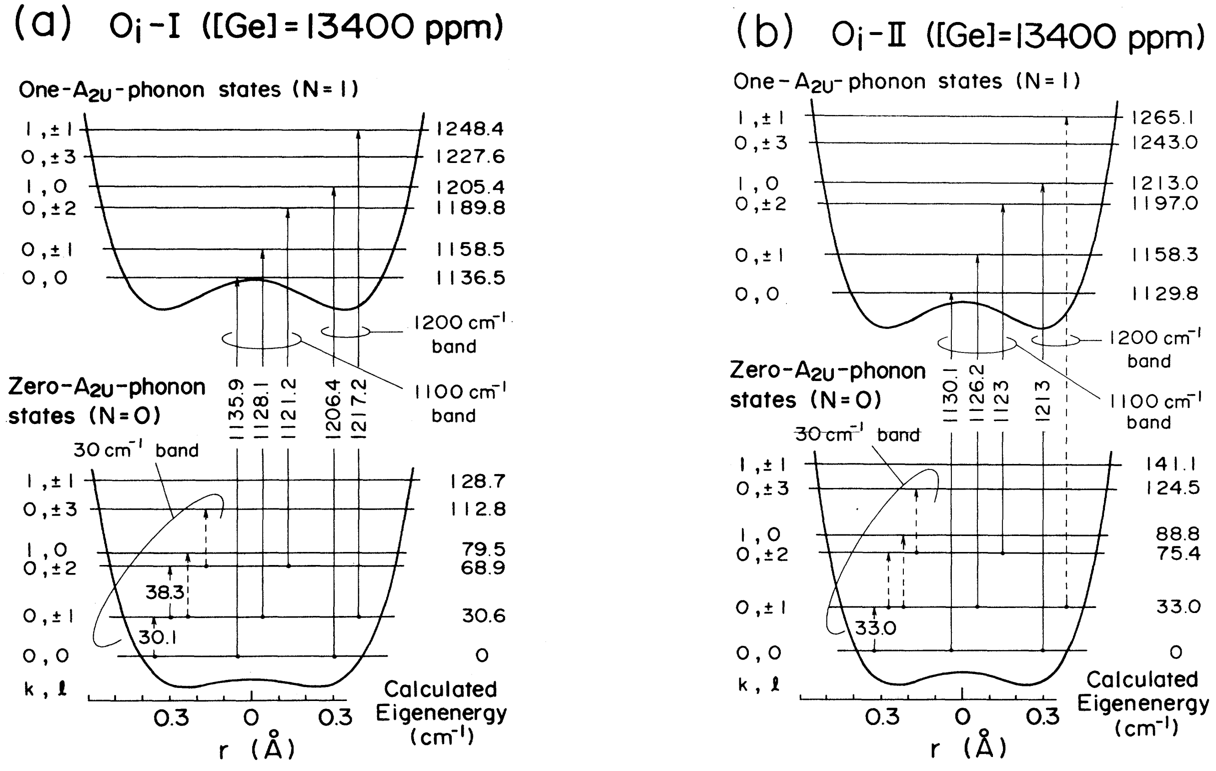

FIG. 5. Energy levels of the A_{2u}-mode-coupled 2D low-energy excitation calculated for Oi-I (*a*) and Oi-II (*b*) in the case of [Ge] = 13 400 ppm. Calculated eigenenergies relative to the ground state $E_{kl,N}-E_{00,0}$ are shown at each level. The value in each solid arrow is the measured energy (Table I) of the peak assigned to each transition. The dashed arrows indicate the transitions which could not be observed as a clear peak. The calculated renormalized potentials for the 2D motion are also shown.

TABLE III. Values of the relevant factors for the oscillator strengths calculated for the transitions $|0,0,0\rangle \rightarrow |0,0,1\rangle$ (1100-cm^{-1} band), $|0,0,0\rangle \rightarrow |1,0,1\rangle$ (1200-cm^{-1} band), and $|0,0,0\rangle \rightarrow |0,\pm 1,0\rangle$ (30-cm^{-1} band). The values for the 30-cm^{-1} band are given in units of meV/Å.^{2} The relative values are also shown in % for each band. For Oi-I ([Ge] = 0 ppm), the ratio between the 1100- and the 1200-cm^{-1} oscillator strengths is 0.043, in agreement with the corresponding experimental value 0.038, the ratio of the area intensities between the 1136.4- and the 1205.7-cm^{-1} peaks (Secs. II A and II C).

Bands (cm^{-1})	Relevant factors for the oscillator strength	Oi-I	Oi-I	Oi-II
		[Ge]=0 ppm	[Ge]=13 400 ppm	
1100	$[(E_{00,1}-E_{00,0})/\hbar\omega]O_{00,00}$	0.946	0.954	0.986
		100%	101%	104%
1200	$[(E_{10,1}-E_{00,0})/\hbar\omega]O_{10,00}$	0.041	0.034	0.007
		100%	83%	17%
30	$(E_{01,0}-E_{00,0})(\hbar/2m\beta)^{1/3}T_{01,00}$	0.253	0.254	0.252
		100%	100%	100%

confirmed as follows: It can be shown that $O_{00,00}$ and $O_{10,00}$ are the functions of $A_0 \equiv \alpha_0[2m/(\hbar\beta)^2]^{1/3}$ and $A_1 \equiv \alpha_1[2m/(\hbar\beta)^2]^{1/3}$.[12] Figures 6(a) and 6(b) show the calculated contours of $O_{00,00}$ and $O_{10,00}$ in the (A_0, A_1) plane. Each type of the Si-O-Si center specified by the parameter values (α,β,ω,g) in Table II corresponds to a point in this (A_0, A_1) plane. We can know from Fig. 6(b) the dependence of $O_{10,00}$ on the parameters (α,β,ω,g), and confirm that the reduction of $O_{10,00}$ is mainly caused by the reduction of $|g|$. We also find that the change in shape of the static potential $\alpha r^2+\beta r^4$ and the change of ω are not essential for this reduction of $O_{10,00}$.

As seen from Table III, the sum of the 1100- and the 1200-cm^{-1} oscillator strengths is kept almost constant 0.98–0.99 for all types of the Si-O-Si centers, implying a kind of conservation rule. From Figs. 6(a) and 6(b), we see that the relation $O_{00,00}+O_{10,00}=1$ holds for the area $A_1 \leq A_0$ and $O_{00,00} \gtrsim 0.8$, in the (A_0, A_1) plane. (This is an approximate relation for $\sum_{k=0,\infty} O_{k0,00}=1$ for all areas.) Hence, when the defect state of the Si-O-Si center changes in this area, the corresponding changes of $O_{00,00}$ and $O_{10,00}$ always cancel each other. Thus from (2) the total oscillator strength $\sum_{k=0,1} I(0,0,0 \rightarrow k,0,1)$ is conserved, so long as the defect state changes in this area retaining the relation $(E_{k0,1}-E_{00,0})/\hbar\omega \cong 1$, $k=0,1$. For change of the defect state from Oi-I ([Ge]=0 ppm) to Oi-II, most of the 1200-cm^{-1} oscillator strength 0.034 is converted into the 1100-cm^{-1} oscillator strength (Table III). But it is very small compared to the original 1100-cm^{-1} oscillator strength 0.946. This is why the change of oscillator strength was clearly observed for the 1200-cm^{-1} band and hardly observed for the 1100-cm^{-1} band.

V. DISCUSSION

In Figs. 1 and 3, the shift of the Oi-III peak from the original Oi-I peak is larger than that of the Oi-II peak. Thus we consider that the location of the Oi-III center is nearer to the Ge atom. For [Ge] = 13 400 ppm, the averaged number of the Si-Si bonds per one Ge atom is about 145. On the other hand, the numbers of the equivalent second-, third-, and fourth-neighbor Si-Si bonds (Fig. 7) are 12, 24, and 12, respectively. Accordingly, if an oxygen atom occupies any Si-Si bond with equal probability, the occupation probabilities for the second- and third-

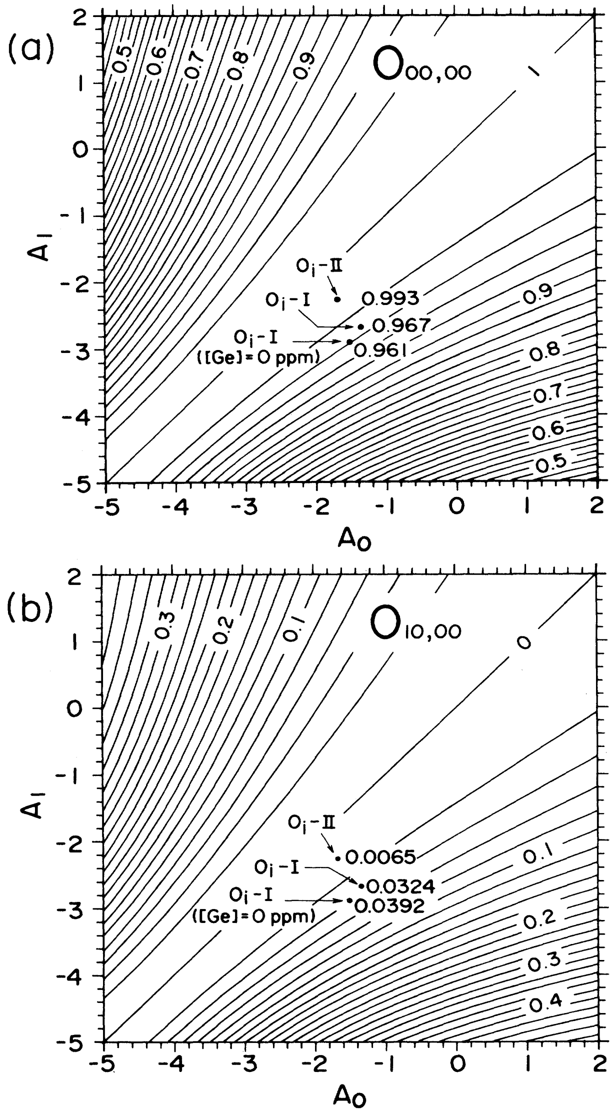

FIG. 6. Calculated contours of $O_{00,00}$ (a) and $O_{10,00}$ (b) in the (A_0, A_1) plane. The figures show the contours of $O_{00,00}$ in the range $0.5 \lesssim O_{00,00} \leq 1$, and those of $O_{10,00}$ in the range $0 \leq O_{10,00} \lesssim 0.4$. The positions (A_0, A_1) corresponding to each type of the Si-O-Si center (Table II) are indicated. The values of $O_{00,00}$ and $O_{10,00}$ at these positions are also shown.

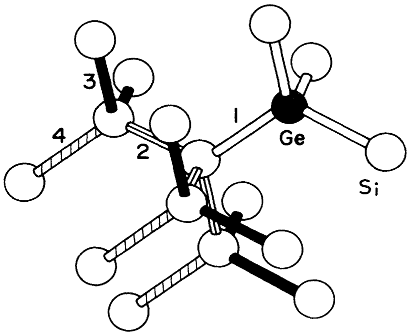

FIG. 7. Part of the silicon crystal lattice around the substitutional germanium atom, showing the first-, second-, third-, and fourth-neighbor bonds to the Ge atom.

neighbor bonds are 8.3% and 16.6%, respectively, for [Ge] = 13 400 ppm. These agree with the measured percentages of Oi-III and -II centers (8±2)% and (22±8)%, respectively. From these we consider that Oi-III is the Si-O-Si center with its oxygen at a second-neighbor bond in Fig. 7, and Oi-II is that with the oxygen at a third-neighbor bond. The absorptions corresponding to the first-neighbor occupation Ge-O-Si were not observed. The first-neighbor bonds Si-Ge may not be preferable for oxygen.

From the previous x-ray and extended x-ray-absorption fine-structure studies,[13] we see that for the third-neighbor and the outer Si-Si bonds (Fig. 7), the bond strains due to Ge doping of 13 400 ppm are the order of 0.1%. This magnitude is comparable to the elastic strain used for the experiment[1] for the stress-induced peak shift. Nevertheless, the shifts of the Oi-II peaks (-6.3, 7.3, and 3.8 cm^{-1} for the 1100- 1200-, and 30-cm^{-1} bands, respectively) and those of the Oi-I peaks for [Ge] = 13 400 ppm (-0.5, 0.6, and 0.8 cm^{-1}) cannot be described in terms of the elastic strain, as seen below. According to Ref. 1 and Table 4 given therein, the stress-induced shifts of the peaks at 1136.4, 1205.7, and 29.2 cm^{-1} (Δ_{1136}, Δ_{1206}, and Δ_{29}) always satisfy an experimental relation $\Delta_{1136} = (0.29 \pm 0.03)\Delta_{1206} - (0.12 \pm 0.05)\Delta_{29}$. However, the shifts of the Oi-II peaks and the Oi-I peaks ([Ge] = 13 400 ppm) both deviate from this relation. These anomalous peak shifts, which we have described as the change of $(\alpha, \beta, \omega, g)$, may be due to electronic mechanism. The anomalous behavior is most noticeable for the 1100-cm^{-1} band: the shifts in this band are negative and too large, considering those in the other two bands. The shift of the Oi-II peak -6.3 cm^{-1} is about one order of magnitude larger than the peak shift[1] for the elastic strain of 0.1%. These large shifts to the low-energy side resulted mainly from competition between the reductions of ω and $|g|$ (Table II). A future problem will be to clarify the mechanism that reduces ω and $|g|$.

VI. SUMMARY AND CONCLUSION

We investigated the effects of germanium doping on the 30-, 1100-, and 1200-cm^{-1} bands of the Si-O-Si center. Two types of the Ge-neighboring Si-O-Si centers caused new absorptions at the largely shifted positions in each band. Compared to the original absorptions for [Ge] = 0 ppm, the separations between the cold and the hot peaks of the new 1100-cm^{-1} absorptions were greatly reduced. Only for the 1200-cm^{-1} band did the new absorptions exhibit large change (reduction) of the oscillator strength. An application of our model[8,9] consistently explained both of the peak energies and the oscillator strengths of these new absorptions. The essential factor for the hot-peak separation reduction (1100-cm^{-1} band) and the oscillator strength reduction (1200-cm^{-1} band) is the weakening of the anharmonic coupling caused by the presence of a Ge atom near the Si-O-Si center. The peak-shift behavior greatly differed from that for the elastic strain,[1] implying that we need electronic consideration to clarify how the Ge atom influences the vibrational characteristics of the Si-O-Si center, e.g., ω and g.

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[11] In our previous calculation for [Ge] = 0 ppm (Ref. 9), the parameters were fitted to the peak energies reported in Refs. 1–6. However, some of them were slightly different depending on the authors, and different from those we measured here. For consistency and precision, we again fitted the parameters to our measured peak energies, and performed our calculation using these new parameter values.

[12] By using the dimensionless distance $R \equiv r/(\hbar^2/2m\beta)^{1/6}$, the

radial Hamiltonian in (1) is rewritten into the product of the constant $[\hbar^4\beta/(2m)^2]^{1/3}$ and the R-represented operator which contains only one parameter $A_N \equiv \alpha_N[2m/(\hbar\beta)^2]^{.1/3}$ [This procedure is analogous to that for Eq. (11) of Ref. 9.] Thus, under the normalization condition for $\xi_{k|l|,N}(r)$, the R-represented eigenfunctions $\xi_{k|l|,N}((\hbar^2/2m\beta)^{1/6}R)$ are determined by one parameter A_N. Accordingly, $O_{k0,00}$ in (3) is determined by two parameters A_0 and A_1.

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