Observation of free-exciton two-electron transitions in wavelength-derivative absorption spectra of impurity-doped silicon*

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Wavelength-derivative absorption spectra have been measured at 1.8 K for silicon doped with different donors and acceptors. The differential spectra have enabled us to reveal fine structure associated with both bound and free excitons, including a no-phonon component and momentum-conserving phonon-assisted components. The TA-phonon replicas of the bound-exciton absorption, which had not been detected for any donor in previous ordinary absorption measurements, have been observed very clearly for all the donors studied in this experiment. The LO-phonon replica of excitons bound to neutral boron acceptors has also been detected. Additional donor-induced structure has been observed nearly at the thresholds of intrinsic absorption due to the creation of free excitons with the emission of momentum-conserving TA and TO phonons. This new absorption structure, which has not been observed in acceptor- (boron- and aluminum-) doped silicon, is interpreted in terms of free-exciton two-electron transitions involving the valley-orbit states of a donor, leaving the donor in the $1s(A_1)$ singlet state. In the TA- and TO-phonon-assisted components of bound-exciton absorption in aluminum-doped silicon, a splitting has been observed, which is caused by differences in the electrostatic interaction between the $J = 0$ and $J = 2$ states formed from the two $j = 3/2$ holes by j-j coupling. The boron spectrum contains no such a splitting, but a weak splitting of the TA- and TO-phonon-assisted components of the free-exciton absorption has been observed, the origin of which is not yet understood.

I. INTRODUCTION

It is well known that the lowest interband transitions in silicon occur between the $\Gamma_{25'}$ valence-band maximum and a minimum along the Δ_1 conduction band in the $\langle 100 \rangle$ direction. The intrinsic optical-absorption spectrum near the indirect gap was precisely measured using pure silicon single crystals by Macfarlane *et al.*[1] and Dean *et al.*[2] The experimental results showed fine absorption structure which arises from indirect allowed transitions, involving the emission or absorption of momentum-conserving phonons. At low temperatures it was shown that indirect free excitons are responsible for the edge absorption, and this result was also confirmed by radiative recombination data on pure silicon crystals.[3] The role of the free exciton in the indirect band-gap absorption process in silicon was well understood by the theory developed by Elliott[4] for the spectral dependence of the absorption coefficient for indirect allowed transitions. Recently, precise measurements of the wavelength derivative of the indirect absorption edge in silicon have resolved more fine structure involving the first excited states of free excitons.[5-7] In particular, we have resolved some weak absorption thresholds attributed to the split-off band exciton with the emission of transverse optical (TO) phonons and indirect excitons accompanied by the simultaneous emission of two phonons.[7]

On the other hand, extrinsic components in silicon containing shallow donor and acceptor centers have been observed in low-temperature photoluminescence spectra which show sharp lines due to the radiative decay of excitons bound to neutral donors or acceptors. Haynes[8] reported first the presence of no-phonon as well as momentum-conserving phonon-assisted components due to these bound excitons, and after then Dean *et al.*[9,10] investigated in detail the low-temperature luminescence due to the decay of excitons bound to a variety of neutral donor and acceptor centers in silicon. In addition, they identified new radiative "two-electron" recombination processes, in which an interbound state transition of a donor electron or acceptor hole is induced during the recombination of both bound and free excitons. Although bound-exciton transitions have also been observed in low-temperature absorption spectra as a sharp absorption line,[11] the absorption due to bound excitons is very weak even for most properly doped silicon.

This paper presents the results of highly-sensitive wavelength-modulated absorption measurements near the indirect edge of impurity-doped silicon, in which "anomalous" structure has been found for the first time nearly at the thresholds of intrinsic free-exciton absorption with the emission of momentum-conserving transverse acoustic (TA) and TO phonons. This structure has been observed at 1.8 K for silicon containing phosphorus, antimony, or arsenic donors between 10^{16} and 10^{18} cm^{-3}, but not observed for boron and aluminum acceptors. The donor-induced components are overlapped with the related intrinsic component of free excitons. This would be the reason why

this structure has not been observed in luminescence spectra from donor-doped silicon, where the components occur at the same energies as the free-exciton components and would be masked by them. The origin of this newly observed donor-induced structure is interpreted in terms of free-exciton two-electron transitions involving the valley-orbit states of a donor in silicon, on the basis of the experimental result that this structure has not been observed for boron and aluminum acceptors in silicon.

II. EXPERIMENTAL

Samples of single-crystal silicon doped with phosphorus, antimony, arsenic, boron, or aluminum in the range 10^{15}–10^{18} cm^{-3} were used in this experiment. The thickness of the specimens, between 0.1 and 1.0 cm, was used to cover a wide range of absorption coefficient near the indirect band gap of silicon. The impurity concentration was obtained from the sample resistivity at room temperature by using resistivity-versus-impurity-concentration curves measured by Sze and Irvin.[12] The preparation of specimens and subsequent absorption measurements were carried out in essentially the same way as described in our previous papers.[13,14] Wavelength-derivative absorption spectra of doped silicon were measured at 1.8 K by immersing the specimen in the pumped liquid helium (and sometimes at 77 K). All wavelength-derivative absorption spectra presented here were taken with a 2-Å wavelength modulation induced by vibrating a quartz plate put inside the exit slit of a grating monochromator.

III. RESULTS AND DISCUSSION

A. Absorption associated with neutral donors

The wavelength-derivative absorption spectrum, taken at 1.8 K, of a silicon crystal containing 1.8 $\times 10^{17}$ cm^{-3} phosphorous donors is shown in Fig. 1. The low-temperature spectrum consists of three major components, in each of which excitons bound to neutral phosphorus-donor centers are clearly observed. The no-phonon (B_P^0) and momentum-conserving TA- and TO-phonon-assisted (B_P^{TA} and B_P^{TO}) bound-exciton components locate, respectively, at the energies of 1.1499, 1.1685, and 1.2078 eV. These energies were estimated from the zero-crossing point in the respective component, corresponding to a peak in the ordinary absorption spectrum. Complicated structure can be seen on the higher-energy side of each phonon-assisted bound-exciton component. It seems to contain an anomalous component overlapped with the intrinsic free-exciton component,

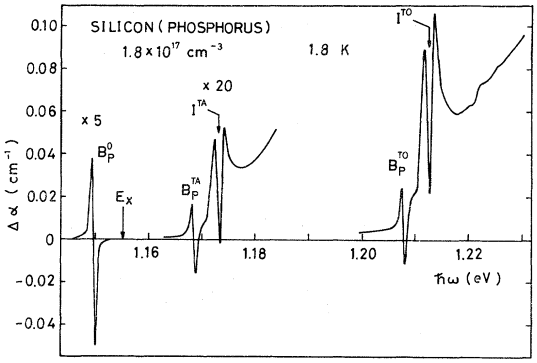

FIG. 1. Wavelength-derivative absorption spectrum of a silicon crystal containing 1.8×10^{17} cm^{-3} phosphorus donors taken at 1.8 K. Arrows labeled E_x, I^{TA}, and I^{TO} denote the exciton energy gap and the intrinsic free-exciton absorption thresholds involving momentum-conserving TA- and TO-phonon emission, respectively. Notation B indicates components associated with bound excitons due to no-phonon (B_P^0) and phonon-assisted (B_P^{TA} and B_P^{TO}) transitions.

and the anomalous component appears strongly in the vicinity of the threshold of the intrinsic free-exciton absorption.

The differential absorption spectrum of Fig. 1 resolves clearly all the no-phonon, TA-, and TO-phonon-assisted components associated with excitons bound to neutral phosphorus-donor centers. The TA-phonon replica has been resolved for the first time in the absorption spectrum of phosphorus-doped silicon. In general, the bound-exciton absorption in silicon containing ~10^{17} cm^{-3} donors is very weak,[15] and particularly the TA replica which is weaker than both the no-phonon component and TO replica has not yet been observed for any donor in silicon in previous ordinary absorp-

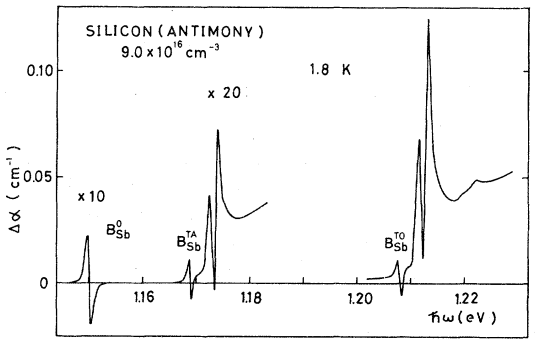

FIG. 2. Low-temperature wavelength-derivative absorption spectrum of a silicon crystal containing 9.0 $\times 10^{16}$ cm^{-3} antimony donors. Notation B indicates a no-phonon component (B_{Sb}^0) and momentum-conserving phonon-assisted components (B_{Sb}^{TA} and B_{Sb}^{TO}) of the bound excitons.

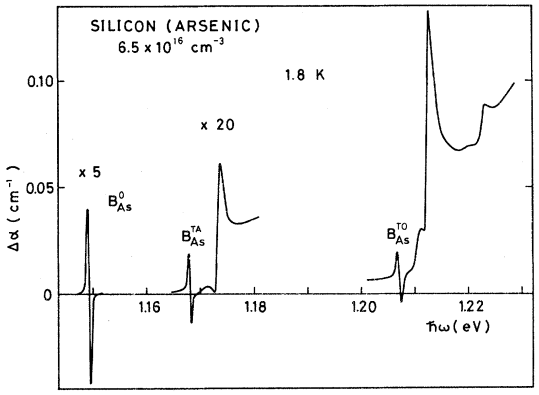

FIG. 3. Low-temperature wavelength-derivative absorption spectrum of a silicon crystal containing 6.5 $\times 10^{16}$ cm^{-3} arsenic donors. Notation B indicates a no-phonon component (B^0_{As}) and phonon-assisted components (B^{TA}_{As} and B^{TO}_{As}) of the bound excitons.

tion measurements.[11] In our wavelength-derivative absorption spectra taken at 1.8 K, the TA-phonon replicas of bound excitons for antimony and arsenic donors have also been observed very clearly, as shown in Figs. 2 and 3. The TA-phonon components due to excitons bound to antimony- and arsenic-donor centers are at 1.1687 and 1.1676 eV, respectively, in agreement with the estimates from their no-phonon and TO-phonon components and also from luminescence data.[10] The energies of the no-phonon and TO-phonon-assisted transitions of the bound excitons are of course consistent with previous data.[10,11] These energies of the bound-exciton transitions in silicon are summarized in Table I. This kind of wavelength-modulation method would therefore be helpful for a study of the weak absorption due to bound excitons as well as indirect free excitons whose faint absorption thresholds can be transformed into a sharp peak by measuring the wavelength derivative of the spectrum.

In the low-temperature differential absorption spectrum of Fig. 1, anomalous components are observed nearly at the thresholds of TA- and TO-phonon-assisted absorption of intrinsic free excitons, labeled I^{TA} and I^{TO}. These newly observed components are of comparable magnitude of those of free excitons and bound excitons, and overlapped with the related free-exciton component. It would be due to this overlapping that these components have not been separated from the corresponding free-exciton component in a detailed study of luminescence spectra from doped silicon.[9,10] These new wavelength-derivative absorption components have been observed for phosphorus-donor concentrations between 10^{16} and 10^{18} cm^{-3}, as shown in Fig. 4. In silicon containing 6.0×10^{15} cm^{-3} phosphorus donors, the spectrum is nearly the same as that of intrinsic silicon,[6] and the intrinsic components associated with the exciton ground state with the emission of longitudinal optical (LO) phonons (I^{LO}) and the $n=2$ exciton excited state with the emission of TO phonons ($I^{TO}_{n=2}$) can be still clearly seen in the spectrum. These intrinsic free-exciton components exhibit a peak corresponding to the photon-energy derivative of the square-root dependence of the absorption coefficient for an indirect allowed exciton: the finite amplitude of the peak is due to lifetime broadening.[16] It has been demonstrated in our previous work[6] that lineshapes of the wavelength derivative of the intrinsic free-exciton absorption can be quantitatively analyzed by the derivative of the absorption coefficient with respect to photon energy. As a result, the transition matrix elements in the indirect process as well as the threshold energies have been estimated.

As can be seen in Fig. 4, there appears an additional component at the phosphorus concentration of 2.2×10^{16} cm^{-3}, which is overlapped with the free-exciton component. This feature becomes clear with increasing phosphorus-donor concentration, but all the components disappear at more than 10^{18} cm^{-3} because of large broadening. Of course, the ordinary, not differential, absorption increases in proportion to the phosphorus concentration even in the high donor-concentration region. Similar behaviors of the concentration dependence were also obtained for the TA-phonon component.

These new phosphorus-donor-induced components which are overlapped with the related free-exciton component were also observed for antimony and arsenic donors, as shown in Figs. 2 and 3. We chose the donor concentration of ~10^{17} cm^{-3}, which is most suitable for a study of the new donor-induced structure, as expected from the data of Fig. 4. The concentration of arsenic donor is a little less than the remainders as more suitable arsenic-doped silicon crystals were not available to us. The new donor-induced components are seen for all the donors at the same energies as the thresholds of intrinsic free-exciton absorption,

TABLE I. Transition energies of excitons bound to neutral donor centers in silicon, determined from the wavelength-derivative absorption spectra taken at 1.8 K. The notation NP indicates no-phonon transitions.

Impurity	Transition energy (eV) NP	TA	TO
Antimony	1.1502	1.1687	1.2080
Phosphorus	1.1499	1.1685	1.2078
Arsenic	1.1491	1.1676	1.2071

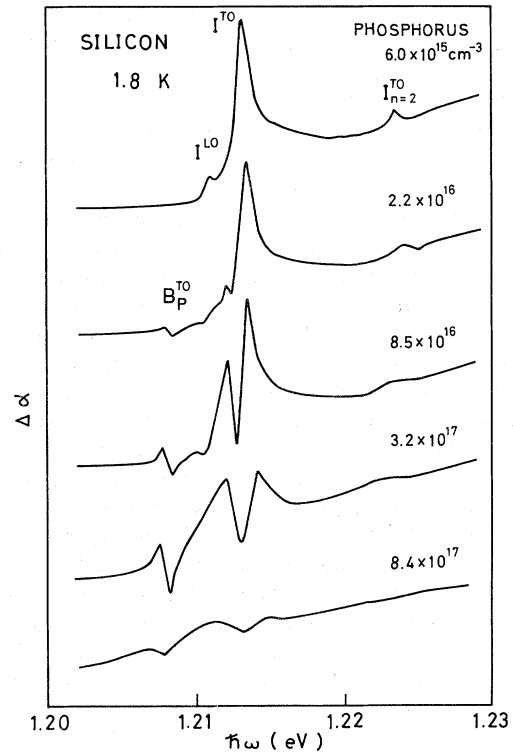

FIG. 4. TO-phonon-assisted component in wavelength-derivative absorption spectra of phosphorus-doped silicon dependent on phosphorus concentration. Intrinsic components associated with the exciton ground state with the emission of LO phonons (I^{LO}) and the $n=2$ exciton excited state with the emission of TO phonons ($I^{TO}_{n=2}$) can be still clearly seen in the spectrum for 6.0×10^{15} cm^{-3} phosphorus concentration.

though the components for arsenic are relatively weak compared with phosphorus and antimony. The weakness in the case of arsenic donor would be due, mainly, to the smaller arsenic concentration used here, as expected from comparison of Fig. 3 and interpolation between the second and third spectrum in Fig. 4. Another effect may contribute, in part, to the weakness in view of the larger oscillator strength of the bound-exicton transitions due to arsenic donors rather than those of phosphorus and antimony donors,[11] but it seems reasonable to consider that the weakness is mostly due to a concentration effect.

B. Free-exciton two-electron transitions

In a detailed study of the low-temperature luminescence from silicon doped with donors and acceptors, new radiative recombination processes were identified by Dean *et al.*[9,10] They found additional weaker impurity-induced luminescence lines, besides strong lines due to the recombination of excitons bound to neutral donor and acceptor centers which had already been recognized by Haynes.[8] These newly observed luminescence lines were identified with "two-electron" recombination processes, in which an interbound state transition of a donor electron or acceptor hole is induced during the recombination of both bound and free excitons. The first experimental observation of the two-electron luminescence process had previously been obtained by donor-doped gallium phosphide only in the recombination of bound-exciton states.[17] Also, Dean *et al.*[9,10] demonstrated that unidentified lines reported by Benoit à la Guillaume and Parodi[18] in the edge luminescence of doped germanium can be interpreted by the two-electron processes.

The wavelength-derivative absorption spectra of impurity-doped silicon show anomalous structure nearly at the thresholds of the intrinsic free-exciton absorption involving TA- and TO-phonon emission, as can be seen from Figs. 1–3. Such anomalies are observed only in the spectra of donor-doped silicon, but not observed for acceptor-doped silicon as will be shown in the next section. This fact suggests that they are associated with the valley-orbit states of a donor since there are no valley-orbit states for acceptors in silicon. Furthermore, these anomalies can be thought of as being related to free excitons rather than bound excitons, because they appear, for all the donors studied in this experiment, nearly at the same energies as the intrinsic free-exciton absorption thresholds. These behaviors lead to the interpretation that two-electron transitions involving a free exciton and the valley-orbit states of a donor are responsible for the anomalous components observed in the wavelength-derivative absorption spectra. This free-exciton two-electron transition involves a free exciton and the valley-orbit states of a donor in which the donor is left in the lowest $1s(A_1)$ singlet state.

The free-exciton two-electron transition involving no change in the valley-orbit states of a donor was not definitely observed in the luminescence from doped silicon, while new extrinsic luminescence bands were obtained and identified with another type of free-exciton two-electron recombination process involving the $1s(A_1)$-$1s(E)$ transition of a donor electron during the recombination of a free exciton.[9,10] However, the existence of the free-exciton two-electron transition involving no change in the valley-orbit states, which seems to be responsible for the anomalous components observed in this experiment, was discussed by Dean *et al.*,[10] based upon a weak luminescence band at the free-exciton energy gap. The weak luminescence which was observed only for phosphorus donor was identified with the no-phonon compo-

nent of free-exciton two-electron recombinations involving no change in the valley-orbit states. The phonon-assisted components were not obtained in the luminescence spectra, since they occur at the same energies as the related free-exciton components and would be masked by them. From the estimate of the relative intensity ratio for the no-phonon components associated with two types of free-exciton two-electron transitions observed in phosphorus-doped silicon, they assumed that the strength of the free-exciton two-electron transition in which the donor is left in the $1s(A_1)$ valley-orbit state is limited by a selection rule.

In the free-exciton absorption process, there are, in general, some differences between the no-phonon and phonon-assisted components. It is therefore not straightforward to expect, from the results on the no-phonon two-electron component in the luminescence spectra, that the strength of the corresponding phonon-assisted components is also limited similarly to the no-phonon component. Considering a momentum-conservation law in the indirect transition process, it would be easier to create a free exciton with help of momentum-conserving phonons rather than in the no-phonon process even if the momentum conservation is relaxed by doping impurities. In fact, no-phonon absorption of free excitons in silicon is very weak and has not been detected by high-resolution measurements of near band-gap absorption of silicon doped with donor or acceptor impurities.[11] There have been some exceptions among a variety of impurities studied there, however. A weak absorption step due to the no-phonon creation of free excitons has been detected only for bismuth and gallium impurities. The no-phonon free-exciton absorption band induced by 2.3×10^{16} cm^{-3} bismuth donors is relatively strong, but only about 20% of the strength of the TA-phonon-assisted intrinsic components. Furthermore, a weak no-phonon radiative recombination line of free excitons has also been observed in the low-temperature luminescence spectra of n-type doped silicon crystals.[10] However, the intensity is very small compared with those of the TA-phonon-assisted intrinsic components. Hence, considering these experimental results, it is not unlikely that the new donor-induced phonon-assisted components arise from free-excition two-electron transitions involving no change in the valley-orbit states, in spite of the absence of the corresponding no-phonon components.[19] This explanation results in the view that the intrinsic free-exciton luminescence bands observed by Dean *et al.*[10] contain significantly two-electron components. The experimental observation of the two-electron transition only in the wavelength-derivative absorption spectra may suggest that the phonon-assisted components exhibit quite different lineshapes of absorption from those of free excitons.

Figure 5 shows details of the TO-phonon-assisted component in the wavelength-derivative absorption spectrum for phosphorus-doped silicon. Around the $n=2$ excited state of free excitons, labeled $I^{TO}_{n=2}$, additional structure can be seen, which appears by doping phosphorus donors in silicon. In luminescence data[10] the most prominent two-electron transition has been seen for TO-phonon-assisted free-exciton two-electron recombinations involving excitation between valley-orbit states of the phosphorus donor. It locates at 13.5 meV below the intrinsic free-exciton luminescence band. In the absorption spectrum the transition is expected to be observed at the energy position marked by the arrow, labeled $I^{TO}+13.5$ meV, in Fig. 5. Hence a weak threshold observed at 1.2260 eV, labeled $B^{TO}_{P(1)}$, may be caused by this free-exciton two-electron process involving the $1s(A_1)-1s(E)$ transition of the donor electron. According to the luminescence data, the most prominent bound-exciton two-electron transition would also be observed in the absorption spectrum at the position

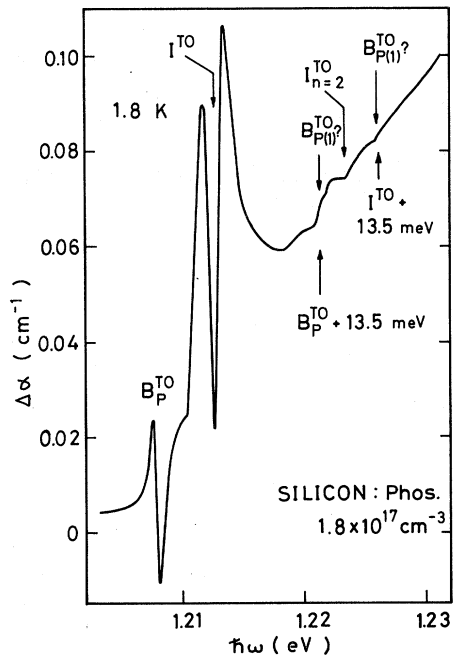

FIG. 5. Detailed TO-phonon-assisted component in the wavelength-derivative absorption spectrum of Fig. 1. Notation is consistent with Figs. 1 and 4, except $B^{TO}_{P(1)}$ indicating two-electron components of free and bound excitons involving the $1s(A_1)$-$1s(E)$ transition in the valley-orbit states of the phosphorus donor (see text).

marked by the arrow, labeled $B_{P(1)}^{TO}+13.5$ meV. Structure seen in the vicinity of 1.221 eV may therefore be explained by this bound-exciton two-electron transition. These identifications are not definite, compared with those in the luminescence study, because such additional structure is overlapped with the continuously increasing component of the free-exciton absorption. However, it is in any event most probable that these two-electron transitions are related to the additional structure observed on the higher-energy side of the threshold of the intrinsic free-exciton absorption with the emission of TO phonons.

It is important to note here that there is another possible explanation of the above mentioned anomalous structure observed in donor-doped silicon: they might be interpreted as due to "interference" between two different paths in the creation of a free exciton. In the free-exciton absorption process in donor-doped silicon, two paths to the same final state of a free exciton can be considered; one is the same normal process as in the intrinsic free-exciton absorption, and another is the process that a free exciton is created via a neutral donor center, leaving the donor state unchanged. This interference effect, which was suggested by Hopfield *et al.*[20] to interpret anomalous absorption structure observed in nitrogen-doped gallium phosphide, occurs when there are two different paths to the same final state or when there are at the same energy two classes of states which are mixed by some perturbation. The interference between the different paths to the same final state of a free exciton might be thought of as the origin of the anomalous structure observed nearly at the thresholds of intrinsic free-exciton absorption with the emission of TA and TO phonons. In order to interpret more completely this anomalous structure further experiment must be performed, and a more detailed luminescence study, such as recent investigations where many extremely sharp luminescence lines have been detected for lightly-doped silicon,[21,22] might be helpful for the complete explanation.

C. Absorption associated with neutral acceptors

Figure 6 shows the wavelength-derivative absorption spectrum of a silicon crystal containing 2.5×10^{17} cm^{-3} boron acceptors. The principal bound-exciton components in the spectrum are very prominent compared with those in the donor spectra discussed above (Figs. 1–3). Even the LO-phonon-assisted bound-exciton component has been clearly obtained, which was not detected for any donor-doped silicon in this study. Because of the significant strength of the bound-exciton components for boron acceptor, the principal components of excitons bound to neutral boron acceptors (the no-phonon component, and the TA and TO replicas) have been clearly observed even at 77 K, though the LO-phonon component could not be detected at the temperature. As is seen in Fig. 6, extrinsic components at the intrinsic free-exciton absorption thresholds labeled I^{TA} and I^{TO} appear a little different from the above mentioned donor-induced phonon-assisted components. Each free-exciton component in the wavelength-derivative absorption spectrum splits into two peaks for both the TA- and TO-phonon-assisted transition. These features differ from those of the donor-induced structure in which an anomalous component is superposed on the free-exciton component, as is seen in the spectra of Figs. 1–3. To make clear the difference between boron-doped and donor-doped silicon, the TO-phonon-assisted component for three different boron concentrations is shown in Fig. 7. Contrary to a sharp dip arising from an anomalous component at the intrinsic free-exciton absorption thresholds for donor-doped silicon, such sharp structure does not appear for boron acceptors. Although the dip between the I_1^{TO} and I_2^{TO} peak in Fig. 7 appears in much the same energy position as the large negative dip in the donor spectra discussed above, the dip in the boron spectrum seems essentially different from that in the donor spectra. In the case of the large dip in the donor spectra, it sometimes exceeds the zero differential absorption line and indicates a negative sign in the differential absorption coefficient, as is clearly seen in the TA-pho-

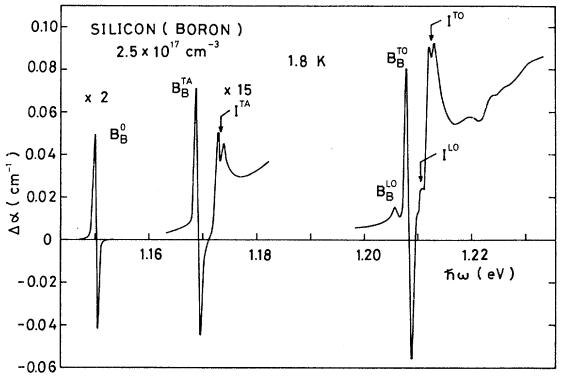

FIG. 6. Wavelength-derivative absorption spectrum of a silicon crystal containing 2.5×10^{17} cm^{-3} boron acceptors taken at 1.8 K. Arrows labeled I^{TA}, I^{LO}, and I^{TO} denote the intrinsic free-exciton absorption thresholds involving momentum-conserving TA-, LO-, and TO-phonon emission. The bound-exciton component with the emission of LO phonons is clearly seen, together with the no-phonon component (B_B^0) and phonon-assisted components (B_B^{TA} and B_B^{TO}).

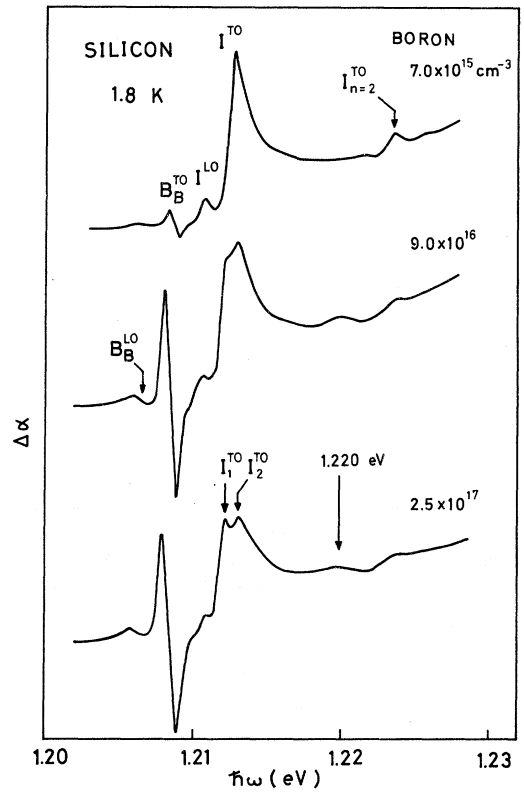

FIG. 7. Low-temperature wavelength-derivative absorption spectra for silicon crystals containing boron acceptors with three different concentrations in the vicinity of the TO-phonon-assisted free-exciton absorption threshold (I^{TO}). Notation is consistent with Fig. 6. The intrinsic free-exciton component is split into two subcomponents (I_1^{TO} and I_2^{TO}) by doping $\sim 10^{17}$ cm^{-3} boron acceptors in silicon (see text).

non-assisted components in the phosphorus and antimony spectra of Figs. 1 and 2. This indicates that the absorption curve decreases with photon energy at the energy of the negative dip. In fact, from comparison of the absorption, not differential, spectra of near-intrinsic and donor-doped silicon crystals, the superposition of additional absorption on the intrinsic absorption curve has been observed in the donor-doped spectrum in the vicinity of the energy position where the sharp negative dip was observed. This fact supports the identification that the large negative feature is due to the superposition of an additional component on the intrinsic free-exciton components.

In the boron spectrum there appears no such large negative structure and hence there is no indication of the superposition of an additional component though a weak splitting of the intrinsic free-exciton components has been observed. The splitting has also been observed for the TA-phonon-assisted free-exciton component shown in Fig. 6. The magnitude of the splitting is about 1 meV. Although it is possible to consider that the splitting of the phonon-assisted free-exciton components may be caused by some perturbation, like inhomogeneous internal strain, in boron-doped silicon crystals used here, further investigation is necessary to establish the identification of the splitting observed in the boron spectra.

Figure 8 shows the wavelength-derivative absorption spectrum of a silicon crystal containing 2.0×10^{17} cm^{-3} aluminum acceptors. The most important thing to note in the aluminum spectrum is that momentum-conserving (TA and TO) phonon-assisted components of free-exciton absorption contain no large negative feature as observed in the donor spectra (see Figs. 1–3), and that the components appear quite similar to those of free-exciton absorption in near-intrinsic silicon crystals. The absence of the negative feature at the intrinsic free-exciton absorption thresholds I^{TA} and I^{TO} leads to the identification that the negative feature arises from free-exciton two-electron transitions involving the valley-orbit states of a donor, leaving the donor in the $1s(A_1)$ singlet state. This result also supports the view that a weak splitting observed for phonon-assisted free-exciton components in the boron spectra is caused by some entirely different origin, as mentioned above.

The aluminum spectrum of Fig. 8 shows much more fine bound-exciton structure than the donor and boron spectra discussed above. Split no-phonon ($B^0_{Al(1)}$ and $B^0_{Al(2)}$), and phonon-assisted ($B^{TA}_{Al(1)}$, $B^{TA}_{Al(2)}$, $B^{TO}_{Al(1)}$, and $B^{TO}_{Al(2)}$) bound-exciton components can be clearly seen in Fig. 8. The energy

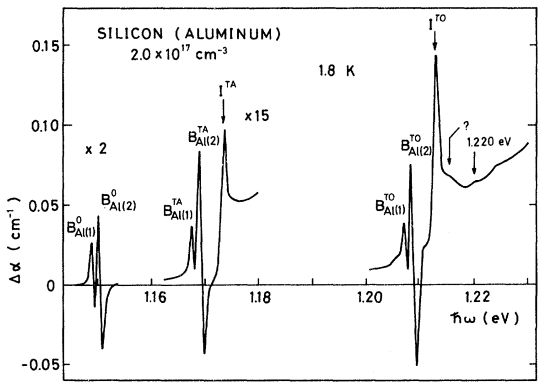

FIG. 8. Low-temperature wavelength-derivative absorption spectrum of a silicon crystal containing 2.0×10^{17} cm^{-3} aluminum acceptors. The three principal bound-exciton components are, respectively, split into two subcomponents ($B_{Al(1)}$ and $B_{Al(2)}$), which arise from the two states, $J=0$ and $J=2$, constructed from the spin-spin interaction between two $j=\frac{3}{2}$ holes.

TABLE II. Transition energies of excitons bound to neutral acceptor centers in silicon, determined from the wavelength-derivative absorption spectra taken at 1.8 K. The bound-exciton absorption components in aluminum-doped silicon are split into two subcomponents (see text).

Impurity	Transition energy (eV) NP	TA	LO	TO
Boron	1.1504	1.1691	1.2063	1.2085
Aluminum	1.1507	1.1694		1.2088
	1.1493	1.1680		1.2073

separation between each $B_{Al(1)}$ and $B_{Al(2)}$ subcomponent is 1.4 meV for the no-phonon and phonon-assisted transitions, as is seen in Table II. The value for the TO-phonon component is less accurate than the remainders because it contains the contribution from the LO-phonon component not definitely observed in the spectrum. On the lower-energy side of the $B^{TO}_{Al(1)}$ component, this LO-phonon-assisted component of bound-exciton absorption can be weakly seen, which is expected to be located 2.2 meV below the TO component. The splitting of the bound-exciton absorption is consistent with the splitting resolved in high-resolution absorption measurements,[11] which was interpreted, based on data for some kinds of acceptor-exciton complexes, by differences in the electrostatic interaction between the $J=0$ and $J=2$ states formed from two $j=\frac{3}{2}$ holes by j-j coupling. Hence, the observed splitting for the no-phonon and phonon-assisted bound-exciton absorption in the aluminum spectrum can be understood by the hole-hole j-j splitting model. This type of splitting in acceptor-exciton complexes should be observed also for boron acceptor though the splitting is small, 0.9 meV according to the previous data.[11] However, it could not be observed for both no-phonon and phonon-assisted components in the differential absorption spectra for boron-doped silicon studied here. This fact may therefore indicate that the absorption bands of excitons bound to neutral boron acceptors are broadened by some unidentified perturbation, and this perturbation may also cause the splitting observed for the phonon-assisted free-exciton components.

On the higher-energy side of the TO-phonon-assisted free-exciton absorption threshold, there appears additional weak, but clearly observed, components marked by the arrow at 1.220 eV, as can be seen in Figs. 7 and 8. The components have not been obtained for 7.0×10^{15} cm^{-3} boron concentration and hence it would not be due to the intrinsic absorption. There is no corresponding bound-exciton luminescence bands which can be assigned to these components, in the luminescence spectra from boron- and aluminum-doped silicon.[10] In the luminescence spectra, there is of course no free-exciton luminescence bands corresponding to these components observed at 1.220 eV. The aluminum spectrum shows another additional component marked by the arrow in Fig. 8, just above the TO-phonon-assisted free-exciton absorption threshold I^{TO}. As can be seen in Fig. 5, there is also an unidentified component around this energy region for phosphorus-doped silicon. However, there is at present no explanation for the origin of these unidentified components in the differential absorption spectra of impurity-doped silicon.

IV. SUMMARY

We have reported the experimental observation of wavelength-derivative absorption spectra of impurity-doped silicon. The low-temperature spectra have enabled us to resolve fine structure associated with both bound and free excitons. In particular, new donor-induced components have been observed nearly at the thresholds of intrinsic absorption due to the creation of free excitons with the emission of momentum-conserving TA and TO phonons. The components, which have been observed for antimony, phosphorus, and arsenic donors, but not observed for boron and aluminum acceptors, had not been detected in previous ordinary absorption measurements for impurity-doped silicon. The behaviors of the newly observed structure in the differential absorption spectra lead to the interpretation that it arises from free-exciton two-electron transitions involving the valley-orbit state of a donor, leaving the donor in the $1s(A_1)$ valley-orbit state. In the TA- and TO-phonon components of the bound-exciton absorption in aluminum-doped silicon, a splitting has been observed, which is caused by differences in the electrostatic interaction between the $J=0$ and $J=2$ states formed from the two $j=\frac{3}{2}$ holes by j-j coupling. The boron spectrum contains no such a splitting, but a weak splitting in the free-exciton components has been observed, which seems different from the newly observed structure in the donor spectra. The splitting may be caused by some perturbation, like inhomogeneous internal strain, in boron-doped silicon crystals used here, but its origin is not yet understood. Additional weak structure has been detected in the TO-phonon-assisted components in both donor- and acceptor-spectra, the origin of which could not definitely be understood. Further study must be made to explain the whole structure observed in this wavelength-derivative absorption experiment.

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