Pseudodonor Electronic Excited States of Neutral Complex Defects in Silicon

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The optical-absorption spectrum of a complex neutral defect in silicon with a lowest bound exciton line at 615.0 meV has been studied. Only transitions to s-like excited electronic states are observed and their binding energies are in good agreement with a deep pseudodonor model for the electronic structure of the defect. A comparison with optical-excitation spectra of other complex defects shows that this type of electronic structure explains the optical spectra of a large class of defects in silicon.

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During the last years, several neutral complex defects with donorlike electronic excited states close to the conduction-band edge have been studied in silicon.[1-4] The electronic states observed have in some cases been identified as those of deep donors,[3] in other cases as those of pseudodonors.[2] A fundamental difference between pseudodonors and donors is that the bound electron of a neutral donor experiences a long-range Coulomb potential already in the ground state, whereas the bound electron of a pseudodonor experiences no such Coulomb potential in the neutral ground state. This potential exists, however, in the excited bound exciton (BE) state due to the positive charge of a bound hole.

An electron bound to a positively charged core of a neutral defect experiences two partly overlapping potentials, the so-called central-cell potential with a short-range interaction and the screened Coulomb potential with a long-range interaction.[5] One important condition for the origin of the central-cell potential is the different character of the local electronic bonds at the defect, compared with the character of those of the undisturbed silicon crystal. The Coulomb potential is due to a positive charge localized to the core, and gives rise to hydrogenlike excited states described by the effective-mass approximation (EMA). Only the binding energies of the lowest s states can be significantly affected by the central-cell potential.[5]

All shallow excited states of a donor in silicon are at least sixfold degenerate due to the six equivalent conduction-band minima. This degeneracy is partly lifted by the so-called valley-orbit interaction, which mainly effects the s states since the wave functions describing these states are the only ones with nonvanishing amplitudes at the defect site. In tetrahedral (T_d) symmetry, all s states split into a singlet (A_1) state, a doublet (E) state, and a triplet (T_2) state.[5] If the symmetry of the defect is lower than T_d, the degeneracy is further reduced.

In this Letter we show in detail an optical-absorption spectrum (Fig. 1) of a defect in silicon with a lowest singlet-to-singlet BE line at 615.0 meV.[6] The structure associated with the same defect observed at higher photon energies is shown in detail in Fig. 1. We give a physical explanation of the observed spectrum in terms of transitions to excited electronic states of a deep pseudodonor. Our results are also compared with other, as we will show, very similar spectra previously found of other complex defects in silicon, confirming a common occurrence of pseudodonor character for deep defects in silicon.

We attribute the transitions observed to symmetry-allowed transitions *from* a nondegenerate ground state of the neutral defect under consideration *to* an excited BE state consisting of a hole tightly bound to the defect with an electron bound in the Coulomb potential of this hole. The electron is described by EMA-like ns states, perturbed by the central-cell potential. Here, n corresponds to the main quantum number of the EMA wave functions. The line at 615.0 meV we associate with a transition to the $1s(A_1)$ pseudodonor state, and the line at 751.3 meV together with the structure at 779.4–781.0 meV we associate with the transitions to $1s(E+T_2)$ states. Transitions to the $2s(A_1)$ state and $2s(E+T_2)$

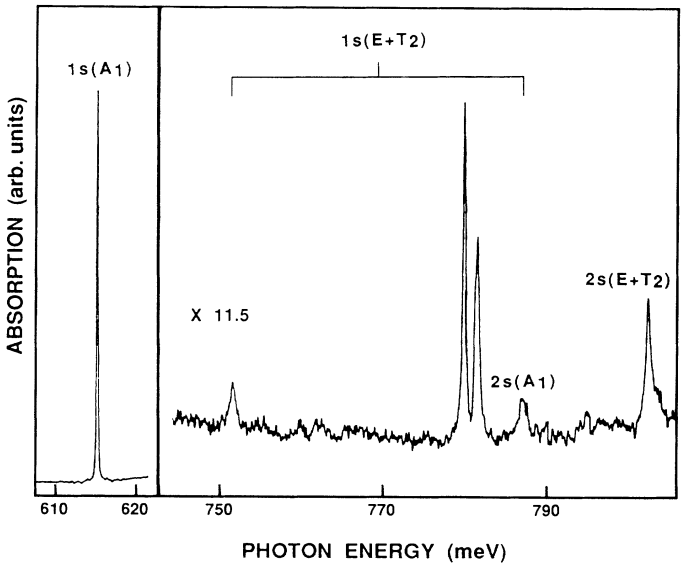

FIG. 1. Absorption spectrum of the 615-meV defect. The spectral resolution is 0.12 meV. (The line at 751.3 meV deviates significantly from EMA. An alternative assignment is therefore possible.)

TABLE I. Optically observed electronic transition energies for the different defects discussed in the text.

Transition (final state)	Photon energy C-line defect (meV)	Photon energy 615.0-meV defect (meV)	Photon energy Ag defect (meV)
$1s(A_1)$	790.0	615.0	
$1C$	...	...	784.3
$1s(E+T_2)$	795.2	751.3	795.8
	800.4	779.4	796.7
	801.8	780.8	781.1
	805.6	781.0	797.7
$2p_0$	816.8	...	814.5
$2s(A_1)$	818.6	786.5	
$2C$			816.0
$2s(E+T_2)$	819.2		
	820.6	802	817.6
$2p\pm$	821.9	...	...

states are associated with the line at 786.5 meV and the structure at 802 meV, respectively, as illustrated in Fig. 1 and Table I. The notation $ns(E+T_2)$ of these states is only one of convenience, since the unknown symmetry of the defect is lower than T_d. We will henceforth use this notation for all s states of the electron that are assumed to have a node at the defect site.

It has been found in previous studies of substitutional donors that the binding energies of the $1s(E)$ states and $1s(T_2)$ states, that have a node at the defect site, are relatively close to the $1s$ EMA value of 31.26 meV.[7] According to our assignments above, the transitions at $\sim$780.4 meV should then approximately correspond to a single $1s$ electronic EMA state. Accordingly, the bound electron's ionization edge would be at $780.4+31.3=811.7$ meV. The transition to the $2s$ state would in this case be at approximately $811.7-8.9=802.8$ meV, using the EMA value of 8.856 meV of the $2s$ state.[7] This corresponds with good agreement to our assignment of the $2s(E+T_2)$ state in Fig. 1.

Since the $1s(A_1)$ and $2s(A_1)$ states have a nonvanishing amplitude at the defect site, they are much more affected by a specific and, in this case, electron-attractive central-cell potential of the defect under consideration than are the $1s(E+T_2)$ and $2s(E+T_2)$ states. There are presently no good theoretical models available that can predict the binding energy of these deep states that are poorly described by EMA. The deviations from the EMA model for the $ns(A_1)$ states can be theoretically estimated, however.[8] The deviation should approximately scale as $1, \frac{1}{8}, \frac{1}{27}, \ldots$ for EMA states with $n=1,2,3,\ldots$, respectively, if it is assumed that the hyperfine constant for the different $ns(A_1)$ states is proportional to $|\Psi_n(0)|^2$, where $\Psi_n(0)$ is the isotropic effective-mass-like wave function at the defect corresponding to the main quantum number n.

Let us compare this estimate with our actual experimental values for the 615-meV BE according to the previous assignments. The deviation from the EMA value for the $1s(A_1)$ state is then approximately $780.4-615.0=165.4$ meV and the corresponding deviation for $2s$ is $802.8-786.5=16.3$ meV, using 780.4 meV as an estimate of the transition energy to the state corresponding to $n=1$ according to EMA. The theoretical value for the deviation of the binding energy of the $2s(A_1)$ state from EMA, using the experimental value for the deviation of the $1s(A_1)$ state, is then $165.4/8=20.7$ meV, which is in fairly good agreement with the experimental value (Table II).

TABLE II. The deviation in binding energy from the EMA value of the $1s(A_1)$ and $2s(A_1)$ states of the different defects discussed in the text. The deviations for the $2s(A_1)$ states given in parentheses are the theoretically estimated values, calculated by dividing the deviation for the $1s(A_1)$ states by 8.

Deviation from EMA	Energy C-line defect (meV)	Energy 615.0-meV defect (meV)	Energy Ag defect (meV)
$1s$(EMA)-$1s(A_1)$	7.0	165.4	10.4
$2s$(EMA)-$2s(A_1)$	0.9	16.4	1.2
	(0.9)	(20.7)	(1.3)

We will now illustrate that the deep pseudodonor model can be applied generally by a comparison with optical-excitation spectra from other reported complex defects in silicon where excited-state structures have been observed, e.g., the so-called C-line defect[1,2] and a defect related to silver (Ag).[3]

As can be seen in Table I and Fig. 2(a), the transmission spectrum related to the Ag defect, reported by Olajos, Kleverman, and Grimmeiss,[3] shows close similarities with the spectrum discussed above. The structure around 800 meV is similar to the structure at $\sim$780.4 meV of the 615-meV defect [Fig. 2(b)]. Olajos, Kleverman, and Grimmeiss have also attributed these lines to transitions to $1s(E+T_2)$ states, although the ground state of the transitions was in their case suggested to be the $1s(A_1)$ ground state of a very deep donor with a binding energy of approximately 831 meV.[3] At 784.3 and 816.0 meV in Fig. 2(a), intense lines labeled $1C$ and $2C$ are observed and suggested to arise from many-particle and spin-orbit effects. Comparing the energy spacing between these lines and the structures labeled $1s(E+T_2)$ and $2s(E+T_2)$, respectively, a similar scaling is found as that expected for the relative deviation of the binding energy from EMA for the $1s(A_1)$ and $2s(A_1)$ states of the 615-meV defect. If the lines $1C$ and $2C$ are reassigned to transitions to the $1s(A_1)$ and $2s(A_1)$ states, the spectrum can be interpreted as being due to the pseudodonor (Table II).

A similar comparison with the spectrum of the C-line defect [Fig. 2(c) and Table I] has been done using the assignments of the lines according to Thonke *et al.*[2] and

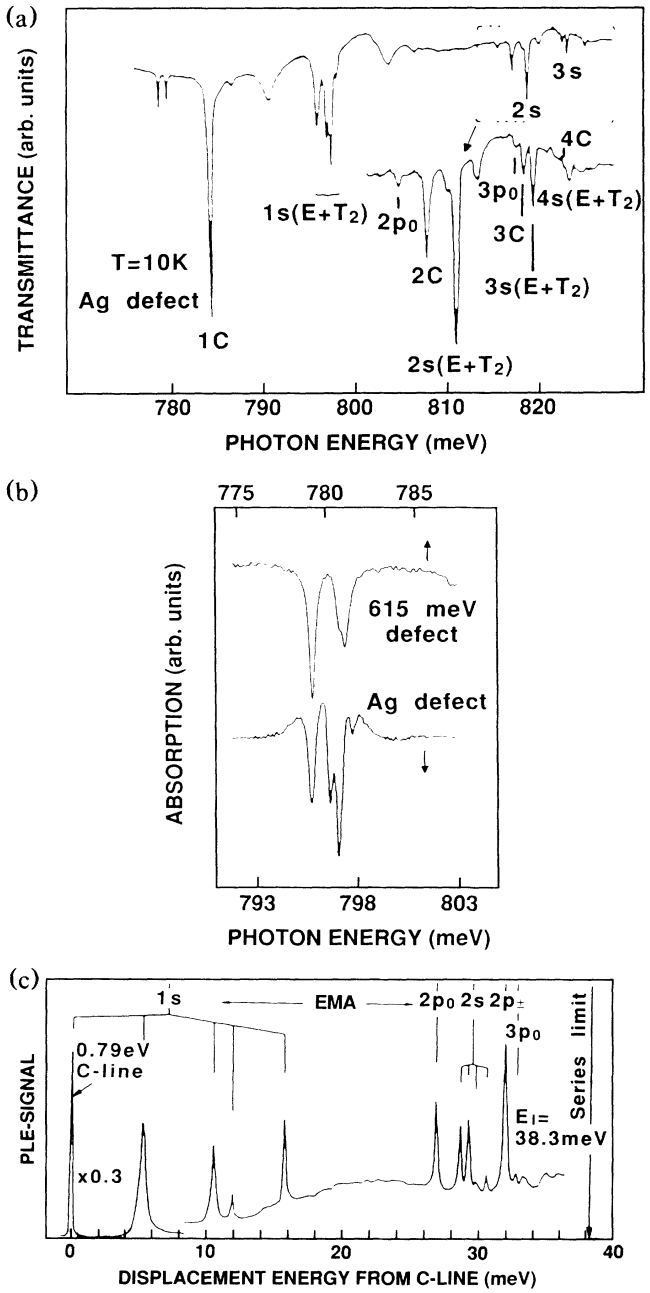

FIG. 2. (a) Transmission spectrum of Ag-doped silicon (see Ref. 3). The lines labeled $1C$, $2C$, etc., and $ns(E+T_2)$ are discussed in the text. (b) Comparison of the lines labeled $1s(E+T_2)$ for the Ag defect and the 615.0-meV effect. (c) Photoluminescence excitation (PLE) spectrum showing the C line and related transitions, and the interpretation of the lines according to EMA (see Refs. 1 and 2).

assuming that the transition to the $2s(A_1)$ state corresponds to the line at 818.6 meV [1,2] and that the continuum edge is at 828.3 meV.[2] The energy of the transition to the $1s$ state according to EMA is then $828.3-31.3=797.0$ meV. The deviation between this energy and the experimental value of the energy of the transition to the $1s(A_1)$ state related to the ionization edge is $797.0-790.0=7.0$ meV, giving an estimated theoretical value of $7.0/8=0.88$ meV for the deviation of the binding energy of the $2s(A_1)$ state from the value according to EMA. The corresponding experimental value is 0.9 meV (Table II).

The three different spectra discussed in this Letter differ from each other in one essential respect. The spectrum related to the C-line defect shows clear transitions to $2p_0$ and $2p\pm$ states, the spectrum related to the Ag defect shows a possible weak transition to the $2p_0$ state and no transitions to $2p\pm$ states, and the defect related to the 615-meV defect does not give rise to any observed transitions to any p state.

The prevalence of transitions to s-like excited states observed in the pseudodonor spectra, as compared with donor spectra, is due to the different excitation schemes of the two cases. In the latter case, the optical spectra show the transitions from the donor ground state to higher states, all in the donor Coulomb potential. In the pseudodonor case, the transitions are from a defect ground state, that is not a donorlike state, to all pseudodonor states. The apparently different orbital symmetry of the ground state of the BE transitions of the pseudodonor, compared with the donor ground state, favors the transitions to even-parity excited states for a pseudodonor, so that transitions to p-like electronic states are hardly observed.

The defects discussed in this work are obviously complex with low symmetry. The most detailed geometrical model is available for the C-line defect, showing the occurrence of both bonds and a lone-pair orbital of the defect atoms (in this case interstitial carbon and oxygen atoms[9]). In general, a pseudodonor electron is expected to have a negative shift in binding energy due to the central-cell potential.[10] The observation of a positive shift of the binding energies can be explained by the model outlined below.

The optical spectra referred to in this work can be interpreted as being due to the creation of a BE state with a very localized bound hole. Such a hole can schematically be understood as being localized to a bond of the defect; i.e., it can be localized within a fraction of a unit cell. Such a bound hole (associated with the deep ground state of the defect) has a quenched orbital angular momentum, i.e., it is spinlike, and naturally gives rise to the lowest states of the BE of triplet-singlet character.[11] The strong localization of such a hole has an important consequence. The basically hole-attractive central-cell potential in the ground state is so localized that once the hole is bound, another part of the defect having an electron-attractive central-cell potential may not be effectively compensated. In the BE state the defect can then have a strong electron-attractive central-cell potential, responsible for the positive central-cell shift of the binding energy always observed for the pseudodonor $ns(A_1)$ electronic state. Obviously, this poten-

tial can dominate over the Coulomb potential of the hole, also allowing strong localization of the $ns(A_1)$ states of the electron, i.e., creating a *deep* pseudodonor, as shown here for the 615-meV BE. The class of transitions with singlet or singlet-triplet character BE lines is indeed very common in silicon and such lines appear at energies well below 0.5 eV.[12] The absorption due to the transitions to the excited states of the deep 615-meV pseudodonor is very weak, approximately 6% of that due to the transition to the $1s(A_1)$ state. This large difference in absorption is not found for the shallow pseudodonors. Since the reported no-phonon lines in silicon normally are weak in absorption,[12] the absorption due to transitions to the excited pseudodonor states can, in general, be very difficult to resolve.

In summary, we have presented an interpretation of the optical-absorption spectrum of a new defect in silicon. The spectrum is interpreted as being due to a deep pseudodonor. We have also compared this spectrum with two other spectra that have previously been interpreted as being due to a shallow pseudodonor and a deep donor. We show that all these spectra can be understood if they are interpreted as being due to pseudodonors with a positive central-cell shift for the binding energy of the $1s(A_1)$ ground state of the pseudodonor electron. A simple theoretical model is found to describe the relative lowering of the binding energy of the different $ns(A_1)$ electronic states in this potential, compared with the binding energies of EMA states. The deep pseudodonor model discussed in this work seems to be able to explain a majority of the optical spectra reported so far which originate from neutral complex defects in silicon.

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