Excited states at deep centers in Si:S and Si:Se

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The spectral distributions of the photoionization cross sections for the dominant sulfur- and selenium-related donor centers in silicon are presented. The measurements have been performed at different temperatures using junction space-charge techniques. The spectra of the electron transitions to the conduction band are best understood in terms of excited states. Two types of excited states are involved: those which are generally referred to as the Rydberg series and those which originate from the multivalley nature of the conduction band. The latter contain sharp peaks with half-widths of the order of 10 meV for the deeper donor levels and 2 meV for the shallower centers. The energy positions of these peaks are independent of temperature. The assignments of the ground states and the excited states are discussed and the results compared with previous data obtained from thermal measurements in Si:S and Si:Se.

I. INTRODUCTION

Good insight into the nature of the impurity centers has been achieved at least for Si and Ge when the foreign atoms belong to the groups of the Periodic Table closest to that of the semiconductor. They introduce localized donor and acceptor levels close to the band edges which are called shallow energy levels. One of the reasons for our good understanding of shallow centers is that they can be described by effective-mass theory. This implies that the centers have a hydrogenlike spectrum of levels.[1] The assignment of these levels and of the ground state has been considerably facilitated by the fact that optical absorption spectra generally exhibit a number of sharp lines.[2]

Apart from transition metals, published optical spectra of crystal defects with large binding energies generally show a smooth energy dependence without any of the detailed structure which is otherwise characteristic of shallow energy levels. This is valid for both excitation and recombination spectra and has often been considered as an indication for the nonexistence of excited states at deep centers.[3] This lack of information on excited states has severely inhibited the energy assignment of deep centers. "Deep" impurities with binding energies much larger than those of "shallow" ones are often generated by replacing an atom of the host lattice by an atom which does not belong to an adjacent group of the Periodic Table.[4] Detailed studies of deep energy states have shown that both the measurements and their interpretation are often far more difficult in compound materials than in elementary semiconductors due to residual impurities, nonstoichiometry, and the formation of complexes. Elementary semiconductors such as silicon are therefore particularly suited for

the study of deep energy states. The possible deep impurities in silicon, sulfur, and other elements from the same row of the Periodic Table are of particular interest. All of them have the same number of core electrons (isocoric impurities) and, hence, the closest resemblance to the host atom.[5]

In two recent papers, evidence was given that both sulfur and selenium create two dominant donor levels in silicon.[6,7] In sulfur-doped silicon the deeper donor level has a "thermal activation energy" of 0.59 eV (the A center), whereas the binding energy of the shallower center (the B center) is $E_c - 0.32$ eV.[6] In Si:Se the corresponding values are 0.52 eV (the A center) and $E_c - 0.30$ eV (the B center), respectively.[7] The A and B centers have about the same concentrations in both Si:S and Si:Se. From a detailed study of electron capture cross sections, it could be shown that the capture of electrons into the sulfur- and selenium-related B levels is best described in terms of a cascade capture process. Within the framework of this model, the data were not in disagreement with the existence of the excited states first observed in optical spectra of Si:S by Sah et al.[8] and Ning and Sah.[9] Although the electron capture cross section of the A centers was too large to be measured with the equipment available, the similar thermal properties of the A and B centers suggested that both centers might have excited states.

Whereas the optical properties of sulfur-doped silicon have been the subject of a number of investigations,[10-17] information on the optical properties of Si:Se (Refs. 17–21) is rather limited. In several of these papers, the A and B centers in both Si:S and Si:Se are considered to be two different charge states of a double donor originating from the same substitutional impurity.[13] We were unable to prove this conclusively,[6,7] although most of our data

are not in contradiction with such a model. It has also been suggested that the A center in Si:S consists of a group of sulfur centers differing only slightly in energy.[22] While our data support this interpretation indirectly, no direct evidence could be given.[7]

The existence of excited states at deep energy levels is of vital importance for a better understanding of deep centers, not only of capture processes[23] but also of the electronic structure in general. In this paper, we wish to present data which show that the electron photoionization cross-section spectra of the A and B centers in Si :S and Si : Se are best understood in terms of excited states. It will be shown that two types of excited states are involved in the spectra: those which are generally referred to as the Rydberg series[4] and those which originate from the multivalley nature of the conduction band.[1] Sulfur is an isocoric impurity in silicon, but selenium is not. Since selenium is isovalent to sulfur, a close resemblance of the electronic properties of the two impurities might be expected as in, e.g., the case of arsenic and phosphorous.[5] However, it will be shown that there are several distinct differences in the optical properties of Si : S and Si : Se.

II. EXPERIMENTAL DETAILS

All measurements were performed on $p^{+}n$ junctions doped with either sulfur or selenium (for details see Refs. 6 and 7). Photoionization cross sections of electrons were measured using the constant capacitance transient technique.[24] This technique implies that the capacitance of the diode is kept constant during the measurements. When the occupancy of the deep centers is changed by illuminating with photons of energy $h\nu$, the change in voltage ΔV needed to keep the capacitance constant is then proportional to the electron occupancy of the center n_T. If, furthermore, the initial conditions of the measurements are such that all centers are filled with electrons, it is readily shown that under these conditions $|d\Delta V(t)/dt|_{t=0}$ is proportional to the photoionization cross section σ_n^0 (initial-slope technique[25]). In order to check whether or not the capacitance transients are simple exponentials in form, the total transient was monitored for several representative energies of the spectra. In all cases, the transients were of exponential form. The initial conditions for measuring the photoionization cross section of the A center, σ_{nA}^0, were chosen to be such that the A center was completely filled with electrons and the B center empty.

The photoionization cross sections of electrons for the B center, σ_{nB}^0, were studied at tempera-

tures well below the freeze-out temperature and for energies $h\nu < E_c - E_A$, where E_A is the energy position of the A center relative to the valence band. In these measurements, care was taken to reduce any disturbance from thermal background radiation.

In the temperature range investigated and for all photon energies smaller than the bandgap E_g, σ_{nA}^0 for the A center was found to be much larger than the photoionization cross sections of holes, σ_{pA}^0, in both Si:S and Si : Se (Figs. 1 and 2). The spectra of σ_{pA}^0 were therefore obtained from steady-state measurements of the photocurrent J_R^0.[26] This procedure was checked with the two-light-source technique,[26] which gave similar results. Since $E_B > E_A > E_c - E_A$, the photoionization cross section of holes for the B center, σ_{pB}^0, could not be studied properly due to the high photocurrent caused by the A center.

Absolute photoionization cross sections were calculated from measured optical emission rates e^0 and photon fluxes ϕ using the relation $e^0/\phi = \sigma^0$. Because of the large differences in sensitivity for intrinsic and extrinsic optical excitations, stray light had to be very carefully excluded
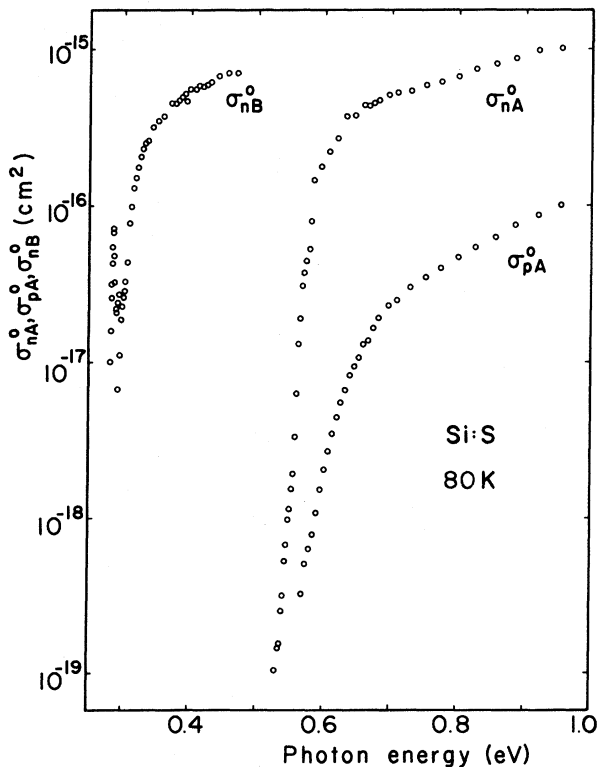

FIG. 1. A survey of the absolute values of the photoionization cross sections σ_{nA}^0, σ_{pA}^0, and σ_{nB}^0 versus photon energy in sulfur-doped silicon at 80 K.
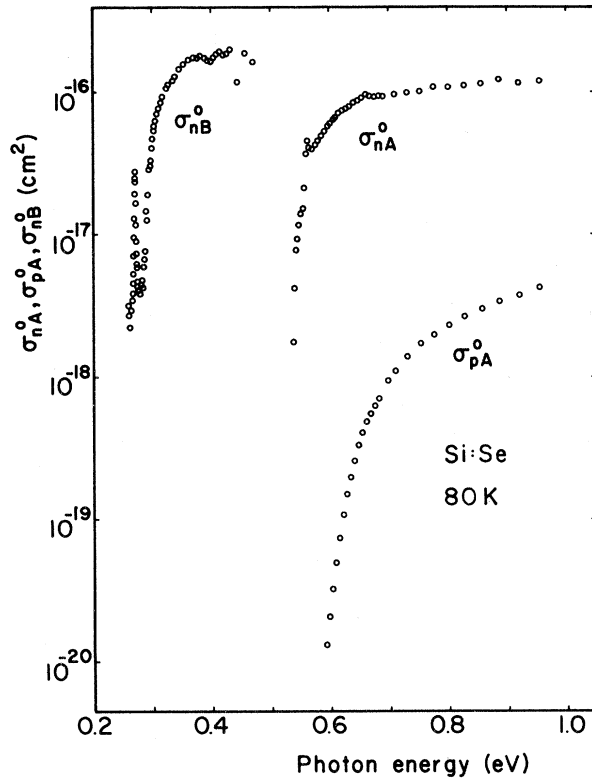
FIG. 2. A survey of the absolute values of the photo-ionization cross sections σ_{nA}^0, σ_{pA}^0, and σ_{nB}^0 versus photon energy in selenium-doped silicon at 80 K.

during the experiments. An incandescent lamp with either a Jarrel Ash double-grating mono-chromator or a Zeiss MM twelve-prism double monochromator was therefore used as a light source. Relative intensities were monitored by a thermocouple; absolute values were measured using a pyroelectric detector. Current measure-ments were performed with a Keithley 616 digital electrometer. For all capacitance measurements a Boonton 72 B capacitance meter was used.

III. EXPERIMENTAL RESULTS

The spectra of σ_{nB}^0, σ_{nA}^0, and σ_{pA}^0 at 80 K are shown in absolute values for both Si:S and Si:Se in Figs. 1 and 2. The corresponding cross sec-tions of the sulfur-related centers are in all cases considerably larger than those of the se-lenium-related centers. Furthermore, whereas the ratio of $\sigma_{nA}^0/\sigma_{pA}^0$ is about 20 at larger photon energies for sulfur, the corresponding value for selenium is about 70. However, it is interesting to see that the curves of σ_{nA}^0, σ_{pA}^0, and σ_{nB}^0 are very similar for both sulfur and selenium.

The logarithm of σ_{nB}^0 versus photon energy is shown for Si:S at two different temperatures in Fig. 3. The spectra in the energy region between

about 0.275 and 0.290 eV are difficult to measure because of the presence of water-absorption bands. For comparison, we have also plotted the values of the enthalpy ΔH at 0.320 eV (F) and the energy separation of the ground state from the $2p_0$ state at 0.302 eV (E_2) as obtained from thermal measurements[7] (Fig. 3). Note that the energy position of the peak at 0.286 eV (T) is in-dependent of temperature.

The data obtained for σ_{nB}^0 in selenium-doped silicon (Fig. 4) are very similar to those in Si:S. For comparison, we have also plotted the values for the enthalpy ΔH at 0.301 eV (F) and the energy separation of the ground state from the $2p_0$ state at 0.286 eV (E_2) as obtained in previous investi-gations of the thermal properties of selenium-doped silicon.[6] The energy position of the peak at 0.270 eV is independent of temperature, as in Si:S.

The photoionization cross sections of electrons σ_{nA}^0 for the A center in Si:S were measured at four different temperatures (Fig. 5). The low-energy part of the spectra below about 0.54 eV shows a strong temperature dependence and could only be studied for temperatures above 120 K. The arrow at 0.587 eV (E_2) indicates the value of the energy separation of the ground state from the lowest state accessible by electron capture as deduced from thermal measurements.[7] It is readily seen from Fig. 5 that the energy position of the peak at 0.428 eV (T) is independent of tem-perature implying a temperature-independent energy separation for transitions between the ground state and this particular excited state.

Similar measurements of σ_{nA}^0 were performed in selenium-doped silicon at three temperatures (Fig. 6). Unlike the spectrum of σ_{nA}^0 obtained in Si:S at 40 K, the low-energy tail of σ_{nA}^0 in se-lenium-doped silicon is very steep and no signal could be detected for energies smaller than 0.537 eV. The spectra in the energy region below about 0.53 eV are strongly temperature dependent and could only be measured for temperatures above 110 K. For comparison, we have also plotted the value of 0.524 eV (E_2) for the energy separation of the ground state from the lowest state acces-sible by electron capture, as obtained from ther-mal investigations of Si:Se.[6] As in Si:S, the energy position of the peak at 0.426 meV (T) is independent of temperature.

The spectra of the photoionization cross section of holes, σ_{pA}^0, were measured at several different temperatures for the A centers in both sulfur- and selenium-doped silicon (Figs. 7 and 8). In both cases, a temperature shift of the low-energy part of the spectra is clearly seen. Furthermore, it is interesting to note that the absolute values of
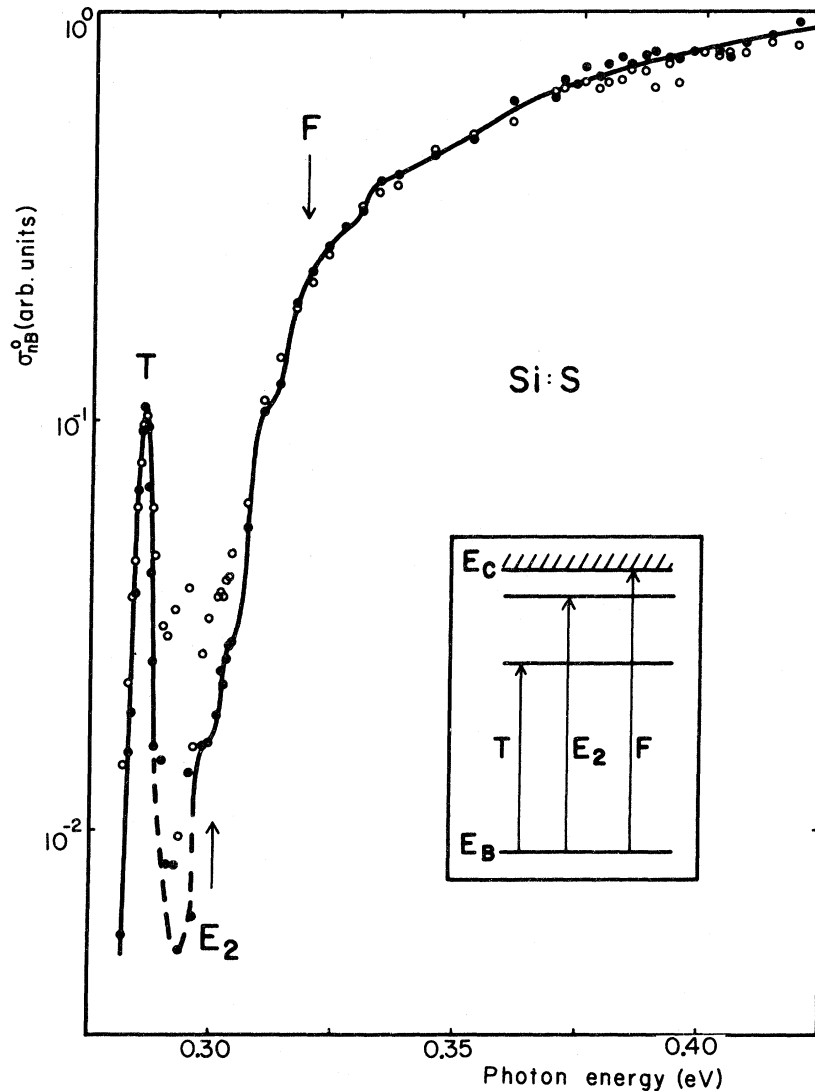
FIG. 3. Spectra of the photoionization cross section of electrons, σ^0_{nB}, for the shallower donor level in Si:S at two different temperatures ($\bullet$=40 K, $\circ$=80 K).

the photoionization cross section σ^0_{pA} at higher energies are independent of temperature in both Si:S and Si:Se.

IV. DISCUSSION

Comparing previous results obtained from thermal measurements in sulfur- and selenium-doped silicon[6,7] with the results presented in this paper, we feel that the spectra of photoionization cross sections can only be understood if it is assumed that both the A and B centers have excited states between their ground states and the conduction band. Transitions from the ground state to excited states are internal transitions and are therefore not expected to cause changes in the diode

capacitance similar to those caused when the charge carriers are excited into the conduction band. Any capacitance signal observed which involves excited states must therefore originate from a two-step photothermal excitation process in which the electron is first excited from the ground state into an excited state by the absorption of a photon and then further excited into the conduction band by absorbing one or several phonons. This type of excitation has been discussed in detail by Kogan et al.[27] They found that the photothermal excitation process is more probable than the simultaneous absorption of a photon and a phonon, provided the electron-lattice vibrational interaction is weak. All published data on electron-lattice interactions suggest that this interaction is probably very weak in silicon.[26,28]
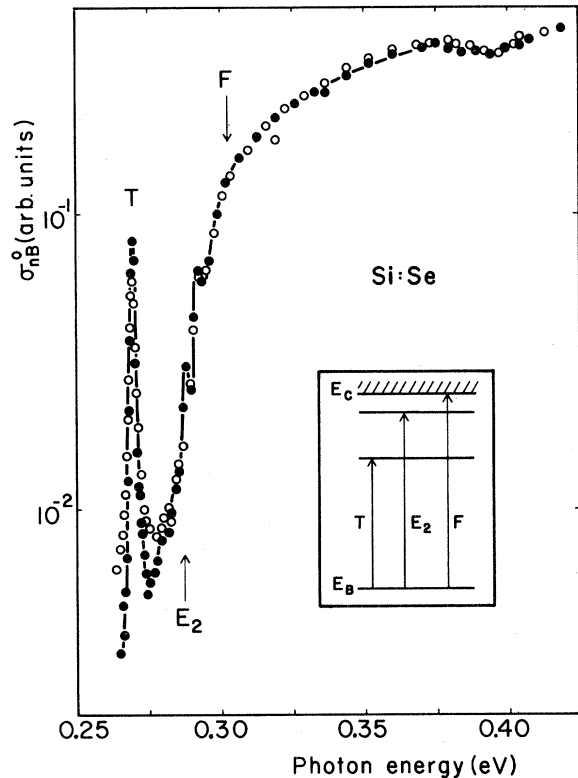
FIG. 4. Spectra of the photoionization cross section of electrons, σ_{nB}^0, for the shallower donor level in Si:Se at two different temperatures ($\bullet$=40 K, $\circ$=80 K).

A. The deeper donor levels (A centers)

Starting our discussion with the A centers, it is clear from what has been said earlier that the part of the spectrum involving the excited states must be thermally activated, in agreement with the results presented in Figs. 5 and 6. A more detailed analysis of the σ_{nA}^0 spectra shows that two types of excited states are involved in the spectra. First, there are those which are generally referred to as the Rydberg series and which lie rather close to the conduction band. Using effective-mass theory, the deepest of these excited states for a donor in silicon should be the $2p_0$ state.[4] Owing to possible broadening effects caused by the high electric field in the junction and the closely spaced energy levels of the excited states, it is not to be expected that these states can be resolved in great detail. Instead, it can be anticipated that the optical signal should increase rapidly for photon energies larger than the energy separation between the ground state and the $2p_0$ state.

It is readily seen from Fig. 6 that for Si:Se the threshold energy of the spectra taken at lower temperatures is about 0.53 eV, which is very close to the value of 0.524 eV for E_2 obtained

from thermal measurements.[6] Using the arguments of Gibb et al.,[29] this result could imply that as for the B centers, the lowest accessible state in the electron cascade process is the $2p_0$ state. Effective-mass theory predicts a binding energy of 11 meV for the $2p_0$ excited state of a single donor in silicon.[4] If the charge states of the A center in Si:Se were known, the binding energy of the ground state could then be deduced. Although we were unable to prove that the A and B centers are different charge states of a selenium-related double donor,[6,7] many of our results are not in contradiction with such an interpretation. Assuming a doubly charged center, the energy separation between the $2p_0$ state and the conduction band is expected to be about 44 meV. Adding this value to E_2 gives a binding energy relative to the ground state of about 0.57 eV. This result is not unreasonable as seen from Fig. 6, where the arrow (F) indicates a value of 0.568 eV. It should be noted, however, that this interpretation is only valid if the lowest state in the electron cascade process is the $2p_0$ state, even though it is separated by about 20 meV from the state immediately above.

Although broadening effects may limit the resolution of the capacitance technique, the σ_{nA}^0 spectrum of Si:Se, nevertheless, shows three clearly resolved peaks in the energy region between 0.53 and 0.56 eV. To demonstrate this, we replot the spectrum at 40 K in this energy region on an expanded scale in Fig. 9. To the best of our knowledge, no detailed information on the excited states of the selenium-related donors in silicon is available and we can therefore only speculate on the origin of these peaks. Scaling the energies of excited states for shallow donors,[2,5] one might expect the energy spacing between the $2p_\pm$ and $2p_0$ excited states to be about 20 meV if we again assume that the A center is doubly charged. Following our previous assignment of the $2p_0$ state, a peak in the spectrum at about 0.54 eV may then be anticipated, in agreement with the data shown in Fig. 9, where the arrow over the first peak indicates an energy of 0.543 eV. Assuming that the peak at 0.543 eV is due to the $2p_\pm$ state, the energies of the $3p_0$ and $4p_\pm$ states can then readily be deduced by again scaling the energies of excited states for shallow donors. According to Refs. 2 and 5 the energy spacings between the $2p_\pm$ state and the $3p_0$ and $4p_\pm$ states are 4 and 17 meV, respectively, if the charge on the empty A center is two. These energy spacings are indicated by the two additional arrows in Fig. 9. The predicted values agree surprisingly well with the other two peaks present in the measured spectrum, although, ob-
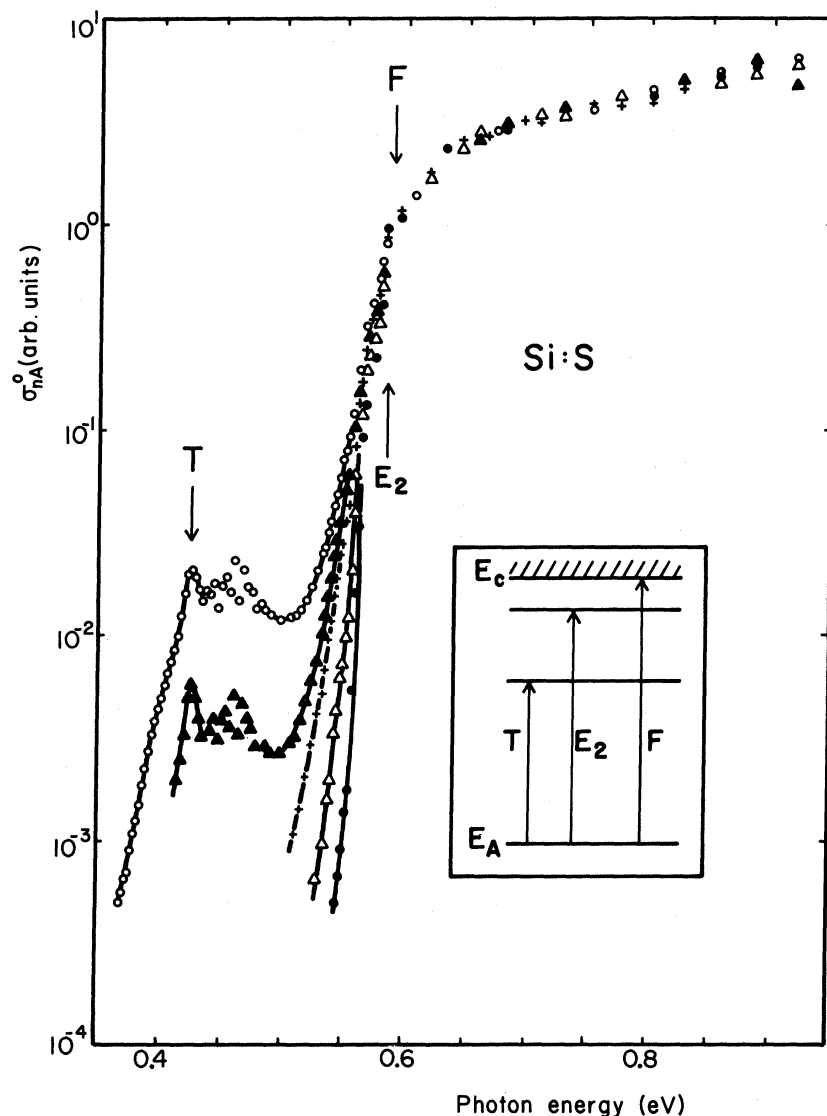
FIG. 5. Spectra of the photoionization cross section of electrons, σ_{nA}^{0}, for the deeper donor level in Si:S at different temperatures (●=40 K, △=80 K, + =120 K, ▲=140 K, ○=160 K).

viously, further investigations are needed before an unambiguous assignment of the spectrum is possible. Adding the scaled effective-mass binding energy of the $4p_{\pm}$ state to the peak energy of the transition from the ground state into the $4p_{\pm}$ state, we arrive at an ionization energy of 0.570 eV for the A center. This is indicated by the arrow F in Fig. 9.

The other type of excited states involved in the spectra is states originating from the multivalley nature of the conduction band.[1] These states may lie well below the conduction band and we believe that the low-energy part of the spectrum below 0.53 eV is produced by such states. Expanding this region of the 110-K spectrum (Fig. 10), three peaks can be distinguished. Of these three peaks,

the one at the lowest energy (labeled T) is clearly resolved, whereas the other two (labeled M and N) are less easily observed. If only the peak at 0.426 eV is due to a transition from the ground state to an excited state, the spectrum can be understood in terms of a center having a T_d symmetry. Although the ground state in this case is split into a nondegenerated A_1 ground state, a triply degenerated T_2 state, and a doubly degenerated E state (without taking spins into account), T_d symmetry only allows a dipole transition from the A_1 ground state to the T_2 excited state. The other two peaks must then be due to other effects. One possibility is that they are phonon replicas of the main peak.[30] If all three peaks are involved in transitions from the ground
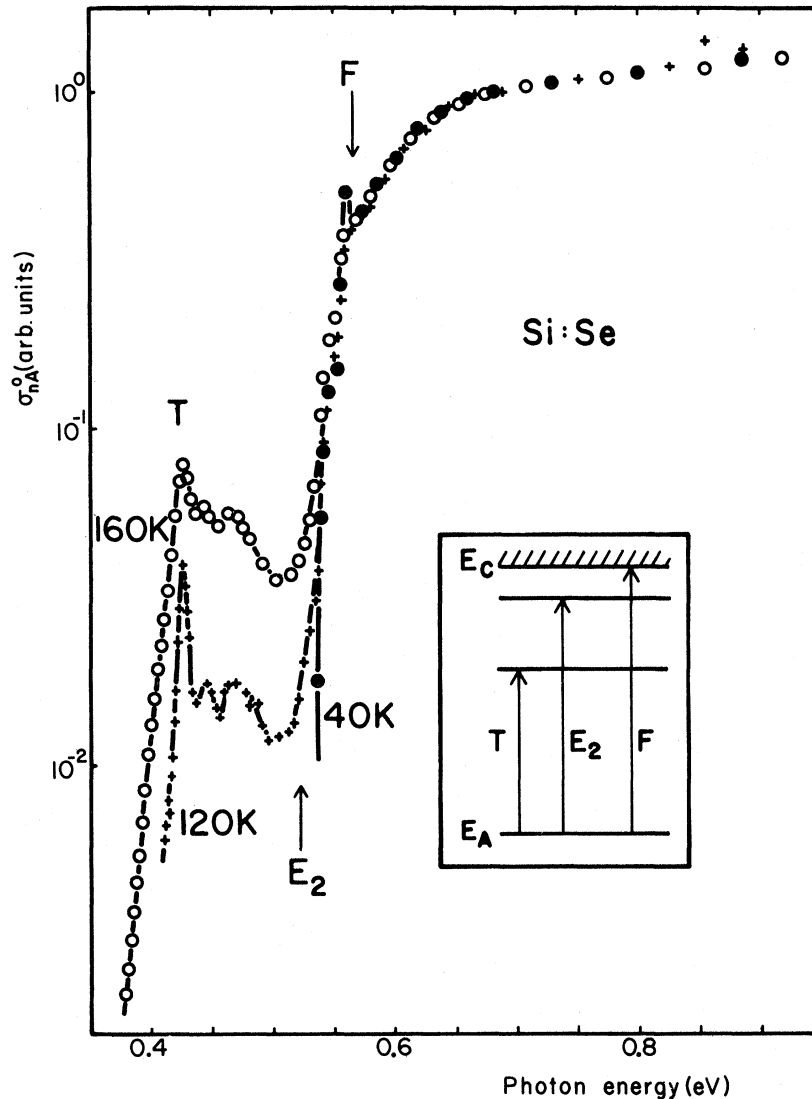
FIG. 6. Spectra of the photoionization cross section of electrons, σ_{nA}^0, for the deeper donor level in Si:Se at different temperatures ($\bullet$=40 K, + =120 K, o=160 K).

state to excited states, the A center must have a lower symmetry. A possible lower symmetry which might account for the presence of three peaks is C_{3V}. Such a symmetry arises, for example, when defects form pairs.

The line shape of the peak at 0.426 eV further confirms the interpretation that the peak is caused by a bound-to-bound transition. In order to show this, we have fitted the experimental data with a Lorentzian line shape whose half-width is 8 meV. It has already been mentioned that the energy position of the peak is constant in the temperature range studied. This implies that the energy position of the ground state may also be independent of temperature if it is assumed that the state causing this peak is effective-mass-like. On the other hand, this could mean that the wave function

of the ground state gets its main contribution from the bottom of the conduction band and that any influence of the valence band is weak. Such a conclusion is supported by the observation that the capture cross section σ_{nA}^0 of electrons probably exceeds the capture cross section σ_{pA}^t of holes by several orders of magnitude and that the photoionization cross section σ_{nA}^0 of electrons is much larger than the photoionization cross section σ_{pA}^0 of holes (Fig. 2).

If the ground state of the A center is pinned to the conduction band, one would expect that the energy spacing between the ground state and the valence band decreases with increasing temperature in the same way as the forbidden energy gap.[31] In Fig. 11, we replot the 40- and 160-K data of Fig. 8. The corresponding decrease of
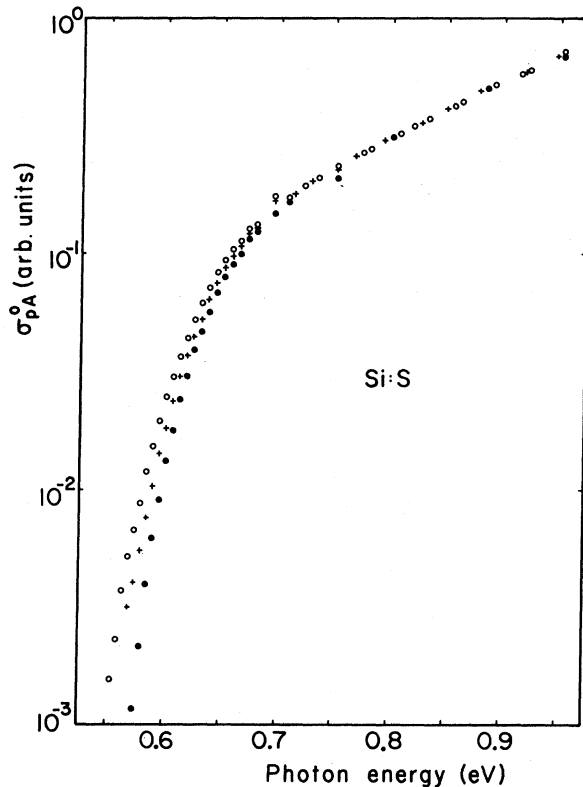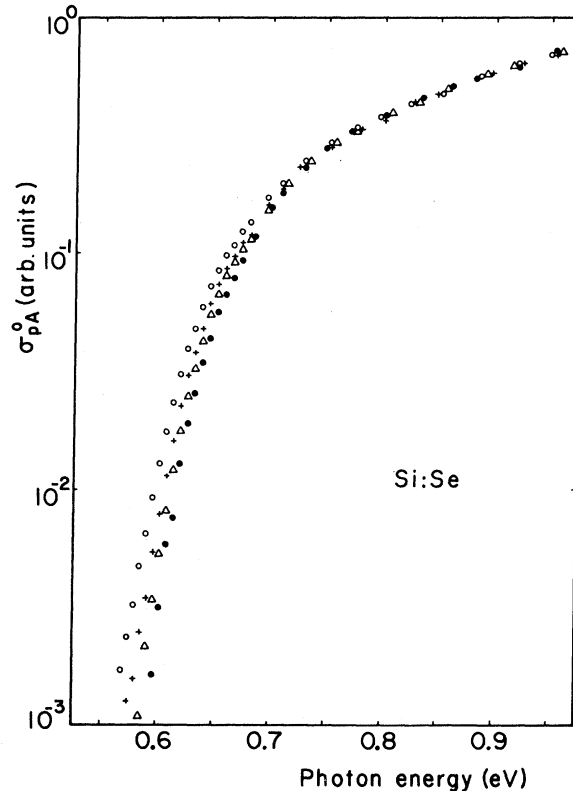
FIG. 7. Spectra of the photoionization cross section of holes, σ_{pA}^0, for the deeper donor level in Si:S at different temperatures ($\bullet$ = 40 K, + = 120 K, o = 160 K).

FIG. 8. Spectra of the photoionization cross section of holes, σ_{pA}^0, for the deeper donor level in Si : Se at different temperatures ($\bullet$ = 40 K, $\triangle$ = 80 K, + = 120 K, o = 160 K).

the band gap in this temperature range is 13.3 meV.[32] Although the shift of the threshold energy is clearly comparable with this value, we did not perform any further analysis due to the lack of well established theoretical models for σ_p^0 and the weak temperature broadening of the spectra, which additionally complicates any attempt at interpretation. No accurate value of the threshold energy E_A can therefore be given. However, with the extrapolation of the data of Figs. 8, 11, and 12, it is readily seen that a value of about 0.59 eV is obtained for E_A at 40 K. Adding E_A to the binding energy of the ground state (about 0.57 eV), a value of 1.16 eV is obtained which is very close to the value of the band gap of silicon at 40 K (1.1695 eV).

It should be mentioned that from the temperature dependence of the thermal emission rate e_{pA}^t an enthalpy ΔH = 0.57 eV is obtained,[6] assuming that the capture cross section of holes, σ_{pA}^t, is independent of temperature. Furthermore, we believe that the weak structure of the 40-K spectrum at about 0.65 eV is probably caused by spin-orbit splitting of the valence band[33] (Fig. 11). It is interesting to note that a linear plot of σ_{pA}^0 (Fig. 12) in the energy interval between 0.67

and 0.77 eV yields a straight line.

The corresponding data for the sulfur-related A center in silicon are, in many respects, very similar to those for Si : Se, although they are several remarkable differences. Unlike the σ_{nA}^0 spectrum in Si : Se, the low-energy part of the σ_{nA}^0 spectrum for the sulfur-related A center increases more slowly at 40 K. This is shown in Fig. 13, where the 40-K data for σ_{nA}^0 have been replotted on an expanded scale. As a consequence of the broader spectrum, more than three peaks are observed in the energy region between 0.53 and 0.59 eV. However, comparing the data in Fig. 13 with those of Fig. 9, the close resemblance of the spectra is quite evident. The three peaks of the σ_{nA}^0 spectrum in Si : S marked with arrows have exactly the same energy spacing and relative position in the spectrum as the three peaks in Si : Se. Although this result does not necessarily justify any further interpretation of the spectrum, it is, nevertheless, tempting to try the same assignment as for Si : Se (Fig. 13). Assuming again that the A center is doubly charged and keeping in mind Krag and Zeigers data,[11] that the $2p_0$ state of sulfur in silicon is 20.6 meV
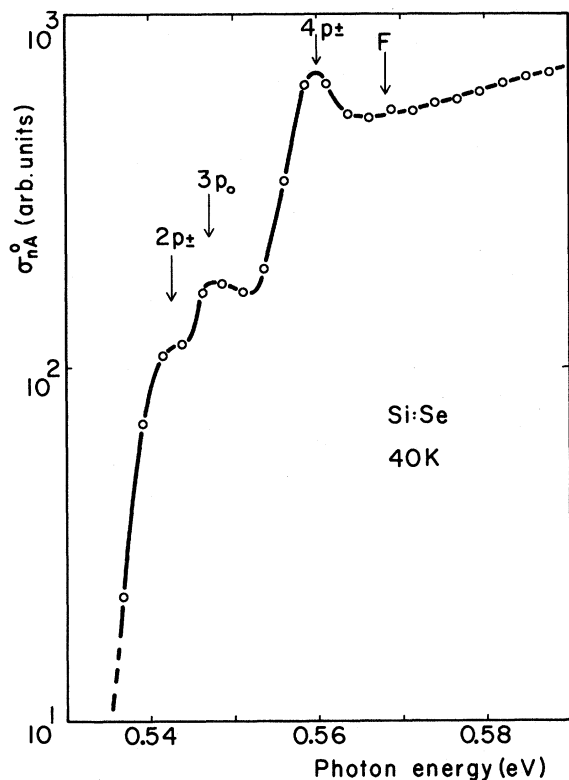
FIG. 9. An enlarged part of the continuum for σ_{nA}^0 in Si:Se, showing the influence and assignment of the excited states.

below the $2p_\pm$ state, one expects the $2p_0$ state to have an energy position at about 0.546 eV. It is readily seen from Fig. 13 that this value is close to the threshold energy of the σ_{nA}^0 spectrum, in agreement with what is expected according to our
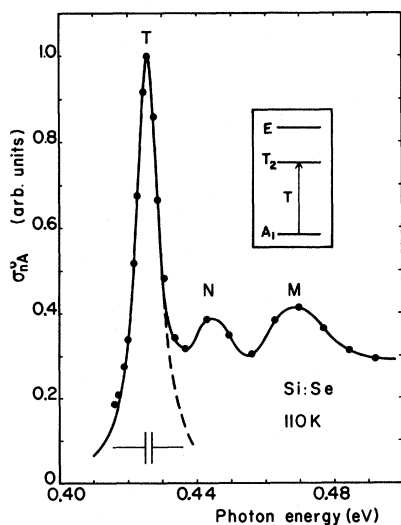

FIG. 10. High-resolution spectrum of the low-energy region for σ_{nA}^0 in Si:Se, showing the Lorentzian behavior of the main peak and some additional structure (see text).
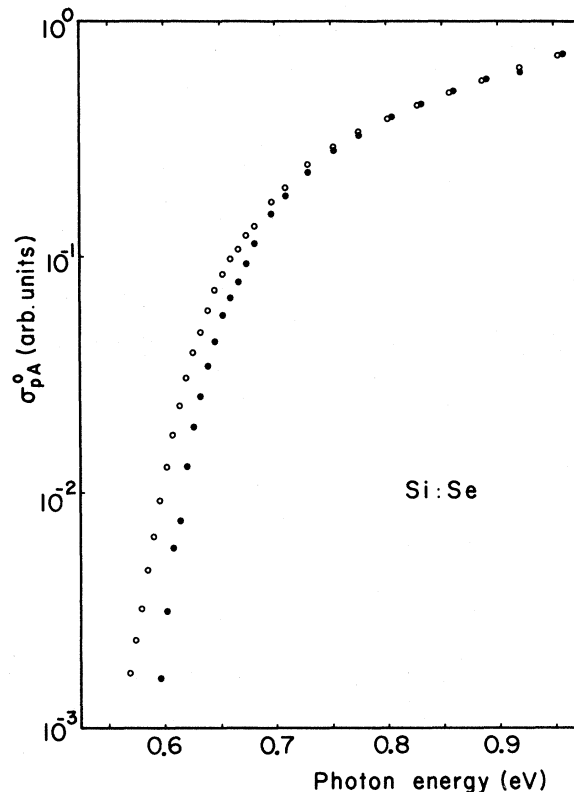

FIG. 11. Comparison of σ_{pA}^0 at 40 K (●) and 160 K (○), showing the energy shift and temperature broadening of the edge region with increasing temperature.

earlier arguments. If it is further assumed that the excited states for the A center in Si:S is effective-mass-like, the lower edge of the conduction band should then lie about 44 meV above the $2p_0$ state at 0.59 eV (Fig. 13, arrow F), in agreement with previous investigations.[8]

These results are in good agreement with the optical spectra but are difficult to understand with respect to previous data obtained from investigations of the thermal emission rate.[7] These studies gave a thermal activation energy of 0.587 eV, which is expected to be the value of E_2, i.e., of the energy spacing between the ground state and the lowest accessible state in the electron-capture cascade process. If this value is taken as the spacing between the ground state and the $2p_0$ excited state, as we did in the case of Si:Se, the binding energy of the A center would be about 0.631 eV. This seems to be far too large compared with the spectrum presented in Figs. 5 and 13 and the threshold energy of σ_{pA}^0 (Fig. 7). On the other hand, the value of 0.587 eV for E_2 is very close to the spacing of the $4p_\pm$ state from the ground state as obtained from the tentative assignment shown in Fig. 13.

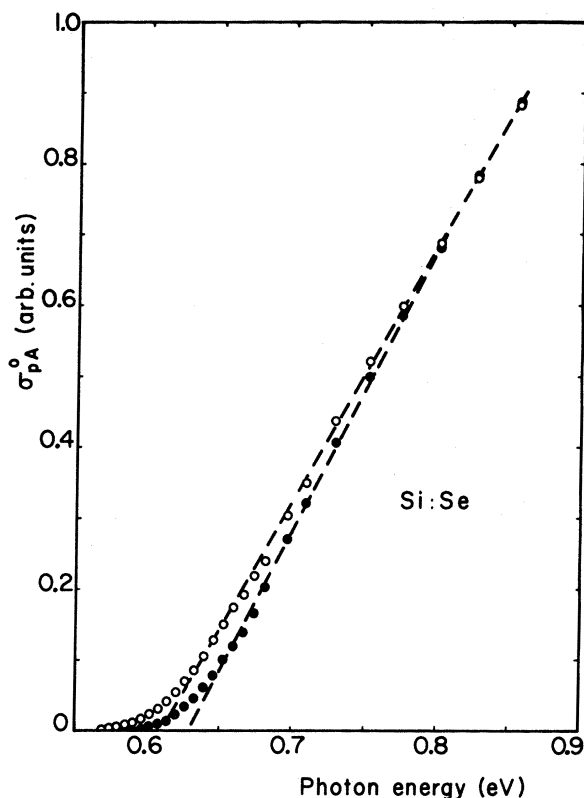In a recent optical study of isotopic effects in

FIG. 12. Linear plot of σ_{pA}^0 at 40 K (●) and 160 K (○), showing the linear behavior of σ_{pA}^0 with photon energy.

FIG. 13. An enlarged part of the continuum region for σ_{nA}^0 in Si : S, showing the influence and assignment of the excited states.

Si : S,[22] Forman reported several absorption lines with peaks at 0.561, 0.569, 0.573 and 0.588 eV. Although the author has a different assignment of the lines (claiming that the strongest three lines all represent $1s - 2p_\pm$ transitions of slightly different centers), these values are in excellent agreement with the spectrum shown in Fig. 13.

At temperatures above 120 K, the Si : S samples became optically sensitive for energies below 0.52 eV (Fig. 5). As in the case of Si : Se, there is reason to believe that this part of the σ_{nA}^0 spectrum originates from the multivalley nature of the conduction band.[2] Replotting the low-energy part of the 160-K spectrum of σ_{nA}^0 on an expanded scale (Fig. 14), it is readily seen that the data for the sulfur-related A center differ somewhat from those obtained in Si : Se (Fig. 10). Although measurements in the energy region between 0.44 and 0.48 eV were not disturbed by interfering absorption bands in air and the data obtained were fairly reproducible, no smooth spectrum in Si : S could be obtained in this energy region. Furthermore, the low-energy tail of the spectrum is considerably broader than for Si : Se, with an unmistakable tendency for a structure to develop (Fig. 15). It is interesting to observe that a value of 0.370 eV obtained from Hall effect and ab-
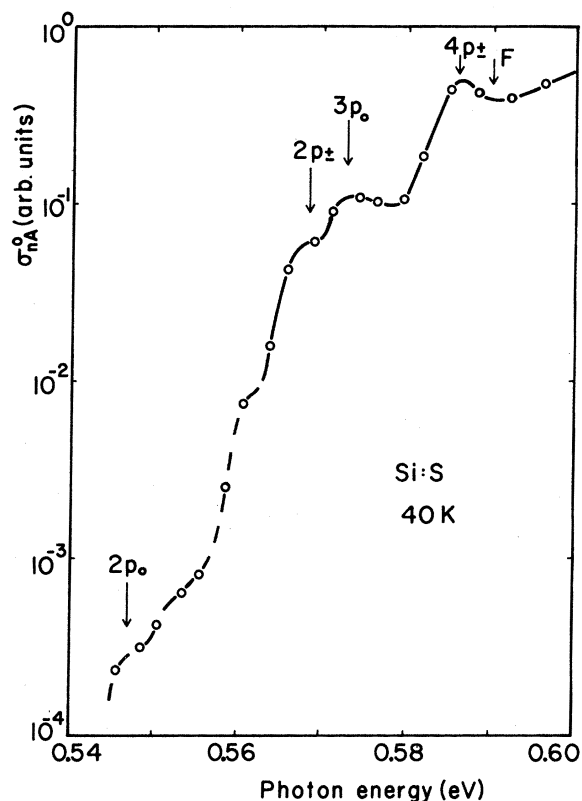
sorption measurements is often quoted in the literature for the energy position of a sulfur-related center[12] in silicon. As can be seen from the data shown in Fig. 14, this is very close to the threshold energy of the σ_{nA}^0 spectrum at temperatures above 120 K. On the other hand, the main peak of the spectrum (Fig. 14) has a half-width of 14 meV and a peak energy of 0.428 eV, which are almost exactly the same values as observed for the corresponding peak in Si : Se. This is remarkable because from a comparison of the data shown in Figs. 9 and 13, it is evident that the A center in Si : S is about 25 meV deeper than that in Si : Se. This result clearly shows that the resemblance between sulfur and selenium in silicon is not at all so close as is sometimes assumed. As mentioned earlier, the energy position of the peak at 0.427 eV is independent of temperature at all temperatures investigated. For an effective-mass-like state, this implies that the ground state of the A center is also independent of temperature. Bearing in mind the fact that the capture cross sections σ_{nA}^t and the photoionization cross sections σ_{nA}^0 of electrons are much larger than the capture cross sections σ_{pA}^t (Ref. 7) and
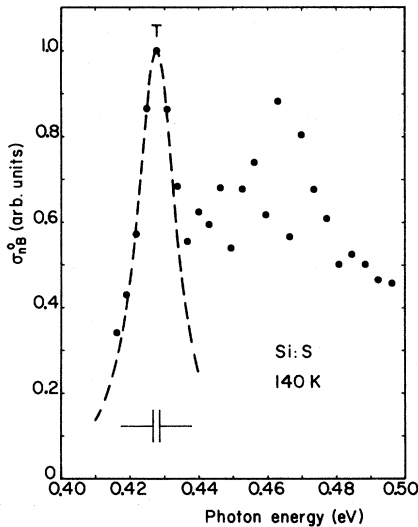
FIG. 14. High-resolution spectrum of the low–energy region for σ_{nA}^0 in Si : S showing the Lorentzian behavior of the main peak and some additional structure (see text).

photoionization cross sections σ_{pA}^0 of holes in Si : S (Fig. 1)and using the same arguments as for Si : Se, it might again be concluded that the wave function of the ground state is mainly built up by contributions from the conduction band.

If the ground state of the A center in Si : S is pinned to the conduction band, the energy spacing between the center and the top of the valence band should decrease with increasing temperature. This is indeed observed, as shown in Fig. 7. We have replotted the spectrum of σ_{pA}^0 for 40 and 160 K (Fig. 15) in order to show that the two spectra coincide for energies larger than about 0.7 eV and that a possible temperature shift of the threshold energy cannot therefore be obtained by simply shifting one of the curves along the energy axes. Closer inspection of Fig. 15 shows that there is a small temperature broadening of the spectra at lower energies, which makes any analysis of the data even more difficult. However, it is readily seen qualitatively that the temperature shift of the threshold energy is of the order of 15 meV, which should be compared with the decrease of the band gap (13 meV) in this temperature range. We therefore feel that these results are not in contradiction with a possible pinning of the A center to the conduction band. It has already been pointed out that a linear plot of σ_{pA}^0 in Si : Se gives a straight line in a limited energy interval. This behavior is still more pronounced in Si : S (Fig. 16), where the linear region extends from about 0.61 to 0.81 eV at 160 K.

As in the case of Si : Se, no comparison was made between measured σ_{pA}^0 data and calculated photoionization cross sections. An attempt can
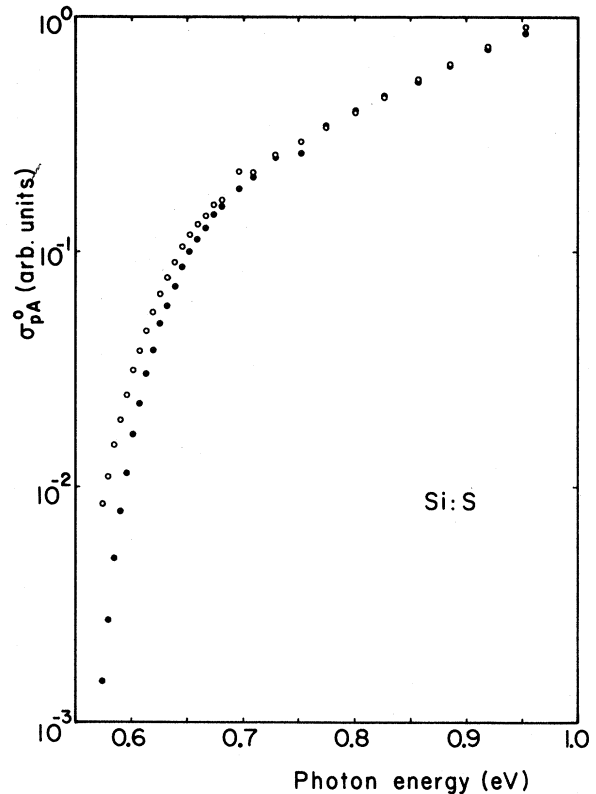

FIG. 15. Comparison of σ_{pA}^0 at 40 K (●) and 160 K (○), showing the energy shift and temperature broadening of the edge region with increasing temperature.

be made to determine the spacing between the A center and the top of the valence band E_A in Si : S at 40 K by extrapolating the corresponding σ_{pA}^0 spectra in Figs. 15 and 16. In both cases, a value of about 0.57 eV is obtained. If the value of 0.59 eV for the binding energy of the A center at 40 K derived above is added to E_A, a value of 1.16 eV is obtained, which is in good agreement with the band gap of silicon at 40 K. This suggests that while the optical data in Si : S are reasonably well understood, the thermal data for the A center[7] still need further interpretation, which is in contrast to the situation in Si : Se, where data of both kinds are accounted for in a satisfactory manner.

B. The shallower donor levels (B centers)

Next, we want to discuss the selenium-related B center in silicon. Closer inspection of Fig. 4 shows that the low-energy part of the spectral distribution is dominated by a peak surprisingly sharp for a spectrum obtained with junction space-charge techniques. We have replotted this part of the σ_{nB}^0 spectrum on an enlarged scale in Fig. 17, where we also compare the experimental data
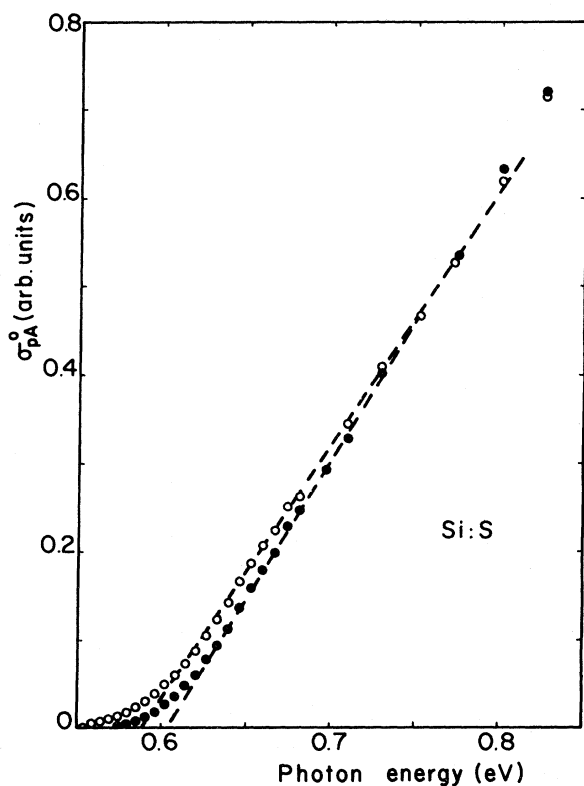
FIG. 16. Linear plot of σ_{pA}^0 at 40 K (●) and 160 K (○), showing the linear behavior of σ_{pA}^0 with photon energy.

with a Lorentzian line shape with a half-width of 1.7 meV. Although the half-width may decrease with improved resolution, the good agreement between the measured and calculated line shapes suggests that the peak at 0.270 eV originates
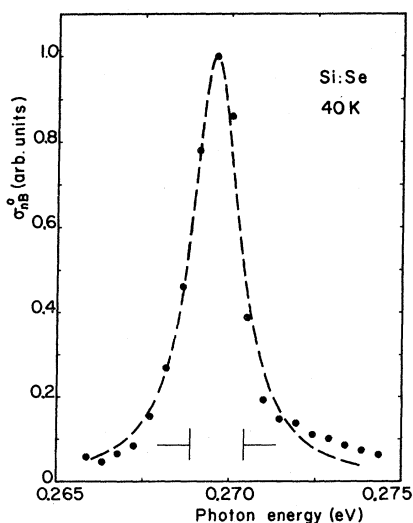

FIG. 17. An enlarged part of a high-resolution spectrum in the low-energy region of σ_{nB}^0 in Si:Se, showing the Lorentzian behavior of the main peak.

from transitions between the ground state of the selenium-related B center and a state generated by the multivalley nature of the conduction band. Further analysis of these data along the lines of that for the A center is at present not possible, since the measurements are disturbed by the presence of water absorption bands in the region between 0.275 and 0.290 eV.

In spite of these disturbances, the measurements were accurate enough to reveal some structure at the edge of the σ_{nB}^0 spectrum above 0.28 eV. The resolution was, however, not good enough to permit a detailed analysis. We tend to believe that this structure can be understood in terms of excited states due to a Rydberg series. Assuming that the B center is effective-mass-like, the deepest of these excited states should then be the $2p_0$ state. If the excited states are broadened due to, e.g., the electric field in the junction, it is anticipated that the photoionization cross section will increase rapidly for energies larger than E_2, the energy separation between the ground state, and the $2p_0$ state, instead of showing a series of well defined sharp peaks. Comparing the absorption data of Forman[22] with the results presented in Fig. 13, it can be anticipated that some kind of broadening effect seems to occur in junction measurements. Previous thermal measurements[6] gave a value of 0.286 eV for E_2 which is in good agreement with the threshold energy of the spectrum shown in Fig. 4. This further supports the assignment that in the case of the B center the value of E_2 is indeed the spacing between the ground state and the $2p_0$ state.[6] Hence, using this result and knowing the spacing between the bottom of the conduction band and the $2p_0$ state, we are able to calculate the binding energy of the selenium-related B center in silicon.

From detailed measurements of capture cross sections and using the arguments of Gibb et al.,[29] a value of 14 meV for the spacing between the conduction band and the $2p_0$ state was previously obtained. For a single donor in silicon, effective-mass theory predicts 11 meV, which is in good agreement with observed values for shallow donors (e.g., 11 meV for Si:P).[2] Neutral selenium (and sulfur) contain two electrons in the bound state and, when one of them is excited, the resulting spectrum is more complicated. If the band minimum were spherical, the spectrum would be analogous to that of the one-electron excitation spectrum of the helium atom. Because of anisotropy, the spectrum is modified. No detailed calculations have been attempted, but it can easily be deduced[34] that, except for additional small multiplet splittings, the spectrum is the same as that of a single shallow donor. The

$2p_0$ equivalent state is, however, expected to have a *larger* binding energy than in the case of a single donor, because selenium and sulfur have two extra protons in the nucleus, one of which is only partially screened by the electron remaining in the ground state.[34] Thus, the value of 14 meV obtained from our analysis is reasonable. Adding 14 meV to E_2 gives a value of 0.301 eV for the binding energy of the selenium-related B center in silicon. This is indicated by an arrow (F) in Fig. 4.

It should be noted that the energy spacing between the peak at 0.270 eV and the optical ionization energy of 0.301 eV is 31 meV. This result is in good agreement with corresponding observations of shallow centers in silicon[2] and very close to the value quoted by Ning and Sah[9] for transition between the ground state and the T_2 excited state in Si:S. Furthermore, the energy position of the peak at 0.270 eV is independent of temperature, which may indicate that the B center is pinned to the conduction band in agreement with previous thermal data.[6]

The overall features of the σ_{nB}^0 spectra for the sulfur-related B center in silicon are very similar to those of Si:Se. The spectral distribution of σ_{nB}^0 has previously been measured by Ning and Sah.[9] They found a peak at 0.285 eV, which they explained as transitions from the $1s\,A_1$ ground state to the $1s\,T_2$ excited state. Replotting the data of Fig. 3 in this energy region on an expanded scale, we observe a peak at 0.286 eV, which fits well to a Lorentzian line shape with a half-width of 2.5 meV (Fig. 18).

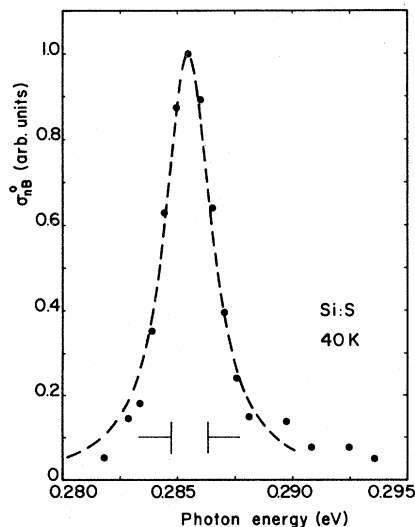The spectral distribution of σ_{nB}^0 at about 0.290

FIG. 18. An enlarged part of a high-resolution spectrum in the low-energy region of σ_{nB}^0 in Si:S, showing the Lorentzian behavior of the main peak.

eV has not been further analyzed because of disturbance from water absorption bands in the air. However, we are convinced that the structure observed above 0.30 eV is not due to experimental difficulties but is caused by Coulombic excited states. Using the same arguments as for the B center in Si:Se, an increase of σ_{nB}^0 is expected for energies larger than E_2, the energy spacing between the ground state and the $2p_0$ state. From the temperature dependence of the thermal emission rate analyzed in terms of a model suggested by Gibb *et al.*,[29] a value of 0.302 eV has previously been obtained for E_2 of the B center in Si:S.[7] Comparing this result with the spectrum shown in Fig. 3, it is quite evident that there is a sharp increase in σ_{nB}^0 at exactly this energy, thus confirming our previous interpretation of E_2. From measurements[7] of the capture cross section σ_{nB}^t we had to conclude that the energy spacing between the bottom of the conduction band and the $2p_0$ state is about 17 meV. Adding this energy value to E_2 gives a value of 0.319 eV for the binding energy of the sulfur-related B center in silicon, which is close to the value quoted by Ning and Sah[9] and in good agreement with the optical data (see arrow F in Fig. 3). The energy separation between the peak at 0.286 eV and the conduction band is then 33 meV, in accordance with a singly charged center derived from previous theoretical considerations.[18]

There appears to be no temperature dependence of the position of the peak at 0.286 eV, also indicating that the position of the ground state is temperature independent if the B center is effective-mass-like. It is then expected that the enthalpy ΔH_{nB} of the center is equal to the optical ionization energy ΔG_{nB}^0. From previous thermal measurements,[7] a value of 0.320 eV has been obtained for ΔH_{nB}, whereas the Gibbs free energy[35] $\Delta G_{nB} = \Delta G_{nB}^0 - kT \ln g$ was temperature dependent and smaller than ΔH_{nB}. If it is concluded from the optical data that the B center is pinned to the conduction band, a degeneracy factor g close to 2 is obtained by putting $\Delta H_{nB} = \Delta G_{nB}^0$. This value of g gives a temperature dependence of ΔG_{nB}, which is in fair agreement with previous experimental results.[7]

It is interesting to note that the peak at 0.286 eV due to intravalley optical transitions is about 16 meV "deeper" than the corresponding peak in Si:Se, in agreement with the 19 meV larger binding energy of the B center in Si:S. However, the dominating peaks of the A centers due to intravalley optical transitions have almost identical energy positions in Si:Se and Si:S, although the A center in Si:S has a 25 meV larger binding energy.

V. CONCLUSION

Two dominant donor levels have been observed in both selenium- and sulfur-doped silicon. One of these centers (the A center) is a midgap level, whereas the other one (the B center) has a binding energy of 0.301 eV in Si : Se and 0.320 eV in Si : S. The spectra of the photoionization cross section of electrons, σ_n^0, have been analyzed by assuming that the B centers are singly charged and the A centers doubly charged. With this assumption, good agreement between our results of the A centers and published data of shallow donors in silicon has been obtained for the Rydberg excited states.

Similar good agreement has been obtained for the valley orbit splitoff states of the B centers and those for shallow centers in silicon. The T_2 state has been found to lie 33 and 31 meV below the conduction band in Si : S and Si : Se, respectively. The corresponding values for the A centers are 163 and 143 meV, respectively.

Within this model we have strong reasons to believe that the energy position of the B centers with respect to the conduction band is independent of temperature. Similar temperature-independent energy positions have been observed for the A centers at $E_c - 0.59$ eV in Si : S and at $E_c - 0.57$ eV in Si : Se. The spectra of the photoionization cross section of holes, σ_{pA}^0, are not in contradiction with a possible pinning of the A centers to the conduction band.

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