Acceptorlike excited states of the isoelectronic *A,B,C* exciton system in silicon

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Excitation spectroscopy of the isoelectronic *A,B,C* exciton system in silicon yields seven new excited states. They can be associated with excited hole states of an effective-mass-like pseudoacceptor split in the axially symmetric field of the binding center. The pseudoacceptor ($E_i = 36.7$ meV) fits excellently into the systematics of common acceptor spectra in silicon.

Excitons bound to isoelectronic traps have been recognized for a long time in several semiconductors. Only recently has photoluminescence been ascribed to isoelectronic centers in silicon, such as the *A,B,C* line system[1]; the *P,Q,R* luminescence lines[2]; neutron-transmutation-induced emission lines at 1.108 eV where long lifetimes hint to the isoelectronic nature[3]; and thallium-related exciton emission.[4] In all cases, deep-level traps of complex, noncubic structure seem to be involved. The best documented case is probably that reported by Weber *et al.*[1] This exciton is localized at an axial center of trigonal symmetry whose chemical nature is not yet known. It recombines preferentially emitting the dipole allowed *A* line at $\lambda = 1.1044$ μm ($h\nu = 1.1223$ eV) from the $J_z = \pm 1$ state. A dipole forbidden *B* line originates from a lower-energy exciton state $J_z = \pm 2$, upon perturbations of the system. The *C* line is due to an excited state split apart from the *A* state by 3.1 meV, and is observed at higher temperatures. Weber *et al.* interpreted the exciton states using the model of Morgan and Morgan.[5] The model refers to excitons at axially symmetric isoelectronic defects and describes the exciton ground-state multiplet in terms of two parameters Δ and ϵ_0; Δ is the *j-j* splitting due to the electrostatic interaction of the electron and the hole in the limit of spherical symmetry, and $2\epsilon_0$ is the hole splitting due to the internal strain field of the axial defect in the limit of vanishing *j-j* coupling. Weber *et al.* presented arguments that the electron is primarily bound to the trap capturing the hole by its Coulombic field.

In the present paper, we study the *A,B,C* exciton by excitation spectroscopy at 4.2 K and determine a set of excited states. The new states can neither be observed in absorption nor in emission. Temperature controlled photoluminescence measurements[1] showed that the exciton is dissociated with an activation energy of $\simeq$44 meV from about 30 K on, too low for the highly excited states to be populated.

The laser used in the experiments was a NaF:Ca(F_2^+)* color-center laser tunable from 1.020 to 1.125 μm. Geometric arrangement, crystal doping and preparation, and other details are described elsewhere.[6–8] The laser was tandem pumped by a HITC dye laser and a Kr^+ laser. Output powers ranged from 150 to 200 mW at a linewidth of $\simeq$0.6 Å. In our experiment, the absorption of laser light by excited states of the exciton was monitored by recording the luminescence of the strong *A* line whose transition upper state is populated by the relaxation of the absorbing excited states. Silicon samples were in the experiments either *p* type (Si:Al, 2.5 Ωcm) or *n* type (Si:P, 115 Ωcm). The samples were immersed in liquid helium at 4.2 K. The luminescence light was dispersed by a 0.75-m grating monochromator and detected by a germanium detector. A polarization filter at the entrance slit of the monochromator reduced excitation light reflected from the sample surface.

The excitation spectrum of an Al-doped sample is shown in Fig. 1. We observe at low excitation

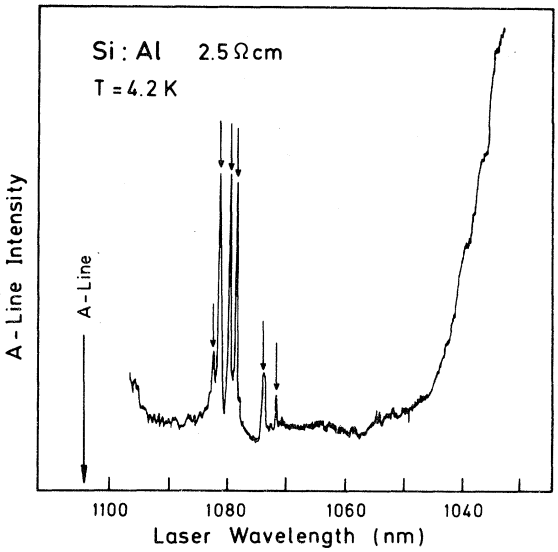

FIG. 1. Excitation spectrum of the localized exciton. Recorded is the *A*-line intensity in function of the laser excitation wavelength. Arrows mark new resonances.

wavelengths around 1.060 μm the quadratic onset of band-to-band absorption. In the spectral region near 1.080 μm six sharp lines show up. On the high wavelength side, the useful recording of the spectrum is limited by the finite suppression of the exciting laser light towards the position of the A line. Therefore we could not see in this experiment the C exciton line.

Figure 2 is a blowup of the excitation spectrum at improved resolution and sensitivity. We distinguish now seven lines which we label D through J persuing the former labeling of the exciton states. This spectrum is at the same relative line intensities obtained for the n-type, phosphorus-doped samples except for lower absolute line intensities.

In the first instance, it has to be made sure that these resonances are related with the A,B,C exciton and are not due to some energy-transfer process to other centers. Energy transfer has, for example, been reported for the GaP nearest-neighbor (NN) pairs to occur between excitons bound to pairs of different pair separation.[9,10] A similar process obviously happens in excitation spectroscopic measurements on the P,Q,R isoelectronic lines in In-doped samples,[2] when we observe the P monitor transition at the excitation energy of the indium acceptor bound exciton.[11] We exclude here every kind of energy transfer since the excitation spectrum is independent of shallow donor or acceptor doping, and since no indication of further optical transitions exists which could be due to other defects or impurities.

We interpret the resonances as originating from acceptorlike excited hole states split in the axially deformed Coulombic field of the primarily bound electron. This interpretation was initiated by some analogy with NN-pair excitation spectra in GaP.[10] In the latter work, a series of resonance lines was observed for each NN pair at individual pair separations converging towards a series limit, and an explanation was given in terms of nS even-parity hole states of a pseudoacceptor. Our interpretation is similar but allows each level to be split into sublevels by the effects of j-j interaction (Δ) and of internal strain ($2\epsilon_0$).

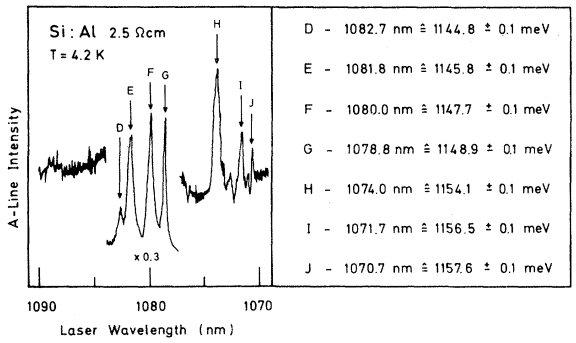

FIG. 2. Detailed excitation spectrum showing lines D through J and line positions.

Using the data of Weber *et al.*,[1] we determine the ground-state parameters of the exciton to be $\Delta = 1.4$ meV and $2\epsilon_0 = 3.6$ meV. Both effects, the j-j splitting as well as the strain splitting, are expected to drop off rapidly for large Bohr radii r of the excited hole. Experimental data as to the functional r dependence seem only to exist for the strain splitting $2\epsilon_0$ and refer to donor-acceptor pairs in GaP.[12] They indicate an approximate relationship $2\epsilon_0 \simeq 1/r^3$. We, on the other hand, do not arrive at a satisfactory explanation of our spectra when we assume that both interactions have to be taken into account in the excited states. Compelled to give predominance to only *one* interaction, we neglect the j-j splitting, thus allowing for strain-dominated doublet splittings of the exciton states. One possible reason for this choice will be advanced below. We associate the doublets with the line pair (D,E) at a level energy of 1.1453 eV ($2\epsilon_0 = 1.0$ meV), and the line pair (F,G) at a level energy of 1.1483 eV ($2\epsilon_0 = 1.2$ meV). The H line is distinctly broader than the other lines, suggesting that it is composed of an unresolved doublet at a level energy of 1.1541 eV ($2\epsilon_0 < 0.2$ meV), and the remaining I and J lines are attributed to levels at 1.565 and 1.1576 eV, respectively ($2\epsilon_0 \simeq 0$).

The level scheme resulting from this coordination is depicted in Fig. 3 and is compared with excited hole states of common acceptors in silicon. The acceptor energies were taken over from bound exciton–two-hole transition data.[13–15] We find an excellent agreement of the excited levels with the boron states when we shift our levels such as correspond to an ionization energy of $E_i = 36.7$ meV of the pseudoacceptor. The dependence on the acceptor species is for the particular states nicely continued in the series from Tl to B and conforms with the value of E_i. Details give support to our interpretation. From Tl to the isocoric Al acceptor, the Γ_8^+ even-parity states shift towards higher energies as a result of the decreasing attractive central-cell potential; for boron the central-cell potential becomes repulsive, leading to a further reduction in the binding energy.[14,15] Thus the A,B,C pseudoacceptor evidences a strong, repulsive central-cell effect. The chemical shift virtually vanishes for high quantum numbers, $n = 3, 4, 5$, since these highly excited states do no longer experience the true core potential. In contrast, the $1\Gamma_8^-$ states of boron and of our pseudoacceptor nearly coincide because their wave functions have a node at the nucleus. We have also made attempts to compare the exciton states with the level scheme of common donors in silicon but could not find a reasonable agreement. The localization energy of the exciton (A line) is, with respect to the band gap, 47.3 meV.[1] We subtract 1.4 meV to come to the center of gravity and find $E_{\text{loc}} = 45.9$ meV. The localization of the electron

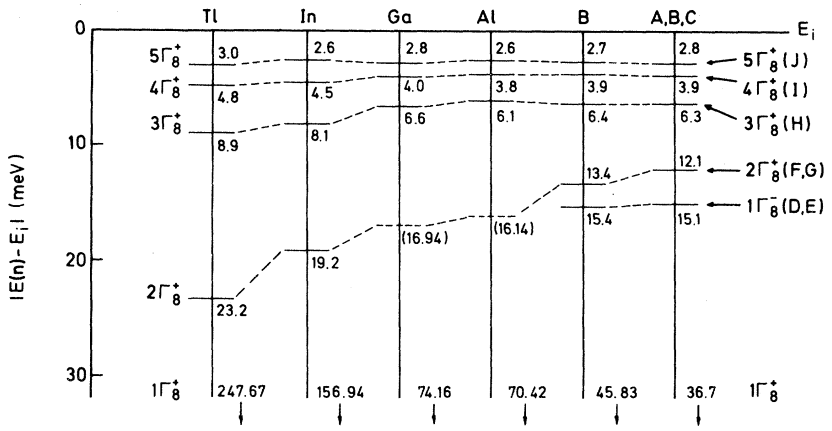

FIG. 3. Experimental *s*-like even-parity-state spectra of Tl, In, Ga, Al, and B acceptors in silicon as taken from bound-exciton-two-hole transition spectra (Refs. 13 and 14). Values for Ga and Al in parentheses are theoretical. The Tl energies were orally communicated [Ref. 14, talk presented at the 15th International Conference on the Physics of Semiconductors, Kyoto, 1980 (unpublished)]. Ionization energies are from Ref. 15. The *A,B,C* pseudoacceptor states are compared on the right-hand side.

at the isoelectronic trap then becomes $E_e = 9.2$ meV, where the acceptor binding energy $E_i = 36.7$ meV was used. This comparatively low figure does not conflict with the present model when we recall that a similar ratio of $E_e/E_i = 0.25$ applies to the accepted case of nitrogen-bound excitons in GaP for the $(NN)_6$ pair.[10]

We have to justify our former choice of a strain splitting dominating the *j*-*j* interaction in the excited states. Actually, if we had chosen the opposite case, we would have found almost the same acceptor levels as quoted before. The reason is that the levels as obtained from the weighted doublet positions in a 3:5 ratio [from $g(J=1):g(J=2)$ in a *j*-*j* interaction model] do not differ from the former ones within experimental uncertainty. So we cannot appeal to a purely experimental decision. We can, however, give an argument in terms of selection rules. The *B* line as the $J_z = \pm 2$ to $J = 0$ transition never shows up in conventional luminescence unless external perturbations are applied, suggesting that the $J_z = M_J$ selection rule works effectively. If the strain effects were negligibly small in the excited states, we would expect *J* to become an even better quantum number than J_z was before, and do not see why transitions from excited $J = 2$ levels could be observable. We find support to this argument from a comparison with excitons at NN nitrogen pairs in GaP.[10] There, the *B* line is strongly seen at low temperatures in the exciton ground state but is absent in the excited states. The sequence of strain splittings $2\epsilon_0$, which we obtain in our interpretation, is consistent with the acceptor model; the values are strongly reduced in the sequence of the Γ_8^+ even-parity states, and for the odd-parity $1\Gamma_8^-$ state, the effect of a smaller orbit may compensate the lower probability density at the binding center of the more *p*-like function.

In conclusion, the explanation of the excited *A,B,C* exciton levels in terms of pseudoacceptor states fits excellently into the systematics of common-acceptor spectra in silicon. Different from familiar isoelectronic systems, doublet splittings of the excited states are observed. An argument is given that they are due to the strain field of the axially symmetric defect. An observable *j*-*j* interaction is then limited to the exciton ground state.

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[1]J. Weber, W. Schmid, and R. Sauer, J. Lumin. 18/19, 93 (1979); Phys. Rev. B 21, 2401 (1980).

[2]G. S. Mitchard, S. A. Lyon, K. R. Elliott, and T. C. McGill, Solid State Commun. 29, 425 (1979); M. L. W. Thewalt, U. O. Ziemelis, and R. R. Parsons, *ibid.* 39, 27 (1981).

[3]J. A. Rostworowskii and R. R. Parsons, Can. J. Phys. 59, 496 (1981).
[4]M. L. W. Thewalt, U. O. Ziemelis, and R. R. Parsons, Phys. Rev. B 24, 3655 (1981).
[5]J. V. W. Morgan and T. N. Morgan, Phys. Rev. B 1, 739 (1970).
[6]J. Wagner, J. Weber, and R. Sauer, Solid State Commun. 39, 1273 (1981).
[7]H. Eisele, H. J. Paus, and J. Wagner, IEEE J. Quantum Electron. 18, 152 (1982).
[8]M. Leduc, H. Eisele, H. J. Paus, and J. Wagner (unpublished).
[9]P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. 35, 1366 (1975).
[10]E. Cohen, M. D. Sturge, N. O. Lipari, M. Altarelli, and A. Baldereschi, Phys. Rev. Lett. 35, 1591 (1975); E. Cohen and M. D. Sturge, Phys. Rev. B 15, 1039 (1977).
[11]Unpublished results of the authors.
[12]T. N. Morgan and H. Maier, Phys. Rev. Lett. 27, 1200 (1971).
[13]M. L. W. Thewalt, Solid State Commun. 23, 733 (1977).
[14]N. O. Lipari, M. L. W. Thewalt, W. Andreoni, and A. Baldereschi, J. Phys. Soc. Jpn. Suppl. A 49, 165 (1980).
[15]N. O. Lipari, A. Baldereschi, and M. L. W. Thewalt, Solid State Commun. 33, 277 (1980).