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Bound-to-bound transitions at neutral zinc in silicon: Effective-mass-like states and hole-hole interaction

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We present infrared absorption measurements on the neutral charge state of the double-acceptor zinc in silicon. An effective-mass-like $P_{3/2}$ spectrum for the excitation of the secondarily bound hole is found. The ground state is calculated to be 319.1 ± 0.3 meV above the valence band. The observed splitting of the ground state into three sublevels is assigned to the hole-hole interaction and crystal-field splitting. The results are compared with recent findings on double acceptors in germanium.

I. INTRODUCTION

Neutral zinc has the electron configuration $3d^{10}4s^2$. When it is incorporated into silicon on a substitutional site four electrons are participating in the bonds leaving the d shell in the configuration $3d^8$. Therefore zinc is expected to act as a double acceptor.

In germanium, two acceptor levels are introduced by zinc, with ionization energies of 33 and 87 meV, respectively.[1] The double-acceptor character of these levels is identified by infrared absorption measurements. A hydrogenlike and a heliumlike series, found for the Zn^0 and the Zn^- charge state, respectively, are well understood within the effective-mass theory (EMT).[1,2]

Similar line spectra for Si:Zn were not reported up to now. Early Hall experiments on Zn-diffused silicon showed two levels which were attributed to the double acceptor. These levels, 0.31 eV above the valence band and 0.55 eV below the conduction band, respectively, were identified with the Zn^0 (Refs. 3 and 4) and the Zn^- (Ref. 4) charge state. Further experiments focused on the photoionization of the various charge states of zinc in n- and p-type silicon, like measurements of photocurrent,[5,6] absorption,[5,7,8] and photocapacitance.[9] The optical cross sections obtained from the latter two methods were explained in the simple model of Lucovsky.[7,9] Thermal-emission rates of holes and electron-capture rates were measured with thermally stimulated current-capacitance[10] and transient-capacitance techniques.[11,12] The values of the Zn^0-level position reported in the literature[1-12] vary between 0.31 and 0.33 eV above the valence band.

All these previous studies are concerned with the rates of carrier emission and capture. In this Rapid Communication, we report bound-to-bound transitions at Zn^0, namely, the excitation of the secondarily bound hole.

II. EXPERIMENTAL DETAILS

For optical measurements, samples from boron-doped float-zone silicon crystals (10^{13} cm^{-3}) and phosphorus-doped Czochralski material (2×10^{15} cm^{-3} and 4×10^{15} cm^{-3}) were cut and cleaned. The samples were then sealed in a quartz ampoule together with zinc ingots and heated up to 1200 °C for 40 h. After the diffusion step, the ampoule was quenched in water. An additional heat treatment at 600 °C was performed for 2 min, to incorporate most of the zinc atoms into the double-acceptor configuration. Finally the samples were mechanically polished to remove metallic zinc and to obtain surfaces of good optical quality.

The absorption spectra were taken with a Fourier spectrometer (Bomem DA 3.01), equipped with a cooled InSb detector. A flow cryostat was used to cool the samples, allowing temperatures from 300 K down to 6 K.

Spreading resistance profiles of similarly treated samples show that the homogeneity of the zinc distribution over the whole sample is better than 10% of the total zinc concentration. From Hall measurements, the zinc concentration is determined to be $(9\pm3)\times10^{16}$ cm^{-3}. All samples resulted in p-type conductivity after the zinc diffusion.

III. RESULTS AND DISCUSSION

Absorption and photoconductivity spectra were measured from 1800 cm^{-1} up to 9000 cm^{-1} (230–1100 meV). At 40 K, all zinc-diffused samples investigated show a strong onset in the absorption spectra at around 2500 cm^{-1} (310 meV). We found an identical onset in photocurrent measurements. No other spectral feature in the absorption is observed at that temperature. In previous studies on absorption,[5,7] photocurrent,[5] and photo-

capacitance[9] of silicon diffused with zinc this spectroscopic structure was found, too, and attributed to the photoionization of the Zn^0 double-acceptor level. In our case, the zinc concentration dominates the shallow dopants and thus determines the Fermi-level position. This explains the observation of the Zn^0 center in nominally boron-doped and nominally phosphorus-doped samples. With the zinc concentration obtained from Hall measurements, we calculate the maximum of the optical cross section to be $\sigma_{max} = (0.5 \pm 0.2) \times 10^{-16}$ cm^2. This value is in fairly good agreement with the previously reported value of $(1-2) \times 10^{-16}$ cm^2 (Ref. 7) and 1×10^{-16} cm^2.[9]

Additional absorption features of the neutral zinc center appear below 40 K. Transitions from the ground state (Zn^0 acceptor level) to effective-mass-like excited states are observed between 2450 and 2550 cm^{-1}. The lines I_1^q through I_4^q, shown in Fig. 1, are due to these transitions. This conclusion is drawn by comparing the I^a series with the absorption spectra of the shallow group-III acceptor indium.[13] Accordance is also found with the recently reported EM-like spectra of the Au and Pt acceptor[14] or the various Be acceptor centers.[15,16] In all cases, the spectra are like the I^a series regarding spectroscopic spacings and line intensities. While the Zn^0 ground state is deep the excited states are satisfactorily described by the EMT, originally developed for shallow single acceptors.[2] The observed lines are due to transitions between a Γ_8^+ ground state and odd-parity EM states originating from the $P_{3/2}$ valence band. The excellent agreement between EMT and the experiment is shown in Table I. This fact allows an accurate calculation of the Zn^0 level position, by adding the binding energy of the excited state —obtained from EMT— to the energy of the corresponding transition. The ground-state level is found to be 319.1 ± 0.3 meV above the valence-band edge. The previously reported values for the Zn^0 level obtained from electrical measurements[10-12] and optical methods[5-9] agree well with the value presented here. The photoionization onset at around 2520 cm^{-1} that governs the absorption spectrum above 40 K is present in Fig. 1, too. A minor low-energy shift of the photoionization onset compared to the series limit obtained by EMT might be caused by a small relaxation of the center.[17]

An additional spectrum with an EMT series is observed in the boron-doped sample. These lines (J series in Fig. 1) belong to an independent center Zn($X2$) (Ref. 18) with

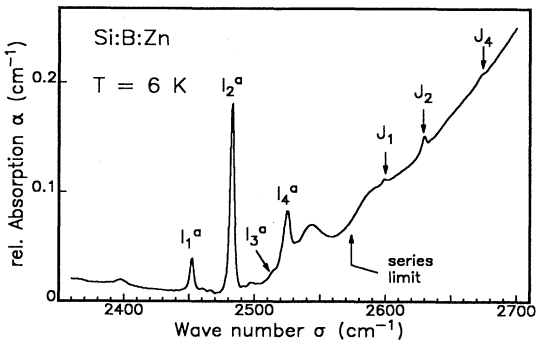

FIG. 1. Zn^0 absorption lines (I series), due to the excitation into the EM-like states; EMT series limit as indicated. J lines belong to the center Zn($X2$) (Ref. 18).

the ground state 337.5 meV above the valence band; see Fig. 1 and Table I.

Additional lines that are weak at 6 K show up with raising temperature in the I^a spectrum of the Zn^0 center. Two new lines at 2459.9 cm^{-1} (I_2^c) and 2466.8 cm^{-1} (I_2^b), respectively, can clearly be resolved at 10 K. Another structure which is found at around 2430 cm^{-1} shows a twofold shape, too. The thermally activated lines are approximately as strong as the remaining I^a lines when the temperature reaches 18 K. The lines of the I^c series become more intense than the lines of the I^b series. Finally at 30 K, the I^a series is weaker than the "hot lines" and additionally all lines are considerably broadened. Between the thermally activated lines the same spectroscopic distances can be found as in the low-temperature spectrum. Generally, to each of the lines I_1^q through I_4^q exists a counterpart in the series I^b and I^c as indicated in Fig. 2. The temperature dependence of the three identical series I^a, I^b, and I^c is characteristic of a ground state that is split into three sublevels a, b, and c. From the shift of the three series, we obtain the ground-state splitting (relative to the lowest level a) $\Delta E_{a,b} = 1.9$ meV and $\Delta E_{a,c} = 2.8$ meV (see Fig. 3). A splitting of the excited states as found for Ge:Be (Ref. 19) is not observed. It could be hidden by the linewidth only and hence must then be smaller than 0.2 meV.

For the line I_2^q, I_2^b, and I_2^c, a quantitative analysis of the temperature dependence is possible. Since I_2^b and I_2^c cannot be resolved over a large temperature range, the sum of

TABLE I. Spectroscopic values ($\bar{\nu}$) of the Zn^0 center and the Zn($X2$) center (Ref. 18), binding energies (E_b) of the EM states, and ground-state position (E_{ion}) relative to the valence band.

Zn		Zn($X2$)		EMT[a]
$\bar{\nu}$ (cm^{-1})	E_b (meV)	$\bar{\nu}$ (cm^{-1})	E_b (meV)	E_b (meV)
I_1 2451.1	15.2	J_1 2598.6	15.3	15.5
I_2 2482.5	11.3	J_2 2629.0	11.5	11.4
I_3 2513.9	7.4			7.3
I_4 2524.7	6.1	J_4 2673.6	6.0	6.0
$E_{ion} = 319.1$ meV		$E_{ion} = 337.5$ meV		

[a]Reference 2.

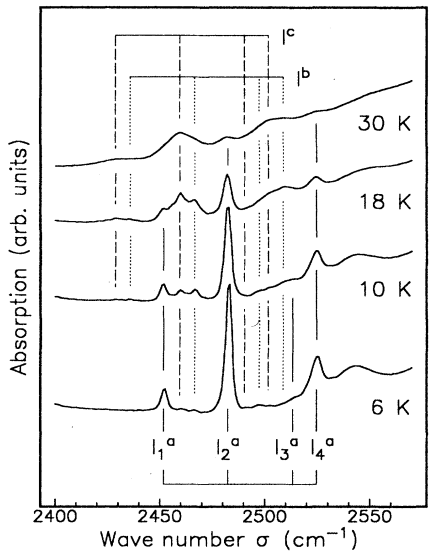

FIG. 2. Thermally activated absorption lines of the Zn^0 center. All lines with corresponding transition starting from the same ground-state level are lumped together. Indication I^a, I^b, and I^c refers to the specific ground-state level; see level scheme in Fig. 3.

both intensities was evaluated. The logarithm of the ratio $(I_2^b+I_2^c)/I_2^a$ vs $1/T$ is plotted in Fig. 3. A linear relation is found in this Arrhenius diagram demonstrating that the intensities reflect the thermal population of the ground-state levels. For the activation energy, we obtain $\Delta E_{\text{therm}}=3.3\pm0.5$ meV. The small deviation from the expected value $(\Delta E_{a,b}+\Delta E_{a,c})/2=2.4$ meV is not fully clear yet.

The observed threefold splitting of the ground state cannot be described in terms of a single acceptor, e.g., by a relaxation of the atom from the highly symmetrical T_d site to a site of lower symmetry. Since a Γ_8^+ state of T_d symmetry splits into two levels when the symmetry is lowered, only a twofold splitting of the line is expected. Hence, an additional interaction is needed in the present case. This is a strong indication that hole-hole interaction together with the crystal field causes the three ground-state levels, as expected for a double acceptor. Taking into account the Pauli principle the coupling of two Γ_8^+ hole states leads to three levels: Γ_1, Γ_3, and Γ_5. In terms of the j-j-coupling scheme, which is not strictly correct, two $j=\frac{3}{2}$ states couple to $J=0$ (Γ_1) and $J=2$ ($\Gamma_3+\Gamma_5$). The latter state may be split further into Γ_3 and Γ_5 by the crystal field. For several double acceptors in germanium, a twofold splitting into $J=0$ and $J=2$ is found: Ge:Hg (0.7 meV),[20] Ge:Zn (2.4 meV) (Refs. 21 and 22) and Ge:Mg (1.8 meV).[23] In the latter two systems a threefold splitting might be possible as well, but could not be resolved, because of the insufficient experimental signal-to-noise ratio. A complete splitting into the three substates as presented here has not yet been reported for double acceptors. On the other hand, previous absorption measurements on excitons bound at the group-III acceptors Al and Ga in silicon (A^0X) show a threefold exciton ground state.[24] The interpretation given there deals with hole-hole interaction and crystal-field splitting, too. Like in our case, see discussion below, the authors conclude the ground-state level to be Γ_1.

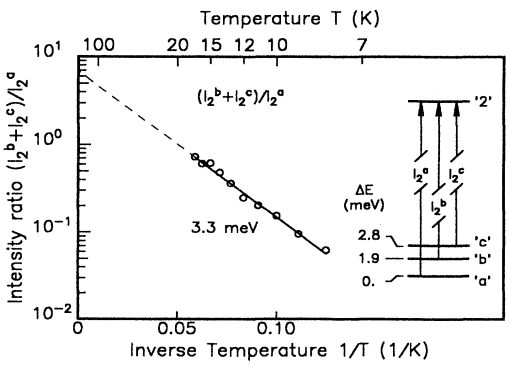

FIG. 3. Thermalization of the lines I_2^a, I_2^b, I_2^c; see text. Scheme of the ground-state levels.

Information about the ordering of the ground-state levels is obtained from temperature-dependent measurements. The high-temperature limit of the ratio $(I_2^b+I_2^c)/I_2^a$ yields 6.9 ± 1.5. This value is determined by the entropy factors of the ground-state levels only.[24] Since Γ_1 is onefold, Γ_3 is twofold, and Γ_5 is threefold degenerate, the lowest ground-state level must be Γ_1 while the upper ground states are Γ_3 and Γ_5. The resulting intensity ratio should then be 5, which is close to the measured value. The ordering of Γ_3 and Γ_5 is more difficult to decide. The faster increasing thermalization of I_2^c suggests the assignment of b with Γ_3 and c with Γ_5. An $J=0$ (Γ_1) ground state was found also in the system Ge:Zn.[21,22] The opposite case, a ground state of $J=2$ ($\Gamma_3+\Gamma_5$), is realized in Ge:Hg.[20] For the latter double acceptor the exchange interaction seems to be more important than in the lighter zinc impurity in germanium and silicon. An exchange term results in the "normal ordering" according to Hund's rule with $J=2$ the lowest.[25] On the other hand, the central-cell corrections seem to dominate in Ge:Zn and in Si:Zn. The central-cell corrections are expected to affect the Γ_1 state more strongly than Γ_3 or Γ_5,[25] which leads to the so called "inverted ordering" with Γ_1 as lowest ground-state level.

Substitutional beryllium as a group-II element is another possible candidate for a double acceptor in silicon. Several centers show up after beryllium diffusion in absorption[15,16] and deep-level transient spectroscopy (DLTS).[26] It is assumed that the BeI center (E_v+192 meV) belongs to the substitutional double acceptor.[15] A splitting of the ground state has not been observed.[15] Hence the data presented here are the first example for the ground-state splitting of a double acceptor in silicon. A comparison of our results with published data for Ge:Zn (Refs. 21 and 22) demonstrates that the hole-hole interaction of Zn in silicon and germanium is of the same size. Fano resonances of the O^Γ phonon as found in the absorption spectra of shallow group-III acceptors[27] or deep acceptor centers in silicon[28] are observed in addition to the I^a series and will be reported elsewhere.

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