PHYSICAL REVIEW B VOLUME 25, NUMBER 6 15 MARCH 1982

Additional $p_{3/2}$ and $p_{1/2}$ infrared excited-state lines of gallium and indium in silicon

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(Received 28 September 1981; revised manuscript received 28 December 1981)

Infrared excitation spectra were measured for the $p_{3/2}$ lines of gallium in silicon. Two missing lines were observed, and a previous weak or doubtful one was confirmed. Spectra were also obtained of the $p_{1/2}$ lines of gallium and indium in silicon, demonstrating for the first time the $4p'$ line for both dopants. There now exists complete correspondence between all observed excited-state lines of gallium and indium in silicon and the lines of boron and aluminum, and with those predicted by theory. From the new spectral data, the spin-orbit splitting of the valence bands is calculated to be 42.62 ± 0.04 meV.

I. INTRODUCTION

The infrared excitation spectra of group-III acceptors in silicon have been the subject of extensive experimental work for many years.[1-4] Meanwhile, extended treatment of the effective-mass theory has produced values of acceptor energy-level positions that are more accurate than those obtained from simpler theories.[5,6] Technological improvements in both spectrophotometry and crystal growth have produced high-resolution acceptor spectra with which to compare the latest theory.[7]

A recent study[8] of the $p_{3/2}$ bands of indium in silicon revealed several lines previously not reported but believed to exist both from theory and from comparison to the spectra of the other group-III acceptors. For the case of gallium in silicon, three lines of the $p_{3/2}$ series were reported by Onton *et al.* as missing or doubtful.[3] In addition, they did not observe the $4p'$ line in the $p_{1/2}$ series of either gallium and indium, although Zwerdling *et al.* had observed the $4p'$ line for both boron- and aluminum-doped silicon.[2]

We report here the observation of the missing or doubtful lines of the gallium $p_{3/2}$ series, and the $4p'$ line for both gallium- and indium-doped silicon. An analysis of the new data also yields a value of the spin-orbit splitting of the valence bands somewhat lower than the values previously calculated.[2,3]

II. EXPERIMENTAL

Gallium-doped samples were cut from two float-zone boules, one grown by Hughes Research Laboratories and the other by Westinghouse Research and Development Center. The Hughes boule had a gallium concentration of 5×10^{16} cm^{-3}, while the Westinghouse boule had a gallium concentration of 3×10^{16} cm^{-3}. The indium-doped samples were cut from a Dow Corning float-zone boule having an indium concentration of 4.2×10^{16} cm^{-3}.

The samples were cooled to 10 K in either a liquid-helium Dewar or a closed-cycle refrigerator for the measurements. All spectra were recorded on a Digilab model FTS-20C Fourier transform spectrophotometer purged with dry nitrogen. The spectrometer was calibrated using known *in vacuo* positions of water vapor and carbon dioxide absorption bands.[9] Our calibration deviated from these standard values by only 0.00 cm^{-1} to -0.02 cm^{-1} in the regions where data is reported. Wave numbers were converted to *in vacuo* energy values

using the factor 0.123 9854 meV/cm^{-1}.[10] The footnote to our previous work on indium-doped silicon spectra[8] should be disregarded, because it was based upon the false assumption that our polystyrene calibration values were referenced to air when they were actually referenced to vacuum.[9] Other experimental details were the same as previously reported.[8]

III. RESULTS AND DISCUSSION

The $p_{3/2}$ excitation spectrum of gallium-doped silicon is shown in Fig. 1. All the $p_{3/2}$ lines, as well as the $p_{1/2}$ lines, were observed in samples cut from both the Hughes and Westinghouse boules. The lines are labeled according to the system of Onton *et al.*[3] and lines 1—4A are essentially the same as reported by them. We do not observe line 4B because of concentration broadening of the lines, since our gallium concentration is about 10—20 times greater than that used by Onton *et al.*[3] While this does introduce a line-broadening penalty, it enables us to observe the additional weak lines.

Figure 2 shows an expansion of the gallium spectrum in the region of the higher-energy lines. Lines 9 and 10 are reported for the first time. Line 7 is also observed, which was reported by Onton *et al.*[3] as "weak or doubtful." A sharper line 7 was displayed by Chandrasekhar *et al.*[4] but they did not list its energy position.

The positions of all gallium $p_{3/2}$ lines are listed in Table I. The position of line 2 is not given because of the optical-phonon broadening phenomenon.[4] Our line positions are higher in energy than those of Onton *et al.*[3] by a mean value of 0.08 meV, with the exception of line 5 whose energy position is 0.21 meV larger. The 0.08-meV difference may include a very slight systematic error (on the order of 0.04 meV) since the estimated experimental error of both sets of data is ±0.02 meV. However, neither experimental error nor a slight systematic error can explain the discrepancy in the

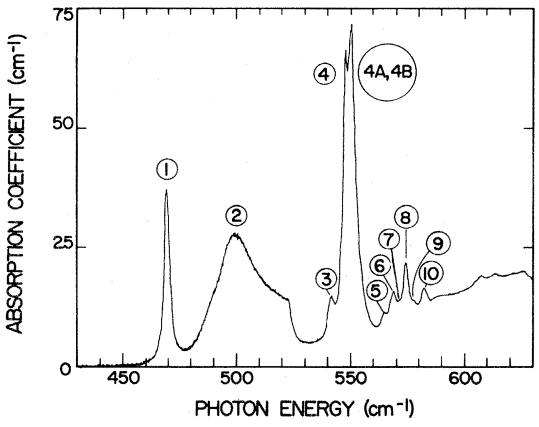

FIG. 1. Absorption spectrum ($p_{3/2}$ series) for gallium in silicon. Gallium concentration 5×10^{16} cm^{-3}. Sample thickness 0.061 cm. Resolution = 0.5 cm^{-1}.

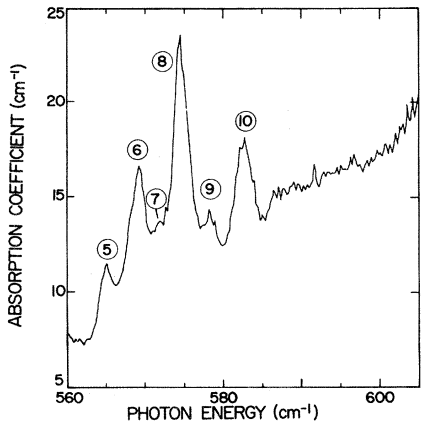

FIG. 2. Expanded absorption spectrum for gallium in silicon in the region containing lines 5 through 10 of the $p_{3/2}$ series. Sample thickness 0.175 cm. Resolution = 0.5 cm^{-1}.

TABLE I. Experimental positions of gallium $p_{3/2}$ excitation lines in silicon.

Line	Line position[a] Wave number (cm^{-1})	Energy (meV)
1	470.0	58.27
2		
3	541.9	67.19
4	548.8	68.04
4A	550.9	68.30
5	565.1	70.06
6	569.2	70.57
7	571.9	70.91
8	574.4	71.22
9	578.2	71.69
10	582.7	72.25

[a]Error is estimated to be ±0.15 cm^{-1} (0.02 meV) for all lines.

TABLE II. Theoretical and experimental $p_{3/2}$ energy-level spacings for boron, aluminum, gallium, and indium in silicon (units of meV).

ΔE	Theory[a]	B[b,c]	Al[b]	Ga[d]	Ga[b]	In[e]
1—3	8.24	7.97( )		8.92	8.89	7.75
3—4	1.22	1.29(1.23)		0.85	0.83	1.04
4—4A	0.33	0.27(0.08)	0.88	0.26	0.30	0.27
4A—5	1.67	1.61(1.78)	1.32	1.76	1.60	1.71
5—6	0.51	0.98(0.69)	0.47	0.51	0.64	0.53
6—7	0.16	0.29(0.59)	0.35	0.34	0.31	0.30
7—8		0.48(0.42)	0.29	0.31	0.31	0.36
8—9		0.59(0.10)	0.51	0.47		0.48
9—10		0.46(0.46)	0.50	0.56		0.51

[a]References 5 and 6.
[b]Reference 3.
[c]Reference 7.
[d]This work.
[e]Reference 8.

line 5 position.

The energy spacing between gallium line positions are listed in Table II, along with those for other group-III acceptors and the most recent theoretical values. Our energy spacings involving lines 7, 9, and 10 are consistent with both theory and the experimental values for the other acceptors, supporting the assignment of lines 7, 9, and 10 as the missing excited-state lines. All of our gallium spacings agree well with the values derived from the data of Onton *et al.*[3] with the exception of 4A—5 and 5—6. We believe our spacings involving line 5 are more consistent with both theory and the recent indium-doped silicon spectra.[8] This comparison, coupled with a pronounced sharpness in our line 5 as compared to that of Onton *et al.*[3] indicates that our line 5 position is the more accurate of the two.

The $p_{1/2}$ spectra for both gallium-doped silicon and indium-doped silicon are shown in Fig. 3 and the energy positions of the lines are listed in Table III. This is the first observation of the $4p'$ line for gallium and indium in silicon. Following Zwerdling *et al.*[2] we constructed a straight-line approximation to an uncorrected Rydberg series describing the line positions. We obtained an uncorrected series limit of 116.79 ± 0.02 meV for the gallium $p_{1/2}$ lines and 199.57 ± 0.02 meV for the indium $p_{1/2}$ lines. Our uncorrected gallium series limit is in agreement with the value of 116.74 ± 0.21 meV of Onton *et al.*[3] but our uncorrected indium series limit differs from their value of 200.16 ± 0.4 meV by more than the total allowable experimental error of both sets of data. We have also fit the data to the corrected Rydberg formula given by Eq. (2) of Zwerdling *et al.*[2] Our corrected series limits are 116.86 ± 0.02 meV for gallium and 199.64 ± 0.02 meV for indium. The uncorrect-

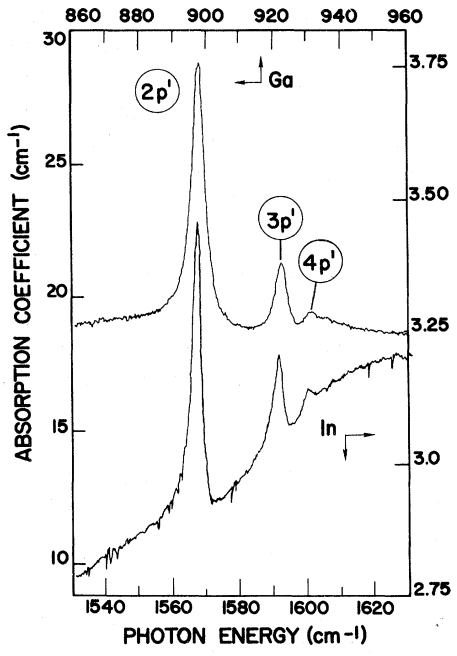

FIG. 3. Absorption spectra ($p_{1/2}$ series) for gallium and indium in silicon. Gallium concentration and sample thickness same as for Fig. 1. Indium concentration 4.2×10^{16} cm^{-3}. Indium sample thickness 0.397 cm. Resolution = 0.5 cm^{-1}.

TABLE III. Experimental positions of gallium and indium $p_{1/2}$ excitation lines in silicon.

Line	Gallium line positions[a] Wave number (cm^{-1})	Gallium line positions[a] Energy (meV)	Indium line positions[a] Wave number (cm^{-1})	Indium line positions[a] Energy (meV)
$2p'$	897.5	111.28	1565.2	194.06
$3p'$	922.0	114.31	1590.0	197.14
$4p'$	931.0	115.43	1598.4	198.18

[a]Error is estimated to be ± 0.1 cm^{-1} (0.01 meV) for $2p'$ and $3p'$; ± 0.2 cm^{-1} (0.025 meV) for $4p'$.

ed and corrected series limits are not identical because a straight line is only an approximate fit to the uncorrected series energy positions.

We have calculated the value of Δ, the spin-orbit splitting, as the energy difference between the corrected $p_{1/2}$ series limit and the $p_{3/2}$ series limit. The $p_{3/2}$ series limit was obtained by adding 3.67 meV to line 6, as prescribed by Lipari *et al.*[6] The energy position of line 6 for indium was obtained from Table I of Ref. 8. For gallium we obtained $\Delta = 42.62 \pm 0.04$ meV and for indium $\Delta = 42.62 \pm 0.03$ meV. The error estimate does not include the unknown error of the theoretical binding energy of the $2\Gamma_6^-$ final state of the line 6 transition. The essentially identical values for Δ support the self-consistency of our gallium and indium spectral data. Our value of Δ is somewhat lower than the 44.1 ± 0.4 meV of Zwerdling *et al.*[2] and ($\leq 44.0 \pm 0.2$) meV of Onton *et al.*[3]

IV. SUMMARY

We have obtained absorption spectra of the $p_{3/2}$ excited-state lines of gallium in silicon. Two missing lines were observed and a third weak or doubtful one was confirmed. The energy spacings of the lines were successfully compared to theory and the other group-III acceptors. We have also measured the $p_{1/2}$ spectra for gallium and indium in silicon, observing the previously unseen $4p'$ lines. From the spectra we calculated new values for the gallium and indium $p_{1/2}$ series limits, and for the spin-orbit splitting of the valence bands.

ACKNOWLEDGMENTS

The authors wish to thank John Baker of Dow Corning Corporation, Harvey Winston of Hughes Research Laboratories, and Timothy Braggins of Westinghouse Research and Development Center for providing the silicon crystals used in this study. We also thank Tim Peterson of the Air Force Wright Aeronautical Laboratories and Steve Smith of the University of Dayton Institute for Hall-effect measurements. Many helpful discussions were held with Dr. Charles DeJoseph, Jr. of the Air Force Wright Aeronautical Laboratories and Professor J. E. Katon of Miami University, Oxford, Ohio.

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