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Photoelectric spectroscopy of indium in silicon

Thomas C. Chandler,* Robert J. Spry, Gail J. Brown, and John J. Rome
Air Force Wright Aeronautical Laboratories, Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433

Richard J. Harris
University of Dayton Research Institute, Dayton, Ohio 45469
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Photoelectric spectroscopy has been used to study $p_{3/2}$, $p_{1/2}$, and Breit-Wigner-Fano excited-state transitions of indium in silicon. The photoelectric spectra were compared to absorption spectra and measured as a function of temperature. All $p_{3/2}$ and $p_{1/2}$ absorption lines are resolved in the photoelectric spectra, with the exception of line $4B$. This is the first observation in photoelectric spectra of lines 3 through 10, $3p'$, and $4p'$. The temperature dependence of the spectra demonstrates that line intensities are governed by a photothermal ionization process; in particular, the activation energy of the line-4 intensity agrees with the theoretical binding energy of the excited state. Details previously observed in the Breit-Wigner-Fano spectra associated with $p_{3/2}$ lines $2-10$ have also been observed for the first time in the absorption spectra.

I. INTRODUCTION

Photoelectric spectroscopy is used to study the energy states of carriers bound to impurities in semiconductors, and to detect small concentrations of impurities.[1] The spectra obtained by this method are produced by a two-step process, optical excitation of the bound carrier to an excited state, followed by thermal ionization of the carrier from the excited state to a band. This photothermal ionization process has received considerable theoretical interest because of its own importance, and because of its direct relationship to the probability of carrier capture into a bound state by a charged impurity.[2-4] Photoelectric spectroscopy has been mainly applied to III-V compound semiconductors[5,6] and to germanium.[7-9]

Absorption spectroscopy has been the major method of determining the energy levels of donors and acceptors in silicon. In particular, the energy position and symmetry have been well established for most of the $p_{3/2}$ and $p_{1/2}$ acceptor states.[10,11] Fourier-transform absorption spectroscopy and improved crystal-growth methods have more recently permitted the detection of the remaining missing or doubtful excited-state transitions of indium and gallium.[12,13] Meanwhile, improvements in the effective-mass theory have produced more accurate acceptor-energy values with which to compare the experimental spectra.[14,15] Absorption spectroscopy was also used for the first observation of the Breit-Wigner-Fano (BWF) resonance spectra associated with the $p_{3/2}$ excited states of boron, aluminum, and gallium in silicon.[16] An unanswered question was why BWF absorption spectra showed an antiresonance dip only in connection with the first-acceptor excited state, but not for the higher-energy excited states.

In silicon, photoelectric spectroscopy has been used to study the energy levels of phosphorous and boron,[1,7,8] and sulfur.[17] Earlier spectral photoconductivity studies of acceptors other than boron, for example, indium,[18] did not resolve discrete lines caused by transitions to excited states. More recently, Baron *et al.*[19] reported photoelectric spectra for aluminum, gallium, and indium in silicon. They observed most of the major $p_{3/2}$ transitions for indium, but as subtractions from the background of X-level photoconductivity. As true, positive photoelectric lines they observed only line 2, while line 1 appeared as a plateau or shoulder, and hints of lines 3 and 4 were present as inflections in the response curve. In the case of $p_{1/2}$ transitions, their data contained the $2p'$ and $3p'$ lines for aluminum and gallium, and the $2p'$ line for indium. Their BWF spectra for indium were highly detailed, containing features associated with all of the $p_{3/2}$ transitions. This is sharply contrasted with the BWF absorption spectra of Watkins *et al.*[16] containing only line 1.

Using a high-resolution, high-signal-to-noise system, we have obtained photoelectric spectra for indium in silicon and compared them to our absorption spectra. We report for the first time all lines $3-10$ (with the exception of $4B$) of the $p_{3/2}$ transitions as positive photoelectric bands. We have made the first photoelectric observation of the indium $3p'$ line of the $p_{1/2}$ series, and the first photoelectric observation of the $4p'$ line for any acceptor. We have also measured the temperature dependence of the photoelectric-line intensities, demonstrating that they are governed by the photothermal ionization process, and have obtained an experimental value of the ionization energy for the $1\Gamma_7^-$ state which agrees with theory. Our BWF spectra show all major features in both absorption and photoconductivity, indicating that the absorption transitions are not particularly weak because of either special selection rules or experimental sensitivity.

II. EXPERIMENTAL

Photoconductivity (photoelectric) and absorption samples were cut from dislocation-free float-zone boules containing $(3-4)\times10^{16}$ indium atoms/cm^3. Residual donor-impurity and acceptor-impurity concentrations were less than 2.3×10^{14} cm^{-3} as determined by Hall-effect analysis. The photoconductivity samples were 1.00-cm long, 0.25-cm wide, and 0.050-cm thick. Ohmic contacts were applied by sparking of indium metal. The electric field was kept below 10 V/cm for all photoconductivity measurements. Optical-absorption samples were 0.40-cm thick.

The photoconductivity samples were maintained at a constant temperature in a "Helitran" flowing-gas refrigerator system.[20] The photoconductivity samples were secured on one end by GE 7031 varnish[21] to a 0.16-cm-thick beryllium oxide slab mounted on the cold finger of the Helitran. This method provided a strain-free thermal contact which kept the samples electrically isolated from the cold finger.

Photoelectric spectra were obtained with a system built around a Spex model 1704 1.0-m spectrometer[22] employing oversize 125 mm$\times$100 mm gratings. The system included a Nernst glower, all-mirror optics, order-sorting filters, a triglycine-sulfate (TGS) detector for intensity calibration, lock-in detection, and a minicomputer for spectrometer control, data acquisition, and data averaging. The spectral resolution was measured to be 0.88 cm^{-1} for data reported here. The wavelength calibration of the system was based upon the line positions of the emission spectra of mercury vapor in a low-pressure lamp.

Absorption spectra were recorded on a Digilab model FTS-20CVX Fourier transform spectrometer at a resolution of 0.5 cm^{-1}. Further details of the absorption experiments were the same as reported earlier.[12,13]

III. RESULTS AND DISCUSSION

Figure 1 contains photoelectric and absorption spectra in the region of lines 1, 2, and 3 of the $p_{3/2}$ series. The photoelectric-line positions agree with the absorption-line positions within the experimental error. The photoelectric and absorption linewidths are also essentially equal. The apparent slight shift to higher energy of line 2 of the 50-K photoelectric spectrum is due to the sloping background shoulder. The absorption-line positions of the $p_{3/2}$ series have been tabulated in detail elsewhere.[12] Line 1 appears here only as a negative photoelectric band caused by subtraction of background signal. Line 2 is seen by background subtraction at 20 K and as a positive photoelectric band at 50 K. Line 3 is a positive photoelectric band at 20 K but loses its distinctive features in the background. Our results are consistent with the 10- and 40-K spectra of Fig. 4 of Baron *et al.*[19] obtained with sample electric fields of 200 and 100 V/cm, respectively. Our photoelectric spectra show line 3 as a distinct band for the first time and our photoelectric linewidths are considerably narrower than those of Baron *et al.*[19]

The comparison between photoelectric and absorption spectra for lines $4-10$ of the $p_{3/2}$ series is shown in Fig. 2. All photoelectric- and absorption-

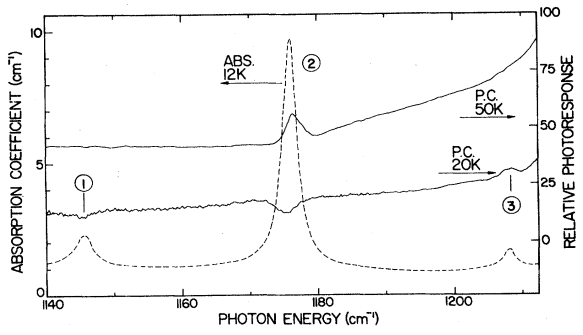

FIG. 1. Photoconductivity and absorption spectra for indium in silicon in the region of lines $1-3$ of the $p_{3/2}$ series.

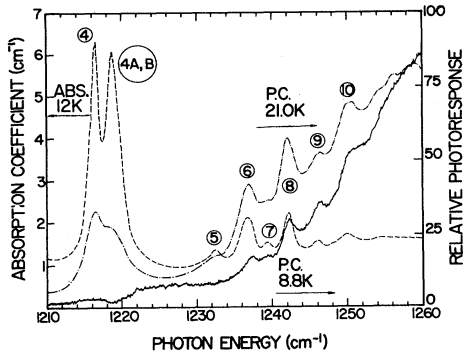

FIG. 2. Photoconductivity and absorption spectra for indium in silicon in the region of lines 4—10 of the $p_{3/2}$ series.

line energy positions agree within experimental error, as do the linewidths. At 8.8 K, lines 4 and combined lines 4*A* and 4*B* appear only as a slight decrease in the background signal, while line 5 is not seen as either a positive or negative signal. However, lines 6, 7, 8, 9, and 10 are all positive photoelectric bands. At 21.0 K, all of lines 4—10 are positive photoelectric bands. Again, the photoelectric-line positions agree with the absorption-line positions within experimental error, and the photoelectric and absorption linewidths are nearly equal. This is the first observation of lines 3—10 as distinct photoelectric bands for indium in silicon. The temperature-dependent intensity of the photoelectric lines according to numerical sequence (and energy position) in Figs. 1 and 2 qualitatively

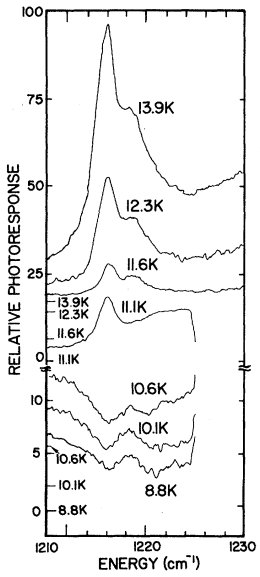

FIG. 3. Temperature dependence of the photoelectric spectra for lines 4, 4*A*, and 4*B* of the $p_{3/2}$ series.

agrees with the behavior expected from photothermal ionization.

The temperature dependence of lines 4 , 4*A*, and 4*B* is shown in Fig. 3. The zero location of the ordinate is different for each spectrum and is indicated for each temperature. Positive photoelectric signals are not seen for data recorded with a sample temperature below 11.1 K. The signal continues to increase above 13.9 K (spectra not shown), but less rapidly and with increased photon broadening.[23]

The intensity of line 4 versus temperature has been analyzed following the methodology of Kogan and Lifshitz[1] and Stillman *et al.*[5] Equation (27) of Stillman *et al.*[5] gives the photothermal ionization probability as

$$I_{n,l}=\frac{R_{n,l}}{R_c}\frac{\sigma}{\sigma_{n,l}}\ , \tag{1}$$

where n and l refer to the principal and angular-momentum quantum numbers of the (n,l) excited state, $R_{n,l}$ is the photoelectric response due to photothermal ionization of the (n,l) excited state, R_c is the photoconductive response from the ground state to the continuum (1280 cm^{-1} used here), $\sigma_{n,l}$ is the optical-absorption cross section for transitions from the ground state to the (n,l) excited state, and σ is the optical-absorption cross section for transitions from the ground state to the continuum.

We have analyzed the photothermal ionization process using peak heights only and the approximation

$$I_{n,l}\propto\frac{R_{n,l}}{R_c}\ , \tag{2}$$

with the following justifications:

(1) σ and $\sigma_{n,l}$ are constant over the (11—14)-K temperature interval.

(2) We have carefully measured the absorption linewidths and found them to change by only 11% over this temperature interval. The size of this broadening is probably no more severe than the overlap of lines 4 and 4*A*, and its effect on the integrated intensity is in a direction opposite to the effect of the overlapping lines.

The data were fit to a simple exponential function which produced an activation energy of 6.4±0.4 meV, where the error is a standard deviation. This activation energy is interpreted to be the separation of the line 4 excited state ($1\Gamma_7^-$) from the valence band. This experimental value compares favorably with the 6.1-meV value of the most recent theoretical calculations.[15] The agreement is much better than that observed for other systems,

such as donors in GaAs,[5] and in addition to the agreement of the photoconductivity- and absorption-line positions, and the qualitative temperature dependence of the photoconductivity-line intensities, is further evidence that the photothermal ionization process is the mechanism producing the discrete photoelectric lines.

More recent theories[2] of photothermal ionization probability do not follow simple exponential behavior.[2-4] We have compared Eq. (31) of Abakumov and Yassievich[2] and Eq. (5) of Jongbloets *et al.*[4] with a simple exponential function, and have reached the following conclusions:

(1) It would be nearly impossible to distinguish between the two more complete theories given the accuracy of most experiments.

(2) The two more complete theories approach simple exponential behavior at lower temperatures, which include the (11 – 14)-K interval.

(3) Our experimental accuracy, as well as the broadening and overlap problems, do not justify attempting to fit the data to any function more complex than a simple exponential over the (11 – 14)-K temperature interval.

We are thus confident that fitting the data to a simple exponential function is a reasonable procedure. This is the first known report of an analysis of the temperature dependence of the intensity of the photoelectric lines for any impurity atom in silicon.

Photoelectric and absorption spectra in the region of the $p_{1/2}$ excitation series[10] and the BWF resonances[16] are shown in Fig. 4. The $3p'$ photoelectric line is clearly resolved for the first time for indium in silicon, and the $4p'$ photoelectric line is seen for the first time for any acceptor in silicon. The energy position of the photoelectric lines agree well with the absorption values, which were reported earlier.[12] The linewidths also are essentially equal.

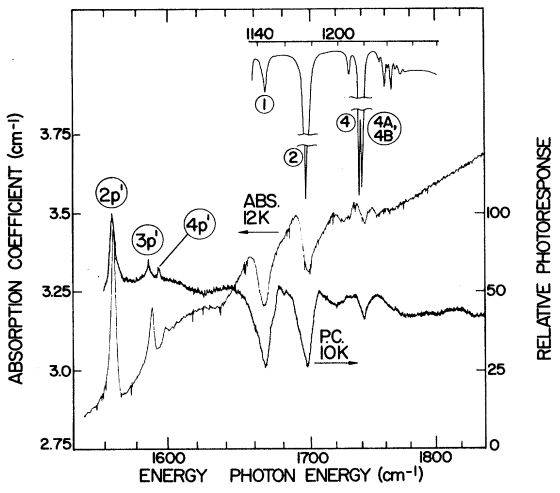

FIG. 4. Photoconductivity and absorption spectra for indium in silicon in the region of the $p_{1/2}$ series lines and the Breit-Wigner-Fano resonances. The $p_{3/2}$ absorption spectrum is also shown displaced by the energy (519 cm^{-1}) of the zone-center optical phonon.

In order to demonstrate the origin of BWF resonances, a $p_{3/2}$ absorption spectrum is also shown in Fig. 4, but is shifted to higher energies by 519 cm^{-1}, the energy value of a zone-center optical phonon. The BWF phenomenon is the resonant interaction of two separate processes: (1) excitation from the indium ground state to the $p_{3/2}$ excited states, followed by absorption of the O^{Γ} phonon to the $p_{1/2}$ continuum, and (2) direct excitation from the ground state to the $p_{1/2}$ continuum. In absorption, a series of resonances and antiresonances are produced, the dip in the antiresonance corresponding almost exactly to the sum of the O^{Γ} phonon energy and the $p_{3/2}$ excitation energy.[16] In photoelectric spectra, the resonance (positive) features are suppressed.[24]

Watkins and Fowler[16] studied the BWF absorption phenomenon in silicon doped with boron, aluminum, and gallium, but not indium. They saw only BWF features associated with line 1 of the $p_{3/2}$ series, and explained the absence of features produced by the other $p_{3/2}$ lines as a mismatch in $\vec{k}$ space between $p_{3/2}$ excited states and the $p_{1/2}$ continuum. Baron *et al.*[19] reported BWF features in photoconductivity corresponding to the major $p_{3/2}$ lines for aluminum, gallium, and indium in silicon. Our photoconductivity spectrum contains the same features reported by Baron *et al.*,[19] but we also see the same major features in the absorption spectrum. Thus, there is no theoretical impediment to the appearance in absorption spectra of BWF resonances associated with lines 2 – 10 of the $p_{3/2}$ series as proposed by Watkins *et al.*,[16] or experimental impediment as implied by Baron *et al.*[19] The dips (antiresonances) in the photoelectric and absorption spectra shown in Fig. 4 occur at very nearly the same photon energy. The displaced $p_{3/2}$ lines do not lie exactly at the minima of the antiresonances but are shifted slightly to lower energies. The data of Baron *et al.*[19] show the same shift for indium in silicon, but not for aluminum or gallium. We do not yet have an explanation for this shift.

IV. SUMMARY

We have obtained photoelectric spectra for indium silicon in the region of the $p_{3/2}$, $p_{1/2}$, and

Breit-Wigner-Fano transitions. The energy positions and linewidths of the $p_{3/2}$ and $p_{1/2}$ photoelectric transitions agree with those in absorption. We report the first photoelectric observation of lines 3–10 of the $p_{3/2}$ series and line $3p'$ of the $p_{1/2}$ series for indium in silicon, and the first observation of line $4p'$ for any acceptor in silicon. The temperature dependence of the photoelectric-line intensities demonstrates that they are governed by a photothermal ionization process. From the temperature dependence of line 4 of the $p_{3/2}$ series, we measured a binding energy of 6.4 ± 0.4 meV for the excited state. We have seen the major features of the $p_{3/2}$-associated Breit-Wigner-Fano resonances in both absorption and photoelectric spectra, demonstrating that there is no fundamental reason to preclude the observation of lines above line 1 in absorption.

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*Present address: Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, OH 45221.

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