Evidence for a shallow Cu acceptor in Si from infrared spectroscopy and photoconductivity

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Copper impurities affect optical and electronic properties in a diverse range of materials. Using IR spectroscopy, we provide evidence for a shallow Cu acceptor in Si. The observation of $P_{1/2}$ excitation lines indicates a Cu acceptor with a hole ionization energy of only 27 meV, which is shallower than any of the group-III acceptors. The observed center has an IR spectrum that is characteristic of a hydrogenic acceptor. Variable-temperature Hall-effect measurements confirm this result. The observation of shallow, hydrogenic behavior is consistent with a universal level model, in which the Cu acceptor level is fixed relative to vacuum, irrespective of the host.

Cu is a ubiquitous impurity in a wide range of electronic and optical materials. In Si, it can be introduced unintentionally during various processing steps [1]. The fast-diffusing interstitial Cu donor [2] passivates shallow acceptors (Al, Ga, In) in Si [3,4] affecting the electronic characteristics of devices. Deep levels [5,6] associated with Cu degrade device performance [7,8] and production yields of Si integrated circuits are reduced by Cu precipitation [9].

Substitutional Cu in Si has been reported to be a deep triple acceptor with energy levels 0.24, 0.37, and 0.52 eV above the valence-band maximum [10–12]. However, these assignments are controversial. While the level at 0.24 eV has been attributed to Cu [13], a later investigation [14] ascribed it to a Cu-O complex. The energy level at 0.52 eV has been attributed to thermal lattice defects, which appear after annealing and are not associated with Cu [15]. The commonly observed photoluminescence peak at 1014.7 meV has been attributed to a "Cu pair" that has a deep donor level [16–18]. Later studies showed that this complex actually contains four Cu atoms [19,20].

Unlike a deep level, which has a localized electronic wave function, a shallow level has a hydrogenic wave function with a large Bohr radius [21]. The excited states of a hydrogenic impurity may be probed by optical spectroscopy, providing accurate information about the electron/hole binding energy [22]. In this paper, we provide evidence that Cu introduces a *shallow*-acceptor level in Si.

A $10\times10\times0.5$ mm^3 Si crystal was cut from a *p*-type float-zone grown wafer. A float-zone sample of different thickness (dimensions $10\times10\times5$ mm^3) was also used. These are referred to as "thin" and "thick" samples, respectively. Samples were doped with Cu by annealing at 1250 °C for 2 h in an evacuated sealed silica ampoule with 300 mg of Cu granules (99.9% purity). Upon completion of annealing, the samples were gradually cooled to room temperature and were mechanically polished. Although the solubility of Cu at the annealing temperature is $\sim10^{18}$ cm^{-3}, after cooling to room

temperature, less than 0.1% of the Cu atoms are electrically active [13]. The large majority of Cu atoms precipitate out of solution and form electrically inactive clusters [23]. As a control, a Si sample was annealed under the same conditions but without Cu granules.

IR spectra were obtained with a Bomem DA8 Fourier transform IR spectrometer with a KBr beam splitter. Samples were maintained at low temperatures in a closed-cycle helium cryostat. For IR transmission measurements, a Ge:Cu photoconductor detector was employed. For photoconductivity (PC) measurements, thin Si samples were fabricated into IR detectors. Contacts were made using sputtered Al followed by annealing at 500 °C for 1.5 h in vacuum. The edges of the samples were attached to wires with silver paint and were connected to an external bias and a preamplifier. An off-axis parabolic mirror, placed inside the cryostat, was used to focus a collimated IR beam onto the sample. The measurements had a spectral range of $500-5000$ cm^{-1} (62–620 meV) and an instrumental resolution of 2 cm^{-1} (0.25 meV).

Hall-effect measurements were performed in the van der Pauw geometry using Al contacts. The thin sample had a room-temperature hole concentration of 2×10^{12} cm^{-3}. After Cu doping, the hole concentration increased to 2×10^{14} cm^{-3}, suggesting the incorporation of Cu acceptors. The control sample showed an electron concentration of 8×10^{12} cm^{-3}, due to trace donor contaminants introduced during annealing. This confirms that the increase in *hole* concentration after Cu diffusion is due to Cu acceptors rather than unintentional contaminants.

Figure 1(a) shows a low-temperature IR absorption spectrum for the thick Si:Cu sample. The absorption spectrum was calculated from

$$\text{Absorbance} = \log_{10}\left(I_R/I\right), \qquad (1)$$

where I_R and I are transmission spectra for the as-received and Cu-diffused samples, respectively. The Si:Cu sample showed IR absorption peaks at 65.8 and 68.7 meV. These peaks were not present in the control sample [Fig. 1(b)]. We attribute the peaks to electronic transitions of neutral Cu acceptors. As shown in Ge [24] such transitions can be modeled by a
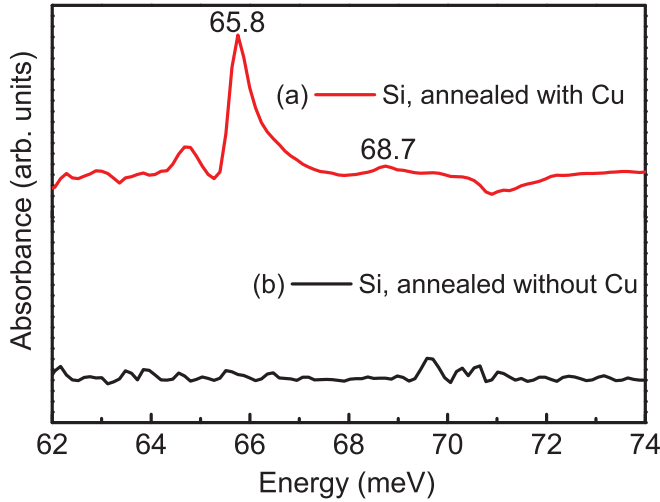
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FIG. 1. (Color online) Low-temperature (10 K) IR absorption spectra of thick Si samples annealed (a) with and (b) without Cu. The peaks at 65.8 and 68.7 meV are due to Cu acceptors. Spectra are shifted vertically for clarity.

single-hole hydrogenic model [25]. The dip at 70.9 meV is due to multiphonon absorption (LO+TA) [26].

The peaks at 65.8 and 68.7 meV were also observed in the thin Si:Cu sample (Fig. 2). Here, IR absorption spectra were calculated using Eq. (1), where I_R and I are the transmission spectra for the sample, before and during exposure to white light, respectively. The increase in the peaks suggests that, prior to illumination, many of the copper acceptors are compensated by donors. During illumination, above-gap light creates electrons and holes. The holes become trapped and neutralize the ionized Cu acceptors, resulting in increased IR absorption. From the increase in the absorption peaks, we estimate at least 60% of the Cu acceptors are compensated by donors. This estimate is a lower bound because illumination does not activate all the ionized Cu acceptors.
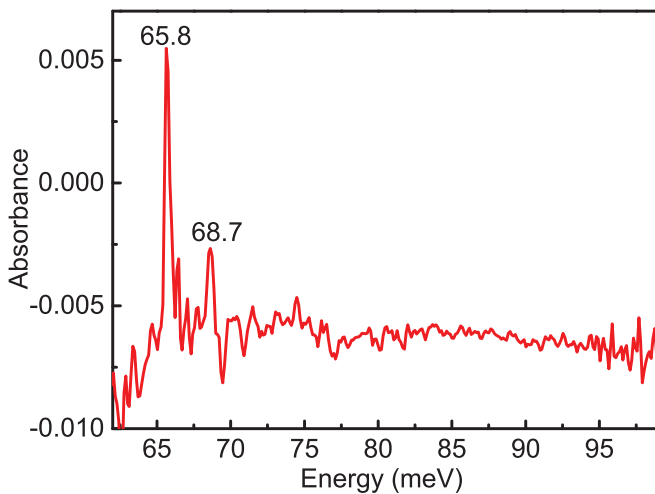

FIG. 2. (Color online) Low-temperature (10 K) IR absorption spectrum of thin Si:Cu sample during exposure to white light. The sample prior to illumination was used as the reference.
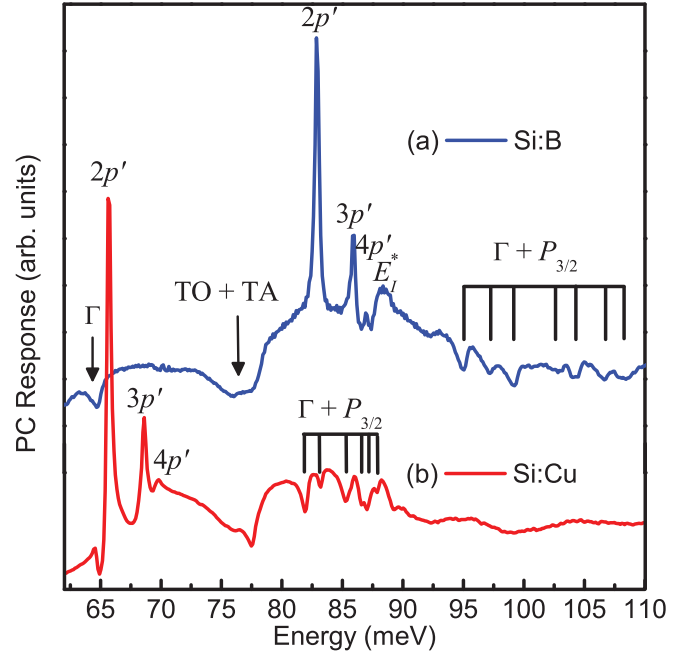

FIG. 3. (Color online) Low-temperature (10 K) PC spectra of (a) Si:B and (b) Si:Cu, showing the acceptor excited state peaks of the $P_{1/2}$ valence band, along with the Fano resonances ($\Gamma + P_{3/2}$). Phonon features (Γ and TO+TA) are indicated. Spectra are shifted vertically for clarity.

To verify that the peaks correspond to electronic transitions, we performed PC spectroscopy. Figure 3 shows a PC spectrum of a Si:Cu sample at 10 K. As shown in the figure, the peaks at 65.8 and 68.7 meV were observed, along with a small peak at 69.8 meV, followed by continuum absorption. The peaks are consistent with hole transitions from the ground state associated with the $P_{3/2}$ valence band to excited states associated with the split-off $P_{1/2}$ valence band. These excited states, denoted $2p'$, $3p'$, and $4p'$, have been observed for group-III acceptors in Si [27–29]. The p' energies are approximately the same for all group-III acceptors. Differences in the IR transition energies are due to chemical shifts of the acceptor ground state (Fig. 4). Therefore, the p' levels provide an excellent means for determining the acceptor binding energy.

For comparison purposes, we performed a PC experiment on the as-received sample [Fig. 3(a)]. This sample showed transitions from the B acceptor at 82.9 ($2p'$), 85.9 ($3p'$), 87.0 ($4p'$), and the series limit (E_I^*) at 88.4 meV [29], followed by continuum absorption. The $2p'$, $3p'$, and $4p'$ transitions of the Cu acceptor are 17 meV redshifted from those of the B acceptor, suggesting that Cu is even *shallower* than B. From the known B acceptor binding energy (44 meV) [29] the Cu acceptor binding energy is estimated to be 44−17 = 27 meV.

In the continuum part of the Si:Cu PC spectrum, there is a broad dip at 77.5 meV due to multiphonon absorption, along with a series of dips in the range 81.9–87.9 meV [Fig. 3(b)]. The as-received Si sample shows similar features in the range 94.8–108.2 meV [Fig. 3(a)]. These dips were observed in previous studies on Si:B. They result from Fano resonances involving the excitation of a Γ phonon and
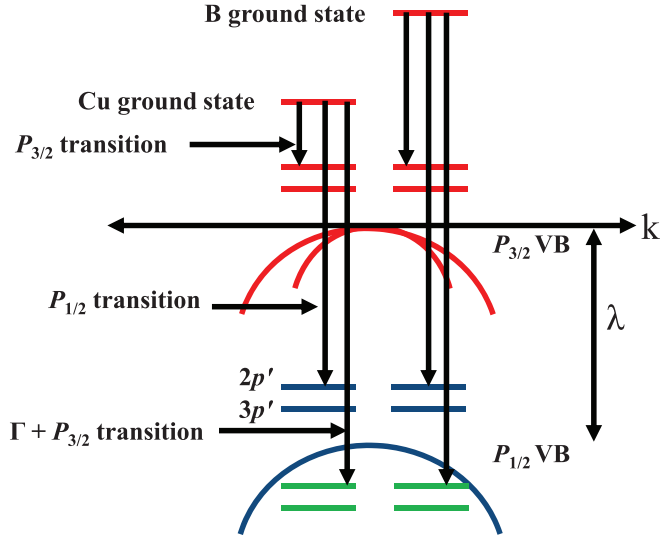
FIG. 4. (Color online) Schematic energy-level diagram of Si showing the Cu and B acceptor levels relative to the $P_{3/2}$ and $P_{1/2}$ valence bands (VB). Hole transitions are indicated by vertical down arrows. The spin-orbit splitting at **k**=0 is indicated by λ.

FIG. 5. Arrhenius plot of hole concentration (p) versus inverse temperature ($1000/T$). The solid line is a model for a heavily compensated acceptor with an activation energy of 27 meV.

bound-to-bound $P_{3/2}$ excitations [30,31]. Figure 4 summarizes the acceptor levels and hole transitions for Cu and B in Si.

The similarity between the Cu spectrum and spectra for group-III acceptors in Si suggests that the observed Cu center is a substitutional acceptor. However, we cannot exclude the possibility that it is a defect complex. Using photothermal ionization spectroscopy, Sirmain *et al.* [32] discovered a Cu complex in Ge with a shallow-acceptor level of only 10 meV. The complex was attributed to a Cu-As pair.

To further test the shallow-acceptor model, Hall-effect data were obtained at low temperatures. Samples were measured in a van der Pauw geometry at a magnetic field of 1 T. As shown in Fig. 5, holes freeze out from the valence band for temperatures below ∼50 K. The solid line is a fit to a standard freeze-out curve [25], with an acceptor activation energy of 27 meV, as determined by the IR measurements. The only adjustable parameters were the concentrations of acceptors ($N_a = 1 \times 10^{15}$ cm^{-3}) and compensating donors ($N_d = 8 \times 10^{14}$ cm^{-3}). The heavy compensation, consistent with our IR measurements (Fig. 2), is likely due to defects such as the Cu pair deep donors mentioned previously.

The observation of a shallow Cu acceptor in Si is consistent with a "universal acceptor level," in which the Cu acceptor level (0/−) is constant relative to vacuum, irrespective of the host [33]. Figure 6 shows band lineups for numerous semiconductors. Valence-band offsets were determined by first-principles calculations [34], while conduction band minima are from the experimental band gaps. The energy values (relative to vacuum) were determined by setting the Si conduction band minimum to its known value of −4.2 eV [35]. If the (0/−) level lies in the gap, then Cu is a deep acceptor. If the (0/−) level lies in the valence band, then Cu is negatively charged (relative to the host), and a hole is weakly attracted to it. In that case, Cu acts as a shallow acceptor, with a hydrogenic level close to the valence-band maximum.
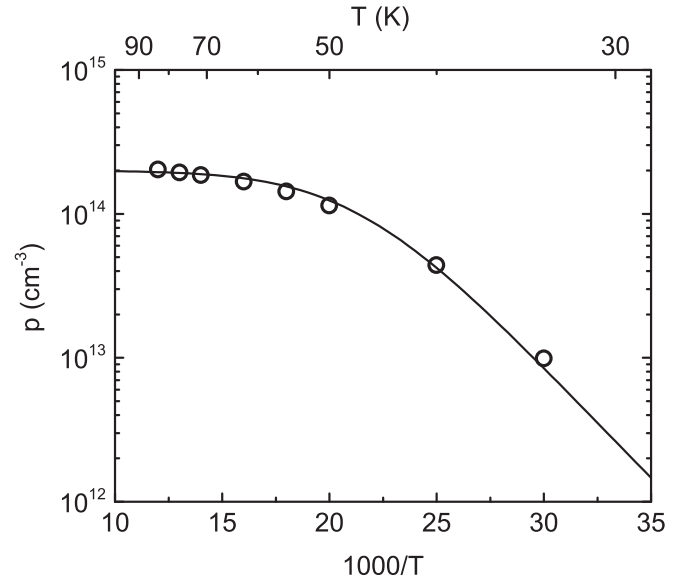
This model accounts for the observations that Cu is a shallow, hydrogenic acceptor in Si (this work) and Ge (Ref. [25]). It shows reasonable agreement with measured deep acceptor energies for GaP [36], InP [37], GaAs [38], GaAs$_{1−x}$P$_x$ [39], ZnO [40], ZnS [41], CdS [40], ZnSe [42], and ZnTe [43]. The model also agrees with first-principles calculations [44] for Cu in CdTe and the qualitative observation that Cu introduces a midgap level in GaN [45]. Note that the universal (0/−) level does not depend on the oxidation state. For example, a neutral substitutional Cu acceptor is denoted Cu^{4+} in Si, Cu^{3+} in GaAs, and Cu^{2+} in ZnO.
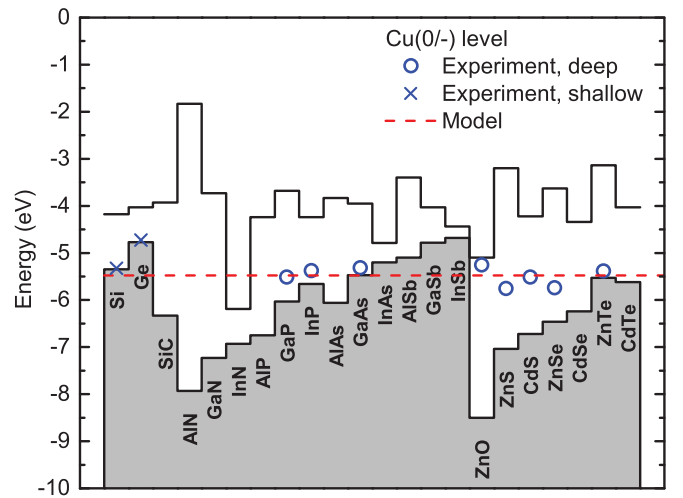

FIG. 6. (Color online) Proposed "universal acceptor level" for Cu in semiconductors. The dashed line shows the model Cu (0/−) acceptor level. When the (0/−) level is in the gap, it gives the deep acceptor level. When the (0/−) level is in the valence band (shaded region), Cu acts as a hydrogenic acceptor, with a shallow-acceptor level near the valence-band maximum.

In conclusion, using IR spectroscopy, we report a shallow Cu acceptor with binding energy of 27 meV. This shallow level is consistent with a universal level for Cu acceptors in semiconductors.

[1] K. G. McGuigan, M. O. Henry, E. C. Lightowlers, A. G. Steele, and M. L. Thewalt, Solid State Commun. **68**, 7 (1988).

[2] A. A. Istratov, C. Flink, H. Hieslmair, E. R. Weber, and T. Heiser, Phys. Rev. Lett. **81**, 1243 (1998).

[3] Th. Prescha and J. Weber, Mater. Sci. Forum **83–87**, 167 (1992).

[4] S. K. Estreicher, Phys. Rev. B **41**, 5447 (1990).

[5] C. D. Latham, M. Ganchenkova, R. M. Nieminen, S. Nicolaysen, M. Alatalo, S. Öberg, and P. R. Briddon, Phys. Scr. **T126**, 61 (2006).

[6] A. Fazzio, M. J. Caldas, and A. Zunger, Phys. Rev. B **32**, 934 (1985).

[7] J. R. Davis, A. Rohatgi, R. H. Hopkins, P. D. Blais, R. Rai-Choudhury, J. R. McCormick, and H. C. Mollenkopf, IEEE Trans. Electron Dev **27**, 677 (1980).

[8] K. Honda, A. Ohsawa, and N. Toyokura, Appl. Phys. Lett. **45**, 270 (1984).

[9] S. A. McHugo, A. Mohammed, A. C. Thompson, B. Lai, and Z. Cai, J. Appl. Phys. **91**, 6396 (2002).

[10] A. G. Milnes, in *Deep Impurities in Semiconductors* (Wiley-Interscience, New York, 1973), p. 14.

[11] S. J. Pearton and A. J. Tavendale, J. Appl. Phys. **54**, 1375 (1983).

[12] S. D. Brotherton, J. R. Ayres, A. Gill, H. W. van Kesteren, and F. J. A. M. Greidanus, J. Appl. Phys. **62**, 1826 (1987).

[13] C. B. Collins and R. O. Carlson, Phys. Rev. **108**, 1409 (1957).

[14] G. I. Voronkova and M. I. Iglitsyn, Sov. Phys. Semicond. **1**, 120 (1967).

[15] J.-W. Chen and A. G. Milnes, Ann. Rev. Mater. Sci. **10**, 157 (1980).

[16] J. Weber, H. Bauch, and R. Sauer, Phys. Rev. B **25**, 7688 (1982).

[17] M. H. Nazaré, A. J. Duarte, A. G. Steele, G. Davies, and E. C. Lightowlers, Mater. Sci. Forum **83–87**, 191 (1992).

[18] H. B. Erzgräber and K. Schmaltz, J. Appl. Phys. **78**, 4066 (1995).

[19] M. L. W. Thewalt, M. Steger, A. Yang, N. Stavrias, M. Cardona, H. Riemann, N. V. Abrosimov, M. F. Churbanov, A. V. Gusev, A. D. Bulanov, I. D. Kovalev, A. K. Kaliteevskii, O. N. Godisov, P. Becker, H.-J. Pohl, J. W. Ager III, and E. E. Haller, Physica B **401–402**, 587 (2007).

[20] M. Steger, A. Yang, N. Stavrias, M. L. W. Thewalt, H. Riemann, N. V. Abrosimov, M. F. Churbanov, A. V. Gusev, A. D. Bulanov, I. D. Kovalev, A. K. Kaliteevskii, O. N. Godisov, P. Becker, and H.-J. Pohl, Phys. Rev. Lett. **100**, 177402 (2008).

[21] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[22] B. Pajot, *Optical Absorption of Impurities and Defects in Semiconducting Crystals I: Hydrogen-Like Centres* (Springer-Verlag, Berlin, 2010).

[23] W. C. Dash, J. Appl. Phys. **27**, 1193 (1956).

[24] E. E. Haller, W. L. Hansen, and F. S. Goulding, Adv. Phys. **30**, 93 (1981).

[25] P. Fisher and H. Y. Fan, Phys. Rev. Lett. **5**, 195 (1960).

[26] M. D. McCluskey and E. E. Haller, *Dopants and Defects in Semiconductors* (CRC Press, New York, 2012).

[27] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Lett. **4**, 173 (1960).

[28] A. Onton, P. Fisher, and A. K. Ramdas, Phys. Rev. **163**, 686 (1967).

[29] D. W. Fischer and J. J. Rome, Phys. Rev. B **27**, 4826 (1983).

[30] G. D. Watkins and W. B. Fowler, Phys. Rev. B **16**, 4524 (1977).

[31] V. V. Rumyantsev, S. V. Morozov, K. E. Kudryavtsev, V. I. Gavrilenko, and D. V. Kozlov, Semiconductors **46**, 1387 (2012).

[32] G. Sirmain, O. D. Dubon, W. L. Hansen, C. S. Olsen, and E. E. Haller, J. Appl. Phys. **79**, 209 (1996).

[33] L.-A. Ledebo and B. K. Ridley, J. Phys. C **15**, L961 (1982).

[34] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

[35] R. L. Lichti, K. H. Chow, and S. F. J. Cox, Phys. Rev. Lett. **101**, 136403 (2008).

[36] H. G. Grimmeiss and B. Monemar, Phys. Status Solidi A **19**, 505 (1973).

[37] K. Zdansky, J. Zavadil, L. Pekarek, V. Gorodynskyy, and H. Kozak, Phys. Status Solidi A **202**, 555 (2005).

[38] K. Leosson and H. P. Gislason, Phys. Scr. **T69**, 196 (1997).

[39] M. Zafar Iqbal, H. G. Grimmeiss, and L. Samuelson, J. Phys. C **18**, 1017 (1985).

[40] F. A. Selim, M. C. Tarun, D. E. Wall, L. A. Boatner, and M. D. McCluskey, Appl. Phys. Lett. **99**, 202109 (2011).

[41] R. Heitz, A. Hoffmann, P. Thurian, and I. Broser, J. Phys.: Condens. Matter **4**, 157 (1992).

[42] G. B. Stringfellow and R. H. Bube, J. Appl. Phys. **39**, 3657 (1968).

[43] K. Saminadayar, N. Magnea, J. L. Pautrat, and B. Pajot, Phys. Status Solidi B **106**, 215 (1981).

[44] S.-H. Wei, S. B. Zhang, and A. Zunger, J. Appl. Phys. **87**, 1304 (2000).

[45] C. Bozdog, K. H. Chow, G. D. Watkins, H. Sunakawa, N. Kuroda, and A. Usui, Phys. Rev. B **62**, 12923 (2000).