Copper Acceptors in Uniaxially Stressed Germanium: $1s^3$ to $1s^2\,2s^1$ Ground-State Transformation

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(Received 20 December 1993)

We have studied uniaxially stressed Ge doped with Cu, a substitutional triple acceptor, by photoconductivity spectroscopy. We find that the ground state of this triple acceptor, normally accommodating three $1s$ holes, reconfigures into an atomic Li-like $1s^2 2s^1$ arrangement by the application of [100] stress. Above 4 kbar the first ionization potential reaches a constant value of 17.4 meV corresponding to the hole excitation from the now partially occupied $2s$ energy level. Excellent agreement was obtained between the experimental results and variational calculations.

PACS numbers: 71.55.Eq, 71.70.Ej, 78.50.Ge

Effective mass theory successfully describes the general spectroscopic nature of shallow impurities in semiconductors. Monovalent dopants such as gallium in germanium produce energy states related to the binding of a single charge carrier by a Coulombically attractive center. The atomic analog to this system is the hydrogen atom. Double acceptors such as beryllium in germanium also have an atomic analog: the He atom. However, acceptors binding a third hole including Be^+ and copper, a substitutional triple acceptor, do not have a direct atomic analog. The fourfold degeneracy at the valence-band edge of Ge and most other cubic semiconductors allows for the accommodation of up to four holes in the $1s$ lowest one-particle level of these acceptors, which would be equivalent in the atomic framework to having electrons with a pseudospin of $\frac{3}{2}$. Variational calculations have shown that, indeed, the analog of Be^+ is a pseudo He^- ion having electrons of hypothetical spin $\frac{3}{2}$ and a $1s^3$ ground-state configuration [1].

The application of uniaxial stress breaks the fourfold degeneracy of the valence-band edge leaving two (time-reversal) doubly degenerate, split bands (in addition to the spin-orbit split-off band which also remains doubly degenerate) [2]. Similarly, uniaxial stress in a [100] direction reduces the symmetry of the acceptor lowest one-particle level (from T_d to D_{2d}) producing two doubly degenerate energy levels [3,4]. For single and double acceptors this means that the bound holes are accommodated in the split level (designated Γ_7 in Fig. 1) that minimizes the total energy of this state. However, for triple acceptors the third hole must necessarily reside in the higher energy split level (designated Γ_6 in Fig. 1) when the applied stress is small but may form an energetically more favorable configuration at higher stresses. Although careful copper-related piezospectroscopy studies have been reported [5,6], neither theoretical nor experimental information exists regarding the effect of *large* uniaxial stresses on Cu-doped Ge.

In this Letter we present photoconductivity measurements which show a large, stress-induced decrease in the first ionization potential of the copper triple acceptor in germanium. We demonstrate that the lowest electronic energy state of neutral copper transforms from a pseudo Li^0, $1s^3$-like configuration to a normal Li^0, $1s^2 2s^1$-like configuration upon the application of a sufficiently large uniaxial stress (> 4 kbar). This is, to our knowledge, the first time that an impurity ground-state transformation of this kind has been observed.

Photoconductivity (PC) response measurements were performed on a copper-diffused, n-type Ge wafer ($n \approx 2 \times 10^{11}$ cm^{-3}). A 200-nm-thick Cu layer was Ar sputtered on either surface of the wafer which was then sealed under vacuum in a quartz ampoule, annealed at 700 °C for 24 h, and finally quenched in ethylene glycol. Two boron implants [(25 keV)/(1×10^{14} cm^{-2}) and (50 keV)/(2×10^{14} cm^{-2})] and subsequent metallization (20

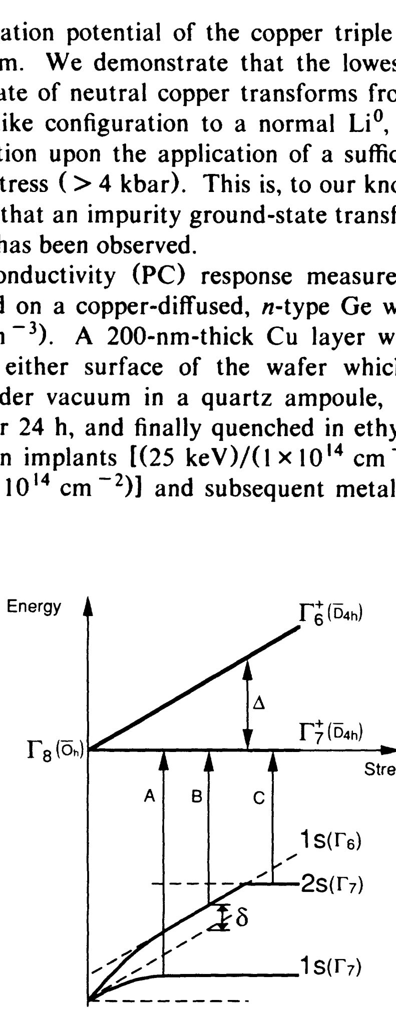

FIG. 1. Schematic of the splitting of the valence band and the copper ground state as a function of a [100] uniaxial stress. The electronic band states change from O_h to D_{4h} symmetry while the impurity states go from T_d to D_{2d} symmetry. Transition A corresponds to that of a hole for a neutral single or double acceptor. Transitions B and C are those of a hole for a neutral triple acceptor such as copper.

0031-9007/94/72(14)/2231(4)$06.00

nm of Pd and 400 nm of Au in this sequence) were performed for later use in the formation of electrical contacts. Thermal annealing at 300 °C for 1 h under Ar flow followed the metallization.

The wafer was cut to produce a $1\times1\times6$ mm^3 final geometry for each sample. All resulting surfaces were $\langle100\rangle$ oriented. Uniaxial stress was applied parallel to the long axis of the bar-shaped samples; therefore, care was taken in maintaining parallelism between the 1×1-mm^2 surfaces. For each sample the two electrical contacts necessary for the PC measurements were masked on one of the 1×6-mm^2 surfaces, and all excess metallization and implanted layers were removed via KBr solution (1 min) and 3:1 HNO_3:HF (30 sec) etches, respectively.

A far infrared Fourier transform spectrometer was used to measure the photoconductivity response of the samples as a function of photon energy. A combination of warm and cold black polyethylene foils was used to block high energy photons with $\omega > 500$ cm^{-1}. A piston-lever apparatus was used for the application of uniaxial compression. The spectra were taken at a temperature of 12 K. At this temperature there is no photoconductivity response caused by residual shallow acceptor impurities, which would have otherwise become neutral by capturing holes photoexcited from copper centers.

Figure 2 shows a series of five photoconductivity spectra as a function of stress between 0 and 8 kbar. The threshold of the PC response in the zero-stress spectrum occurs at a photon energy of 350 cm^{-1}, as expected from previously reported data on the first ionization potential of copper [5]. The large dips appearing, for example, in the 350–400 cm^{-1} region are caused by absorption arising from optically active multiphonon modes [7]. This coupling reduces the number of photons available for absorption by the copper centers thus decreasing the PC response. As the applied stress increases, the threshold of the PC response shifts to lower energies becoming constant at stresses above 4 kbar. The binding energy is reduced from 43.2 meV (349 cm^{-1}) to 17.4 meV (141 cm^{-1}). In addition, we performed Hall effect measurements which showed that only the binding energy and not other freeze-out characteristics of the holes changed with stress. This indicates that there was not a stress-induced structural change in the defect.

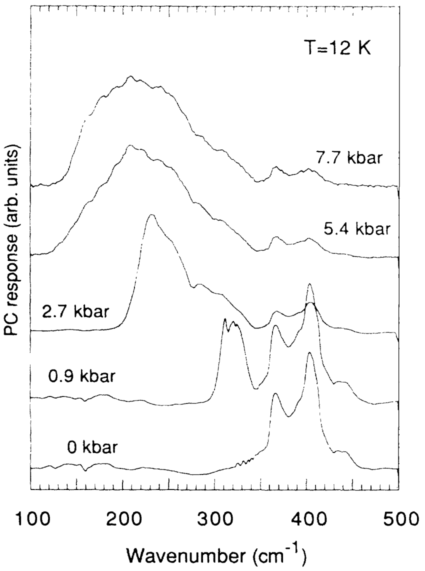

FIG. 2. Photoconductivity (PC) response spectra as a function of stress. The shift of the PC threshold is caused by the reduction of the first ionization potential of copper with increasing stress.

The stress dependence of the hole binding energy for group III, single acceptors is well documented [8–10]. Photoconductivity spectroscopy measurements of stressed Be-doped Ge have been performed as well [11]. The energy shift of the first ionization potential in each of these is approximately 5 meV less than the zero-stress value compared to 26 meV for Cu. The decrease of the binding energy is limited to approximately this value because the separation between the lower lying, split $1s(\Gamma_7)$ level (in which the holes reside) and the split Γ_7^+ valence band (to which the holes are excited) changes only slightly in the high stress limit (transition *A* in Fig. 1).

Copper differs from single and double acceptors by the fact that it binds *three* holes. When stress is applied and the one-particle states split, two holes are accommodated in the $1s(\Gamma_7)$ level and the third in the higher energy $1s(\Gamma_6)$ level. An increase in the stress significantly reduces the energy with which the third hole is bound since the split $1s(\Gamma_6)$ level—which it populates—increases in energy with respect to its zero-stress value (transition *B* in Fig. 1). Therefore, the separation between this level and the split valence band has a strong dependence on the applied stress.

At sufficiently high stresses the excited one-particle levels associated with the lower Γ_7^+ valence band should cross the $1s(\Gamma_6)$ level of the third hole. The lowest lying and thus the first excited level that crosses is the $2s(\Gamma_7)$. When the $2s(\Gamma_7)$ level is lower in energy than the upward-moving $1s(\Gamma_6)$ level, the ground state of copper reconfigures from its usual $[1s(\Gamma_7)]^2[1s(\Gamma_6)]^1$ configuration to the more stable one $[1s(\Gamma_7)]^2[2s(\Gamma_7)]^1$. The binding energy of the third $2s$ hole becomes roughly constant as in the case of the bound excited Γ_7 states of shallow levels (transition *C* in Fig. 1). A conceptually similar crossing of states has been observed in the photoluminesce spectra of bound multiexciton complexes containing three holes in uniaxially stressed silicon [12,13].

A transformation of the ground-state configuration, as described above, occurs if there is a crossover in the minimum total energy of the system. Therefore, we have estimated the pressure-dependent total energies and first ionization potentials of both configurations by a variational calculation. We calculated the $1s^3$ total energy following the method of Wu and Falicov [14] and obtained a value of $-8.62+\Delta$ a.u., where Δ is the splitting of the valence band as a function of pressure and the atomic unit (a.u.) for Ge is $m^* e^4/\varepsilon\hbar = 22.4$ meV. The $1s^2 2s^1$ state was obtained from the observed lithium spectrum [15], by adding (in a.u.) the ionization potentials of Li^0, Li^+, and Li^{++}. It yields an equivalent total energy of $-0.20-2.79-4.50$ a.u. $=-7.49$ a.u.

For either neutral ground-state configuration the removal of one hole from the neutral copper center produces a $1s^2$ (free hole) final state, which has an energy of $-2.79-4.50$ a.u. $=-7.29$ a.u. Thus, we arrive at the first ionization potentials (IP's): $\mathrm{IP}(1s^3) = 1.33-\Delta$ a.u. and $\mathrm{IP}(1s^2 2s^1) = 0.20$ a.u. Because the final state is the same in both cases, the crossover from the $1s^3$ to the $1s^2 2s^1$ ground state occurs at the pressure for which the ionization potentials are equal.

The experimentally observed, zero-stress value of $\mathrm{IP}(1s^3)$ is 43.2 meV compared to the calculated value 29.8 meV. The difference between these two is the central cell correction, 13.4 meV $=0.60$ a.u. The central cell correction of the $1s^2 2s^1$ configuration, estimated from the variational values of the wave functions at the Cu site, increases $\mathrm{IP}(1s^2 2s^1)$ by 12.9 meV $=0.58$ a.u. Therefore, the $1s^2 2s^1$ configuration becomes the stable one for $\Delta > 1.15$ a.u. $=25.8$ meV, and the central-cell adjusted values of the ionization potentials are

$$\mathrm{IP}(1s^3) = 43.2 - \Delta \text{ meV}$$

valid for $\Delta < 25.8$ meV, and

$$\mathrm{IP}(1s^2 2s^1) = 17.4 \text{ meV}$$

valid for $\Delta > 25.8$ meV.

Figure 3 is a plot of the measured binding energy of the outer hole as a function of stress. The binding energy was measured from spectra such as those in Fig. 2 and was evaluated at the photon energy at which the onset of the PC threshold occurs. The valence band splitting (Δ) was determined from the equation

$$\Delta = 2b(S_{11} - S_{12})T ,$$

where T is the applied stress, b is a deformation potential, and S_{11} and S_{12} are elastic constants. For germanium

$$\Delta = 6 \text{ meV/kbar} \quad \text{(applied stress in kbar)} .$$

The lines represent the binding energies (i.e, the IP's) obtained from the variational calculations.

Deviation between the experimental results and the $1s^3$ calculated line results from the approximation made in the calculations that the splitting of the $1s$ energy level equals the splitting of the valence band. Although appropriate for large stresses, this approximation is not valid at low stresses (below 1 kbar); therefore, the calculated IP's are slightly larger than the actual values by an amount δ (as indicated in Fig. 1) and $\mathrm{IP}(1s^3) = 43.2 - \delta - \Delta$. Nevertheless, the data presented in Fig. 3 agree very well with the calculated values in two important features: (1) the stress at which the configurational transformation should occur and (2) the magnitude of the IP subsequent to the transformation. Therefore, our experimental observations are properly (and we believe unequivocally) interpreted as a change of the copper ground-state configuration.

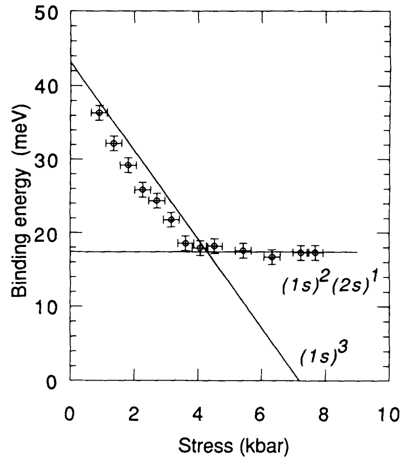

FIG. 3. Measured and calculated binding energies as a function of stress. The experimental points were determined from the PC response spectra. Above a pressure of 4 kbar, the experimental binding energies cease to depend on stress. This is in strong agreement with the stress dependence of the calculated ionization potentials (solid lines); above 4.3 kbar the ground state of the neutral copper acceptors changes from a $1s^3$ to a $1s^2 2s^1$ configuration, the latter having a stress-insensitive first ionization potential.

In conclusion, we have observed a large, stress-induced reduction in the first ionization potential of copper triple acceptor in germanium. Our analysis demonstrates that the electronic configuration of neutral copper changes from a pseudo Li^0, $1s^3$-like to a normal Li^0, $1s^2 2s^1$-like configuration when a stress greater than 4 kbar is applied along a ⟨100⟩ direction.

In the future we hope to investigate the optically accessible, bound excited states of each configuration. Our variational calculations indicate that two distinct sets of excited states (one set for each configuration) should be observable. Up to now, PC measurements have not revealed such states. This may be caused by inhomogeneities in the applied stress.

This research was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 and in part by U.S. NSF Grant No. DMR 91-15856. C. Wang wishes to acknowledge partial support from CONACyT (Consejo Nacional de Ciencia y Tecnología, México) and from Grant No. IN-103493-UNAM (México). O. Dubon acknowledges support from the National Physical Science Consortium.

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