Giant Negative Piezoresistance Effect in Copper-Doped Germanium

O.D. Dubon, W. Walukiewicz, J.W. Beeman, and E.E. Haller
Engineering Division

September 1996
Presented at the
23rd International
Conference on the
Physics of Semiconductors,
Berlin, Germany,
July 21-26, 1996,
and to be published in
the Proceedings
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Giant Negative Piezoresistance Effect in Copper-Doped Germanium

O.D. Dubon,¹,² W. Walukiewicz,² J.W. Beeman,² and E.E. Haller¹,²

¹University of California
Berkeley, California 94720

²Engineering Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

September 1996

This work was supported by the Director, Office of Energy Research, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
GIANT NEGATIVE PIEZORESISTANCE EFFECT IN COPPER-DOPED GERMANIUM

O. D. DUBON (1,2), W. WALUKIEWICZ (2), J. W. BEEMAN (2), and E. E. HALLE (1,2)

(1) University of California, Berkeley, California 94720, U.S.A.
(2) Lawrence Berkeley National Laboratory, Berkeley, California 94720, U.S.A.

We have observed a stress-induced decrease of over ten orders of magnitude in the low-temperature electrical resistivity of copper-doped germanium single crystals. The application of large uniaxial stresses in a <001> direction leads to a change in the copper ground-state wavefunction from the highly localized 1s(2s) to the much more extended 1s(2p)(2s) configuration. We attribute the decrease in the resistivity to impurity band conduction by the 2s holes of the high pressure configuration.

1. Introduction

The fourfold degeneracy at the valence-band edge of Ge allows for the accommodation of up to four holes in the 1s lowest one-particle level of acceptors, which would be equivalent in the atomic framework to having a 1s(3) ground-state configuration in the case of the copper triple acceptor. Uniaxial stress breaks the fourfold degeneracy of the valence-band edge and splits the acceptor lowest one-particle level into two, doubly-degenerate levels. In the case of the copper triple acceptor, we have previously shown that at sufficiently high stresses (>4 kbar), the 2s one-particle level associated with the lower 1s split level crosses the higher energy 1s level transforming the copper ground-state from a pseudo Li(0), 1s(3)-like to a normal Li(0), 1s(2p)(2s)(2s)-like configuration having a first ionization potential of 17 meV. In this study we show that this ground-state transformation produces a giant decrease in the electrical resistivity which is attributed to the stress-induced onset of impurity band conduction due to the extended nature of the 2s-like one-particle level of the 1s(2p)(2s) high-pressure configuration.

2. Experiments and Results

Three germanium crystals were Ar-sputtered with copper, annealed separately at 700 °C, and quenched in ethylene glycol leading to a copper acceptor concentration of 2 to 4x10^15 cm^-3 for each. We have measured the 4-point resistivity of two Ge:Cu single crystals as a function of temperature with and without stress (Fig. 1a). Uniaxial compression was applied to <001>-oriented sample surfaces. The magnitude of the stress is estimated to be at least 3 kbar from infrared spectroscopy measurements. Figure 1b shows the 2-point resistivity measured at 4.2 K as a function of stress for the third crystal. The application of
uniaxial pressure results in a reduction of the sample resistivity of many orders of magnitude that is most pronounced in the range of 2 to 4 kbar.

Figure 2a is a plot of the hole concentration versus inverse temperature for the sample represented in Figure 1a (squares). The filled squares represent zero-stress measurements while the clear squares correspond to hole concentrations obtained for the sample under the same uniaxial stress for which the resistivity is shown in Fig. 1a. The hole concentration of the uniaxially stressed sample exhibits an Arrhenius behavior with an activation energy of 3.1 meV. Figure 2b shows the sample's photoconductive response corresponding to the non-zero stress for which the Hall measurements are presented in Fig. 2a.

3. Discussion

The low-temperature conductivity, $\sigma$, of a moderately to heavily doped semiconductor results from carrier (electron/hole) transport via impurity states. Hopping conduction is one form of impurity conduction. It involves the phonon-
Figure 2. (a) Hole concentration as a function of inverse temperature measured by the Hall effect. The squares correspond to the sample represented by squares in Figure 1. The line represents the calculated hole concentration for a Ge crystal having the same impurity concentrations as the sample and with a binding energy of 17 meV for the majority impurity. The calculation includes effects from having an applied stress. (b) Photoconductive response corresponding to the sample in (a) under the same stress as displayed by the clear squares.

assisted motion of carriers through ionized (empty) dopant states and therefore requires the presence of compensating minority impurities. "$e_2$ conduction" is a process characterized by an activation energy $e_2$ that decreases with increasing majority impurity concentration. Unlike hopping $e_2$ conduction depends only on the majority and not the minority impurity concentration. At a critical concentration, $n_c$, $e_2$ vanishes and the resistivity becomes essentially temperature independent similarly to a metal. This metal-insulator transition has been shown to occur in a wide variety of solid state systems that obey the simple relation $n_c^{1/2}a^*=0.26$ where $a^*$ is the impurity Bohr radius. A critical concentration $n_c$ of approximately 1 to $2 \times 10^{17}$ cm$^{-3}$ has been observed for germanium doped with hydrogenic impurities.

Our results indicate that the observed giant negative piezoresistance effect arises from $e_2$ conduction via the copper acceptor states. The resistivity measurements demonstrate that this phenomenon occurs in Ge:Cu whether or not the copper acceptors are partially compensated. Although the Hall effect reveals a very small activation energy of 3.1 meV for the "freeze-out" of holes, the photoconductive spectrum (Fig. 2b) shows that the holes are bound at copper acceptors with an energy of about 17 meV leading to an essentially neutral (not
thermally ionized) copper acceptor level in the sample having a shallow acceptor background (represented by triangles in Fig. 1a). Holes can move even when occupying acceptor states. Therefore, the Hall energy is small because it is related to $e_2$ rather than the thermal ionization of the shallow acceptors.

For the $(1s)^2(2s)^1$, lithium-like copper ground-state, the Bohr radius can be estimated by scaling the hydrogenic $a^*$ with the ratio between the Bohr radius of the hydrogen atom (0.53 Å) and that of the lithium atom (1.59 Å). This results in a radius of $(1.59/0.53)80$ Å or 240 Å for which $n_c=1.27x10^{15}$ cm$^3$. This large Bohr radius does not take into account any central cell effect. The binding energy derived from effective mass theory is 4.5 meV.$^1$ The estimated central cell correction using the quantum defect model$^4$ is therefore $(4.5/17)^{1/2}$ which gives an $a^*$ of 123 Å and $n_c$ equal to $9.3x10^{15}$ cm$^3$. This Bohr radius is significantly larger than the estimated $a^*$ for the $(1s)^2$-like configuration, 48 Å, which yields a critical concentration of $1.6x10^{17}$ cm$^{-3}$. A critical concentration in the range of $10^{15}$-$10^{16}$ cm$^{-3}$ clearly implies the existence of $e_2$ conduction at and even below these concentrations.

In conclusion, uniaxially stressed copper-doped germanium provides a new medium for studying $e_2$ conduction. The existence of an isolated copper related impurity band within the bandgap of Ge makes stressed Ge:Cu a unique semiconductor system for studying new phenomena.

Acknowledgments

The authors would like to thank K. Roderick and L. Hsu for their technical support. This research was supported in part by the Director, Office of Energy Research, Materials Sciences Division, of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098. O. D. Dubon acknowledges support from the National Physical Science Consortium.

References