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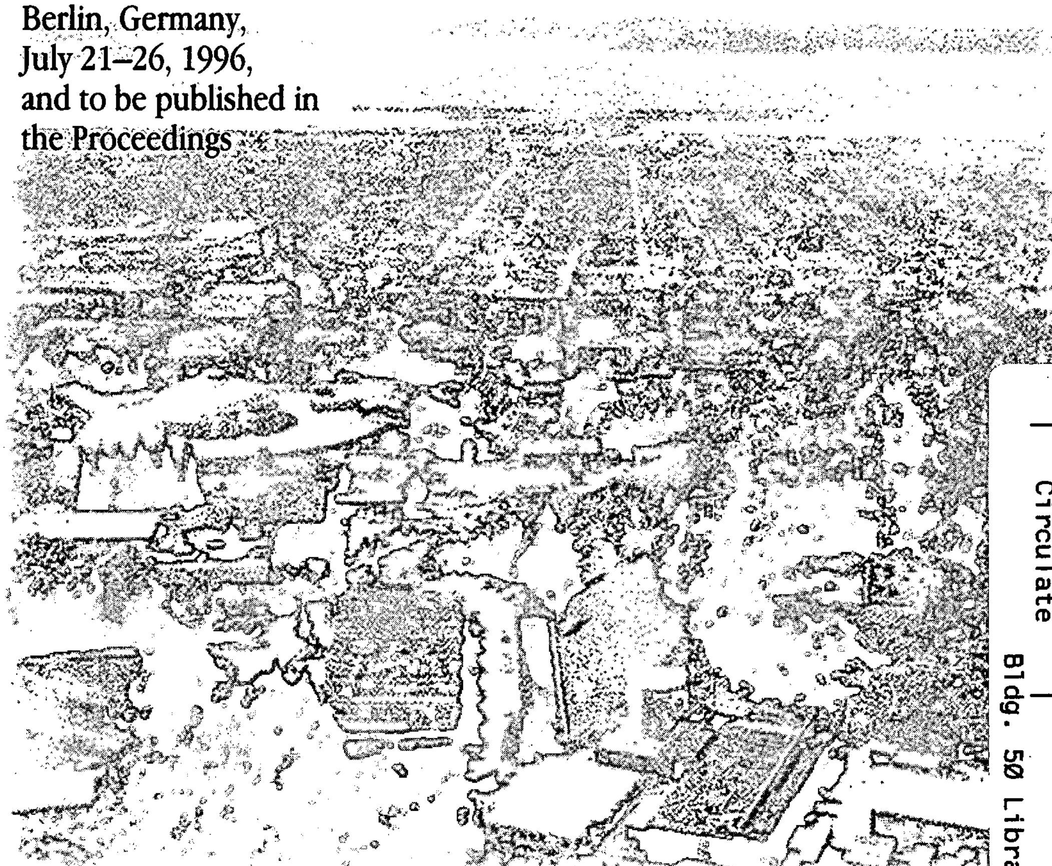

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GIANT NEGATIVE PIEZORESISTANCE EFFECT IN COPPER-DOPED GERMANIUM

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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 $(1s)^3$ to the much more extended $(1s)^2(2s)^1$ 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, $(1s)^2(2s)^1$-like configuration having a first ionization potential of 17 meV.[1] 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 $(1s)^2(2s)^1$ 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 4×10^{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

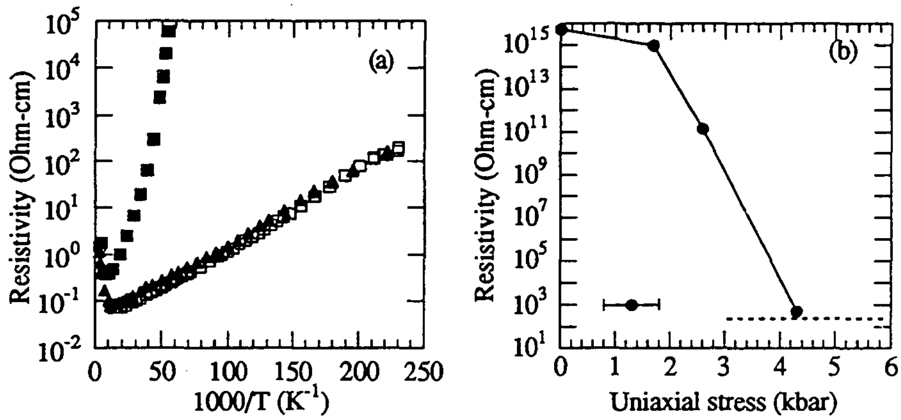

Figure 1. (a) Resistivity as a function of inverse temperature. The filled squares represent the zero-stress resistivity of Ge sample with a copper concentration of $3x10^{15}$ cm^{-3}. The copper is compensated by $4x10^{11}$ cm^{-3} donors. The clear squares were obtained for the same sample with an applied stress of at least 3 kbar. The filled triangles represent a similarly stressed sample having roughly the same copper concentration but with a residual shallow acceptor concentration of $3x10^{13}$ cm^{-3}. (b) Resistivity as a function of stress at 4.2 K for a sample having a copper concentration of $3x10^{15}$ cm^{-3} and with a residual shallow acceptor concentration of $4x10^{10}$ cm^{-3}. The dashed line reflects the value of the piezoresistivity from (a) extrapolated to 4. 2 K.

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, σ, 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-

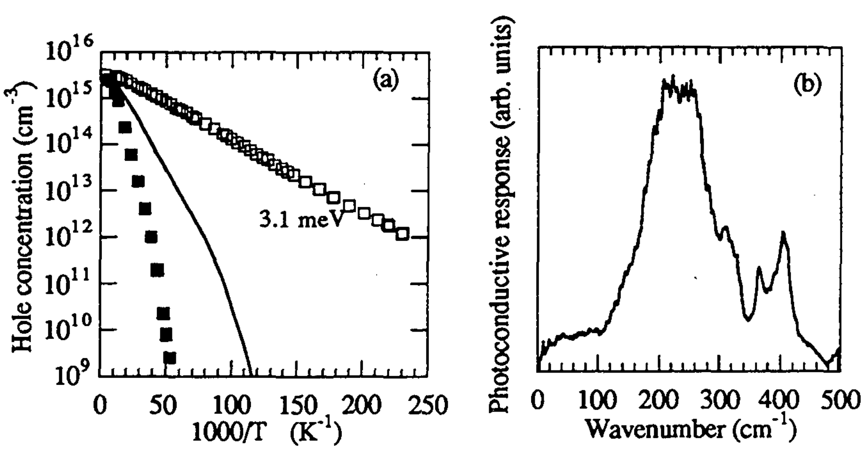

Figure 2. (a) Hole concentration as a function of inverse temperature measured by the Hall effect. The squares correspond to the sample represented by squares in Figure 1. The line represents the calculated hole concentration for a Ge crystal having the same impurity concentrations as the sample and 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. "ε_2 conduction" is a process characterized by an activation energy ε_2 that decreases with increasing majority impurity concentration. Unlike hopping ε_2 conduction depends only on the majority and not the minority impurity concentration. At a critical concentration, n_c, ε_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 $n_c^{1/3}a^*=0.26$ where a* is the impurity Bohr radius.[2,3] A critical concentration n_c of approximately 1 to 2×10^{17} cm^{-3} has been observed for germanium doped with hydrogenic impurities.

Our results indicate that the observed giant negative piezoresistance effect arises from ε_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 ε_2 rather than the thermal ionization of the shallow accpetors.

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 $(1s)^3$-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 ε_2 conduction at and even below these concentrations.

In conclusion, uniaxially stressed copper-doped germanium provides a new medium for studying ε_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.

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References

1. O. D. Dubon, J. W. Beeman, L. M. Falicov, H. D. Fuchs, E. E. Haller, and C. Wang, *Phys. Rev. Lett.* **72**, 2231 (1994) and references therein.
2. P. P. Edwards and M. J. Sienko, *Phys. Rev. B* **17**, 2575 (1978).
3. N. F. Mott and M. Kaveh, *Advan. Phys.* **34**, 329 (1985).
4. B.K. Ridley, *Quantum Processes in Semiconductors* (Clarendon Press, Oxford, 1988).

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