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Pressure Dependence of the Carrier Concentrations in p-Type Alloys of $Hg_{1-x}Cd_xTe$ at 4.2 and 77 °K*

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Electrical transport measurements have been made on p-type samples of $Hg_{1-x}Cd_xTe$ with x near 0.15 at temperatures of 4.2 and 77 °K and at hydrostatic pressures up to 9 kbar. A sharp transition is observed in both the Hall coefficient and conductivity versus pressure at 4.2 °K. The pressure dependence of the carrier concentrations and mobilities has been obtained from magneto-Hall and magnetoresistance data. Analysis using $\vec{k}\cdot\vec{p}$ theory yields values for the Fermi energy, measured with respect to the valence-band edge, of more than 9 meV, which are independent of pressure. A possible model to account for this behavior is described. Magnetic freeze-out effects have been observed and attributed to the lowest-energy, spin-split, zero-order Landau level passing through the Fermi energy. A value of 7×10^{-6} eV/bar is obtained for the pressure coefficient of the energy gap at 77 °K. Non-Ohmic behavior has been observed at 4.2 °K during the magnetic freeze-out.

INTRODUCTION

A continuous range of $Hg_{1-x}Cd_xTe$ alloys can be formed between the semimetal HgTe and the semiconductor CdTe. The general features of the band structure are now well established (see review papers by Long and Schmit[1] and Harman[2]). HgTe is a semimetal with an inverted band structure, like that proposed for gray tin,[3] with a negative Γ_6-Γ_8 energy gap of 0.3 eV, at low temperature. The energy gap increases approximately linearly with x, going through zero for $x\simeq0.15$ at low temperature. At higher values of x the alloys are semiconducting with a band structure qualitatively like that of the direct-gap III-V compounds. A large number of investigations (see review papers for references) have established that the dispersion relation for the conduction band is well described by Kane's $\vec{k}\cdot\vec{p}$ model.[4] A recent determination[5] from magnetoreflection measurements yielded a value of 8.4×10^{-8} eV cm for the Kane matrix element.

The behavior of n-type $Hg_{1-x}Cd_xTe$ is now relatively well understood, but the valence-band parameters have yet to be established. Reported values for the heavy-hole mass range from $0.3m_0$ to $7m_0$,[5-11] and the band overlap energy in the semimetallic alloys, due to the warping of the heavy-hole band, has not been reliably determined. In general, the electrical transport properties of the p-type alloys have proved complex and difficult to interpret.[5,12-14]

The object of this work was to obtain information on the valence-band structure and on acceptor levels near the valence-band edge. Measurements of the electron and hole concentrations have been made on p-type, nearly zero-band-gap semiconducting samples, as the energy gap was opened up with hydrostatic pressure. Because of the high electron-to-hole mobility ratio the minority electrons can dominate the transport properties in the semimetallic state and large changes in the transport coefficients occur during the semimetal-semiconductor transition produced by applying pressure.

Hydrostatic pressure measurements have been made previously only on n-type $Hg_{1-x}Cd_xTe$[15] and HgTe[16,17] at 300 and 77 °K, and on p-n junctions in $Hg_{1-x}Cd_xTe$.[18] The values obtained for the pressure coefficient of the energy gap vary from 8 to 14×10^{-6} eV/bar.

In this paper we describe first the experimental procedure, then the results obtained, and finally the analysis and interpretation of the results.

EXPERIMENTAL PROCEDURE

Sample Preparation

Single crystals of $Hg_{1-x}Cd_xTe$ were grown by a

new technique[19] which is believed to involve mass-transport-induced growth and simultaneous temperature-gradient annealing in a vertical ampoule 1.8 cm in diameter.

The composition x of the ingot was a function of distance along the growth direction. Slices were cut from the ingot perpendicular to the growth direction and etch polished to a thickness of about 0.50 mm. The composition x within a slice was found to be constant within the accuracy of the electron microprobe ($\Delta x = \pm 0.005$). The slices were further cut into rectangular parallelepiped wafers $1.2 \times 0.4 \times 0.05$ cm.

The samples that we will report on are from three wafers: 7B with $x = 0.149$, 7B1 with $x = 0.149$, and 8B with $x = 0.138$. The latter two were used unannealed. To reduce the acceptor concentration, wafer 7B (thickness 0.3 mm) was annealed for four days at 400 °C in Hg vapor. It was verified to be homogeneous in carrier concentration by Hall measurements on a sample progressively thinned by etching. (The unannealed wafers, cut from a large crystal, are expected to be homogeneous in thickness. Several small samples cut from each wafer showed the same carrier concentration within the accuracy of about 10% of the measurement of the Hall constant.)

Unoriented single-crystal samples, typically of dimensions $3.0 \times 0.7 \times 0.3$ mm, were cut from the wafers with a 0.005-in. nichrome-wire saw using a Carborundum-oil slurry.

Just before etching, the samples were rinsed for three minutes in turn in hot xylene, in acetone, and in hot methyl alcohol. The samples were not exposed to air but were left in the bottom of a beaker covered by a small amount of methyl alcohol. The etchant consisting of 20% bromine and 80% methyl alcohol (by volume) was poured into the beaker and agitated. The etching was stopped after about 10 sec by pouring a large quantity of methyl alcohol into the beaker. The usual, more dilute, Br-methanol etches can yield conducting surface layers, which have been observed at 4.2 °K on larger-gap semiconducting, p-type $Hg_{0.70}Cd_{0.30}Te$. The above etch[20] left no detectable conducting layer on $Hg_{0.70}Cd_{0.30}Te$ samples with resistivities as high as $10^5\ \Omega$ cm.[21] Since the resistivity of the samples discussed here was always below $10^3\ \Omega$ cm, the surface conduction left by the etching should be insignificant.

Six contacts were made to the samples by electroplating gold and then indium, as follows: The samples were held down on a microscope slide by the sharp tip of a spring-loaded tungsten wire, and the sample and most of the wire were covered by microstop (a red lacquer). When it was dry, 0.02-cm strips were cut in the microstop on the glass. These strips terminated at the sample and were peeled off, exposing the parts to be plated. Using the tungsten wire to make electrical contact, a thin layer of gold followed by a thicker layer of indium was plated on. Gold wires (0.001-in. diam) were indium soldered to the plated regions. These contacts were able to withstand the temperature and pressure cycling involved in the experiments.

Measurements

The samples were mounted in a Be-Cu pressure bomb (1.43-cm o.d., 0.32-cm i.d.), which, when pumped to the desired He-gas pressure (0–9 kbar), could be lowered into a Dewar. The Hall and resistivity voltages were displayed on an xy recorder as a function of magnetic field. (The sample mounting and pressure techniques have been described in more detail in Ref. 22.)

For the 4.2 °K measurements the bomb was slowly lowered into the Dewar, so that the pressurized helium solidified from the bottom up. There may be some uncertainty about the final pressure in the bomb. For example, helium at 8 kbar solidifies at 55 °K.[23,24] If it then cools to 4.2 °K at constant volume, the pressure would drop by about 8%. Most of this drop, however, occurs in the first 15 °K of cooling. Differences in temperature between the two ends of the bomb cavity (length 10 cm) during the cooling are expected to be higher than 15 °K. Therefore, assuming that within the bomb cavity solid helium cannot support a pressure gradient,[24,25] a large portion of the pressurized helium in the bomb cools through the first 15 °K after solidification at constant pressure. When the helium in the 0.050-cm-i.d. pressure tubing, which is connected to the top of the bomb, finally solidifies, the bomb becomes effectively sealed and the rest of the cooling takes place at constant volume. In the following we assume that the pressure in the bomb at 4.2 °K is the externally maintained pressure. In view of the above considerations, this is thought to be closer to fact than the assumption of cooling at constant volume.[25]

RESULTS AND PRELIMINARY ANALYSIS

Figures 1 and 2 show the zero-field resistivity and low-field Hall coefficient as a function of pressure for the three samples at 4.2 °K. A clear transition is indicated by the sharp rise in resistivity and the sudden change of sign of the Hall coefficient, which results from the removal of the minority electrons. For samples 7B and 7B1 the transition occurs between 3 and 4 kbar, and for sample 8B between 7 and 8 kbar. In sample 7B (annealed sample), the resistivity increases by more than three orders of magnitude, indicating that only a small fraction of the conductivity at atmospheric pressure is due to holes.

In order to obtain the concentrations and mobil-