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Growth and Transport Properties of Bi-Sb Single Crystal Alloys*

Since the details of this investigation are to be published elsewhere,[1,2] it is our purpose to only briefly summarize the results here.

The purpose of this study was (1) to investigate the methods required to produce homogeneous single crystal Bi-Sb alloys[1] and (2) to study the band structure by performing transport phenomena measurements and analyzing them for a given composition ($Bi_{85}Sb_{15}$) as a function of doping.[2]

Crystal growing

Homogeneous crystals of Bi-Sb solid solutions are difficult to grow, but are important for the basic understanding of the electron transport properties and band structure of these materials. The problems arise from (1) the low melting temperature (approximately 300°C) which makes it difficult to achieve a large thermal gradient at the crystal growing interface, (2) the small liquid diffusion coefficient, which was estimated to be between 2×10^{-5} and 3×10^{-5} cm^2/sec at 300°C,[3] and (3) a segregation coefficient so large[4] (5 to 10) as to favor growth of undesirable cellular substructure. From existing theories of crystal growth,[5] the conditions necessary for producing crystals with Sb compositions from 5 to 15%, free of macro- and micro-inhomogeneity, are as follows: A zone melting technique is used to grow the crystals. If the temperature gradient in the molten zone is about 60°C/cm, as can be attained by the use of a water cooling jacket, the growth rates must be between 1 and 0.4 mm/hr to grow homogeneous Bi-Sb alloys of from 5 to 15% Sb.

The degree of homogeneity can be determined by etching studies, chemical analysis, and electron beam microprobing. This latter technique revealed a typical variation of ±15% about the mean Sb concentration over a 0.2 mm interval on a specimen grown at 1.6 mm/hr. A lower growth rate (0.4 mm/hr) produced no detectable micro-inhomogeneities.

Transport properties and band structure

The slope of ln (resistivity) versus $1/T$ curves in the exponential region, for variously doped n- and p-type $Bi_{85}Sb_{15}$ crystals, were found to increase as one progresses from Te doped n-type crystals through high purity n- and p-type samples to heavily doped p-type crystals. This situation is similar to that found in InSb, where the electron to hole mobility ratio is large.[6] The thermal gap for a $Bi_{85}Sb_{15}$ alloy, as deduced from the temperature variation of resistivity on the high purity n- and p-type samples, is 0.024 ± 0.003 eV, a significantly higher value than the previously measured[7] maximum gap (0.014 eV) for this system.

The low-field Hall coefficient anisotropy, due to crystal asymmetry and the nature of the mobility tensor, was essentially eliminated at high magnetic fields ($H \geq 2 \times 10^4$ gauss). This provided a means of directly determining the total electron concentration[8] at 20°K in the Te doped sample. Combining these results with those of quantitative chemical analyses, we obtained a ratio of Te atoms to electrons equal to 2.

Seebeck coefficient measurements were used to determine the Fermi levels of electrons in doped and undoped n-type samples, being respectively 0.02 eV above and 0.002 eV below the band edge at 20°K. Carrier concentrations calculated for these samples, assuming bismuth-like effective masses and an ellipsoidal-parabolic model,[9] indicate that most of the electrons must reside in three bismuth-like tilted ellipsoids. Most of the transport measurements are consistent with this conclusion. However, the relative magnitudes of the second power magnetoresistance tensor components[10,11] $\rho_{33,11}$ and $\rho_{33,33}$ may may indicate the possible presence of a small number of electrons in an ellipsoid along the trigonal axis.

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* A summary.

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Discussion

L. S. Lerner: Does the 15% antimony concentration correspond to the maximum band gap in the alloy system? Jain puts it at 11-12% antimony.

Dale Brown: I don't know. Our work was done mostly at this one concentration. It is not likely that the maximum occurs at lower concentrations. Jain gets a smaller gap at 11%.

Yi-Han Kao: Experimental and theoretical studies have shown that the conduction band in bismuth is nonparabolic, so that the interpretation must be based on a nonparabolic model. In work done last year at Watson Laboratory, I observed the de Haas - Shubnikov effect and Azbel'-Kaner type cyclotron resonance in a dilute Bi-Sb alloy with antimony concentration nearly 1 wt. %. We found from the cyclotron resonance data that one cyclotron mass is changed upon alloying bismuth with antimony. This is consistent with the nonparabolic model. Assuming E_g and effective masses are unchanged in the alloys, we calculated that for pure bismuth $E_F = 24.4$ meV, $E_g = 14.5$ meV, by using our data in alloys and the cyclotron masses and de Haas - van Alphen periods in bismuth. These values are in agreement with the Lincoln Laboratory measurements ($E_F = 25$ meV, $E_g = 15$ meV) and the values given by G. E. Smith this morning ($E_F = 27.6$ meV, $E_g = 15.3$ meV). This agreement suggests that E_g and effective masses are held fixed in dilute Bi-Sb alloys.

Brown: We are dealing in the 15% Sb alloy with a *thermal band gap* of 24 meV. It would not be surprising that as one alloys bismuth, and produces a band gap, the amount of nonparabolicity would decrease.

A small amount of nonparabolicity is evident in our data. In the tellurium-doped sample where $N = 4.8 \times 10^{17}$/cc and $E_F = 21$ meV (20°K), as deduced from Hall coefficient versus field and Seebeck coefficient data respectively, a density-of-states effective mass of $0.052\ m_0$ was consistent with a 3 ellipsoid parabolic model. In the undoped sample where $E_F \simeq -2$ meV (below the band edge) a slightly smaller density-of-states effective mass ($0.044\ m_0$) was required to calculate N in this sample, indicating some nonparabolicity.

C. A. Nanney: Can you compare the mobility of the tellurium-doped alloys with the mobility of the undoped alloys?

Brown: In the *n*-type samples at 20°K the mobility tensor components in the undoped material are about a factor of 2 larger than those in the tellurium-doped samples. In these latter samples, the mobility is about 4×10^5 cm²/volt sec.

W. E. Henry: What etch did you use?

Brown: The most common one consisted of 50% nitric acid and 50% water. This attacks the bismuth preferentially and leaves a light film on the surface. The white oxide film is removed by a nitric acid-HF etch.

Henry: Have you made a qualitative estimate of the effect of growth rate and temperature gradient on the defect (dislocations, etc.) concentration in the material?

Brown: No.

W. M. Yim: According to our results at RCA we agree with the authors that one should use a much slower growth rate and a much higher temperature gradient than usual in order to grow a homogeneous single crystal of Bi-Sb alloys. However, the slower the growth rate, the more frequent is the chance of growth striations to occur. These striations are parallel to the growth interface and resemble so-called resistivity striations observed in some semiconductors grown from the melt. Did you observe these striations? If so, what would be the effect of the striations on the electrical properties of Bi-Sb alloys?

Brown: We have not observed any so-called resistivity "striations" in the middle sections of the single-crystal ingots, where a high degree of electrical uniformity is found from samples taken from different slices in this region.

A. N. Friedman: Have you investigated the possibility of annealing to smooth out the microstructure?

Brown: We tried that but saw no effect.

Milton Green: Slow pulling of crystals during growth produces an impurity concentration gradient in the direction of pull. Rupprecht [*Z. Naturf.* **16a**, 395 (1961)] has demonstrated with measurements on InSb that this produces an anisotropy in the magnetoresistivity that is not observed if the crystal is pulled fast. In the latter case, the impurity gradient is not observed or is extensively diminished.

Brown: Pulling too fast produces constitutional supercooling, and zone leveling will then cause complete segregation.

M. H. Cohen: Barrett, in his studies of the lattice parameters of Bi, Sb, and BiSb, required very perfect crystals for accurate determination of the internal displacement parameters. This was particularly difficult for the BiSb alloys. The way Barrett solved the problem was to *speed up* his zone leveling process rather than to slow it down. The sufficiently rapidly pulled crystals were homogeneous, showed extremely sharp Bragg reflections, and had very low dislocation counts. However, this technique worked only for antimony concentrations of less then 8%, whereas Drs. Brown and Silverman have been particularly concerned with alloys of order 15% concentration.