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A systematic study of the electrical properties of Fe-doped InP single crystals

The doping of indium phosphide (InP) single crystals with iron (Fe) to induce semi-insulating properties is a well established procedure [1–4] but no detailed systematic investigation of changes in electrical resistance, carrier concentration and Hall mobility induced by changes in Fe concentration and which occur due to normal segregation effects, has been reported. In view of the importance of minimizing Fe concentration because of the possibility of out-diffusion into epitaxial layers grown onto semi-insulating Fe-doped substrates, this paper reports the electrical properties determined along InP single crystals grown using melts containing between 0.005 and 0.15 wt% Fe, in order to cover the complete range of electrical properties from n-conducting to semi-insulating.

All crystals used in this investigation were grown on the ⟨1 1 1⟩ axis by the liquid-encapsulation Czochralski (LEC) technique [5] incorporating the crucible weighing method of automatic diameter control [6, 7]. The melts were contained in silica crucibles surrounded by a carbon susceptor and radio-frequency heating (450 kHz) was employed. Nitrogen gas at a pressure of 30 atm was used throughout and all the crystals were grown at pulling and rotation rates of 15 mm h^{-1} and 10 rpm, respectively. The boric oxide used as the encapsulant was supplied by BDH Limited and the polycrystalline InP starting material was provided by MCP Limited. In control experiments, where no Fe was added to the melt, the polycrystalline InP was converted into single crystals which had a residual free-electron concentration, ($N_D - N_A$), consistently within the range 2 to 4×10^{15} cm^{-3} and a Hall mobility within the limits 25 000 to 35 000 cm^2 V^{-1} sec^{-1}, both these properties being measured at 77 K. A detailed chemical analysis of these materials is published elsewhere [8].

Five different concentrations of Fe were studied; the concentrations as added to the starting charge prior to melting in the form of metallic Fe were: 0.005 wt% (L781, L857), 0.01 wt% (L776, L808), 0.02 wt% (L772, L775), 0.04 wt% (L749, L750) and 0.15 wt% (L677, L729), the numbers in brackets denoting the crystal reference code. For the conducting samples, resistivity, Hall mobility and the free-electron concentration were determined at both 77 K and 298 K using the Van der Pauw technique. Resistivities for all samples were determined by measuring the resistance of a bar sample, typically 1.2 cm long. The amount of Fe present was determined in some of these samples by spark-source mass spectrometry (SSMS).

Resistivity is plotted as a function of mass fraction of melt converted into single crystal (g) for the five pairs of crystals in Fig. 1; for clarity, at the highest Fe levels, not all the results available have been plotted but all substantiate the trends shown. The Van der Pauw resistivities for the lightly-doped crystals, L781 and L857, have been included for completeness but the bar resistivities are

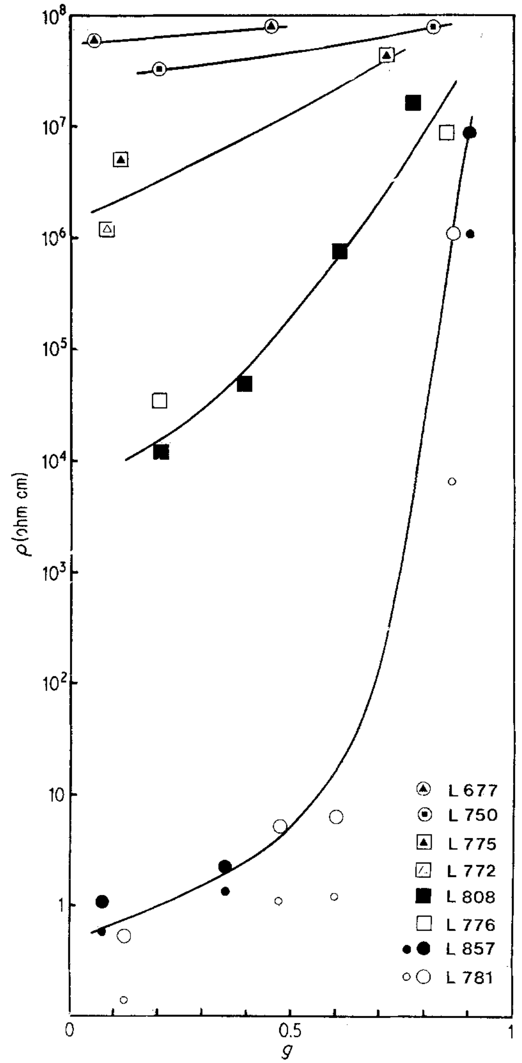

Figure 1 Resistivity plotted as a function of mass fraction of crystal solidified from InP melts with five different Fe concentrations added (1) L781 and L857 = 0.005 wt% Fe (2) L776 and L808 = 0.01 wt% Fe (3) L772 and L775 = 0.02 wt% Fe (4) L750 = 0.04 wt% Fe (5) L677 = 0.15 wt% Fe. The small circles for L781 and L857 are Van der Pauw measurements, the remainder are bar measurements.

considered to be more accurate due to the larger sample size. It is apparent from Fig. 1 that all the crystals become semi-insulating along some part of their length but that an Fe concentration in the melt greater than 0.01 wt% is necessary for all the crystal to have a resistivity in excess of 10^4 ohm cm, the value generally produced by doping with Cr [5]. It is also evident that the resistivity of the material increases with g at all levels of Fe used although the effect is least pronounced at the high doping levels where resistivities greater than 10^7 ohm cm can be produced throughout. Higher levels of Fe cannot be added to the melt without precipitation of phosphides of iron during crystal growth [2, 3], hence it seems unlikely that crystals with a completely uniform resistivity along their length can be produced by a unidirectional crystal growth process.

The results do show, however, that the resistivities from crystal to crystal are substantially reproducible for a given Fe concentration.

The least-doped crystals, L781 and L857, provide the most marked change in resistivity with a gradual increase from $g = 0$ to $g = 0.6$ followed by a rapid rise from $g = 0.7$ to 0.8. These changes are reflected in the free-electron concentration and mobility values, plotted for these crystals in Fig. 2, which decrease markedly in the range of g associated with the rapid rise in resistivity. The spread of data at high g values merely reflects the difficulty of measuring such low values accurately. It is reasonable to suppose that these changes reflect the increase in Fe concentration which must occur along the length of the crystal due to normal segregation of an added element and should follow a relationship of the type

$$C_g = kC_0(1-g)^{k-1}, \qquad (1)$$

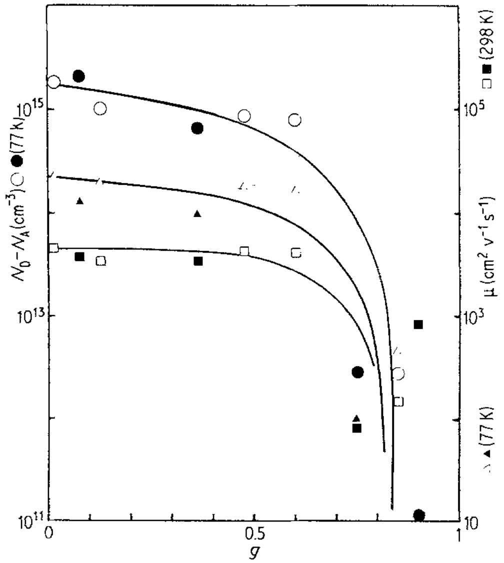

Figure 2 Hall mobility (77 and 298 K) and free electron concentration, ($N_D - N_A$) (77 K), plotted as a function of mass fraction of melt solidified for lightly Fe-doped InP crystals: L781 (open shapes) and L857 (closed shapes).

where k is the distribution coefficient, C_0 is the concentration of Fe added to the melt and C_g is the concentration at the mass fraction solidified, g. The value of k for Fe in InP quoted in the literature and derived from electron-spin resonance (ESR) measurements is 1.6×10^{-3} [2]. On this basis, a value of C_g ($g = 0.7$) equal to 1.3×10^{16} atoms cm^{-3} Fe can be calculated for the point of rapid change from n-conducting to semi-insulating behaviour shown in Figs 1 and 2 for crystals L781 and L857. This is a factor of four times greater than the maximum residual free-electron concentration ($N_D - N_A$) measured in the undoped starting material and would suggest that more Fe is present than would be required to in duce semi-insulating behaviour on a 1:1 donor: acceptor basis For one of these crystals, L781, it has been shown recently that the electron traps necessary to induce semi-insulating behaviour are derived from excited states of Fe^{2+} close to the middle of the band gap [9].

In order to check these deductions on Fe concentration, SSMS analysis has been carried out on crystal L857 at the transition point from n-conducting to semi-insulating behaviour ($g = 0.7$) and a level of 0.08 ppma has been determined. This is equivalent to 3.2×10^{15} atoms cm^{-3} Fe and balances almost exactly the residual donor concentration in the undoped starting material; however, it must be remembered that SSMS analysis is quoted only to an accuracy of × 3. Using Equation 1, a value of $k = 4 \times 10^{-4}$ can be calculated, which is an order of magnitude lower than that derived from the ESR data [2].

A SSMS analysis of crystal L677 grown from a highly doped melt (0.15 wt% Fe), typical of dopant levels now available commercially, gave Fe concentration values of 0.30 ppma ($g = 0.05$) and 0.35 ppma ($g = 0.45$) which are equivalent to 1.2×10^{16} and 1.4×10^{16} atoms cm^{-3} of Fe, respectively. Again, using Equation 1, values of $k = 1.5 \times 10^{-4}$ and 1.0×10^{-4} can be calculated for the respective mass fractions. The good agreement between the k values at different mass fractions substantiates that normal segregation according to Equation 1 is occurring. The k values for the two widely different melt concentrations of Fe also show good agreement and suggests that the distribution coefficient for Fe in InP shows little concentration dependence. The 1:1 correlation determined between residual donors and the added acceptors clearly suggest that in crystals L781 and L857, Fe is present in the lattice predominantly as Fe^{2+}, at least until the balance with residual donors is achieved and the material is fully compensated. Beyond this point, the Fe^{3+} observed in ESR studies on more heavily doped crystals [2] will gradually predominate as the Fe content is increased. This implies that in the fully semi-insulating crystals such as L677, only a small fraction of the total Fe will be present as Fe^{2+}; on the present data, the minimum amount of Fe^{2+} present must be some 3×10^{15} atoms out of a total of 2×10^{16} atoms cm^{-3} of Fe, i.e. about 10%.

In summary, it is shown here that by using low dopant concentrations, the Fe incorporated into InP single crystals at the transition point between n-conducting and semi-insulating behaviour can be identified and shown to be almost equal to the residual donor concentration in the undoped material used as a starting charge. However, the Fe concentration must be increased by an order of magnitude for the whole crystal to become semi-insulating with a resistivity $> 10^7$ ohm cm. A mean value of 2.5×10^{-4} has been determined for the distribution coefficient of Fe in InP using SSMS analysis; this is an order of magnitude lower than that determined previously from ESR data.

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On the growth process of precipitate colonies

The appearance of precipitate colonies has been reported for a variety of alloy systems e.g. iron [1–6], copper [7, 8] and semiconductor materials [7–14]. Interpretations of the experimental observations have been proposed in terms of a repeated precipitation caused by the autocatalytic nucleation on the dislocations generated during precipitation [1] and in terms of the repeated precipitation on a climbing (partial or perfect) dislocation [2, 6–8].

It is the purpose of this note to derive a model for colony growth on the basis of observations by means of transmission electron microscopy on the growth of precipitate colonies of silver from supersaturated copper–silver solid solutions.

Single crystals (Cu–5 wt% Ag) were homogenized for 90 h at 700° C and subsequently quenched in water. Growth of precipitate colonies was induced by annealing the crystals at 500° C for various times between 3 and 60 min. Specimens suitable for transmission electron microscopy were prepared by slicing the crystals with a spark cutter and electropolishing (jet method) in a solution of 67% methanol and 33% nitric acid at −23° C and 20 V. The residual contamination at the surface of the electropolished specimens was removed by a subsequent bombardment with 6 kV argon ions (10 min, 30–40 μA). The transmission electron microscopy studies were carried out using a 200 kV electron microscope (Jeol 200A).

From the investigation of about 65 colonies the following facts emerged as the "typical features" of the colonies. The precipitate colonies observed had the shape of circular discs with rod-shaped silver precipitates arranged radially in a spoke-like fashion (Figs 1 and 2). The diameter of the rods was about 46 nm. The lengths varied between 25 and 300 nm. The spacing, *s*, (Figs 1 and 3) between neighbouring silver precipitates was approximately constant. If two neighbouring precipitates were divergently oriented, a new silver precipitate was observed to be formed in between if the spacing between the two precipitates became larger than about 2*s* (Figs 1 and 3). Each colony was surrounded by a chain of small precipitates (8 to 20 nm diameter) arranged along a dislocation loop. Occasionally the loop was observed to be removed from the chain of small precipitates (Fig. 1). From contrast experiments (Fig. 4) (**g.b**–

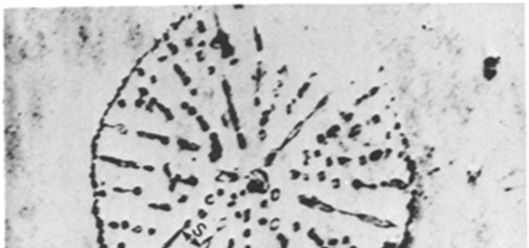

Figure 1 Bright-field electron micrograph of a precipitate colony in a Cu–5 wt% Ag alloy. In the region marked by an arrow the dislocation loop is separated from the chain of small precipitates surrounding the colony. The inserted diffraction pattern shows the parallel crystallographic orientation of the silver precipitates (weak diffraction spots) and the surrounding copper matrix (strong diffraction spots).

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