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The SnSe–SnSe$_2$ Eutectic; a *P–N* Multilayer Structure

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The conditions required to grow a two-phase *P–N* heterojunction from a eutectic melt are discussed from general principles. It is shown that the lamellar SnSe–SnSe$_2$ eutectic exhibits 10^3 to 10^4 *P–N* heterojunctions per cm, and the crystallographic relationship between the SnSe- and the SnSe$_2$-lamellae is reported. A simple, chemical vapour-etching technique is discussed which enables the components of the eutectic to be identified.

1. Introduction

Directional lamellar two-phase materials can be obtained by unidirectional solidification of suitable eutectic melts. The lamellae grow perpendicular to the solidification front. The interlamellar spacing is regular and inversely proportional to the square root of the growth rate if the eutectic phases exhibit non-faceted growth [1-5]. This regularity is lost in the case of faceted growth, but then, too, lamellar formation is possible.

In view of the interesting possibilities of *P–N* heterojunctions it is of value to consider whether it is possible to grow *in situ*, a lamellar two-phase eutectic, in which the lamellae of the one phase (I) consist of a *P*-type semiconductor and the lamellae of the other phase (II) of an *N*-type semiconductor. In principle, such a structure can be obtained if both eutectic phases are semiconducting and if an added dopant acts as a donor in phase I and as an acceptor in phase II. However, as will be pointed out in section 2, anisotype heterostructures of this kind can also be obtained without intentionally doping with a third component. As an example the SnSe–SnSe$_2$ system has been investigated (section 3). Section 4 reports a simple chemical method to identify the constituent single phases of the eutectic mixture.

2. *P–N* Heterojunction Eutectics

The occurrence of *P–N* heterojunctions in a eutectic mixture can be understood on the basis of a binary lamellar composite AB–AB$_2$, grown from a eutectic melt, where AB and AB$_2$ are semiconducting compounds. The same reasoning is valid if the composite originates from solid state disproportionation, or if one or both constituent phases are semiconducting elements.

It is well known from chemical defect considerations [6-9] that a semiconducting compound AB contains a small amount of randomly distributed native defects *A and *B, the concentrations of which are given by:

$$[{}^*\mathrm{A}]\,[{}^*\mathrm{B}] = K_1 \qquad (1)$$

where K_1 is a constant at a given temperature. *A may for example correspond to an interstitial A-atom or to a B-vacancy in the AB crystal. If A is less electronegative than B, then the ionisation reactions $^*\mathrm{A} \rightleftharpoons {}^*\mathrm{A}^+ + \mathrm{e}$ and $^*\mathrm{B} \rightleftharpoons {}^*\mathrm{B}^- + \mathrm{h}$ give rise to the equilibrium relations;

$$\frac{[{}^*\mathrm{A}^+]n}{[{}^*\mathrm{A}]} = K_2 \qquad (2)$$

and

$$\frac{[{}^*\mathrm{B}^-]p}{[{}^*\mathrm{B}]} = K_3 \qquad (3)$$

where n and p are the concentration of electrons (e) and holes (h) in the conduction band and the valence band respectively. From equations 1 to 3 and using

$$n\,p = K_4 \qquad (4)$$

and the electroneutrality relation

$$n + [{}^*\mathrm{B}^-] = p + [{}^*\mathrm{A}^+] \qquad (5)$$

it follows that, if [*B] $\gg$ [*A] (which is possible if AB is saturated with B), AB is *P*-type semiconducting. Similarly it can be argued that AB_2 saturated with A can be *N*-type semiconducting. Thus, a lamellar eutectic mixture consisting of AB saturated with B, and AB_2 saturated with A, may exhibit about 10^3 to 10^4 anisotype heterojunctions per cm if the lamellar width equals about 1 to 10 μm. This is found to be the case with the SnSe–$SnSe_2$ eutectic.

3. The SnSe–$SnSe_2$ Eutectic

The phase diagram of the Sn–Se system exhibits a eutectic between the compounds SnSe and $SnSe_2$ at 640° C and at 61 at. % Se [10]. SnSe is a semiconductor with a band gap, $E_g = 0.9$ eV [11, 12] and has an orthorhombic structure at room temperature with a cleavage plane perpendicular to the *c*-axis (space group *Pcmn*) [13]. $SnSe_2$ is a semiconductor with a band gap $E_g = 1$ eV [14] and has the hexagonal CdI_2 structure with a cleavage plane perpendicular to the *c*-axis [14].

A mixture of very pure Sn and very pure Se with atomic ratio Sn/Se = 0.99 (1 % excess Se) was heated for four days at 50° K above the melting temperature in an evacuated silica tube to obtain good homogenisation; then the melt was unidirectionally solidified, the growth rate and the temperature gradient being 5×10^{-4} cm sec^{-1} and 50° K cm^{-1} respectively. The resulting *P*-type single crystal of SnSe, saturated with Se, contained small precipitates of $SnSe_2$, and had a value $n_h = 3 \times 10^{18}$ cm^{-3} with a mobility $\mu_h = 100$ cm^2 V^{-1} sec^{-1} at 300° K (el. resistivity and Hall voltage measurements).

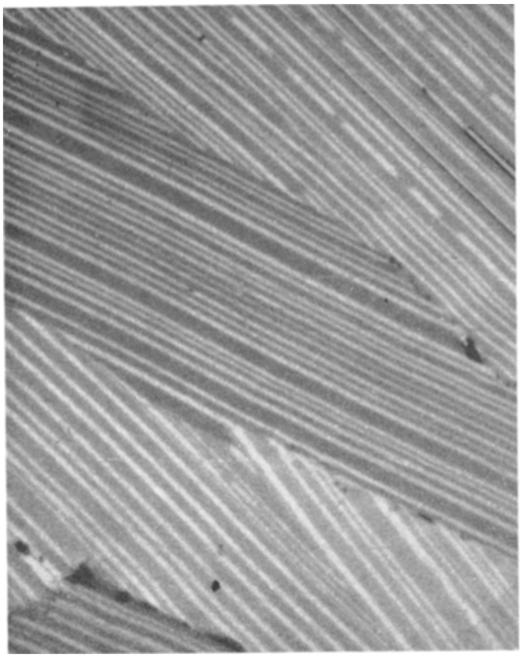


Figure 1 Transverse section of the unidirectionally grown SnSe–$SnSe_2$ eutectic mixture showing the random domain orientation (× 580).

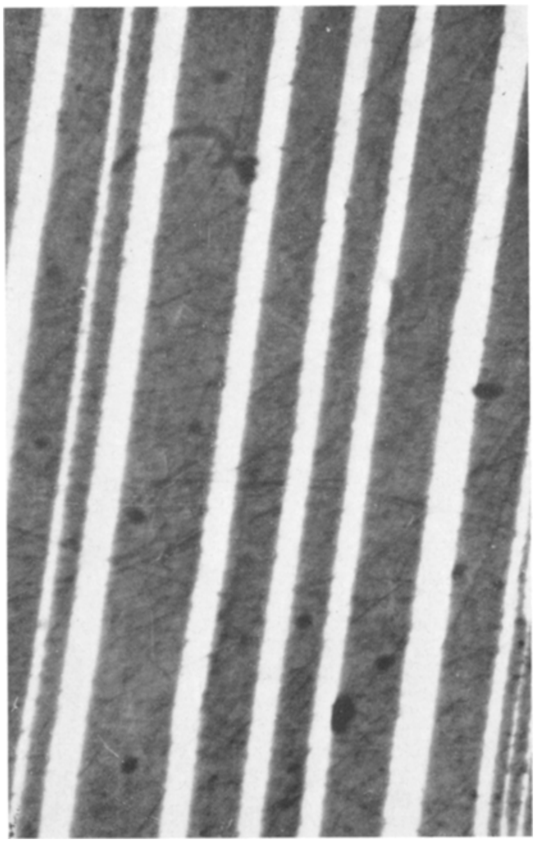


Figure 2 Section of the lamellar SnSe–$SnSe_2$ composite before vapour-etching (× 1265).

Similarly, a single crystal of $SnSe_2$, this time saturated with Sn, was prepared. It was *N*-type semiconducting. At 300° K, $n_e = 2 \times 10^{18}$ cm^{-3} and the electron mobility $\mu_e = 10$ cm^2 V^{-1} sec^{-1}.

The SnSe–$SnSe_2$ eutectic was obtained by unidirectional solidification. From longitudinal sections through the solidified sample and by microscopic observation during growth of the eutectic in a thin, flat silica cell it was concluded that the lamellae grew perpendicular to the solidification front. Perpendicular to the growth direction, however, the lamellae exhibited a parallel arrangement in domains 0.01 to 0.1 cm in size, which showed a random mutual orientation to one another (fig. 1). The variation of the interlamellar spacing (see also fig. 2) originates from the faceted character of the solid-liquid interface during growth.

X-ray analyses and Seebeck coefficient measurements confirmed the presence of single crystalline lamellae which were alternatively *N*- and *P*-type (i.e. $SnSe_2$ and SnSe).

The crystallographic relationship existing between the constituent single-crystalline phases of the SnSe–$SnSe_2$ mixture was obtained from X-ray measurements (diffractometer, Weissenberg, Von Laue back-reflection) on both isolated and coupled SnSe and $SnSe_2$ lamellae. At the SnSe–$SnSe_2$ interface the mating planes are the cleavage planes (see fig. 3) such that:

$$(0\,0\,1)_{SnSe} \,//\, (0\,0\,1)_{SnSe_2}$$
$$[1\,1\,0]_{SnSe} \,//\, [1\,\bar{1}\,0]_{SnSe_2}$$

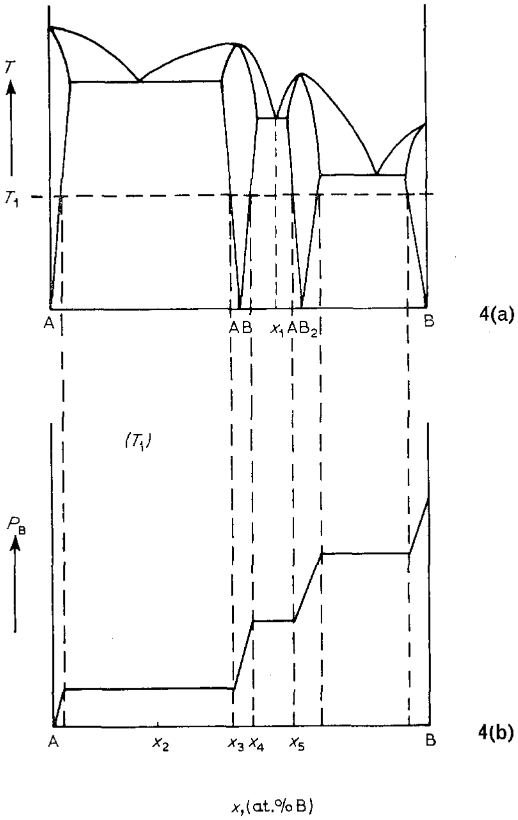


Figure 4 The A–B system containing two compounds. (a) The *T*–*x* projection; the gas line has been omitted; (b) Schematic representation of the dependence of the equilibrium B vapour pressure, P_B, on the gross composition of the condensed phases (*P*, *T* and *x* in arbitrary units).

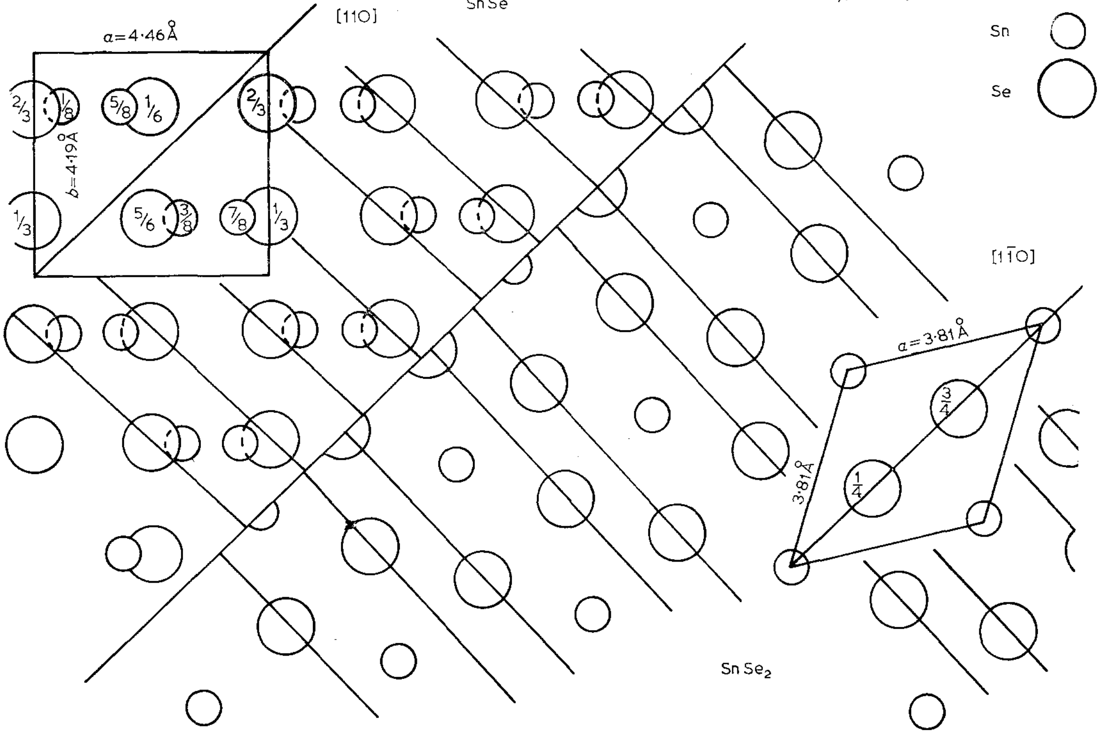


Figure 3 Crystallographic relationship between the SnSe- and the $SnSe_2$-lamellae in the SnSe–$SnSe_2$ eutectic. Projection on the (001) plane.

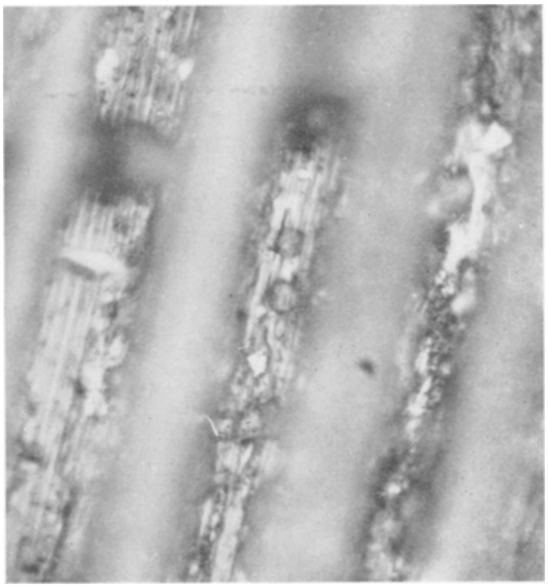
4. Identification of the Single Phases of the Solid Eutectic by a Simple Chemical Vapour Etching Technique

The phases of a eutectic mixture can be identified in various ways, for example by etching with specific chemical solutions or by means of the electron probe microanalyser. However, for a number of systems the phases can be identified within a few hours by means of a very simple chemical vapour-etching method, which requires no specific know-how or expensive and sophisticated apparatus.

Suppose the eutectic melt between the compounds AB and AB$_2$ of composition x_1 (fig. 4a) has been solidified and subsequently annealed at a temperature T_1. Then at equilibrium a composite material consisting of AB of composition x_4 and AB$_2$ of composition x_5 will be obtained. The partial vapour pressure of B, P_B, in the coexisting gaseous phase at T_1 as a function of the gross concentration of B in the condensed phases has been schematically represented in fig. 4b. The equilibrium partial vapour pressures at the A-rich boundary and at the B-rich boundary of a compound (e.g. for AB the compositions x_3 and x_4 respectively) generally differ by many decades.* When the AB-AB$_2$ eutectic mixture is annealed at temperature T_1 together with a large amount of A + AB (e.g. of composition x_2, fig. 4a) the AB phase will remain intact and shift from composition x_4 to x_3. The AB$_2$ phase, however, will be destroyed and converted to AB. If a flat polished sample of the mixture and short annealing times are used, the AB$_2$ phase will be only partially destroyed and will transform into areas of nucleated AB in a matrix of AB$_2$. At the same time the original AB$_2$ region may shrink if the molar volume of AB is smaller than that of AB$_2$. Both effects can be easily observed by optical means.

This procedure has been carried out on the SnSe–SnSe$_2$ eutectic composite. A polished sample (5 × 5 × 3 mm^3; fig. 2) was annealed at 500° C with a 5 g mixture of Sn and SnSe (geometrically separated from it) of gross composition 27 at. % Se, in an evacuated silica tube for 2 h. The result (figs. 5a and b) shows that the unattacked white phase is SnSe, whilst the attacked black and white speckled area indicates the SnSe$_2$ phase (originally black, see fig. 2). The latter had been etched away to a depth of 10 μm (fig. 5b).

(a)



(b)

Figure 5 The surface of the SnSe–SnSe$_2$ composite after annealing with a mixture of Sn and SnSe. (a) The white regions represent SnSe (focused on the white area, × 1500). (b) The speckled area represents the original SnSe$_2$ regions (focused on the speckled area, × 1500).

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*For example, for the semiconducting compound SnS at 730° C the partial pressure of the co-existing sulphur vapour, P_{S_2}, equals 10^{-6} and 10^2 torr for SnS saturated with Sn and saturated with S, respectively [15].

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