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Silicon- and germanium-based eutectics

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A survey has been made of the microstructures produced by unidirectional solidification of selected eutectic systems based on the semiconductors silicon and germanium. The aim of the work was to identify those systems which produce an aligned rod-type structure consisting of metallic rods in a semiconducting matrix.

The systems $NbSi_2$-Si, $TaSi_2$-Si and Ti Ge_2-Ge have been found to produce structures of this type which may be of use in future electronic applications.

1. Introduction

Materials produced by unidirectional solidification of eutectic systems are now well known for their useful mechanical properties. However, such materials have also been shown to possess other interesting physical properties [1, 2]. Of special interest in this context are two phase eutectic systems consisting of aligned metallic rods in a semiconducting matrix. For example, it has been demonstrated [3] that a material of this type, the NiSb-InSb eutectic, has several potential applications in commercial devices [2]. Extensive investigations into other systems based on the III-IV semiconducting compounds have also been carried out [4-6] by the same group.

The purpose of the investigation reported here was to examine the microstructure of various eutectic systems based on the widely used group IV semiconductors silicon and germanium. The exact material requirements of course, depend to a large extent on the particular application envisaged but in general the metallic rods should be highly aligned, of the order of 1 μm in diameter and present at a low volume fraction. Since the electrical properties of semiconductor materials are highly sensitive to small additions of certain elements, a very low solubility in the matrix of the other elements present in the eutectic is also desirable.

In general, in eutectic systems in which one phase is present at a low volume fraction, this phase will form a rod-like structure. However, where a high anisotropy of crystallization exists there is a strong tendency for low energy planes to be formed which can, in extreme cases, result in the formation of a lamellar structure [7]. Intermediate cases can also exist in which the minor phase forms rods which are faceted in accordance with planes of low surface energy. In some cases platelets of the minor phase are also formed, being interspersed with the faceted rods. The type of structure which occurs in all these cases is likely to be affected by the addition of other elements, present either in the form of impurities or dopants. In the latter case this can enable the microstructure of certain systems to be modified to meet a given requirement.

In the case of the elemental semiconductors, silicon and germanium, several binary eutectics, of the form MSi_2-Si and MGe_2-Ge respectively, have been reported in the literature [8-10]. These were investigated where there was a possibility of producing a suitable structure. In some cases, where a eutectic of this type was reported in a silicon system and little or no information was available on the analogous germanium system, preliminary investigations were carried out on the latter. This approach led to the discovery of a promising germanium based system, the previously unreported $TiGe_2$-Ge eutectic.

No attempt was made during this investigation to determine the eutectic temperatures of the systems investigated.

2. Experimental

2.1. Unidirectional solidification

As the aim of the present investigation was to determine the eutectic morphology a large num-

ber of selected systems rather than to produce high quality single crystal material, a relatively simple unidirectional growth apparatus was constructed. This apparatus enabled a range of growth rates from 0.6 to 6 cm h^{-1} to be achieved. The design of the apparatus was such as to allow the pull rod to be rotated at a constant rate (in this case 7 rpm) independently of the growth rate to promote thermal symmetry in the melt.

Unidirectional solidification was carried out using a Stockbarger technique. The constituents required to give the known or estimated eutectic composition were placed in a conical based silica crucible having a 1 cm i.d. and being approximately 5 cm in length. The crucible was placed inside a graphite susceptor which was suspended by carbon string from the pull rod of the growth apparatus. Induction heating was used to produce a hot zone through which the susceptor and its contents could be raised and lowered at controlled speeds. The eutectic alloys were prepared under argon, at a pressure slightly in excess of atmospheric, within a borosilicate glass furnace tube.

TABLE I

Element	Form	Purity
Germanium	Ingots	5N
Hafnium	Rods	3N
Molybdenum	Powder	4N
Niobium	Powder	3N
Praseodymium	Ingots	2N7
Silicon	Granules	6N
Tantalum	Powder	2N7
Thorium	Powder	3N
Titanium	Sponge	3N+
Tungsten	Powder	3N5
Vanadium	Powder	2N5
Yttrium	Powder	3N
Zirconium	Sponge	2N8

Purity is given by means of the symbol "N" where 2N7 indicates a purity of 99.7% with respect to impurities, 3N = 99.9% and 5N = 99.999%. The "+" symbol indicates a purity better than that stated.

No attempt was made to control the temperature gradient in the melt during solidification. Measurements taken using an optical pyrometer showed this to be between 20 and 50° C cm^{-1}.

2.2. Preparation of ingots

The constituents used were obtained from Koch Light Laboratories in the form and with the quoted purities shown in Table I.

For previously documented eutectics, weighed quantities of the constituents were added to a silica crucible to give the eutectic composition. Where no phase diagram information was available, initial ingots were prepared such that the minor elemental constituent was present at 10 wt %. Examination of the microstructure of such ingots showed which phase was present in excess of the eutectic composition and enabled the composition of subsequent ingots to be adjusted towards that of the eutectic. After the chamber had been flushed several times with argon the charge was melted by being raised into the induction coil, where it was held for approximately 1h to allow homogenization to take place. It was then lowered at a controlled rate so that it was solidified unidirectionally.

In the initial investigation intermediate growth rates of between 1 and 2 cm h^{-1} were used. Where these yielded promising microstructures, ingots were prepared over a wider growth rate range to determine whether this produced any marked changes in microstructure.

3. Observed microstructures

3.1. Silicon-based systems

Of the reported metal silicide-silicon eutectic systems [8], five were chosen as being likely to produce a rod-type morphology. The observed microstructures of these systems are summarized in Table II. Of these, only the systems containing niobium and tantalum produced suitably aligned rod-type structures.

3.1.1. Niobium-silicon

In the niobium-silicon system the microstructure was in all cases aligned with the rods being evenly distributed. The size and nature of the rods did, however, vary considerably.

In the majority of ingots, the $NbSi_2$ phase occurred as both platelets and rods of triangular cross sections, the latter being the most common form (Fig. 1). Occasionally, interspersed with these were rods which displayed no faceting, being much smaller in diameter than the faceted type. Near the surface of most ingots large faceted $NbSi_2$ precipitates occurred, probably arising from nucleation in the melt ahead of the solidification front; their predominance at the edges of the ingots suggested that this nucleation was caused by impurities in the melt introduced from the crucible.

TABLE II Microstructure of silicon-based eutectic systems

Minor eutectic phase	Eutectic data [8]		Observed microstructure
	Composition (wt % Si)	Temperature (°C)	
$MoSi_2$	95	1410	Faceted: predominantly platelet with some rods
$NbSi_2$	92	1405	Both faceted and non-faceted: predominantly rod type
$TaSi_2$	94	1405	Non-faceted: rod type
VSi_2	95	1385	Highly faceted: irregular
WSi_2	95	1400	Only a small amount of two phase regions observed owing to difficulties of density segregation and incomplete reaction; highly faceted

Two of the ingots gave considerably different microstructures from the remainder. In these, very little faceting occurred, the disilicide phase being present mostly as circular rods (Fig. 2) the diameters of which were appreciably smaller than the faceted type found in the other ingots. In one ingot, grown at 0.6 cm h^{-1}, this non-faceted structure was observed throughout its length. In the case of the other ingot, grown at 2 cm h^{-1}, this structure was only observed in the upper region, there being a well-defined interface between this and the faceted structure observed in the remainder of the ingot. Sections taken perpendicular to the growth direction showed the large difference in the rod size between the two regions (Figs. 1 and 2). Accurate measurements of rod size were difficult because of the irregularity in rod shape which occurred as a result of faceting. However, in this ingot, the average diameter was approximately 1.5 μm for the non-faceted rods as opposed to between 3 and 5 μm in the faceted case. Measurements of rod sizes in ingots prepared at other growth rates showed that the average rod diameter (d) was related to the growth rate (R) by the relationship d^2R = constant, for both the faceted and non-faceted structures. The constant was however, different, being smaller by a factor of three to four in the latter case.

Although no definite conclusions were reached during this study as to the reason for this growth rate independent change in morphology, preliminary analysis by mass spectrometry of the ingots produced did give indications that it was an impurity dependent effect, although the exact nature of this was not ascertained.

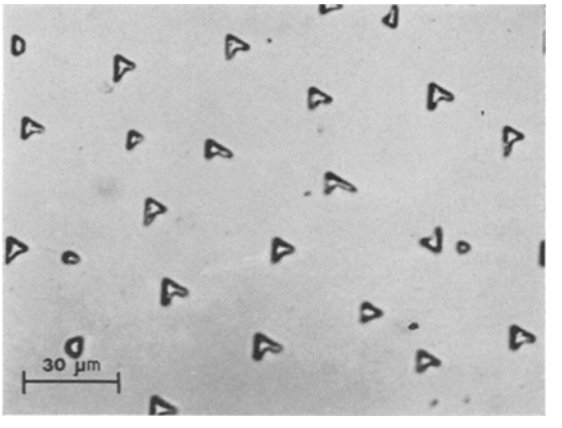

Figure 1 $NbSi_2$-Si eutectic unidirectionally solidified at 2 cm h^{-1}. Section perpendicular to growth direction showing faceted $NbSi_2$ rods.

3.1.2. Tantalum-silicon

This system displayed an aligned rod-type microstructure (Fig. 3). The rods were non-faceted and approximately circular in cross-section with average diameters of between 1 and 3 μm over the range of growth rates studied.

The rod size varied noticeably within all the ingots and the distribution of rods was irregular (Fig. 4). This occasionally resulted in sizeable regions of primary silicon. There was also some

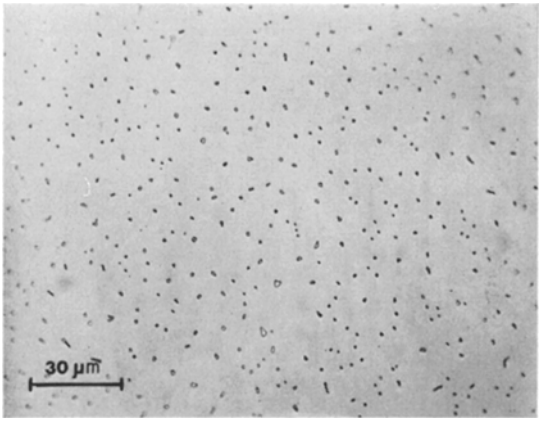

Figure 2 $NbSi_2$-Si eutectic unidirectionally solidified at 2 cm h^{-1}. Section perpendicular to growth direction showing fine non-faceted $NbSi_2$ rods.

occurrence of large faceted disilicide precipitates at the edge of the ingots as in the $NbSi_2$-Si system.

Because of the variability of rod size and distribution precise measurements could not be obtained from the ingots produced. However, approximate values indicated that this system also showed the characteristic dependence of rod size on growth rate (d^2R = constant).

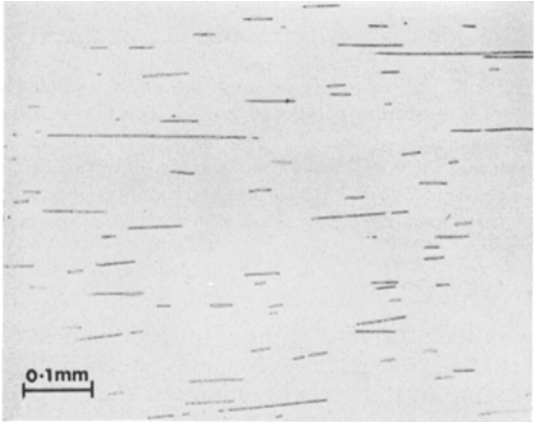

Figure 3 $TaSi_2$-Si eutectic unidirectionally solidified at 2 cm h^{-1}. Section parallel to growth direction, showing rods of $TaSi_2$. The apparent difference in length of the rods is owing to the small differences in the angle they make with the surface and is only an indication of their actual length in so far as it shows the minimum length.

3.2. Germanium-based systems

Eleven germanium-based systems were prepared by unidirectional solidification. Some of these systems were chosen on the basis of previously reported phase diagrams while others were chosen by analogy with silicon based systems. The microstructures observed in these systems are summarized in Table III.

Of the systems studied only the titanium-germanium system produced a well aligned rod type structure.

3.2.1. Titanium-germanium

Very little information is available on the

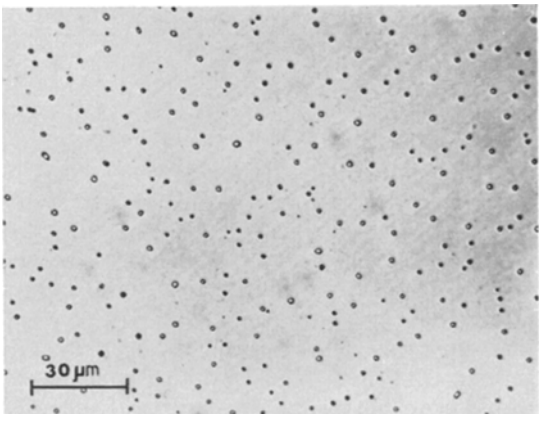

Figure 4 $TaSi_2$-Si eutectic unidirectionally solidified at 2 cm h^{-1}. Section perpendicular to growth direction showing irregular size and distribution of $TaSi_2$ rods.

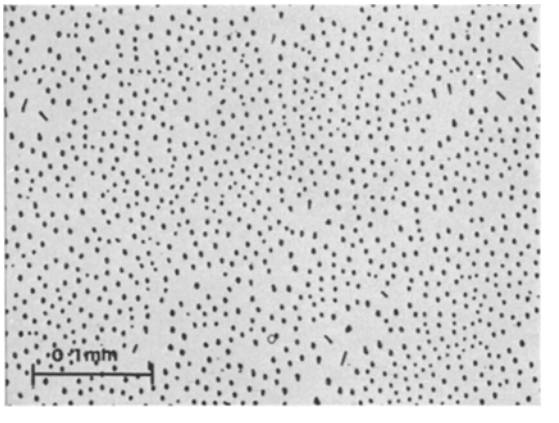

Figure 5 $TiGe_2$-Ge eutectic unidirectionally solidified at 2 cm h^{-1}. Section perpendicular to growth direction showing typical structure of $TiGe_2$ rods.

TABLE III Microstructure of germanium-based eutectic systems

Minor eutectic phase	Previously reported eutectic data		Composition obtained from present work (wt % Ge)	Observed microstructure
	Temperature (°C)	Composition (wt % Ge)		
$HfGe_2$	—	90 [9]	96	Irregular
$MoGe_2$	—	95 [10]	95 to 98	Irregular
$NbGe_2$	—	—	—	No eutectic observed
$PrGe_2$	825 [9]	—	92	Degenerate lamellar
$TaGe_2$	—	—	—	No eutectic observed
$Th_{0\cdot9}$ Ge_2	approx. 900 [10]	70 to 90	85	Rod; poorly aligned
$TiGe_2$	—	—	98.1	Rod; well aligned
V Ge_2	—	—	98	Platelet
W	—	Simple eutectic reported with no data [9]	—	No structure observed possibly owing to segregation lack of reaction
YGe_3	—	—	80 to 90	Lamellar; aligned
$ZrGe_2$	933 [8]	—	99	Irregular

germanium rich region of this system but in the corresponding silicon system a eutectic is reported containing 86 at. (78 wt) % Si. Unidirectional solidification of this silicon system [11] did not produce a rod-type structure. However, because of the difference in melting points of germanium and silicon (936 and 1420°C respectively) it was thought that a rod-type structure was more likely to occur in the germanium system, since in this case the eutectic would probably have a smaller titanium content [12].

An ingot containing 90 wt % germanium was prepared but on examination this was found to contain an excess of $TiGe_2$. Subsequent ingots were prepared containing 98 wt % germanium which was found to be close to the eutectic composition. In general, an aligned continuous rod-type structure was produced, especially at the faster growth rates (Figs. 5 and 6). However, at growth rates below 2 cm h^{-1} there was an increase in the proportion of the platelets present in the structure. These, in some cases, showed preferred orientation and were accompanied by faceted rod growth. The total impurity level was typically between 50 and 150 ppm, of which the majority appeared to consist of contamination from the silica crucible.

Measurements made on the ingots determined the eutectic composition as 98.1 wt % germanium (6.2 vol % $TiGe_2$). A graph was also plotted (Fig. 7) of the number of rods per unit area (ρ) against growth rate (R). This was substantially linear over the range of growth rates investigated,

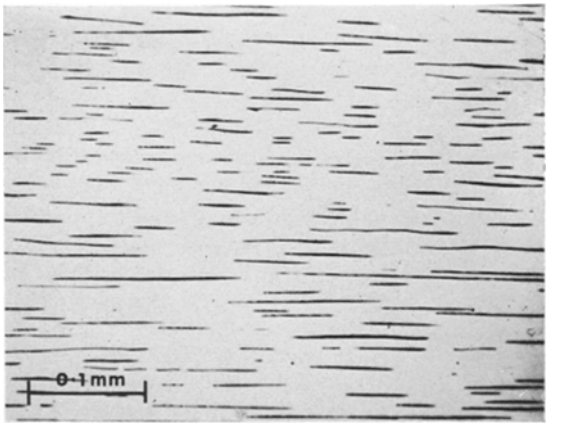

Figure 6 $TiGe_2$-Ge eutectic unidirectionally solidified at 6 cm h^{-1}. Section parallel to growth direction showing well aligned $TiGe_2$ rods. The apparent differences in length of the rods is owing to the small differences in the angle they make with the surface and is only an indication of their actual length in so far as it shows the minimum length.

with the exception of the ingot produced at 0.6 cm h^{-1}, where measurements were difficult because of the irregular nature of the structure produced at this, the slowest, growth rate. The linearity of the graph shows that the $\lambda \propto R^{-\frac{1}{2}}$ relationship holds for this system, where λ is the average rod spacing, since it has been shown [13] that $\lambda \propto \rho^{-\frac{1}{2}}$. Using the volume fraction of rods (v_r) and the number of rods per unit area (ρ) observed, it was possible to calculate the

average rod diameter (d) at the various growth rates, as shown in Table IV from the expression

$$v_r = \frac{\rho\pi d^2}{4}.$$

TABLE IV Average rod diameters of $TiGe_2$ at various growth rates

Growth rate (cm h^{-1})	Average rod diameter (μm)
0.6	4.6
1.0	5.9
1.5	4.2
2.0	3.8
4.0	2.5
6.0	2.0

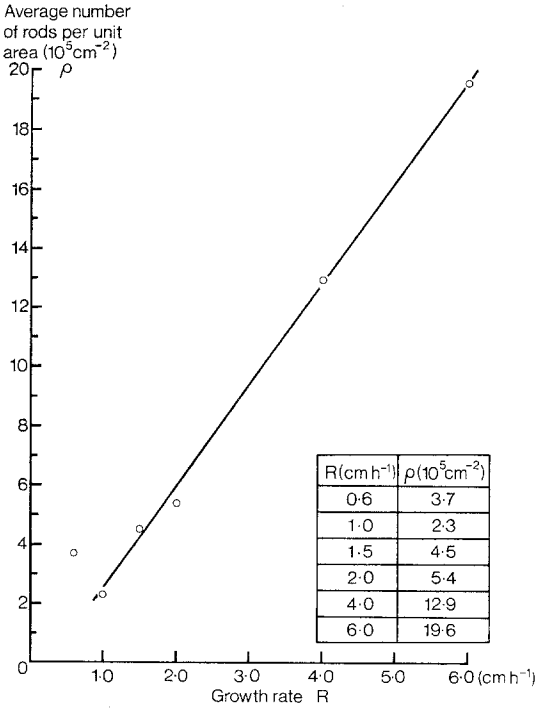

Figure 7 Variation of number of rods per unit area (ρ) against growth rate (R) for the unidirectionally solidified $TiGe_2$-Ge eutectic system.

4. Conclusions

This survey of eutectic systems based on silicon and germanium has shown that at least three systems exist with microstructures which may be of use in electronic applications [1]. These are niobium-silicon, tantalum-silicon and titanium-germanium. In all three cases, a well-aligned rod type structure obeying the $\lambda^2 R$ = constant diffusion relationship was obtained, with the rod phase being present at less than vol %. However, in general, the silicon- and germanium-based systems studied produced irregular structures with a pronounced tendency to faceting of the minor phase.

In the case of the niobium-silicon system, two different microstructures were observed, one in which the rod phase was highly faceted and the other, with considerably smaller diameter rods, in which it was apparently non-faceted. During this study, however, the exact growth conditions under which each structure occurred were not fully determined and this aspect requires further investigation.

In all cases the material produced in this study was polycrystalline. In the systems producing rod-type structures it would be interesting to produce single crystals, by Czochralski growth, which would be more suitable for evaluation of the anisotropic electrical and optical properties of these materials.

This investigation was primarily aimed at surveying the microstructure of eutectic systems based on the semiconductors silicon and germanium. In this respect the directional growth apparatus was designed to be simple and reliable. enabling a rapid through-put of samples. It did, however, lack the stability and control which can be obtained with more sophisticated equipment. It may be, therefore, that with improved growth conditions several of the systems reported here would produce more regular microstructures.

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