

# The solid state reaction between Cu<sub>3</sub>P and silicon or germanium

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## THE SOLID STATE REACTION BETWEEN $\text{Cu}_3\text{P}$ AND SILICON OR GERMANIUM

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### ABSTRACT

The phase relations in low-phosphorus parts of the ternary systems Cu-Si-P and Cu-Ge-P have been determined for alloys annealed in evacuated capsules at 500 °C.

The reaction of  $\text{Cu}_3\text{P}$  with silicon in diffusion couples that have been annealed in vacuum, is never faster than the reaction between copper and silicon.  $\text{Cu}_3\text{Si}$  and phosphorus vapour are formed during the reaction. A peculiar morphology, that of isolated  $\text{Cu}_3\text{Si}$  columns separated by large gaps, develops when the reaction is hindered. When a diffusion couple is annealed in a closed capsule,  $\text{Cu}_3\text{Si}$  and presumably SiP are formed.

The reaction between  $\text{Cu}_3\text{P}$  and germanium takes place at a rate comparable with that of the copper-germanium reaction and leads to the formation of  $\text{Cu}_3\text{Ge}$  and phosphorus vapour. Because of plastic deformation of  $\text{Cu}_3\text{Ge}$  no peculiar morphology of the reaction layer was observed.

### INTRODUCTION

We have studied the influence of traces of phosphorus in copper on the solid state reactions of copper with silicon. It was found that the segregation of phosphorus to the copper surface changes the reaction kinetics [1]. Auger electron spectra have shown, that even in copper with a bulk phosphorus concentration of 30 ppm the surface concentration is about 25 atom-% phosphorus. Since the copper surface resembles a  $\text{Cu}_3\text{P}$  surface, we have studied the reaction of  $\text{Cu}_3\text{P}$  with silicon. This reaction has many interesting aspects. Again it is the behaviour of phosphorus, especially its volatility, that predominates in the reactions that take place.

We have determined the low-phosphorus parts of the ternary phase diagram Cu-Si-P at 500 °C by the preparation and a study of the ternary alloys. In addition, the products formed in the diffusion couples provide information on the shape of the ternary phase diagram. The kinetics of the

reaction between  $\text{Cu}_3\text{P}$  and silicon in diffusion couples and the products formed, have been studied both in vacuum and in closed, evacuated capsules at temperatures between 400 and 550 °C. We have compared silicon systems with those of germanium. The low-phosphorus part of the ternary phase diagram Cu–Ge–P at 500 °C has been determined. The reaction of  $\text{Cu}_3\text{P}$  with germanium in diffusion couples is described.

#### LITERATURE SURVEY ON THE TERNARY PHASE DIAGRAMS Cu–Si–P AND Cu–Ge–P

The binary Cu–Si [2] and Cu–Ge [3] phase diagrams have been described previously.

The solubility of phosphorus in copper at 350 °C was found to be 1.2 atom-% and at 714 °C (the eutectic temperature) it was 3.5 atom-% [4]. In the binary Cu–P system, two compounds are known:  $\text{Cu}_3\text{P}$  and  $\text{CuP}_2$  [5]. Because of the high phosphorus content  $\text{CuP}_2$  is of no consequence to the study discussed here.  $\text{Cu}_3\text{P}$  has a hexagonal crystal structure [6] with  $a$  0.694 nm and  $c/a = 1.028$ . The structure resembles that of  $\text{Cu}_3\text{Si}$  [7].

The most recent silicon–phosphorus phase diagram (1986) [8] shows SiP to be the only compound in this system. But depending on the preparative techniques employed  $\text{SiP}_2$  [9],  $\text{Si}_3\text{P}_2$  [10] and  $\text{Si}_2\text{P}$  [11] have been reported. There is some confusion about the structures of these compounds: an orthorhombic structure with  $a$  1.36,  $b$  2.05 and  $c$  0.35 nm is attributed both to SiP [12] and to  $\text{SiP}_2$  [9], while for  $\text{SiP}_2$  an alternative orthorhombic structure with  $a$  1.399,  $b$  1.009 and  $c$  0.343 nm [13] is also reported. The data on the stability of SiP are contradictory: SiP is reported to be stable in water and in air [14], but on the other hand SiP must be regarded as hazardous material [15] because it decomposes into  $\text{SiO}_2$  and  $\text{PH}_3$  on contact with humid air [16].

One ternary Cu–Si–P compound has been described in the literature:  $\text{CuSi}_2\text{P}_3$ , a semiconductor [17], crystals of which have the sphalerite structure with a random distribution of copper and silicon atoms about the cation sites [18]. The lattice constant,  $a$ , is 0.525 nm. No further information has been found on the ternary system.

There is only one compound known to be in the germanium–phosphorus system, viz. GeP [5].

Up to now no phase diagram of the ternary system Cu–Ge–P has been published. One ternary compound,  $\text{CuGe}_2\text{P}_3$  [18] analogous to  $\text{CuSi}_2\text{P}_3$ , is known. It is also a semiconductor [19] with a zincblende type structure having a lattice parameter of 0.5372 nm [18]. Germanium can dissolve in the compound which markedly varies the lattice parameter [20].

## EXPERIMENTAL PROCEDURES

Alloys were prepared by arc-melting together lumps of copper (MRC, VP quality),  $\text{Cu}_3\text{P}$  (Alpha Products, balls containing 15 wt.-% phosphorus according to supplier, some balls contained an excess of copper), and silicon (Vieille Montagne, polycrystalline n-type) or germanium (Ventron, m6N purity). During melting considerable losses occurred, presumably as phosphorus vapour, which condensed on the inner walls of the glass container of the apparatus. The limited choice of raw materials restricted the overall composition of the alloys made: the maximum phosphorus content was below the line  $\text{Cu}_3\text{P}$ -Si(Ge). In the  $\text{Cu}_3\text{P}$ -Si system, a series of alloys was prepared containing less than 30 atom-% silicon and varying (2–15 atom-%) amounts of phosphorus. Alloys containing high amounts of silicon (about 40 atom-%) were prepared without the addition of copper to silicon and  $\text{Cu}_3\text{P}$ . Alloys containing 75 atom-% copper and varying amounts of silicon were prepared from  $\text{Cu}_3\text{P}$  with  $\text{Cu}_3\text{Si}$ . In the  $\text{Cu}_3\text{P}$ -Ge system similar alloys were prepared, as were alloys containing higher amounts of germanium.

The alloys were equilibrated in evacuated silica capsules for one to two months at  $500^\circ\text{C}$ . The sealed capsules ensured that the alloys were annealed under an equilibrium pressure of phosphorus. No losses were found to occur during the annealing treatment. After quenching in brine the specimens were cut with a water-cooled SiC saw, ground on SiC paper, and polished with diamond paste. On occasions the characteristic odour of  $\text{PH}_3$  was perceived. The composition of the phases was determined with EPMA (JEOL 733 Superprobe) operating at 20 kV, 10 nA, with the BAS [21] correction program.

Diffusion couples were prepared with polished slices, which were pressed together under a load of 20 kg and heated in a vacuum furnace (pressure lower than 0.1 mPa) [1]. After the reaction the couples were cut perpendicular to the reaction layer. After the metallographic preparation the couples were studied by optical microscopy (Reichert MeF2, equipped with a calibrated eyepiece) and with electron microscopy. Quantitative analyses were carried out with EPMA.

DETERMINATION OF THE TERNARY SYSTEMS AT  $500^\circ\text{C}$ 

The composition of the various phases in the Cu-Si-P alloys, annealed in evacuated silica capsules at  $500^\circ\text{C}$  are shown in Fig. 1. The overall compositions of the alloys studied are indicated. It was found from the observed compositions in the equilibrated alloys that the  $\text{Cu}_3\text{P}$  phase is in equilibrium both with  $\text{Cu}_{15}\text{Si}_4$  and  $\text{Cu}_3\text{Si}$ ; both silicides contain some phosphorus. Furthermore a three-phase triangle exists between  $\text{Cu}_3\text{P}$ ,  $\text{Cu}_3\text{Si}$ , and  $\text{CuSi}_2\text{P}_3$ . Another equilibrium exists between  $\text{Cu}_3\text{Si}$ , silicon, and a ternary compound

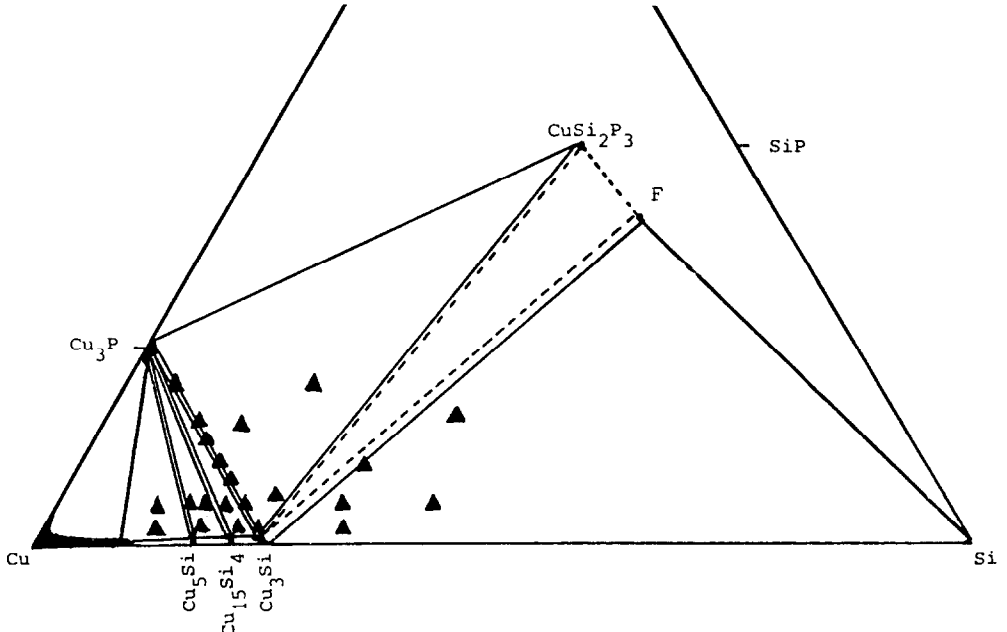


Fig. 1. Phase relations in the ternary system Cu–Si–P determined with EPMA in alloys, equilibrated in evacuated silica vessels at 500 °C. ▲ denotes overall compositions of the alloys; the dotted lines are described in the text.

containing 16 atom-% Cu, 43 atom-% Si, and 41 atom-% P, denoted F in the diagram. This last compound lies nearly on the connecting line between  $\text{CuSi}_2\text{P}_3$  and Si.

There are three possible compositions of F:

- (i) F is a submicroscopic mixture of  $\text{CuSi}_2\text{P}_3$  and Si. A variable composition would strongly support this idea, but in all alloys with an overall composition within the  $\text{Cu}_3\text{Si}$ –Si–F triangle the same composition was found.
- (ii) F is in fact  $\text{CuSi}_2\text{P}_3$ , but with a maximum of dissolved Si, analogous to  $\text{CuGe}_2\text{P}_3$  [20].
- (iii) F is a true ternary compound.

Since we have not been able to prepare alloys with an overall composition in the triangle  $\text{Cu}_3\text{Si}$ – $\text{CuSi}_2\text{P}_3$ –F we cannot decide whether (ii) or (iii) is true.

Figure 2 shows the results of the analyses of the Cu–Ge–P ternary alloys, annealed in evacuated silica capsules at 500 °C.  $\text{Cu}_3\text{P}$  contains at the most 1 atom-% Ge. The compound is in equilibrium with  $\text{Cu}_3\text{Ge}$ ,  $\text{Cu}_5\text{Ge}$ , and with the primary solid solution. Both germanides contain 1 atom-% P as a maximum at the apex of the three-phase triangles. Another three-phase triangle exists between  $\text{Cu}_3\text{P}$ ,  $\text{Cu}_3\text{Ge}$  and germanium.

This situation is common to most germanium-rich alloys, but sometimes unique material is found. In the back-scattered electron image (Fig. 3) this

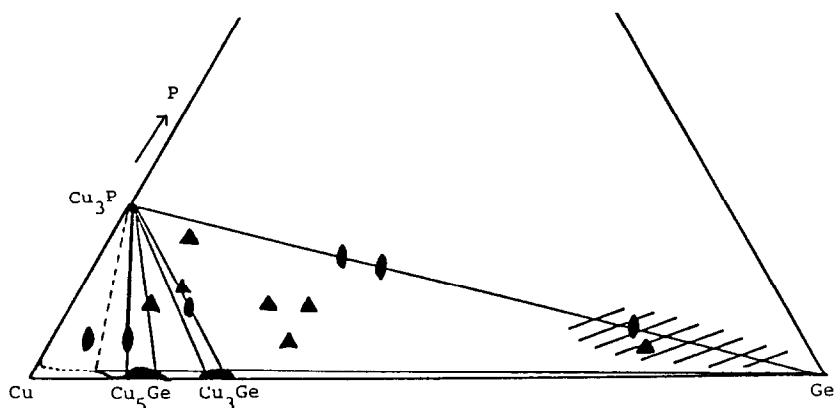


Fig. 2. Low-phosphorus part of the ternary phase diagram Cu-Ge-P. The alloys were equilibrated at 500 °C in evacuated silica vessels. The compositions were determined with EPMA. Hatched areas indicate regions of non-equilibrium “compositions” sometimes observed, and are described in the text.

material appears as bright areas, although the brightness is not uniform. Furthermore the areas are surrounded by brighter or darker lines, which indicate that changes in the electrical conductivity take place in these specific spots. Attempts to make quantitative analyses (EPMA) of this material, revealed a very large spread in composition, even within one

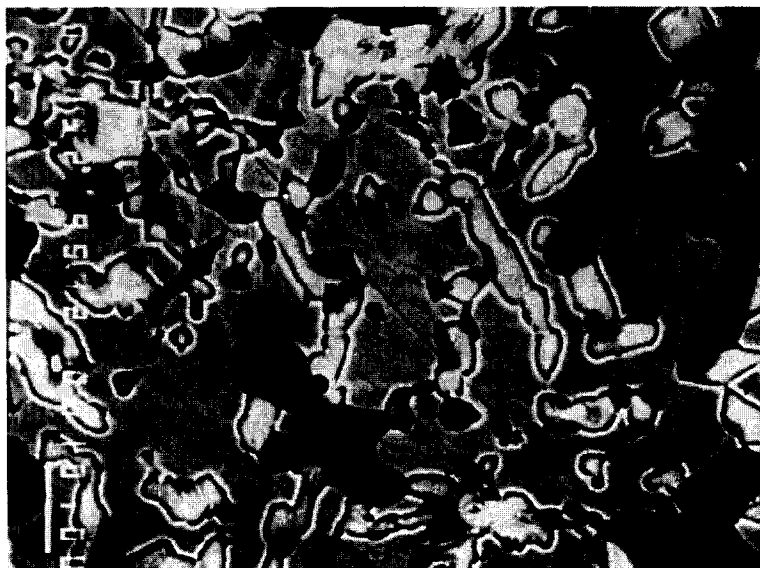


Fig. 3. Back-scattered electron image of a ternary alloy of overall composition  $\text{Cu}_{60}\text{Ge}_{30}\text{P}_{10}$ . The alloy contains  $\text{Cu}_3\text{P}$  (dark),  $\text{Cu}_3\text{Ge}$  (grey) and a ternary composition (bright, bounded by black and white lines). Bar indicates 10  $\mu\text{m}$ .

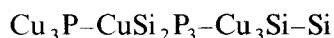
“crystal”. In Fig. 3 the compositions (as normalised atomic percentages) are depicted as hatched areas. A careful study of the result, especially the measured weight percentages, reveals total amounts of between 95 and 105% which is unusual because the specimen is in the focus of the electron beam, has good overall conductivity, and no other components were detected with EDS (energy dispersive spectrometry). We have no explanation for this phenomenon. We suppose that this is a non-equilibrium situation, perhaps a microscopic mixture so finely-divided that the electron probe also irradiates the “grain boundaries”. The normalised compositions suggest that this material is a mixture of the original  $\text{Cu}_3\text{P}$  and Ge used to prepare the alloys. Since it is clearly not an equilibrium compound, we have not included it in the ternary diagram of Fig. 2.

In contrast to the Cu–Si–P system, no ternary compounds were found by us to be present in the Cu–Ge–P system with relatively low phosphorus content in the evacuated silica capsules at  $500^\circ\text{C}$ .

#### THE SOLID STATE REACTION OF $\text{Cu}_3\text{P}$ WITH Si IN VACUUM

##### *Product formation*

We prepared diffusion couples from polished slices of  $\text{Cu}_3\text{P}$  and Si, which had been annealed beforehand in a vacuum furnace. The vacuum pressure is less than 0.1 mPa. From the phase diagram in Fig. 1, we see that the slope of the tielines changes from  $\text{Cu}_3\text{P}$  via  $\text{Cu}_3\text{Si}$  to  $\text{CuSi}_2\text{P}_3$ . Thus the following sequence should have been present in the  $\text{Cu}_3\text{P}$ –Si diffusion couple [22]:



However, we observed only  $\text{Cu}_3\text{Si}$ , which had grown into columns separating the original slices, although they had been pressed together with a weight of 20 kg. This is shown for a real couple in Fig. 4 and schematically in Fig. 5. The separation of the  $\text{Cu}_3\text{P}$  and Si discs deserves mention, since in a diffusion couple, in which reaction is hindered and proceeds only locally, the original interface remains intact (Fig. 6).

The  $\text{Cu}_3\text{Si}$  crystals in the  $\text{Cu}_3\text{P}$ –Si diffusion couple are embedded in the silicon layer, and show a perfect, pore-free interface, but the contact with the  $\text{Cu}_3\text{P}$  layer is remarkable: the smallest crystals have lost contact with the  $\text{Cu}_3\text{P}$  layer, as if the  $\text{Cu}_3\text{P}$  slice had already been lifted away by the faster-growing crystals before the smaller crystals could react, or grow larger. Contacts with the large crystals is also rather unusual. The  $\text{Cu}_3\text{Si}$  column only touches the  $\text{Cu}_3\text{P}$  platelet, but is not embedded in it. This morphology indicates that not only the immediate contact area but the whole of the  $\text{Cu}_3\text{P}$  surface takes part in the reaction. Thus the surface diffusion of copper on the  $\text{Cu}_3\text{P}$  surface is very fast.

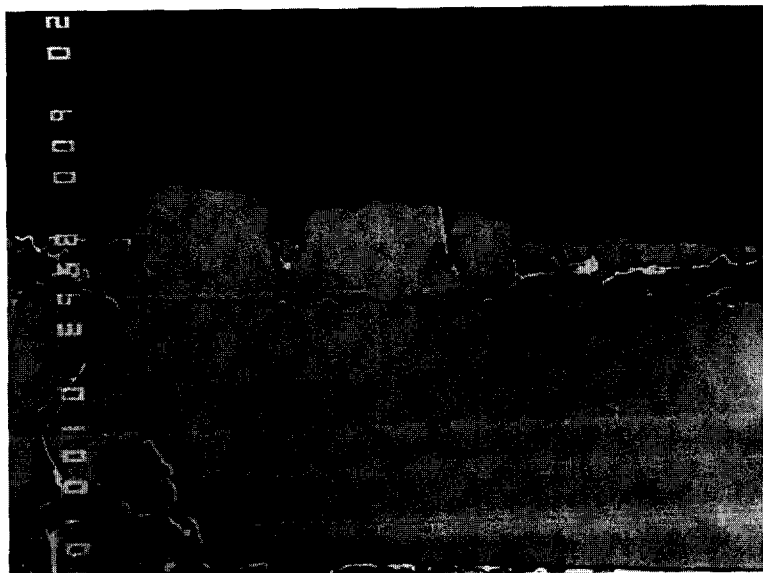


Fig. 4. Back-scattered electron image of a  $\text{Cu}_3\text{P-Si}$  diffusion couple, annealed at  $430^\circ\text{C}$  for 145 h, showing large columns <sup>A</sup> and small crystals <sup>B</sup> of  $\text{Cu}_3\text{Si}$  and the gap <sup>C</sup> between the original Si <sup>D</sup> and  $\text{Cu}_3\text{P}$  <sup>E</sup> discs. Bar indicates  $100\ \mu\text{m}$ .

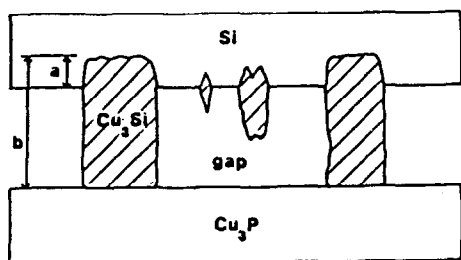


Fig. 5. Schematic representation of a  $\text{Cu}_3\text{P-Si}$  diffusion couple. a: the amount of silicon consumed. b: the amount of  $\text{Cu}_3\text{Si}$  formed.

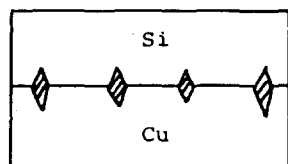


Fig. 6. Schematic representation of a diffusion couple, in which the reaction takes place in localized patches of the contact area.



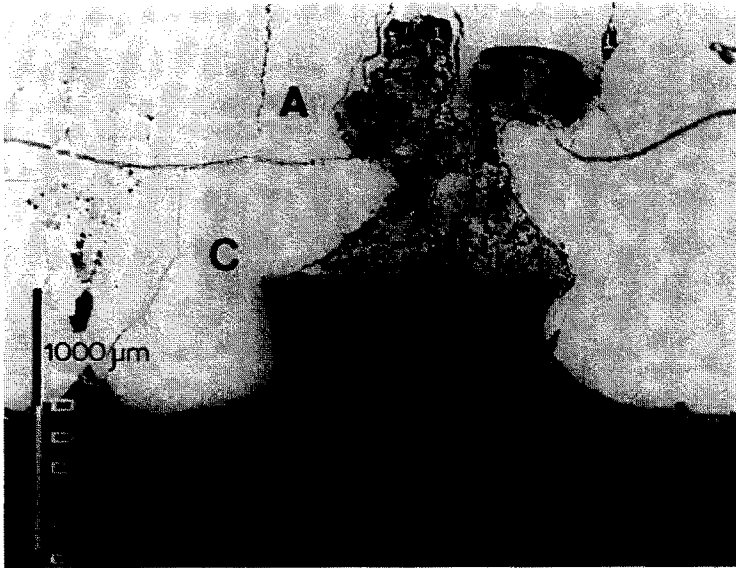
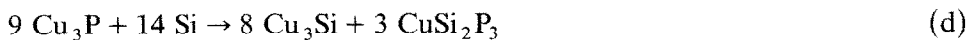


Fig. 7. Secondary electron image of a  $\text{Cu}_3\text{P}^{\text{A}}\text{-Si}^{\text{B}}$  diffusion couple annealed at  $550^\circ\text{C}$  for 73 h, showing the plastically deformed  $\text{Cu}_3\text{Si}$  columns  $^{\text{C}}$ .

At  $550^\circ\text{C}$  anvil-shaped columns are formed (Fig. 7): instead of usual straight-sided ones. We attribute this to plastic deformation, since the reaction temperature is relatively high,  $T \approx 0.73 T_m$  and the 20 kg load is carried by only a few  $\text{mm}^2$  of product surface, to result in local stresses of about 20 MPa.

The product formed is  $\text{Cu}_3\text{Si}$  containing less than 0.02 atom-% phosphorus. There is no concentration gradient in the product layer. The absence of phosphorus in the product layer contradicts the mass balance: if  $\text{Cu}_3\text{P}$  does decompose, and the copper reacts with silicon, a phosphorus-containing compound should also be formed. Judging from the shape of the ternary diagram, we expected this compound to be present at the  $\text{Cu}_3\text{P}\text{-Cu}_3\text{Si}$  interface. Since the reaction was carried out in vacuum, it is possible that if the product is gaseous and would thus have been removed. There are a number of reactions possible:



We know the volumes per formula unit of  $\text{Cu}_3\text{Si}$  [23] =  $0.049 \text{ nm}^3$  and Si [24] =  $0.021 \text{ nm}^3$ . Therefore we can calculate the ratio of the amount of silicon consumed (a in Fig. 5) to the amount of  $\text{Cu}_3\text{Si}$  formed (b in Fig. 5).

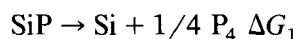
Both for reaction (a) and (b) this ratio is  $21/49 = 0.41$ . Both reactions are similar in respect of the nature of the products formed i.e. the second product, in addition to  $\text{Cu}_3\text{Si}$ , does not contain silicon. If silicon is a constituent of the second product, this ratio becomes 0.71 for reaction (d) and 0.82 for reaction (c).

This ratio can be determined for the diffusion couples if the location of the original silicon surface is known after the reaction. Since the unreacted silicon surface is still mirror-like, we have assumed that the surface we observed in the side view is the original silicon surface. The average ratio determined from the diffusion couples at 400, 430 and 500 °C is 0.43. Only the couples at 550 °C give ratios that deviate from this value, probably because of the deformation of the  $\text{Cu}_3\text{Si}$  columns. From this ratio we conclude that the gaseous product contains no silicon.

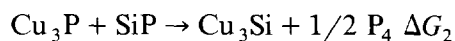
No  $\text{CuP}_2$  could be detected. This leaves as the most probable reaction, the formation of phosphorus vapour, which should be accompanied by weight losses in the diffusion couples. The weight losses determined at 500 °C are consistent with the formation of phosphorus vapour.

The generation of free phosphorus is not in agreement with the diagram presented in Fig. 1. This is because of the differing reaction conditions, especially in regard to the vapour pressure: the alloys were equilibrated in closed capsules, so as to establish an equilibrium phosphorus-pressure. Because the diffusion couples were annealed in a vacuum, any phosphorus vapour formed will have been removed.

$\text{SiP}$  has marginal stability in the vacuum furnace, as can be seen from its Gibbs energy (for data see Barin and Knacke, [25])



$\Delta G_1 = 37987 \text{ J}$  at 700 K and  $32703 \text{ J}$  at 800 K, leading to phosphorus pressures of  $4.6 \times 10^{-7} \text{ Pa}$  at 700 K and  $2.9 \times 10^{-4} \text{ Pa}$  at 800 K. Therefore, in the dynamic vacuum of  $10^{-4} \text{ Pa}$  in the furnace, the decomposition of  $\text{SiP}$  into Si and  $\text{P}_4$  is likely. This is even more so in the presence of  $\text{Cu}_3\text{P}$ , because then the reaction



takes place.

The stability of  $\text{SiP}$  in the presence of  $\text{Cu}_3\text{P}$  can be estimated from the change in the Gibbs free energy  $\Delta G_2$ . Although the Gibbs free energy of  $\text{Cu}_3\text{Si}$  is not known, an estimate can be made on the basis that the structure of  $\text{Cu}_3\text{Si}$  and those of  $\text{Cu}_3\text{P}$  and  $\text{Cu}_3\text{As}$  are analogous. The values for the Gibbs energy of  $\text{Cu}_3\text{P}$  and  $\text{Cu}_3\text{As}$  have been found to be very close to each other [25], thus we took the values for  $\text{Cu}_3\text{P}$  to be those for  $\text{Cu}_3\text{Si}$ . This leads to values of  $+17650 \text{ J}$  at 700 K and  $+7625 \text{ J}$  at 800 K for  $\Delta G_2$ . This corresponds with phosphorus vapour pressures of 230 and  $10^4 \text{ Pa}$ , respectively. From these values we decided that  $\text{SiP}$  would decompose in the

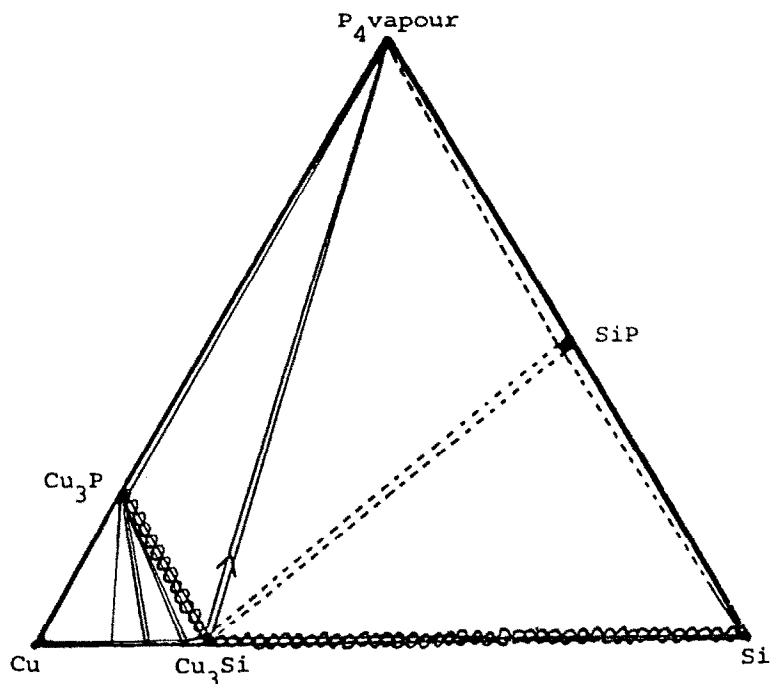


Fig. 8. A ternary Cu-Si-P diagram illustrating the formation of phosphorus vapour in a  $\text{Cu}_3\text{P}$ -Si diffusion couple in vacuo. The arrow denotes the formation of vapour, the dotted lines denote possible instability, the circles denote the diffusion path.

presence of  $\text{Cu}_3\text{P}$  with the formation of phosphorus vapour in a dynamic vacuum system, of which the pressure is 0.1 mPa. A consequence is that the phase relations in a closed system will be different from those in an evacuated system. The phase diagram in a vacuum system is depicted schematically in Fig. 8. The diffusion path in  $\text{Cu}_3\text{P}$ -Si diffusion couples is outlined and shows the formation of  $\text{Cu}_3\text{Si}$  and phosphorus vapour.

### *Reaction kinetics*

The time dependence of the thickness of the  $\text{Cu}_3\text{Si}$  layer in  $\text{Cu}_3\text{P}$ -Si diffusion couples has been determined at 4 different temperatures. The results are listed in Fig. 9. The spread in the data is rather large, since the crystals obtained were thin and scarce. Thus it is difficult to decide whether a particular crystal is really the largest one obtained at a specific time and temperature.

The thicknesses for the couples at 550°C are corrected for the plastic deformation. This was performed by measuring the thickness of  $\text{Cu}_3\text{Si}$  in the silicon slice and multiplying this value by 1/0.41, the ratio of the amount of silicon consumed to the amount of  $\text{Cu}_3\text{Si}$  formed if the columns are straight.

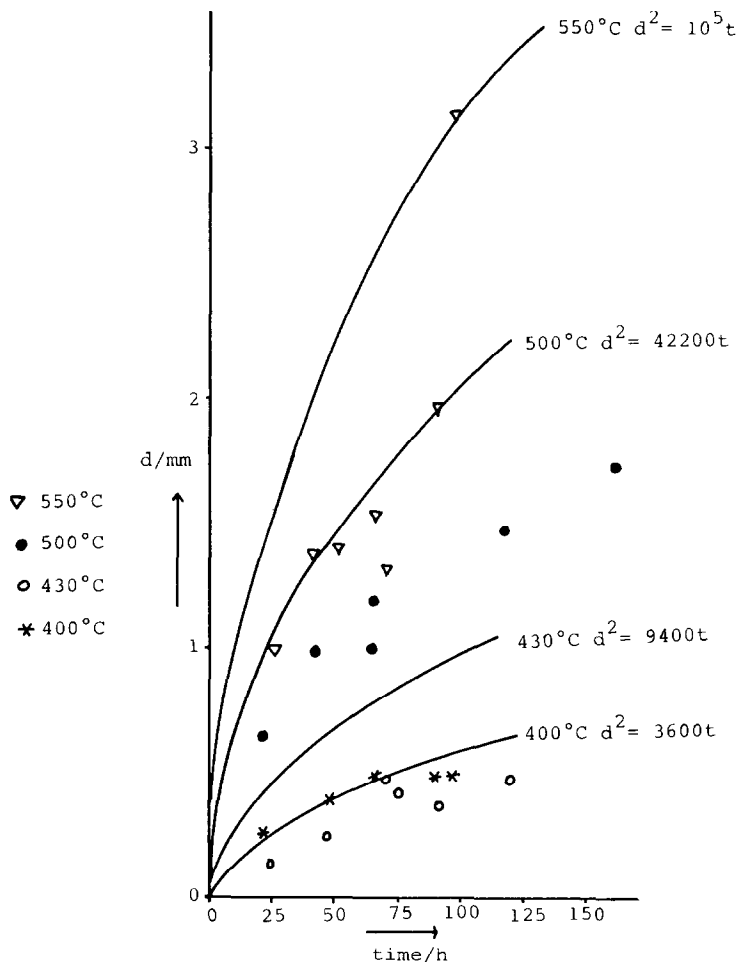


Fig. 9. The thickness of the  $\text{Cu}_3\text{Si}$  layer in  $\text{Cu}_3\text{P-Si}$  diffusion couples, plotted as a function of reaction time for several temperatures. The couples were annealed in a dynamic vacuum system. The parabolic growth curves, derived from the reaction rate constants determined from the Arrhenius plot for pure copper vs. silicon (ref. 1,2), are plotted for comparison.

We have previously reported the rate constants for the reaction between pure copper and silicon [1,2]. From these data we obtained the solid lines in Fig. 9. It is clear that the reaction in  $\text{Cu}_3\text{P-Si}$  couples is never faster than in couples between pure copper and silicon.

#### *Morphology of the reaction product*

The formation of gaps in the reaction layer is surprising, since this is certainly not usual. We see that the overall growth is retarded in such cases. Furthermore the shape of the  $\text{Cu}_3\text{Si-Cu}_3\text{P}$  interface shows that the whole  $\text{Cu}_3\text{P}$  platelet is involved in the reaction instead of just the contact area. If a

closed reaction layer is formed, the diffusion couple must decrease in height, since phosphorus vapour is lost at the  $\text{Cu}_3\text{Si}$ - $\text{Cu}_3\text{P}$  interface. The layer thickness is determined by the diffusion of copper through the silicide layer as long as there is good contact between  $\text{Cu}_3\text{Si}$  and  $\text{Cu}_3\text{P}$ . When this contact is lost,  $\text{Cu}_3\text{P}$  is removed to allow the reaction to continue at another place, leaving a  $\text{Cu}_3\text{Si}$  crystal that is only in contact with silicon. The gap that remains is the space originally occupied by  $\text{Cu}_3\text{P}$ . The overall reaction rate is slower than in those couples in which a closed layer is formed.

#### THE SOLID STATE REACTION BETWEEN $\text{Cu}_3\text{P}$ AND Si IN A CLOSED SYSTEM

One diffusion couple was prepared in a stainless steel clamp, and annealed in an evacuated silica capsule at  $500^\circ\text{C}$ . After 65 h the capsule was allowed to cool down slowly and was carefully opened. The specimen became warm on contact with air and the characteristic smell of  $\text{PH}_3$  pervaded. Optical microscopy showed that the outside of the reaction layer was covered with small, white crystals, definitely different from  $\text{Cu}_3\text{Si}$ . Metallographic preparation of the specimen turned out to be difficult, since the second phase formed (Fig. 10) either had been crushed by the pressure arising during the heat treatment or had decomposed in contact with air and water.

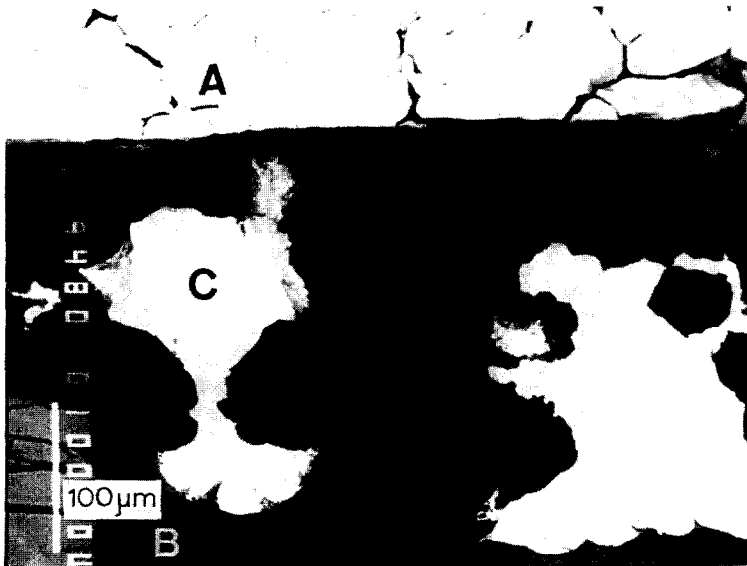


Fig. 10. Secondary electron image of a  $\text{Cu}_3\text{P}^{\text{A}}$ - $\text{Si}^{\text{B}}$  diffusion couple annealed in a sealed vessel at  $500^\circ\text{C}$  for 65 h. The bright reaction product is  $\text{Cu}_3\text{Si}^{\text{C}}$ , the crumbly second phase is probably  $\text{SiP}^{\text{D}}$ .

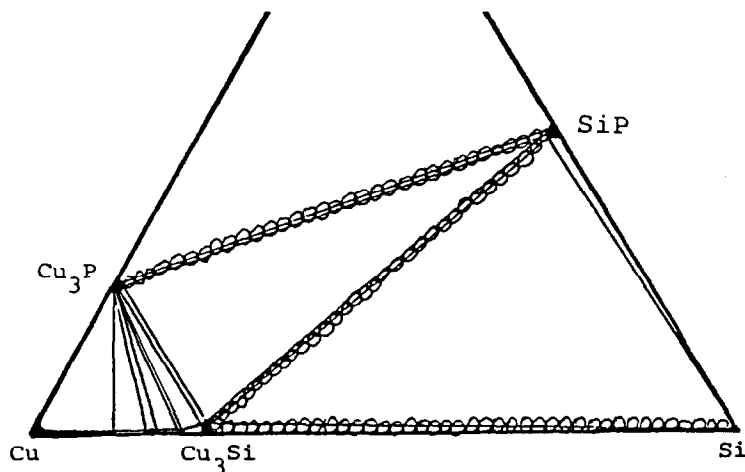


Fig. 11. Ternary phase diagram for the Cu-Si-P system in sealed, evacuated vessels, together with the diffusion path for  $\text{Cu}_3\text{P}$ -Si diffusion couples.

The EPMA shows that one product,  $\text{Cu}_3\text{Si}$ , is in contact with silicon. A second phase was formed, however, no quantitative analyses could be performed. Qualitatively, silicon and oxygen, but no copper or phosphorus were detected. This suggests that this second phase originally consisted of  $\text{SiP}$ , which decomposes into  $\text{SiO}_2$ , and  $\text{PH}_3$  [16] identified from its characteristic smell. This reaction could account for the fact that the specimen became warm and was impossible to polish.

According to the phase diagram given in Fig. 1 we expected the formation of  $\text{CuSi}_2\text{P}_3$  at the  $\text{Cu}_3\text{P}$ - $\text{Cu}_3\text{Si}$  interface. If this were the case, however, and this compound decomposes, some copper should be left amongst the products. Since no copper was detected, no  $\text{CuSi}_2\text{P}_3$  was formed. We must conclude that Fig. 1 is irrelevant to this experiment, because of the difference in phosphorus pressures and that Fig. 11 is more appropriate for the circumstances used in the experiment.

The thickness of the reaction layer is smaller than in case of a vacuum-annealed couple indicating that the diffusion of copper through  $\text{SiP}$  might be rate determining.

#### THE REACTION BETWEEN $\text{Cu}_3\text{P}$ AND GERMANIUM IN A VACUUM SYSTEM

Previously [3], we have seen that there is no difference between the reaction of copper or  $\text{Cu}_3\text{P}$  with germanium, which is in contrast to their reaction with silicon.

From the ternary diagram (Fig. 2) we can see that an equilibrium exists between  $\text{Cu}_3\text{P}$  and germanium, so it is not immediately clear how the reaction takes place in the  $\text{Cu}_3\text{P}$ -Ge diffusion couple. Furthermore the absence of a phosphorus-containing reaction product is incompatible with

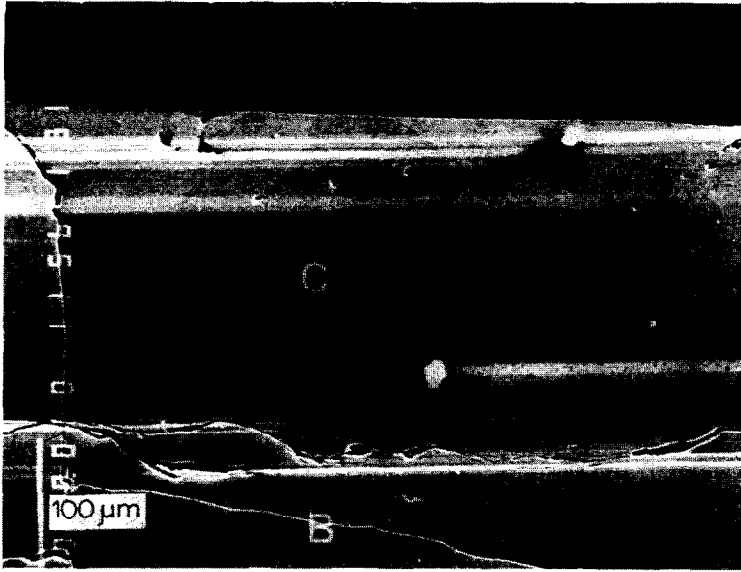


Fig. 12. Secondary electron image of a  $\text{Cu}_3\text{P}^{\text{A}}-\text{Ge}^{\text{B}}$  diffusion couple, annealed at  $500^\circ\text{C}$ , 162 h, showing large crystals of  $\text{Cu}_3\text{Ge}^{\text{C}}$ . Note the absence of  $\text{Cu}_5\text{Ge}$  and the primary solid solution.

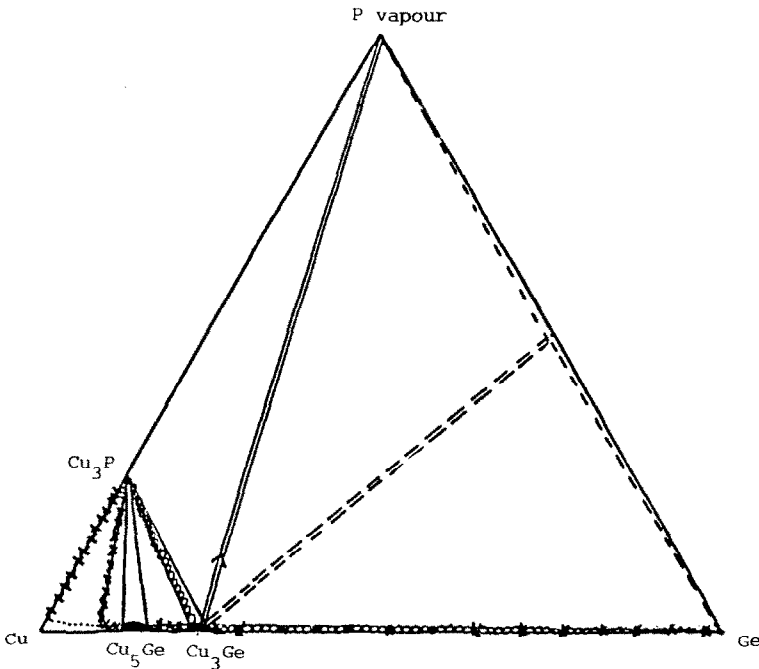


Fig. 13. Part of the ternary  $\text{Cu}-\text{Ge}-\text{P}$  diagram proposed for dynamic vacuum conditions. The diffusion paths in a  $\text{Cu}_3\text{P}-\text{Ge}$  couple ( $\text{O}$ ) and a couple between phosphorus containing copper and germanium ( $\times$ ) [1,3] are denoted. The arrow denotes the evolution of phosphorus vapour.  $\text{GeP}$  is considered to be unstable.

the mass balance. In contrast to the copper–germanium couples, neither the solid solution nor  $\text{Cu}_3\text{Ge}$  was formed (Fig. 12) in the  $\text{Cu}_3\text{P}$ –Ge couples. So again we must conclude that the phase diagram determined for ternary alloys, equilibrated in evacuated vessels, does not apply to diffusion couples annealed in vacuo. As there are no thermodynamic data on GeP or  $\text{Cu}_3\text{Ge}$ , we can not calculate whether GeP is stable towards  $\text{Cu}_3\text{P}$  in a vacuum system. The fact that GeP melts incongruently at  $725^\circ\text{C}$  shows that this compound is not particularly stable [26]. Therefore we propose a phase diagram (Fig. 13) for the vacuum system, analogous to the Cu–Si–P diagram: in the reaction between  $\text{Cu}_3\text{P}$  and Ge,  $\text{Cu}_3\text{Ge}$  and phosphorus vapour are formed.

From the observed reaction rate it follows that the formation of phosphorus does not inhibit the reaction. Furthermore, the morphology of the reaction layer suggests that the contact at the  $\text{Cu}_3\text{P}$ – $\text{Cu}_3\text{Ge}$  interface remains good. This difference from the  $\text{Cu}_3\text{P}$ –Si reaction might well be caused by a difference in hardness, since  $\text{Cu}_3\text{Si}$  is nearly three times as hard as  $\text{Cu}_3\text{Ge}$  [27]. Therefore  $\text{Cu}_3\text{Ge}$  undergoes plastic deformation more readily and can thus conform to the irregularities of the contact interface.

#### DISCUSSION AND CONCLUSIONS

The main problem encountered in this study of the reactions of  $\text{Cu}_3\text{P}$  with silicon or germanium, is the phosphorus pressure. We are sure that the phosphorus pressure during the annealing treatment of the alloys is different from that in the experiments on diffusion couples.

In the Cu–Si–P system  $\text{Cu}_3\text{Si}$  is formed in all cases, but phosphorus is found in various compounds viz.  $\text{CuSi}_2\text{P}_3$  (and possibly a second ternary compound) is formed in the alloys, in diffusion couples in a vacuum system phosphorus vapour is generated, whereas during annealing of a diffusion couple in a closed capsule, SiP seems to be formed.

$\text{Cu}_3\text{Ge}$  is formed in the Cu–Ge–P system. In the alloys, phosphorus is found in  $\text{Cu}_3\text{P}$ , which is in equilibrium with germanium, whereas in a vacuum system  $\text{Cu}_3\text{P}$  reacts with germanium to give phosphorus vapour and  $\text{Cu}_3\text{Ge}$ .

The diffusion couples between  $\text{Cu}_3\text{P}$  and Si show a remarkable morphology, that of isolated  $\text{Cu}_3\text{Si}$  columns, separated by gaps, between the original slices. The columns form when  $\text{Cu}_3\text{P}$  diffuses away once reaction has ceased. This morphology is accompanied by a generally retarded growth rate if we compare it with the reaction between copper and silicon.

This unique morphology is not found in  $\text{Cu}_3\text{P}$ –Ge diffusion couples, in which the reaction rates are the same as those of the copper–germanium diffusion couples. This difference is best attributed to the plastic deformation of  $\text{Cu}_3\text{Ge}$ , so that even if a small gap forms,  $\text{Cu}_3\text{Ge}$  is still pressed onto the  $\text{Cu}_3\text{P}$  disc and the reaction continues.



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