

The solid state diffusion reaction of copper with germanium : a comparison between silicon and germanium

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THE SOLID STATE DIFFUSION REACTION OF COPPER WITH GERMANIUM; A COMPARISON BETWEEN SILICON AND GERMANIUM

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ABSTRACT

The solid state reaction between copper and germanium has been studied in diffusion couples in the range 400 to 575 °C. The main product is coarse-grained Cu_3Ge , but Cu_5Ge and the (Cu, Ge) solid solution are also formed, albeit in thin layers. The reaction rate is determined by bulk diffusion of copper through the germanide layer, with an activation energy of 104 kJ/mol. Above 570 °C a sudden acceleration occurs. At 500 °C the interdiffusion coefficient in the solid solution is $6 \times 10^{-12} \text{ cm}^2/\text{s}$, $\bar{D}(\text{Cu}_5\text{Ge}) = 4 \times 10^{-11} \text{ cm}^2/\text{s}$ and \bar{D} in Cu_3Ge is raised from $1 \times 10^{-10} \text{ cm}^2/\text{s}$ at 22 atom-% Ge to $1 \times 10^{-8} \text{ cm}^2/\text{s}$ at 25 atom-% Ge. Contrary to the copper–silicon reaction, no reaction barrier has been observed, and so the presence of phosphorus in copper does not influence the reaction between copper and germanium.

INTRODUCTION

We reported recently [1] that the solid state reaction between copper and silicon is strongly influenced by the presence of an oxidation layer on silicon and by the presence of a trace of phosphorus in the copper. We wondered whether such a large effect by an impurity could occur in other similar systems. An obvious example would be the reaction between copper and germanium. Silicon and germanium are very much alike: they have the same crystal structure and show similar chemical behaviour. Furthermore the phase diagrams of the copper–silicon and the copper–germanium systems are much alike.

To our knowledge the solid state reaction between copper and germanium has not been described previously. Thus we have studied the solid state reaction between copper and germanium in diffusion couples between 400 and 575 °C. Special attention was paid to the occurrence of incubation times

and the influence of phosphorus on reaction kinetics. The composition of the products was determined. The diffusion coefficients in the various products were determined from the concentration profile. The results on the copper–germanium reaction are compared with those of the copper–silicon reaction.

EXPERIMENTAL

Alloys were prepared by arc melting germanium (Ventron, m6N purity) with copper (MRC, Marz quality), and were left to equilibrate for 1 month in evacuated silica capsules at 500 °C. Diffusion couples were prepared with polished slices and were heated in a vacuum furnace (see [2] for details). Cu₃P was prepared by arc melting copper with lumps of Cu₃P (Alpha Products) to give a total phosphorus content of 1 atom-%. After heating the diffusion couples were sliced perpendicular to the reaction layer.

Both alloys and diffusion couples were prepared metallographically and studied by optical (Reichert MeF2, equipped with a calibrated eyepiece) and electron (JEOL 733 Superprobe) microscopy. Quantitative analyses were carried out by use of electron probe micro analysis (EPMA). The pure element was used as calibration standard, as were a beam current of 10 nA, an accelerating voltage of 20 kV, and a BAS correction program [3].

THE COPPER–GERMANIUM PHASE DIAGRAM

Figure 1 shows the copper–germanium phase diagram according to Hansen [4] and Hultgren [5]. The solubility of germanium in copper is large: 9.5 atom-% at 300 °C, with a maximum of 11.8 atom-% at 823 °C. The solubility of copper in germanium is negligible; the maximum copper content is less than 3×10^{-4} atom-% at 875 °C [4].

In the low-temperature range two compounds exist: the ζ phase or Cu₅Ge and the ϵ phase or Cu₃Ge. There is some confusion as to the composition of these phases: Hansen [4] states that the ζ phase ranges from 11.4 to 18.7 atom-% Ge, but Schubert [6] places the limits at 11.9 and 19.4 atom-% Ge. The ζ phase has a hexagonal close-packed (h.c.p.) structure (A3 type), and is regarded as a 3 : 2 electron compound, based on the composition Cu₅Ge, with 16.7 atom-% Ge [7]. The ϵ phases consist of a group of 3 compounds. The ϵ phase which is evident at low temperature has an orthorhombically distorted A3 type structure with a 0.2645, b 0.4553, c 0.4202 nm at 25 atom-% Ge [6], Hansen [4] does not give homogeneity boundaries, but those at 24.25 and 25.5 atom-% Ge are suggested. This is supported by Hultgren [5]. Above 570 °C the ϵ_1 phase takes over, the structure becomes h.c.p. with a 0.420 nm, $c/a = 1.20$. The ϵ phase is cubic with about 27.5 atom-% of Ge [4]. Reynolds and Hume-Rothery [8], how-

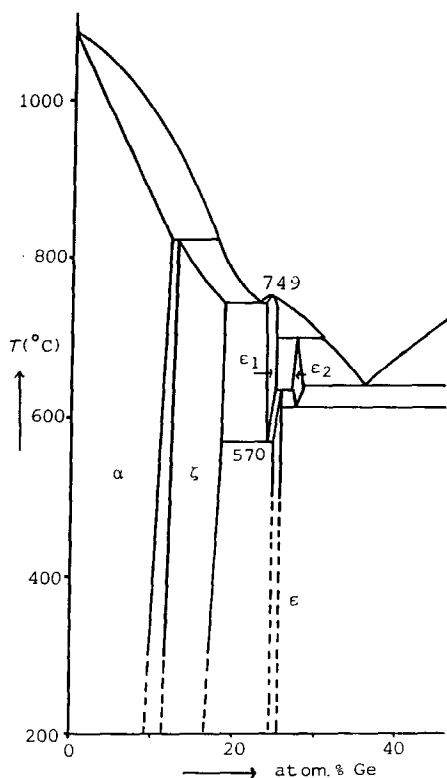


Fig. 1. The copper-germanium phase diagram [4].

ever, give a different interpretation of this region as is shown in Fig. 2. The homogeneity region of the ϵ phase is much wider, and the transition to ϵ_1 occurs at 550°C.

The Cu-Si and Cu-Ge phase diagrams show a close resemblance [8]. In both systems the complicated sequence of solid phases is confined to the first 27 atom-% of the solute. A maximum in the solidus-liquidus curve is found at approximately 24 atom-%. The extent of the primary solid solutions is of the same order. The range of compositions from 11 to 19 atom-%, in the Cu-Ge system has only one h.c.p. ζ phase, whereas in the Cu-Si system there are several phases, some having h.c.p. structure. Both Cu_5Ge and Cu_5Si are considered to be 3:2 electron compounds. The copper-silicon η phases have composition ranges similar to those of the copper-germanium ϵ and ϵ_1 phases. In each there are high and low temperature modifications. The ϵ_2 compound has no counterpart in the copper-silicon system, and the reverse applies to $\text{Cu}_{15}\text{Si}_4$.

We determined, by EPMA, the concentrations at the phase boundaries at 500°C. The maximum solubility of germanium in copper is 10.5 atom-% Ge. The low germanium limit of Cu_5Ge was not detected in Cu-Ge alloys, because the gap between this phase and the primary solution is so small that

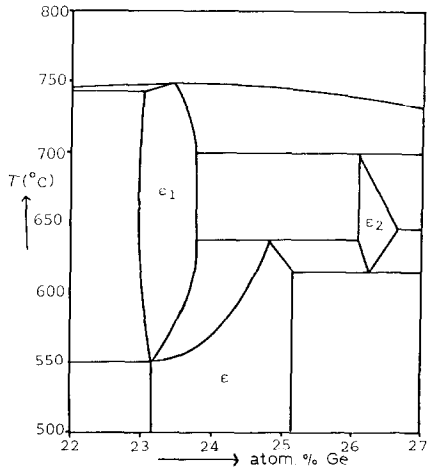


Fig. 2. Detail of the copper-germanium phase diagram [8].

no two phased alloys could be prepared in this region. The germanium-rich side of Cu_5Ge in Cu-Ge alloys contains 17.2 atom-% Ge, which is less than has been reported in the literature. The boundaries for Cu_3Ge in the alloys are 21.7 and 24.2 atom-% Ge, again rather low compared with published values. In diffusion couples the composition of Cu_5Ge is in the range 11.6 to 17.8 atom-% Ge. The maximum germanium concentration in Cu_3Ge is 24.8 atom-% Ge. These values are consistent with those found for the alloys (within experimental error). The homogeneity range for Cu_5Ge seems to be smaller than that found in the literature, whereas that for Cu_3Ge is wider.

DIFFUSION REACTION BETWEEN COPPER AND GERMANIUM

Diffusion experiments were carried out in a vacuum furnace at 400 to 575°C. Below 570°C the reaction between copper and germanium is considerably slower than that between copper and silicon, but permits better slices to be prepared [2]. High mechanical stresses are induced in the diffusion couples, sometimes resulting in spectacular flea-like jumps of the germanium platelet away from the couple after the removal from the furnace.

The influence of the applied compressive stress has been tested explicitly and found to be non-existent; between 2 and 9.6 MPa the reaction layer thickness is independent of the stress. The influence of the phosphorus concentration in copper was also tested and once more no significant influence was found. Copper containing < 1 ppm (Cu MRC Marz), 1 atom-% (Cu₁P), and 25 atom-% (Cu₃P) phosphorus all react at the same rate within experimental error. As can be seen in Figs. 3 and 4 straight lined

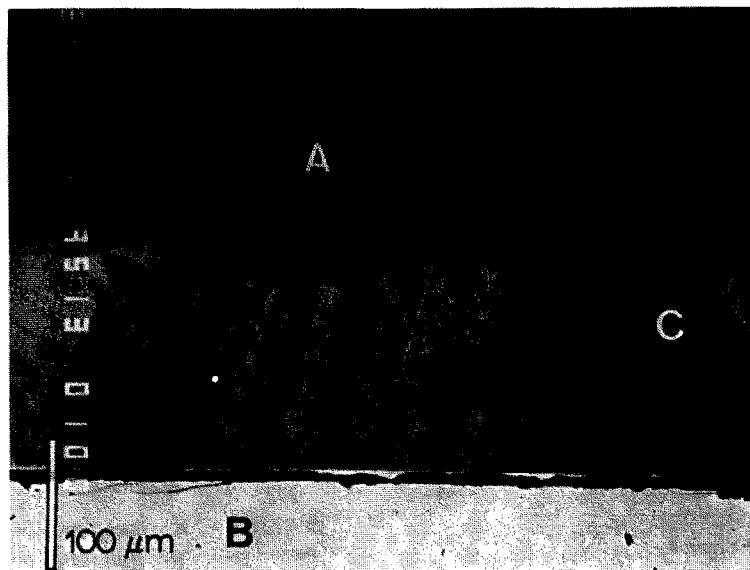


Fig. 3. Back scattered electron image of a diffusion couple between pure copper (A) and germanium (B), showing straight-lined interfaces and coarse Cu_3Ge (C) crystals; annealed at 500°C for 48 h.

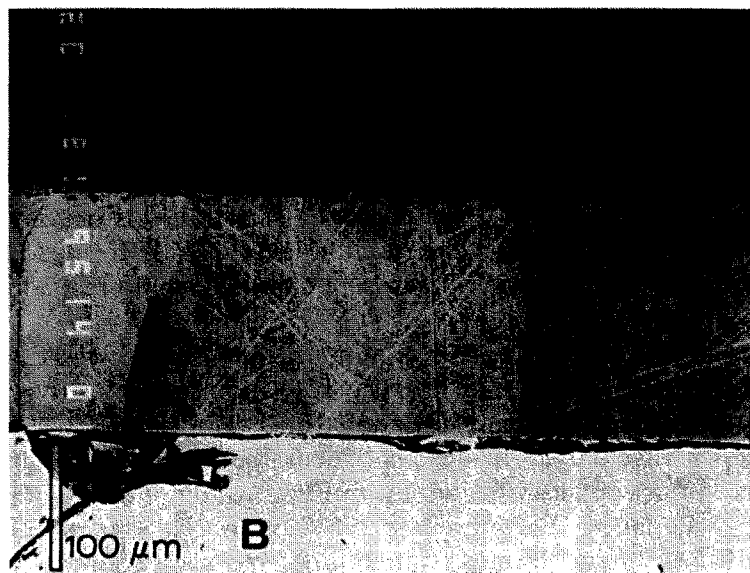


Fig. 4. Back scattered electron image of a diffusion couple between Cu_3P (A) and germanium (B) showing large Cu_3Ge (C) crystals and Cu_3P (D) formed at the copper-germanides interface; annealed at 500°C , 48 h.

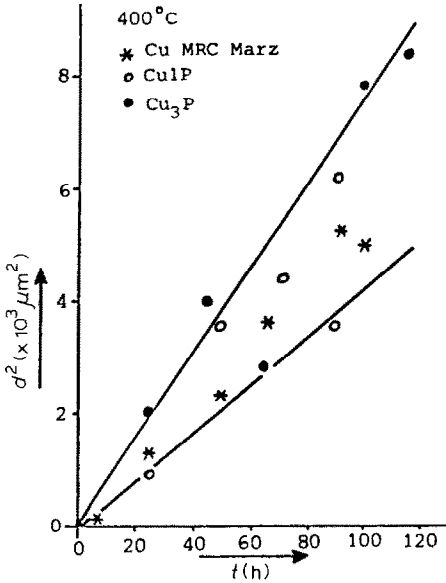


Fig. 5. The thickness of the reaction layer in copper-germanium diffusion couples as a function of reaction time at 400°C.

reaction layers are formed. In all cases the main product Cu_3Ge is coarse-grained. Cu_5Ge was also formed, in thin layers. In diffusion couples with Cu1P , crystals of Cu_3P are present at the copper-germanide interface (Fig. 4). Copper is the only diffusing element in the copper-germanium system.

The dependence of the reaction layer thickness in copper-germanium diffusion couples on time is plotted in Fig. 5. It is clear that significant experimental error exists. It is this experimental error which forced us to average the results for all types of copper, since we could not distinguish between them. Both at 400 and 500°C the parabolic growth law is obeyed, so that the diffusion of copper through the reaction layer already formed is the rate limiting process. No incubation times were observed, so no reaction barrier exists.

The dependence of the reaction rate constant on temperature was determined between 400 and 550°C (Fig. 6). The activation energy derived from this plot is 104 kJ/mol, standard deviation 12 kJ/mol (least-squares method). Since copper is the only diffusing component, the activation energy is attributable only to this copper diffusion. From Figs. 3 and 4 it is obvious that Cu_3Ge is coarse-grained. Therefore the diffusion is likely to occur through the bulk of the crystals, since there are not enough grain boundaries to supply the reaction interface with copper atoms. The observed value for the activation energy is rather low for bulk diffusion, and it is then likely that the crystal structure of Cu_3Ge offers routes for easy diffusion.

At 570°C [4] or 550°C [8] a change in structure occurs in Cu_3Ge . This change is manifested by sudden enhancement of the reaction rate above

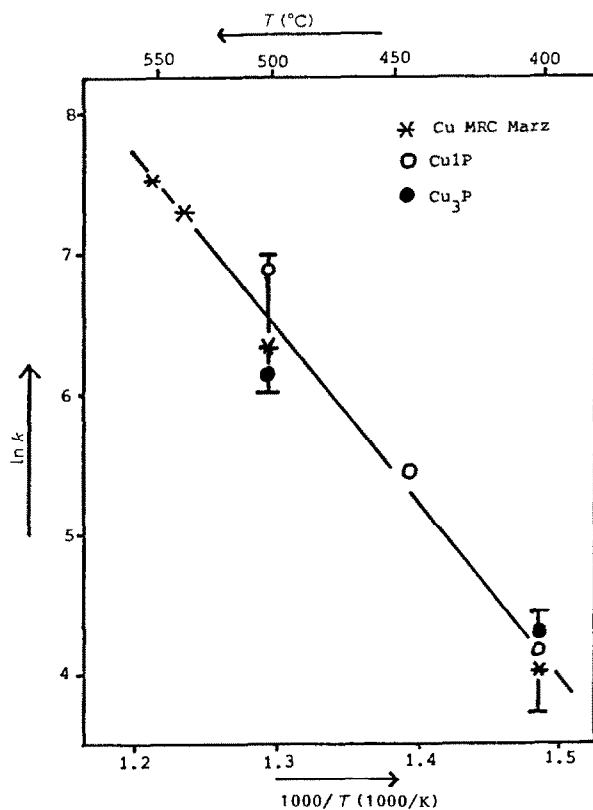


Fig. 6. Arrhenius plot of the reaction rate constant for copper-germanium diffusion couples.

570 °C. At 575 °C the reaction rate constant is $1.3 \times 10^6 \mu\text{m}^2/\text{h}$, compared with $2 \times 10^3 \mu\text{m}^2/\text{h}$ at 550 °C. The reaction rate is too fast to be measured because of the effects of the heating and cooling procedures. The different crystal structure of ϵ_1 leads to a different activation energy and a different pre-exponential factor for the diffusion of copper.

DETERMINATION OF THE DIFFUSION COEFFICIENTS

In Cu/Ge diffusion couples all the expected compounds are formed, viz., the (Cu, Ge) primary solid solution, Cu_3Ge , Cu_3Ge and all layers show a concentration gradient. This gives us the opportunity to determine the interdiffusion coefficients according to the formula derived by Sauer and Freise [9]:

$$\tilde{D}(Y)^* = \frac{V_m(Y)^*}{2t} \left(\frac{dx^*}{dY} \right) \left[(1 - Y^*) \int_{-\infty}^{x^*} \frac{Y}{V_m(Y)} dx + Y^* \int_{x^*}^{+\infty} \frac{(1 - Y)}{V_m(Y)} dx \right]$$

where $Y = \frac{N_i - N_i^{-\infty}}{N_i^{+\infty} - N_i^{-\infty}}$

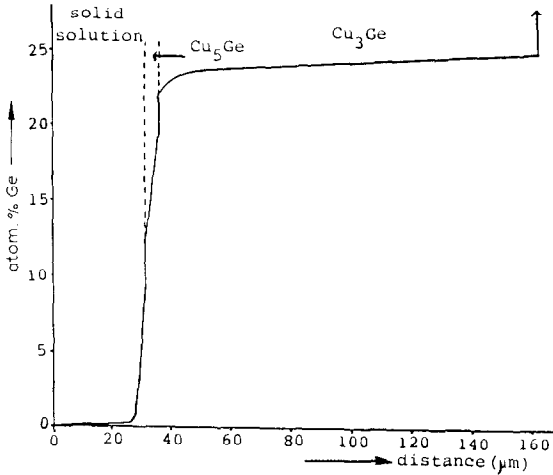


Fig. 7. Concentration profile for a copper-germanium diffusion couple annealed at 500 °C for 30 h, as determined with EPMA.

and N_i denotes the mole fraction of component i . V_m is the molar volume of the phase at position x , and x^* is the position where the diffusion coefficient is determined. The molar volumes of Cu_3Ge and Cu_5Ge were calculated from data taken from ref. 10. A unit cell of Cu_3Ge , containing 2 molecules of Cu_3Ge has a volume of 0.10116 nm^3 , the molar volume is $7.61 \text{ cm}^3/\text{mol Cu}_{0.75}\text{Ge}_{0.25}$. For Cu_5Ge this value is $7.55 \text{ cm}^3/\text{mol Cu}_{0.83}\text{Ge}_{0.17}$. For pure copper and germanium these values are 7.11 and $13.63 \text{ cm}^3/\text{mol}$ respectively, [11]. This results in a contraction of 13% during the formation of Cu_3Ge from the elements.

The concentration profile of a copper-germanium diffusion couple is in Fig. 7. The couple was annealed for 30 h at 500 °C, subsequent graphical integration yielded the diffusion coefficients. The results are summarized in Fig. 8. Two sets of values are given, both deduced from the same profile, showing the experimental error in this type of determination. This arises mainly from uncertainty in the determination of the concentration gradient which is rather steep at the phase boundaries. The average diffusion coefficient in the solid solution is $6 \times 10^{-12} \text{ cm}^2/\text{s}$, while in the Cu_5Ge phase the diffusion coefficient is $4 \times 10^{-11} \text{ cm}^2/\text{s}$. In Cu_3Ge the interdiffusion coefficient increases from about $1 \times 10^{-10} \text{ cm}^2/\text{s}$ at 22 atom-% of Ge to about $1 \times 10^{-8} \text{ cm}^2/\text{s}$ at 25 atom-% of Ge. In the diffusion couples this high diffusion coefficient leads to a thick Cu_3Ge layer containing about 24–25 atom-% Ge, with a small concentration gradient.

We can compare these values with those published on the catalytic activity of copper-germanium alloys in the formation of germanes [12], in which the diffusion coefficient can be determined from the amount of germanes formed. Although Chong and Skaates have assumed that germanium does, in fact, diffuse, in contrast to our findings, the average

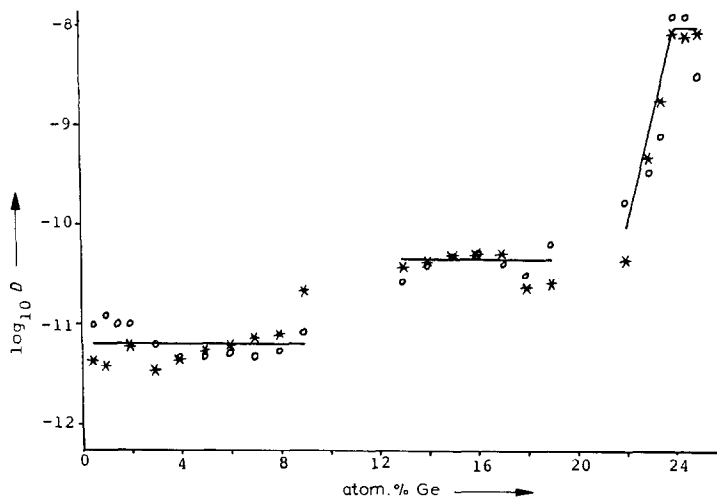


Fig. 8. Calculated diffusion coefficients as a function of the concentration in a copper-germanium diffusion couple at 500 °C; \circ and $*$ denote two different sets of values derived from the profile of Fig. 7.

interdiffusion coefficient \tilde{D} determined by them gives a measure of the total transport in the alloys. At 700 K they find in Cu_5Ge $\tilde{D} = 5 \times 10^{-11} \text{ cm}^2/\text{s}$, in Cu_3Ge $\tilde{D} = 5 \times 10^{-10} \text{ cm}^2/\text{s}$. From these values, together with the activation energy, determined by us, (104 kJ/mol) we estimate the value of $\tilde{D}(\text{Cu}_5\text{Ge})$ to be $3 \times 10^{-10} \text{ cm}^2/\text{s}$ and that of $\tilde{D}(\text{Cu}_3\text{Ge})$ to be $3 \times 10^{-9} \text{ cm}^2/\text{s}$ both at 773 K).

COMPARISON OF GERMANIUM WITH SILICON

If we compare the results obtained for the solid state reaction between copper and germanium with those for the reaction between copper and silicon [1], there are three aspects in which differences occur.

(a) In copper-silicon diffusion couples only Cu_3Si is observed, whereas in copper-germanium couples all the compounds expected are present.

(b) In copper-silicon diffusion couples there are two activation energies, 175 and about 100 kJ/mol, related with bulk and grain boundary diffusion of copper through Cu_3Si . In copper-germanium diffusion couples only one activation energy was observed that of 104 kJ/mol, related with bulk diffusion of copper through Cu_3Ge .

(c) A reaction barrier is present in the copper-silicon diffusion couples which results in an incubation time at low temperature. Connected with this, the reaction is influenced by the presence of phosphorus in the copper and by the applied compressive stress. These phenomena are absent in copper-germanium diffusion couples.

TABLE 1

Diffusion coefficients in the Cu–Si and Cu–Ge systems at 500 °C

Compound	\tilde{D} (cm ² /s)
Cu ₃ Si	$> 2 \times 10^{-5}$ *
Cu ₁₅ Si ₄	$> 1 \times 10^{-8}$ *
Cu ₃ Ge	10^{-10} – 10^{-8} **
Cu ₅ Ge	4×10^{-11} **

* Ref. 1.

** This work.

The thickness of each layer in diffusion couples depends on the respective diffusion coefficients in the system. The diffusion coefficients as derived for the copper–silicon system [1] and the copper–germanium system are listed in Table 1.

From these data it can be seen that the Cu₁₅Si₄ layer will be extremely thin compared with that of Cu₃Si, since the diffusion coefficient is about a 1000 times as small. The same is true for Cu₅Ge, compared with Cu₃Ge, but to a lesser extent. Thus in a copper–germanium diffusion couple Cu₅Ge is indeed observed, albeit in thin layers.

Furthermore we can see from these data that the reaction in copper–germanium couples is much slower than in the copper–silicon couples, since the diffusion coefficient for copper in Cu₃Ge is about a 1000 times smaller than in Cu₃Si.

If the data for the interdiffusion coefficients are combined with those for the activation energies, we can calculate the lower limit for the frequency factor D_0 according to:

$$\tilde{D} = D_0 \exp(-Q/RT)$$

Thus for Cu₃Ge, D_0 is 0.06 cm²/s and for Cu₃Si, D_0 is $> 1.5 \times 10^7$ cm²/s. The value obtained for Cu₃Ge is normal for bulk diffusion [13], but that for Cu₃Si is very high.

To compare the activation energies for the diffusion of copper into Cu₃Si and Cu₃Ge, the fact that the melting point T_m of Cu₃Si (1132 K) is 100 K higher than that of Cu₃Ge (1022 K) must be taken into account. We can allow for this difference by plotting the results as a function of the relative temperature T/T_m in the same way as Tiwari did when he compared the self-diffusion coefficients in cubic metals [14]. Figure 9 depicts the Arrhenius plot for the reaction rate constants as a function of the reciprocal relative temperature, the slope of this plot gives Q/T_m .

Several remarks can be made. The relative temperature ranges, in which Cu₃Si and Cu₃Ge form coarse-grained layers seem to be similar. The activation energies for bulk diffusion of copper through Cu₃Si and Cu₃Ge are unequal (175 and 104 kJ/mol respectively) [2]. The values for Q/T_m are

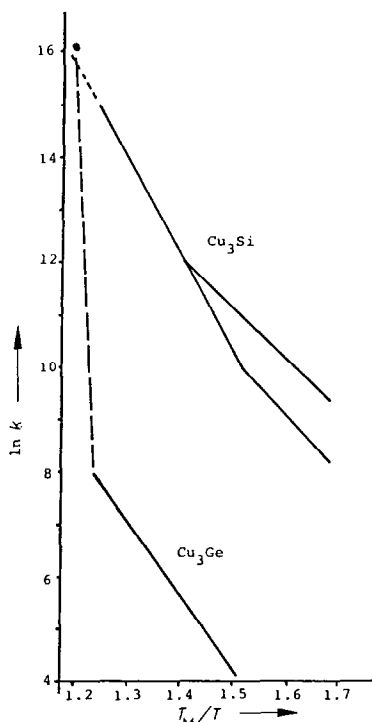


Fig. 9. Arrhenius plot of the reaction rate constants for Cu-Si and Cu-Ge diffusion couples as a function of the relative temperature. T_M is the melting point.

also unequal, but to a lesser extent, viz. 150 J/mol K and 100 J/mol K for Cu_3Si and Cu_3Ge , respectively. For comparison Tiwari found the self-diffusivity in cubic metals to be 145 J/mol K [14].

These data suggest that bulk diffusion does occur, but in addition there are rapid diffusion routes. Although the structures of Cu_3Ge and Cu_3Si are closely related [8], in Cu_3Si the frequency factor is abnormal, whereas in Cu_3Ge the activation energy is abnormal. These differences probably stem from detailed differences in structure, while the difference in size between silicon and germanium may be the most important.

The reaction rate for the Cu/Ge reaction at 575°C fits the extrapolation of the Cu_3Si bulk diffusion at higher relative temperatures. This implies that the diffusivity in the ϵ_1 phase is comparable with that in Cu_3Si . Furthermore we expected a change in slope in the Cu_3Ge curve, similar to that in the Cu_3Si curve, to occur at low temperatures, above $T_m/T = 1.5$. In order to determine this transition experiments ought to have been conducted in the temperature range between 200 and 400°C. The rate of reaction however is too small, so that experiments are virtually impossible.

The reaction of silicon with copper is characterized by interfacial problems [1]. Silicon is covered with a silicon dioxide layer, which is nearly

impenetrable by copper. If the conditions are such that this layer is removed (high compressive stresses, phosphorus impurity in the copper, or after long incubation times) then the reaction proceeds, and the morphology of the reaction layer is strongly influenced by nucleation phenomena. The reaction of copper with germanium is smooth and simple; there is no incubation time, no influence by compressive stress, no influence by traces of phosphorus in the copper. The reactions of silicon are determined by the presence of an oxidation layer. Evidently the stability of the oxidation layer on germanium is much less.

Some evidence for this statement has been found in the literature, viz. the oxidation of copper–silicon and that of copper–germanium alloys has been studied. When Cu_3Si is oxidized, SiO_2 is formed and the layer underneath is enriched in copper [15]. If, however, Cu_3Ge is oxidized, GeO and Cu_2O are formed at 400 and 500 K [16]. Only at 600 K is this surface converted into $\text{Cu} + \text{GeO}_2$. This suggests that SiO_2 is more stable than GeO_2 with respect to copper. No reaction barrier exists as the results of the diffusion couples clearly show. Since there is no reaction barrier, the reaction between copper and germanium is not influenced by compressive stress or the presence of phosphorus.

CONCLUSIONS

In copper–germanium diffusion couples all the products expected are formed. Cu_3Ge is the main product, but thin layers of Cu_5Ge and the primary (Cu, Ge) solid solution are also observed. Copper is the only diffusing component in this system. The reaction proceeds in a diffusion-limited process, having an activation energy of 104 kJ/mol between 400 and 550 °C. On the basis of the morphology of the product layer, copper diffuses by bulk diffusion. Because of the relative instability of the oxidation layer on germanium the reaction with copper is not hindered by a reaction barrier.

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