

The influence of phosphorus on the solid state reaction between copper and silicon

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THE INFLUENCE OF PHOSPHORUS ON THE SOLID STATE REACTION BETWEEN COPPER AND SILICON

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ABSTRACT

The solid state reaction between copper and silicon has been studied in the temperature range 350 to 650 °C. The rate-limiting step is the diffusion of copper through the main product Cu_3Si . When pure copper is used, a bulk diffusion mechanism is operative above 470 °C, and the activation energy is 175 kJ/mol. Below 470 °C incubation times occur. The reaction proceeds by grain-boundary diffusion, with an activation energy of 110 kJ/mol. When phosphorus-doped copper is used, bulk diffusion of copper through Cu_3Si occurs above 530 °C. Below this temperature grain-boundary diffusion occurs with an activation energy of 92 kJ/mol. No incubation times were observed. The segregation of phosphorus at the reaction interface removes the reaction barrier. $\text{Cu}_{15}\text{Si}_4$ and Cu_5Si seem to be absent from the diffusion couples because of kinetic factors.

INTRODUCTION

Solid state reactions in binary diffusion couples have been widely studied and are generally well understood. The reactions proceed by the diffusion of one or both components under the influence of a chemical potential gradient. A phase diagram of the system shows which compounds can be expected in a diffusion couple. The parabolic growth law permits prediction of how much of each product is formed in a certain time. Such systems are usually regarded as binary if the amount of impurities is less than 0.1 atom-%. Very little attention has been paid to the influence of a third component which is present in much lower concentrations, although it has already been shown in oxidic systems that both the reaction kinetics and the product morphology can be influenced by such an impurity [1].

In this article we will show what influence phosphorus concentrations (in ppm) have on the reaction between copper and silicon. Preliminary diffusion experiments [2] between silicon and various types of copper have revealed

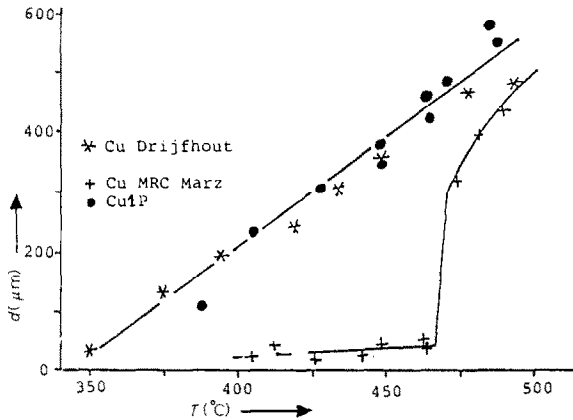


Fig. 1. The thickness of the Cu_3Si layer against temperature in diffusion couples between silicon and various types of copper, annealed for 4 h.

that “pure” copper obtained from one supplier (Cu Drijfhout), reacts with silicon to Cu_3Si at low temperatures (Fig. 1), whereas “pure” copper from another supplier (Cu MRC Marz) showed very little reaction. The main difference between the two types of copper was a difference in the phosphorus content: Cu Drijfhout contains 30 ppm phosphorus (by mass spectrometry), whereas Cu MRC Marz contains less than 1 ppm (supplier’s figures). This leads to strong phosphorus segregation in Cu Drijfhout at 400°C (AES), whereas no segregation was observed for Cu MRC Marz [2].

The aim of this study was to determine why the presence of phosphorus has such a large influence on the reaction between copper and silicon. Furthermore we wanted to find out whether the differing amounts of phosphorus present in the copper samples may have been responsible for the conflicting results of this reaction, published by other investigators.

LITERATURE SURVEY ON THE REACTION BETWEEN COPPER AND SILICON

On the basis of the phase diagram of the copper–silicon system [3] we expected the formation of Cu_3Si (η), $\text{Cu}_{15}\text{Si}_{14}$ (ϵ) and Cu_5Si (γ) in copper–silicon diffusion couples below 550°C (Fig. 2).

Veer et al. [4] have studied the reaction between copper and silicon in the temperature range between 350 and 550°C . The only product observed is Cu_3Si . The reaction is a diffusion limited process, but there is an incubation time. Experiments with inert markers show that copper is the only diffusing component. Activation energy of 78 kJ/mol is low and is attributed to bulk diffusion through the highly defective Cu_3Si structure [5]. Ward and Carroll [6] upon reexamining these data, found an activation energy of 107 kJ/mol for the rate constant, defined as $k = d^2/t$ ($\mu\text{m}^2/\text{h}$).

Ward and Carroll [6] have electroplated copper onto silicon. At low temperatures (between 250 and 350°C) and after short reaction times

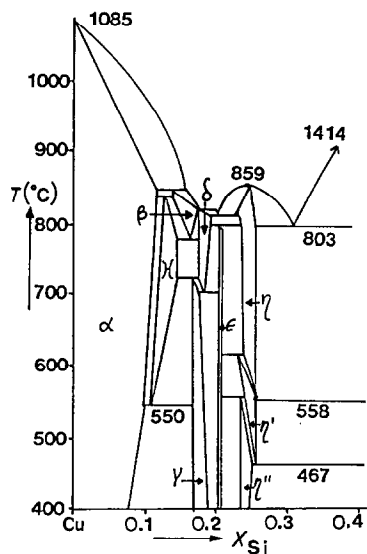


Fig. 2. The copper-rich side of the copper-silicon phase diagram [3].

(≈ 100 s) only Cu_3Si formed during a diffusion controlled process. The activation energy is 105 kJ/mol.

Onishi and Miura [7] have studied the influence of compressive stress on the thickness of the reaction layer. If this stress is larger than 8 MPa, the thickness is independent of the applied stress. Between 420 and 465°C at 12 MPa the reaction is a diffusion limited process with an activation energy of 150 kJ/mol. The formation of Kirkendall pores at the copper-silicide interface indicates that copper is the only diffusing component, and only Cu_3Si was observed.

Weber and coworkers [8] dipped silicon slices in a bath of molten copper(I) chloride. The reaction layer that formed consisted of Cu_3Si with copper precipitates, indicating that the process cannot be a purely binary diffusion mechanism. They described it as a diffusion-controlled reaction. The activation energy is 69.4 kJ/mol between 425 and 455°C.

Although we expected the formation of three compounds, in all these investigations only Cu_3Si was found, with the added complication that the reaction kinetics were found to be conflicting.

EXPERIMENTAL

Diffusion couples are prepared by using slices cut from the raw materials with a SiC saw. The silicon slices (Veille Montagne, polycrystalline, n-type) were of dimensions $1 \times 1 \times 0.2$ cm; copper slices were circular with a diameter of 0.9 cm. The slices were ground on SiC paper, polished on nylon cloth with diamond paste, and on soft cloth with alumina. For each sample a

different piece of cloth was used, so as to prevent contamination. Between the various steps the slices were cleaned with alcohol or refined petrol. As a final step the slices were washed with acetone and carefully but quickly dried in order to limit oxidation. After preparation the slices were placed immediately in a vacuum furnace, to minimise oxidation.

The diffusion experiments [9] were conducted in a vacuum furnace. The vessel was evacuated to less than 0.1 mPa; the compressive stress was 3 MPa, which was a compromise between the limitations of the furnace and the stress recommended by Onishi et al. [7]. After the heat treatment the couples were cut perpendicular to the reaction layer, and products were studied by optical microscopy (Reichert MeF2, equipped with a calibrated eye-piece) and with electron probe micro analysis (EPMA), JEOL 733 Superprobe, operating with an acceleration voltage of 20 kV and a beam current of 10 nA. Some samples were etched with a nitric acid/water mixture (1/1 by volume).

The influence of phosphorus was studied with Cu₃P as a model system. It was prepared by arc-melting Cu MRC Marz with Cu₃P (Alpha Products), so that the material contained 1 atom-% of phosphorus. As can be seen from Fig. 1, this material reacts in the same way as Cu Drijfhout, which contains 30 ppm phosphorus.

PRODUCT FORMATION

The composition of the silicides was determined by EPMA [9]. The phase boundaries found in the binary alloys are listed in Table 1.

In diffusion couples the main product is copper-rich Cu₃Si. No concentration gradient was observed. Although the reaction layer consisted of columns, no texture was present. Depending on the temperature, thin (Fig. 3) or thick (Fig. 4) columns are formed. In diffusion couples with phosphorus-doped copper grain size is suddenly reduced from 100 μm at 530 °C to 10 μm at 520 °C. In diffusion couples with pure copper the average grain size decreases gradually between 530 and 470 °C.

TABLE 1

Concentrations at the phase boundaries in the copper–silicon system at 500 °C, by EPMA after calibration on a homogeneous copper–silicon alloy containing 23.6 atom-% Si

Phase	Cu-rich boundary (atom-% Si)	Si-rich boundary (atom-% Si)
solid solution		10.02 ± 0.06
Cu ₅ Si	16.72 ± 0.05	17.54 ± 0.05
Cu ₁₅ Si ₄	21.70 ± 0.04	21.86 ± 0.06
Cu ₃ Si	23.46 ± 0.02	24.23 ± 0.03

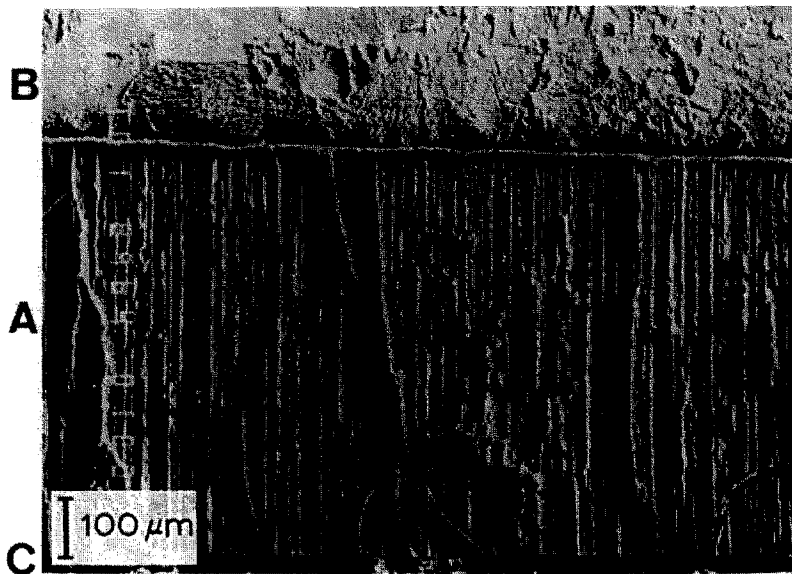


Fig. 3. Secondary electron image of an etched diffusion couple between Cu MRC Marz (B) and silicon (C), showing thin columns of Cu_3Si (A). The couple was annealed at 430°C , for 65 h.

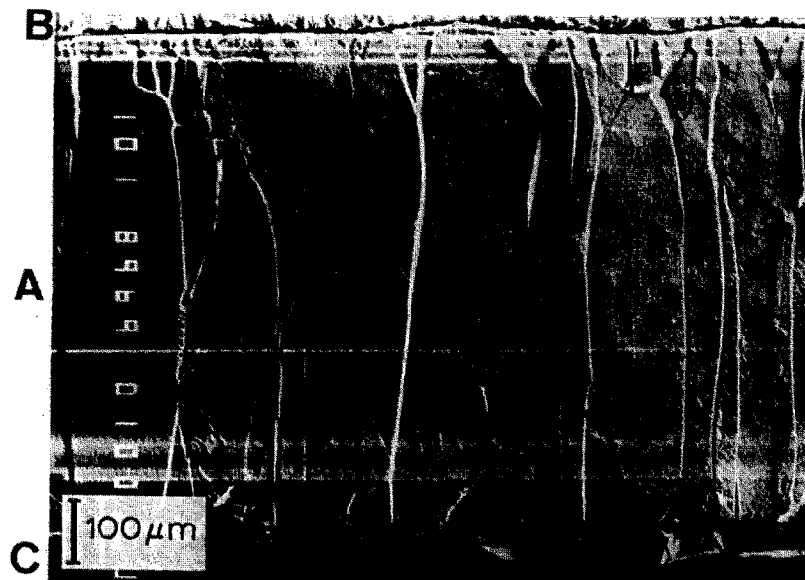


Fig. 4. Secondary electron image of an etched diffusion couple between Cu MRC Marz (B) and silicon (C), showing the heavy grains of Cu_3Si (A). The couple was annealed at 500°C , for 8 h.

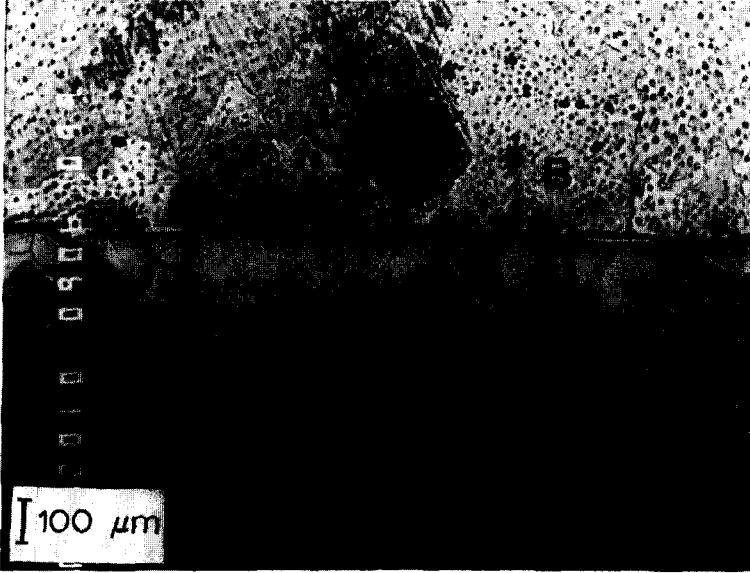


Fig. 5. Back-scattered electron image of the formation of $\text{Cu}_{15}\text{Si}_4$ (A) in a diffusion couple between Cu_1P (B) and a Cu-Si alloy (C) containing 23.1 atom-% Si at 500°C , for 16 h.

In diffusion couples between silicon and phosphorus-doped copper, Cu_3P precipitates are formed at the copper/silicide interface.

$\text{Cu}_{15}\text{Si}_4$ was formed in some diffusion couples with an overall retarded growth rate, so when the reaction between copper and silicon is hampered, copper reacts with Cu_3Si to form $\text{Cu}_{15}\text{Si}_4$. The formation of $\text{Cu}_{15}\text{Si}_4$ has also been observed, albeit on rare occasions, in diffusion couples containing phosphorus, which indicates that $\text{Cu}_{15}\text{Si}_4$ and Cu_5Si are not absent for thermodynamic reasons. We tested the hypothesis that $\text{Cu}_{15}\text{Si}_4$ and Cu_5Si are absent for kinetic reasons with the following experiment: a diffusion couple was made between Cu_1P and Cu-Si alloy containing 23.1 atom-% Si, i.e. one containing Cu_3Si and a small amount of $\text{Cu}_{15}\text{Si}_4$ at the grain boundaries (Fig. 5). The choice of Cu_1P instead of Cu MRC Marz will be clarified later on. After 16 h at 500°C about $120\ \mu\text{m}$ of $\text{Cu}_{15}\text{Si}_4$ and $12\ \mu\text{m}$ of Cu_5Si were found to have formed (Fig. 5). Since there is virtually no concentration gradient in the diffusion couples, we can apply the equation for the integrated diffusion coefficient, as defined by Wagner [10]:

$$\begin{aligned}
 D\gamma_{\text{int}} = & \int_{N_i(\gamma')}^{N_i(\gamma'')} \tilde{D} \, dN_i = \frac{(N_i(\gamma) - N_i^{-\infty})(N_i^{+\infty} - N_i(\gamma))}{N_i^{+\infty} - N_i^{-\infty}} \left(\frac{d_\gamma^2}{2t} \right) \\
 & + \frac{d_\gamma}{2t} \left[\frac{N_i^{+\infty} - N_i(\gamma)}{N_i^{+\infty} - N_i^{-\infty}} \int_{-\infty}^{x(\gamma-1,\gamma)} \frac{V_{m,\gamma}}{V_m(x)} (N_i - N_i^{-\infty}) \, dx \right. \\
 & \left. + \frac{N_i(\gamma) - N_i^{-\infty}}{N_i^{+\infty} - N_i^{-\infty}} \int_{x(\gamma,\gamma+1)}^{+\infty} \frac{V_{m,\gamma}}{V_m(x)} (N_i^{+\infty} - N_i) \, dx \right]
 \end{aligned}$$

where $N_i(\gamma'')$ and $N_i(\gamma')$ are the unknown limiting-mole fractions of component i in the line compound γ with layer thickness d_γ ; $N_i(\gamma') \approx N_i(\gamma) \approx N_i(\gamma'')$; $x(\gamma - 1, \gamma)$ and $x(\gamma, \gamma + 1)$ are respectively the positions of the left-hand and right-hand boundaries of the γ layer; $V_{m,\gamma}$ is the molar volume of γ ; $N_i^{-\infty}$ and $N_i^{+\infty}$ are the mole fractions of component i at the left-hand and right-hand ends of the diffusion couple, respectively.

Since this integrated diffusion coefficient is a material constant, there is a [9] relationship between the thickness of the $\text{Cu}_{15}\text{Si}_4$ layer in a diffusion couple between the elements (d_ϵ^1) and the thickness of the $\text{Cu}_{15}\text{Si}_4$ layer in a couple between copper and the alloy $\text{Cu}_{76.9}\text{Si}_{23.1}$ (d_ϵ^{II}). If we ignore the small amount of Cu_5Si formed and the small amount of $\text{Cu}_{15}\text{Si}_4$ present in the alloy, we get:

$$(d_\epsilon^{\text{II}})^2 = \frac{(1 - N_\epsilon)N_\eta}{N_\eta - N_\epsilon} \times (d_\epsilon^1)^2 + \frac{(1 - N_\eta)N_\epsilon}{N_\eta - N_\epsilon} \times d_\epsilon^1 \times d_\eta^1$$

where ϵ denotes the $\text{Cu}_{15}\text{Si}_4$ phase and η the Cu_3Si phase. $\text{Cu}_{15}\text{Si}_4$ contains 21.7 atom-% of Si, so $N_\epsilon = 0.217$; Cu_3Si contains 23.5 atom-% of Si in the diffusion couples, so $N_\eta = 0.235$. In a diffusion couple between copper and silicon at 500°C after 16 h, $1200 \mu\text{m}$ Cu_3Si will be formed, so $d_\eta^1 = 1200 \mu\text{m}$. Since $120 \mu\text{m}$ of $\text{Cu}_{15}\text{Si}_4$ was formed ($d_\epsilon^{\text{II}} = 120 \mu\text{m}$) in the diffusion couple between copper and the alloy, we found that $d_\epsilon^1 = 1 \mu\text{m}$. Thus the formation of $1 \mu\text{m}$ $\text{Cu}_{15}\text{Si}_4$ in a copper-silicon diffusion couple at 500°C takes place when the Cu_3Si layer is $1200 \mu\text{m}$ thick. At shorter reaction times and at lower temperatures even less $\text{Cu}_{15}\text{Si}_4$ will be formed.

It may be concluded that kinetic factors limit the formation of $\text{Cu}_{15}\text{Si}_4$ and Cu_5Si in copper-silicon diffusion couples. The layer is formed, but is usually too thin to be observed, unless the reaction between copper and silicon at the $\text{Cu}_3\text{Si}/\text{Si}$ interface is disturbed, in which case copper reacts with Cu_3Si to form $\text{Cu}_{15}\text{Si}_4$ with an overall retarded growth rate.

The integrated diffusion coefficients for $\text{Cu}_{15}\text{Si}_4$ and Cu_3Si are 1.6×10^{-11} and $2.2 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively. Since no concentration gradient was observed interdiffusion coefficients could not be determined. The minimum values can be estimated by modifying the definition for the integrated diffusion coefficient:

$$D_{\text{int}} \approx \tilde{D}_{\text{av}} \times \Delta N$$

Since the difference in mole fraction, ΔN , in the growing layer from the silicon side to the copper side is less than 0.001 (EPMA limit), it follows that \tilde{D}_{av} for Cu_3Si is $> 2.2 \times 10^{-5} \text{ cm}^2/\text{s}$ and for $\text{Cu}_{15}\text{Si}_4$ is $> 1.6 \times 10^{-8} \text{ cm}^2/\text{s}$.

DETERMINATION OF THE DIFFUSING COMPONENT

The solid-state reaction between copper and silicon can, in principle, proceed by three mechanisms: diffusion of copper through the layer already formed, diffusion of silicon through the same or diffusion by both components through the layer. The last mechanism can be ruled out, since it would lead to the formation of a marker plane inside the silicide layer, which was not observed. The presence of natural markers (inclusions, pores) at the interface between copper and the copper silicide suggest that this plane is the marker plane and that copper is the only diffusing component. Similar deductions were made by Onishi and coworkers [7] on the basis of the positions of the Kirkendall pores, and by Kolster [5] who used tungsten markers. The latter method has the disadvantage that the diffusion couple suffers from deformation around the wires.

A more suitable technique is to study the diffusion couple between silicon and a copper-silicon alloy, in which Cu_3Si is formed in two ways: (i) by decomposition of the alloy and (ii) by the diffusion reaction. The two products can readily be distinguished by the marker plane, where crystals nucleated from both sides meet (Fig. 6). If only silicon diffuses, this marker plane would coincide with the silicon-silicide interface. If only copper diffuses the ratio of the thickness of the two layers can be calculated. The alloy used in this experiment is a two-phased alloy with 18.0 atom-% of Si,

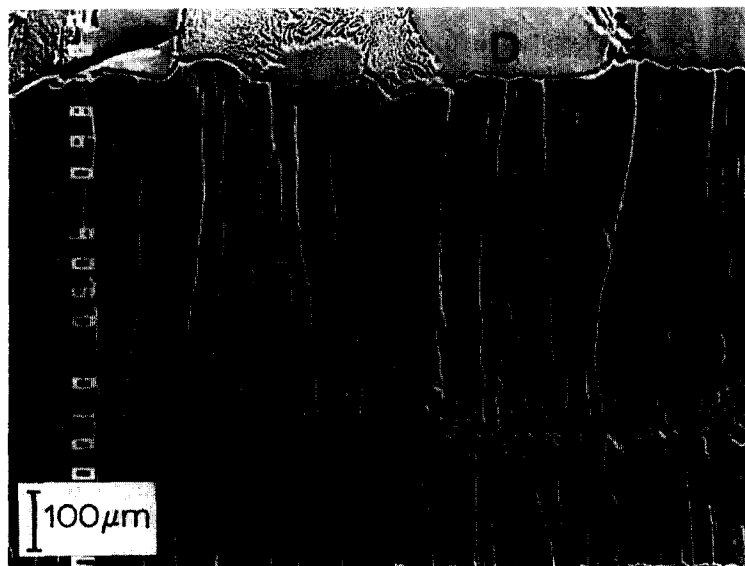


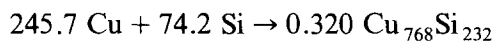
Fig. 6. The markerplane (A) in the Cu_3Si (B) layer in a diffusion couple between silicon (C) and an alloy (D) containing 18.0 atom-% Si, which separates the Cu_3Si formed by decomposition (top) from the Cu_3Si formed by reaction diffusion (bottom).

consisting of Cu_5Si (17.5 atom-% of Si, $\text{Cu}_{825}\text{Si}_{175}$) and a small amount of $\text{Cu}_{15}\text{Si}_4$, not uniformly distributed over the alloy. The compound Cu_3Si was formed, and was found to contain 23.2 atom-% Si: $\text{Cu}_{768}\text{Si}_{232}$. Since no concentration gradient was observed we derived a set of equations for:

(a) the decomposition of Cu_5Si ,



(b) the diffusion reaction between copper and silicon,



The ratio between the layers formed according to (a) and (b) is $0.754/0.320$ or $2.36/1$. If we take $\text{Cu}_{82}\text{Si}_{18}$ as a starting material this ratio is $2.66/1$. The observed ratio varies between 2.33 and 2.65, which can be explained in terms of the non-uniform distribution of $\text{Cu}_{15}\text{Si}_4$ through the alloy. These results confirm the hypothesis that only copper diffuses in Cu_3Si .

REACTION KINETICS

The dependence of layer thickness on reaction time

The relation tested in this section is the parabolic growth law. In a diffusion limited process the product layer thickness will show the following dependence on the reaction time:

$$d^2 = k \times (t - t_0)$$

Here t_0 is the time necessary for the process to become limited by diffusion through the product layer (the incubation time). During the incubation time layer growth is generally very slow compared with diffusion limited growth, owing to the presence of a reaction barrier. k is the reaction rate constant in $\mu\text{m}^2/\text{h}$.

There is a large difference in the time dependence of the layer thickness between couples with pure copper and those with phosphorus-doped copper. In diffusion couples between silicon and pure copper (Cu MRC Marz) there is a large incubation time (Fig. 7). The time necessary to remove the reaction barrier decreases as the temperature is raised: at 400°C it may be as long as 25 h, at 430°C it is 5 h, and above 465°C there is no incubation at all. This is demonstrated in Fig. 7. The incubation time is not a constant but varies from one experiment to another, and causes the relatively large spread in the measurements shown in Fig. 7. The lability of the diffusion couples precludes the reheating of a diffusion couple, which would reveal the time dependence in one couple using only the incubation time. But in all cases, after some time, the reaction becomes diffusion-limited and the rate con-

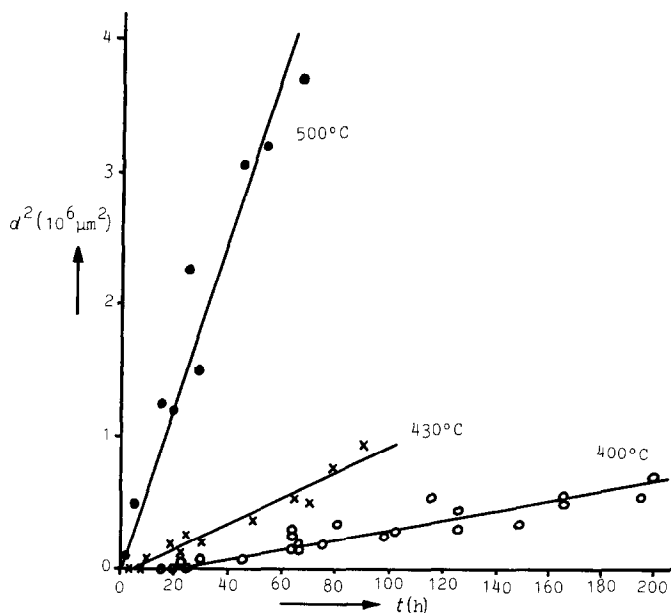


Fig. 7. The thickness of the Cu_3Si layer in diffusion couples between pure copper and silicon as a function of the reaction time at various temperatures. For proper testing of the parabolic growth law with incubation time, the data were plotted as the squares of the thickness against time.

stant can be determined, although with a relatively large experimental error (Table 2).

The dependence on time is completely changed if traces of phosphorus are present in the copper used. The amount of phosphorus does not have much influence so that Cu Drijfhout (30 ppm P) and Cu1P (1 atom-% P) react in the same way, viz. the incubation time is eliminated, because the reaction barrier is removed by migration of phosphorus to the copper surface during the initial stages of heating. Furthermore the rate constant is much higher when phosphorus is present: $k = 10500 \pm 200 \mu\text{m}^2/\text{h}$ at 400°C .

TABLE 2

Reaction rate constants determined by least-squares for diffusion couples between pure copper and silicon

T ($^\circ\text{C}$)	k ($\mu\text{m}^2/\text{h}$)	$\ln k$
400	3600 ± 400	8.2 ± 0.1
415	7900 ± 2300	9.0 ± 0.4
430	9400 ± 800	9.2 ± 0.1

Dependence of the rate constant on temperature

Figure 8 shows the dependence of the rate constant on temperature as an Arrhenius plot. Such a plot gives the activation energy of the rate-determining step of the process. We have already shown that the reaction is diffusion limited (from the parabolic growth law) and that the diffusing component is copper. Therefore, we can determine the activation energy for the diffusion of copper through the Cu_3Si layer, assuming that the homogeneity range of Cu_3Si is not temperature dependent.

There is a distinct difference between pure copper, and copper containing phosphorus. At high temperature the activation energy for diffusion of copper is 175 ± 3 kJ/mol (least-squares method), both for doped and undoped copper. Cu_3Si is formed in large crystals as shown in Fig. 4. Undoped copper reacts with this activation energy down to 470°C , while the grain size is gradually reduced. Below 470°C the activation energy is 110 ± 12 kJ/mol, and Cu_3Si forms thin columns, as shown in Fig. 3. These

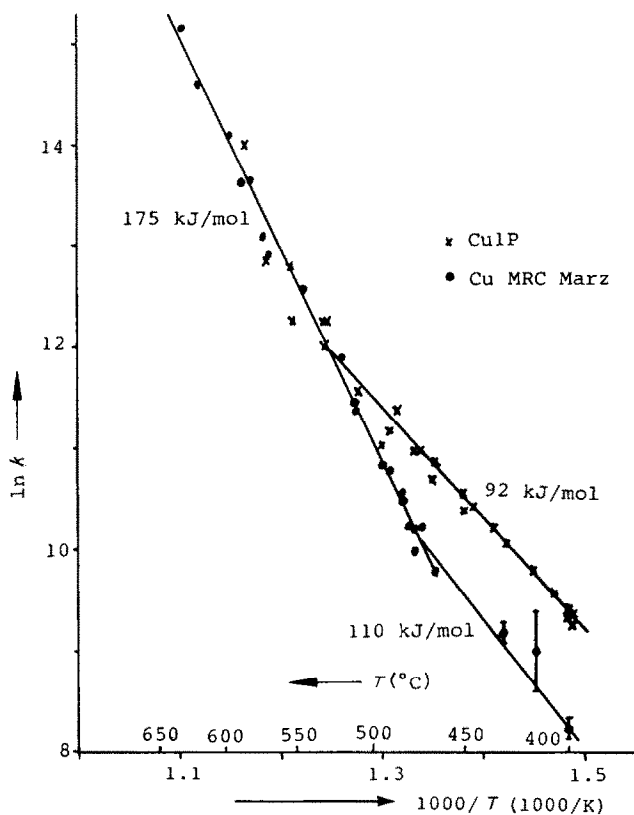


Fig. 8. Arrhenius plot of the reaction rate constant versus temperature, both for phosphorus-doped (Cu1P) and pure (Cu MRC Marz) copper in copper-silicon diffusion couples.

values indicate that at high temperatures copper diffusion takes place by a bulk diffusion mechanism, whereas at low temperatures a grain boundary mechanism dominates, which is known to proceed with a lower activation energy. The morphology of the reaction layer supports this.

In doped diffusion couples the situation is somewhat different: at 530 °C the mechanism changes from bulk diffusion to grain boundary diffusion, which is shown both by the activation energy and the thin columns present in the reaction layer. The presence of phosphorus causes early nucleation of many crystals, so that grain boundary diffusion provides a large amount of the copper supply at high temperatures.

The activation energy at low temperature in the presence of phosphorus is 92 ± 4 kJ/mol. On the basis of our data we cannot conclude whether the activation energies in the presence and absence of phosphorus (110 ± 12 kJ/mol) are equal within experimental error. There is no theoretical basis for the two values to be equal, considering the possibility of the presence of phosphorus at the grain boundaries. So these two processes can proceed with different activation energies. Clearly the pre-exponential or frequency factors are different. Since these factors incorporate terms such as the number of sites available for diffusion, we conclude that the presence of phosphorus induces the formation of more nuclei, resulting in more grain boundaries available for diffusion.

THE ROLE OF PHOSPHORUS IN THE REMOVAL OF THE REACTION BARRIER

The fact that incubation times have been noted for reactions using pure copper suggests that there is a reaction barrier. This is removed when phosphorus is present. A possible reaction barrier that will always be present is an oxidation layer, probably of silicon dioxide on silicon. Even when suitable precautions are taken silicon is covered with an oxide layer of 2 nm thickness [11]. Furthermore it is known that the diffusion of copper through silicon dioxide is an extremely slow process [12].

To find out whether this oxidation layer hampers the reaction, we conducted experiments with pre-oxidized silicon slices. Polished silicon slices were oxidized in a furnace at 1000 °C for half an hour in pure oxygen which resulted in violet discoloration of the slices. The oxide layer formed was approximately 200 nm thick, which gives rise to a reaction barrier that is so large, that pure copper does not react even at 500 °C after 65 h. The situation is completely different with Cu₃P. Both at 400 and 500 °C the thickness of the Cu₃Si layer is comparable to the results of experiments with non-pre-oxidized silicon. After 16 h at 500 °C a layer of 1050 μm was found to have formed, while a layer of 1200 μm is the norm. At 400 °C for 66 h annealing the layer thickness was: 680 μm observed and 830 μm expected.

The effect of a silicon dioxide layer on the reaction with copper has also

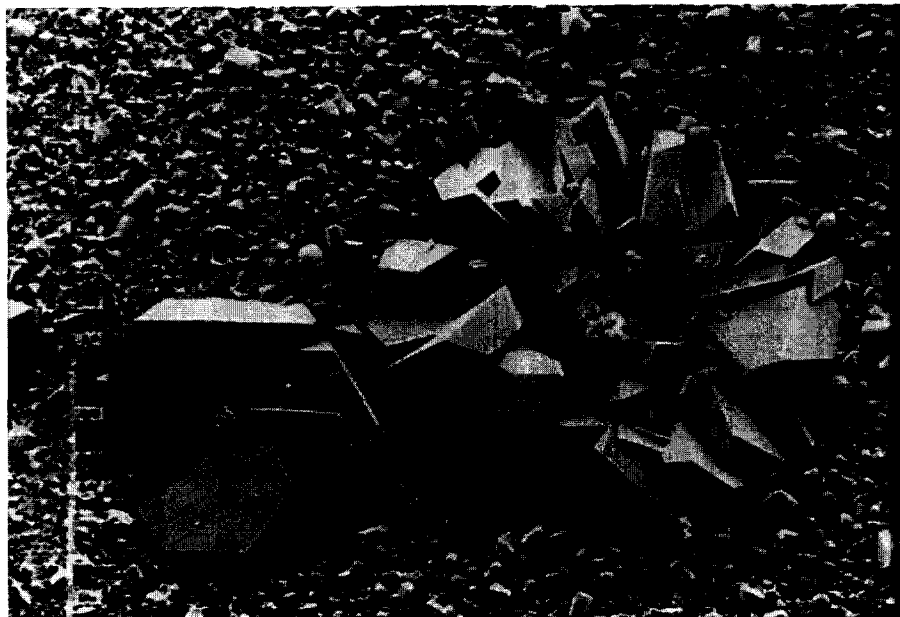


Fig. 9. The hexagonal crystals of a compound, containing silicon, phosphorus and oxygen, formed during the reaction of phosphorus vapour with silica in the presence of copper at 500 ° C.

been demonstrated with Cu_3Si alloys, which undergo spontaneous oxidation and are always covered with SiO_2 . These always react with Cu_3P to give only $\text{Cu}_{15}\text{Si}_4$. No reaction has ever been observed with pure copper.

We can think of several ways in which phosphorus removes this reaction barrier (i) phosphorus could induce crystallization in the amorphous silicon dioxide layer, so that copper can diffuse through defects in the oxide layer, (ii) the formation of volatile phosphorus oxides which are subsequently removed by the vacuum system.

A third possibility is the formation of silicon phosphates. Formation of $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$ in the bulk phase has been described [13]. We have observed the formation of hexagonal crystals (Fig. 9), containing silicon, phosphorus and oxygen, during the reaction between phosphorus powder and silica. The presence of copper seems to be necessary, since no products formed in the absence of copper.

DISCUSSION AND CONCLUSIONS

We asked ourselves two questions: why is Cu_3Si the only product formed in copper–silicon diffusion couples, and can the presence of phosphorus account for the fact that various types of copper react so differently?

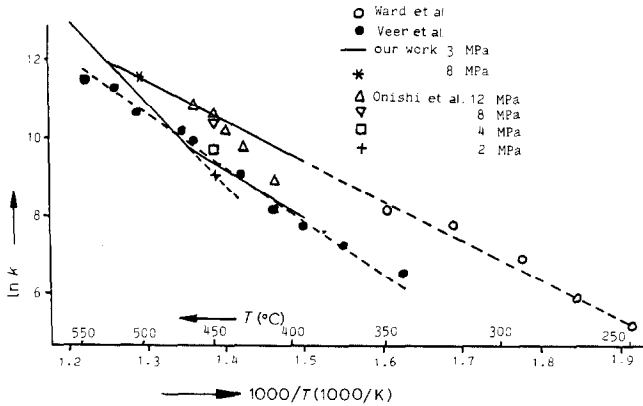


Fig. 10. Comparison of the results of our study with those of Ward et al. [6], Veer et al. [4] and Onishi et al. [7].

We have shown, that $\text{Cu}_{15}\text{Si}_4$ and Cu_5Si seem to be absent in diffusion couples, because their growth rate is very small. These phases are observed after long reaction times and when the reaction between copper and silicon is obstructed. In diffusion couples between copper and Cu_3Si they are formed if the reaction barrier formed by the silicon dioxide layer on Cu_3Si is removed.

The formation of Cu_3Si obeys the parabolic growth law: the rate-limiting step is the diffusion of copper through the silicide layer.

In the case of pure copper a reaction barrier exists at low temperatures, which leads to an incubation time for the reaction. This is caused by the presence of an oxidation layer on silicon. This layer is removed by phosphorus segregation to the original interface so that copper can react with silicon without an incubation time. This is one reason why phosphorus-containing copper reacts differently from pure copper. The other reason is that the presence of phosphorus raises the temperature from 470 to 530 °C below which the grain boundary diffusion mechanism is dominant.

In Fig. 10 there is a comparison between our results and those taken from the literature. Although different techniques and materials were used, there is a close similarity. The data of Ward and coworkers [6] fit well into an extrapolation of our results for the phosphorus-doped samples. The lack of incubation time is attributable to the experimental technique which prevented the formation of an oxidation layer on silicon will be formed. The results of Veer and coworkers [4] and Kolster [5] are similar to ours for the phosphorus-free diffusion couples, although a grain boundary mechanism is sustained up to higher temperatures. Onishi and coworkers [7] have eliminated the incubation times by use of large stresses. Their results lie between the two curves we have obtained in this study. The data for high stresses are consistent with the rapid phosphorus-doped reaction; while the

data for very low stresses suggest that a bulk diffusion mechanism is maintained till lower temperatures. The results of Weber and coworkers [8] are not included in the diagram, since they describe the growth of a two-phase layer. If we correct their data for the inclusion of copper precipitates, their layer thicknesses are similar to our results with phosphorus-doped couples.

It was found that in copper-silicon diffusion couples Cu_3Si is the main product. It can be formed by grain boundary or bulk diffusion of copper through the silicide layer. The predominance of either process depends on the reaction conditions; a subtle interaction between various reaction barriers, impurities and stresses determines the precise mechanism and thereby the morphology of the reaction layer.

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