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STUDY OF THE REACTIVITY OF A SINGLE CRYSTAL OF SILICON WITH MOLTEN COPPER(I) CHLORIDE

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ABSTRACT

When a single crystal of silicon is dipped into a molten bath of copper(I) chloride between 425 and 480°C, relatively rapid formation of the intermetallic compound Cu_3Si occurs. For reaction times less than 4 min the nuclei always present a geometrical pyramidal structure with a square [on Si(100)] or triangular [on Si(lll)] basis. The nucleation growth kinetics on Si(100) are obtained by a method of nuclei counting and the overall reaction rate seems to be controlled by the nucleation rate of the Cu_3Si phase. At longer reaction times, when the nuclei are overlapping each other, a continuous layer of Cu_3Si forms on silicon with a thickness proportional to the square root of the reaction time. The layer growth mechanism is governed by the diffusion of copper at the Si-Cu_3Si interface.

INTRODUCTION

The intermetallic compound Cu_3Si (rj-phase) is an important inter¬ mediate in the industrial manufacture of chlorosilanes and a detailed knowl¬ edge of the chemical processes that occur during the reaction of copper or copper(I) chloride with silicon is of interest from both a theoretical and a practical point of view [1], Some papers [2-9] have appeared concerning the formation conditions of Cu_3Si from mixtures of silicon and copper or silicon and copper compounds [6]. When such a mixture is formed from silicon and copper(I) oxide, copper(I) formate or copper(I) aluminate, this reaction has to be carried out at a high temperature (1000°C) in a hydrogen atmosphere so as to favour Cu_3Si formation. However, a silicon-copper(I) chloride mixture is much more reactive [8,10,11] and seems to be the most amenable to Cu_3Si formation at low temperatures. Several kinetic studies have been carried out with such a mixture, but the reaction is restricted to the

nucleation growth stage of the metallic phase [12-15]. Only a few workers have investigated the growth mechanism of Cu_3Si from copper-silicon diffusion couples [16-19], Various preparation methods are available for contacting copper and silicon. In particular, by electroplating copper on to boron-doped silicon wafers, the rate of Cu_3Si formation is favoured at low temperatures (from 250 °C). A higher reaction temperature (350-500 °C) was necessary when the diffusion couples were prepared by another experi¬mental procedure [16-19]. Relatively rapid diffusion occurs and a new phase with the approximate composition Cu_3Si grows in the interfacial region. The main conclusions concerning the rate of growth were that, on the one hand, the copper atoms diffuse through the Cu_3Si deposit to the underlying silicon and, on the other, the silicon atoms diffuse in the opposite direction. However, Veer et al. [17] found, from marker experiments, that copper is the only diffusing species and that the rate of Cu_3Si formation is controlled by the diffusion of copper. The growth of the Cu_3Si follows Fick's law. Onishi and Miura [18] reported similar results when single-crystal silicon and copper were pressed together with compressive stresses from 0.8 to 12 MPa. More recently, Becht et al. [19] examined the influence of phosphorus on Cu_3Si growth in the temperature range 350-500 °C. Phosphorus-free copper reacts slowly with silicon below 467 °C and the layer thickness is a linear function of time. Above this temperature, growth is accelerated and the layer thickness becomes a function of the square root of time. The above-men¬tioned studies dealt exclusively with solid-solid or gas-solid reactions when silicon is initially reacted with a metal, salt or metallic oxide.

The purpose of this work was to study the nucleation growth mechanism, and the formation of a continuous Cu_3Si layer by reaction of silicon with molten copper(I) chloride [20,21] according to the following theoretical equation:

$$Si(s)_{excess} + 3CuCl(l) \rightarrow SiCl_4(g) + Cu_3Si(s)$$

The intention was to investigate the evolution of the degree of reaction from the beginning, where the first nuclei are observed, to the end, where a thick continuous layer is formed on the single crystal substrate. Until now, studies of these two stages have not been comparative because the nucleation has been studied with a mixture of silicon and CuCl powder and the growth of the Cu_3Si layer has been carried out from Cu-Si diffusion couples.

EXPERIMENTAL

Samples

The crystals were Czochralski grown in the form of cylindrical rods with a Si[100] growth axis. Wafers of n-type with Si(100) and Si(lll) surface

orientation were prepared by mechanical grinding and chemical polishing. The polishing solution was a freshly prepared mixture of concentrated nitric acid, hydrofluoric acid and acetic acid. The characteristic resistivity and thickness were 50 Ω cm and 0.4 mm for Si(100) and 6 Ω cm and 2 mm for Si(111). Before each experiment, the sample was cleaned with trichloroethylene, then acetone and dried with ethanol.

Chemically pure copper(I) chloride was used (Puratronic, 99.999%).

Apparatus

The apparatus used to study the action of molten copper(I) chloride on polished silicon surfaces is shown in Fig. 1. The silicon wafer was maintained vertically above the bath of copper(I) chloride heated between 430 and 480 °C in pure nitrogen, which prevented oxidation of molten CuCl. The wafer was then quickly transferred into the bath with the mobile holder.

Identification of reaction products

The Cu_3Si phase was identified by means of X-ray diffraction, optical metallography, scanning electron microscopy (SEM) and electron microprobe analysis. The morphological analyses were carried out with sample sections that had been previously mounted in a synthetic resin.

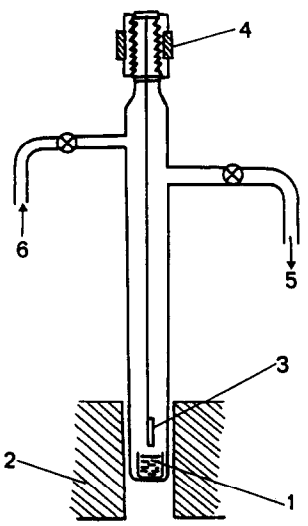

Fig. 1. Schematic diagram showing the experimental set-up for studies on the Si–CuCl system in a molten medium. 1 = Glass boat containing molten CuCl; 2 = furnace; 3 = silicon; 4 = mobile holder; 5 = to diffusion pump; 6 = inlet of pure nitrogen.

RESULTS

Morphology of Cu_3Si precipitates

As soon as the wafer had been transferred to the bath we observed numerous precipitates crystallized epitaxially on to the single crystal substrate. These precipitates were discrete provided that the reaction time did not exceed 4 min at 430°C. The morphological analysis showed that each precipitate was, in turn, partly covered with an outer porous skin composed predominantly of free copper and CuCl. After dissolution of this porous skin in concentrated-ammonia solution we observed the geometrical pyramidal structure of these precipitates with a square [on Si(100)] or triangular [on Si(111)] basis (Figs. 2 and 3).

To describe their inner bulkiness we performed successive dissolutions in concentrated nitric acid (11 *M*) and sodium hydroxide (1 *M*). The cavity created in the matrix had the same geometrical shape as previously with a Si(111)–Cu_3Si nucleus–matrix interface (Figs. 4 and 5). From these morphological considerations, we can speculate that the main growth direction for Cu_3Si is Si⟨110⟩, this direction being the most close-packed direction in silicon. The crystallite growth occurs by progressive copper diffusion through the Si(111)–Cu_3Si interface. Such a mechanism seems to be independent of the copper(I) chloride state, as suggested by the observation of a very similar behaviour of a silicon-gaseous copper(I) chloride reaction [11].

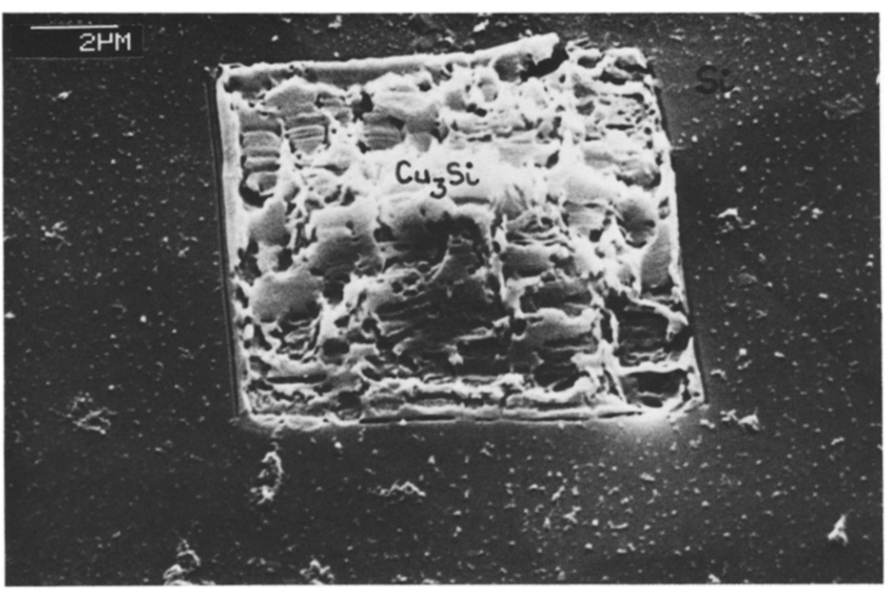

Fig. 2. Microphotograph showing a Cu_3Si precipitate on Si(100) after 3 min at 450°C.

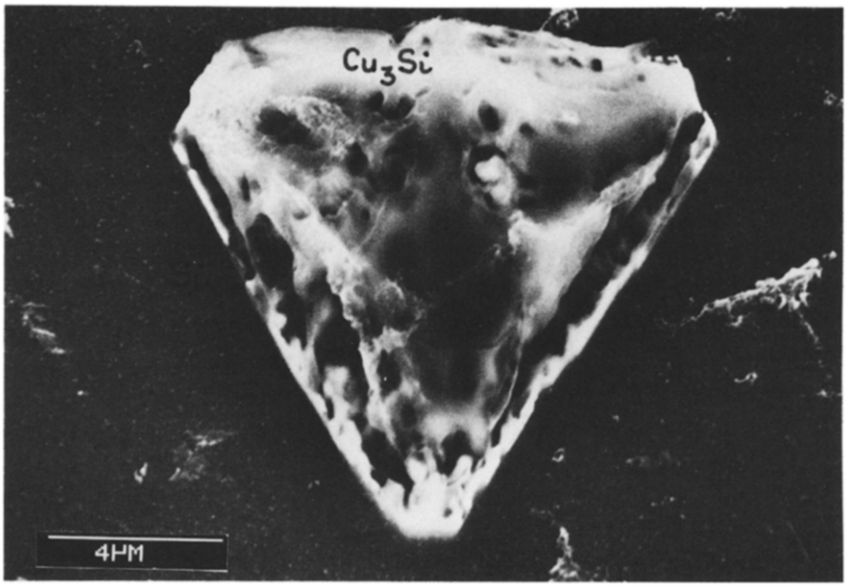

Fig. 3. Microphotograph showing the growth of Cu_3Si precipitate on Si(111). Time and temperature of reaction, 90 s and 450°C, respectively.

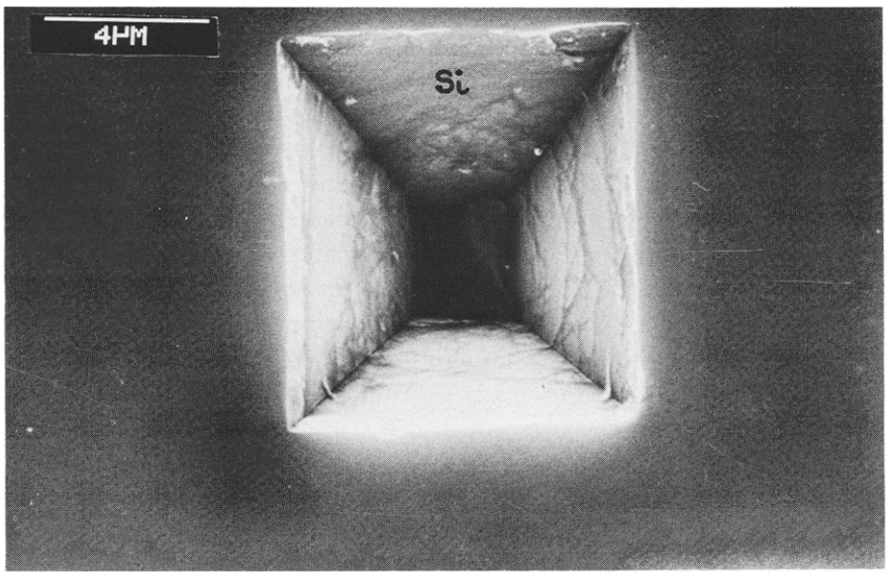

Fig. 4. Cavity of square-pyramidal shape on Si(100) revealed by dissolving Cu_3Si successively with nitric acid (11 *M*) and sodium hydroxide (1 *M*).

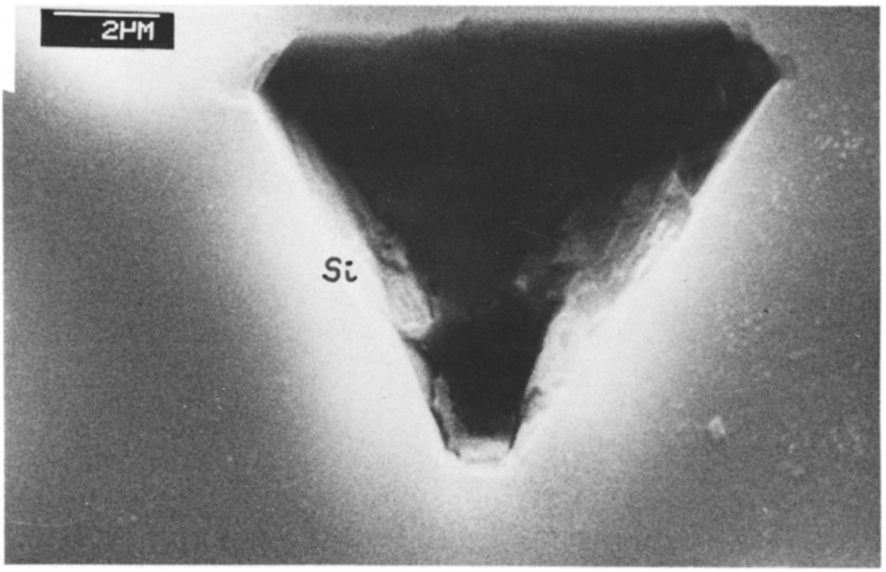

Fig. 5. Cavity of triangular pyramidal shape on Si(111) revealed by dissolving Cu_3Si successively with nitric acid (11 *M*) and sodium hydroxide (1 *M*).

Statistical study of nuclei counting on Si(100)

This study who carried out in order to establish a correlation between the kinetic characters and basic parameters such as the nucleation rate. In order to describe the nucleation kinetics, and the ratio between the nucleation rate and growth rate, we counted the nuclei for respective reaction times of 30 s, 1 min and 3 min (when the silicon wafer was maintained above the bath before reaction, no nuclei were observed on the silicon sample by SEM).

The counting and sizing of the nuclei were carried out on the scanning electron micrographs. Fig. 6 shows such a nuclei distribution. The error in the measurement of nuclei was 1 mm. After waking corrections due to the magnification of the micrographs we obtained the real sizes of the nuclei. The repartition histograms (Fig. 7) were assimilated to Gaussian curves. Hence the nucleation laws represent statistical laws, but they apply to a good approximation owing to the relatively large number of nuclei. All this work was carried out with the hypothesis of uniform nucleation.

Nucleation kinetics

In order to investigate the nucleation process, the number of nuclei per unit area, i.e., the density, γ, was used; γ was thus given by the expression (Fig. 8)

$$\gamma = 1.02 \cdot 10^4 [t - (-113)] \tag{1}$$

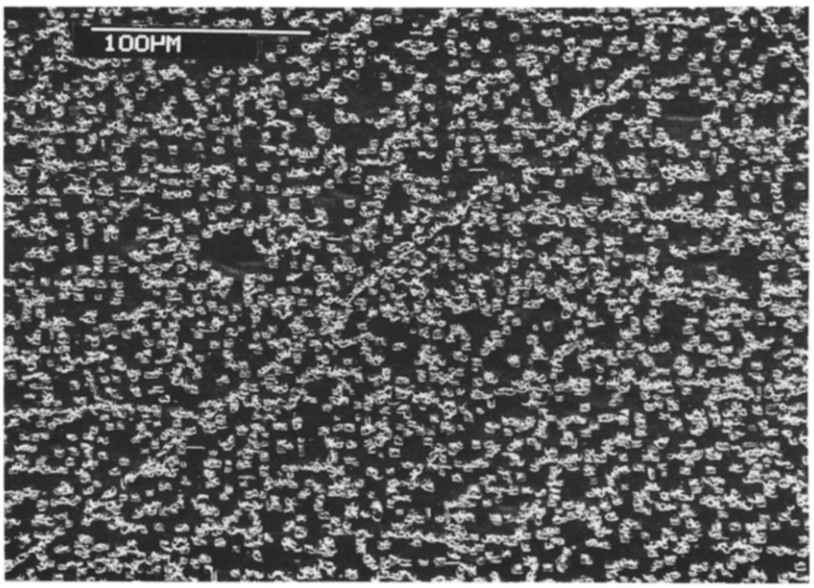

Fig. 6. Microphotograph showing the growth of Cu_3Si precipitates after 3 min at 450 °C.

with time (t) in s and γ in cm^{-2}. In this equation the value $t = -113$ characterizes a negative latent period, which is thus fictitious. This value determines advanced-early nucleation of Cu_3Si metallic alloy. Two assumptions can be proposed to explain this result: the nuclei are generated before the initial state, or the linear dependence is no longer true below 30 s.

The second assumption seems highly unlikely, because after 15 s numerous crystallites had already been generated on the substrate. Therefore, this population would be created by adsorption of copper(I) chloride vapour on silicon during the homogenization period (40 min) of the bath at the reaction temperature.

According to these considerations, the rate law is defined by the differential coefficient of eqn. 1:

$$d\gamma/dt = 1.02 \cdot 10^4 \text{ cm}^{-2} \text{ s}^{-1} \quad (2)$$

This law characterizes a constant nucleation rate.

Growth kinetics of the precipitates

Before the later steps, i.e. when the nuclei are not yet overlapping to give a protective layer, the growth of nuclei is limited. For reaction times of 30 s, 1 min and 3 min, the mean size ($\bar{x}$) corresponds approximately to the maxima of the curves (Fig. 7, Table 1). It can be seen from Fig. 8 that these values vary according to

$$\bar{x} = -3.8 \cdot 10^{-3} t + 4.8 \quad (3)$$

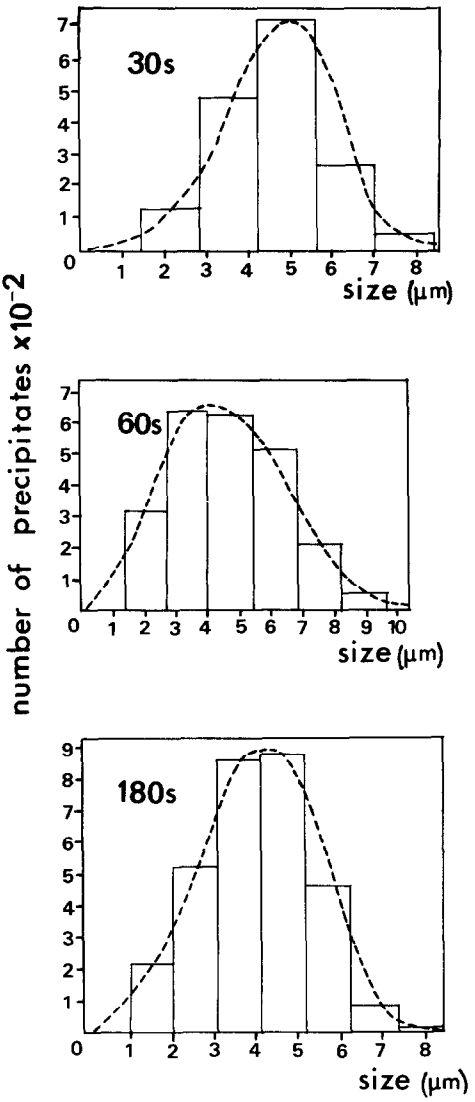

Fig. 7. Diagrams showing the evolution number of Cu_3Si precipitates versus size for successive reaction times (30, 60 and 180 s) at 450 °C.

The derivative of eqn. 3 versus time defines the growth rate, which theoretically may be estimated between t_1 and t_2, especially when no nucleus is generated during this time interval. However, it has been found that the size of the nuclei varies slightly. Hence it is difficult to evaluate the growth rate since for a reaction time of 30 s the nuclei already have a mean size of about 4.6 μm. This can be associated with a high growth rate. Thus, this value will be attributed to artificial growth.

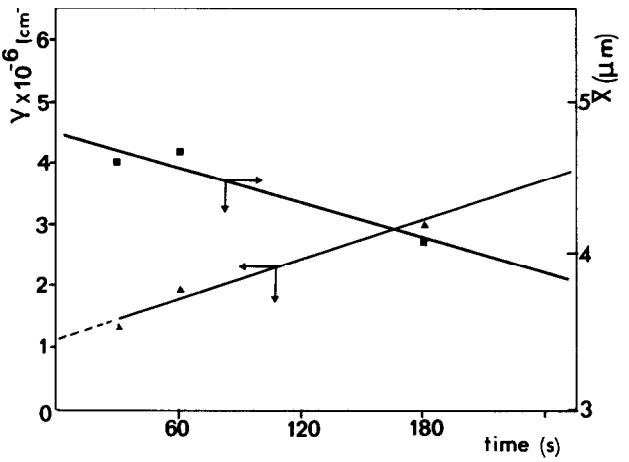

Fig. 8. The number (γ) and mean size ($\bar{x}$) of Cu_3Si precipitates per unit area of silicon as a function of reaction time.

Growth kinetics of the Cu_3Si layer

The growth was studied in the Si⟨100⟩ direction at temperatures between 425 and 455 °C. The analysis by SEM of the cross-section of a sample showed mainly the formation of Cu_3Si with a porous external skin adhering weakly to Cu_3Si and composed of free copper and CuCl (Fig. 9). At the Si–Cu_3Si interface, the silicon exhibits a large number of cracks attributed to the expansion of the Cu_3Si phase [1,13]. It is difficult to explain this phenomenon but these cracks cannot be generated only by mechanical stresses during the sample preparation because of their repreducibility in the location and with the reaction time. As stated previously, the external thin layer of CuCl is porous whereas Cu_3Si adheres strongly to the substrate. However, the compaction of this layer appears to be perturbed by the presence of defects in which the copper is detected. With increasing layer thickness with longer reaction times or higher temperatures, the segregation of copper appears to be more important.

The layer growth at the internal interface in the Si⟨100⟩ direction is controlled by the rate of diffusion of copper atoms resulting from the CuCl

TABLE 1

Dependence of γ and $\bar{x}$ on reaction time

Reaction time (s)	γ (cm^{-2})	$\bar{x}$ (μm)
30	$1.30 \cdot 10^{-6}$	4.6
60	$1.96 \cdot 10^{-6}$	4.7
180	$2.95 \cdot 10^{-6}$	4.1

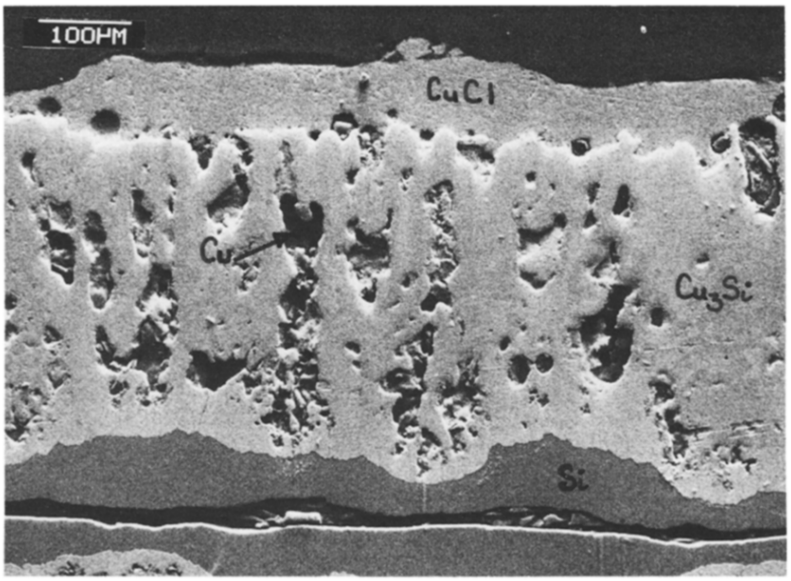

Fig. 9. Cross-sectional view of Cu_3Si covered by a porous skin of copper(I) chloride after 1 h at 450 °C. Copper precipitates are indicated by an arrow.

reduction by silicon. Fig. 10 shows a plot of the Cu_3Si layer thickness (e) versus the square root of time for temperatures ranging from 425 to 455 °C. In this temperature range the diffusion coefficient can be represented by an Arrhenius relationship and varies from $1.89 \cdot 10^{-7}$ cm^2 s^{-1} (425 °C) to

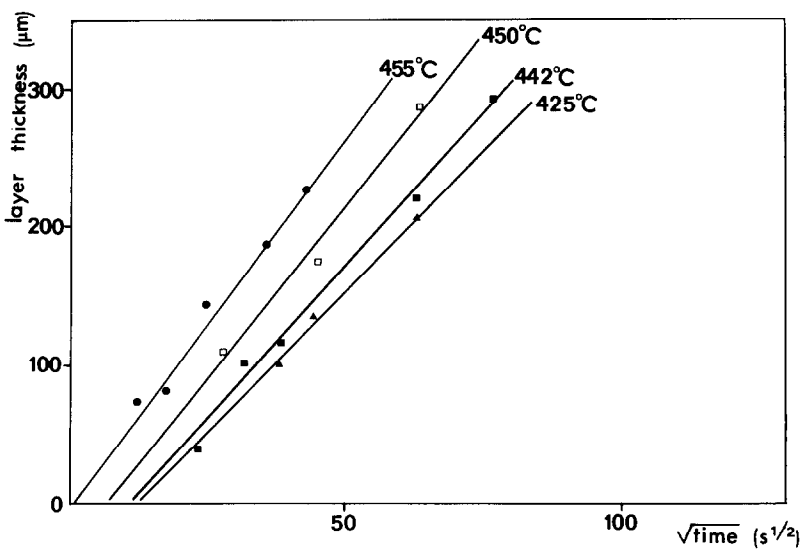

Fig. 10. Thickness of Cu_3Si layer versus square root of time.

$3.12 \cdot 10^{-7}$ cm^2 s^{-1} (455 °C). The activation energy is 69.4 kJ mol^{-1}. The time lag extrapolated to $e = 0$ can be interpreted as the time necessary for establishing the diffusion process. The temperature dependence decrease of this time lag can be represented by

$$t_{lag} = -4.89T + 2248 \quad (4)$$

with t in s and temperature (T) in °C.

DISCUSSION AND CONCLUSION

In this investigation the Cu_3Si phase was obtained with molten copper(I) chloride in the presence of silicon as a reducing agent. As the experimental values were relatively scarce, the results found from the kinetic study of the nucleation growth only partially established the reaction mechanism in molten medium. However, several conclusions can be drawn: the fictitious latent period indicates the presence of nuclei generated before the initial state; the law of nucleation of the nuclei is of zero order, which means that the nuclei are generated at a constant rate; and the growth rate seems very large compared with the nucleation rate.

When a protective layer is obtained, its growth in the Si⟨100⟩ direction results from a diffusion mechanism, the copper being the predominantly diffusing species. However, it should be realized that the presence of copper in the Cu_3Si layer for a long reaction time (e.g., 4 h at 430 °C) or at high temperatures (e.g., 30 min at 470 °C) is unexpected. A conceivable explanation can be found by considering the successive reactions:

$$Si(s)_{excess} + 3CuCl(l) \xrightarrow{k_1} \tfrac{4}{3}SiCl_4(g) + 3Cu(s) + Si(s)$$

and

$$Si(s) + 3Cu(s) \xrightarrow{k_2} Cu_3Si(s)$$

These explain the formation of Cu_3Si but provide no information on the morphology of the layer. During the growth, the silicon atoms of the matrix diffuse with increasing difficulty, thus diminishing the formation of gaseous silicon chloride and consequently the rate of progression of the Si–Cu_3Si interface. The competitive reaction

$$Cu_3Si(s) + 4CuCl(g) \rightarrow SiCl_4(g) + 7Cu(s)$$

can be considered between Cu_3Si and CuCl, as demonstrated experimentally. In this reaction CuCl can be in the gaseous, solid or liquid state.

The silicon vacancies formation in Cu_3Si alloy favours atomic mobility. The pure copper formed in excess by prolongation of the reaction time diffuses and partially reacts with silicon, whereas the remaining copper can

be trapped in vacancies. Although not detected by the usual experimental methods, other copper alloys such as $\epsilon(Cu_{15}Si_4)$ and $\gamma(Cu_5Si)$ may be present in the vicinity of these precipitates. It should be emphasized that these impurities probably hamper diffusion, leading to the low activation energy (69.4 kJ mol^{-1}). This value and the literature data are very close, the slight difference probably being due to the different experimental procedures and to the purity of the silicon.

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