Growth kinetics and morphologies of iron silicide layers

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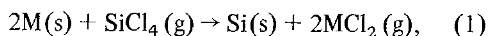
The production of iron silicide layers by the vapour deposition of silicon on to iron has been studied over the temperature range 800 to 1200° C. Silicon was deposited from silicon tetrachloride by either a combination of hydrogen reduction and replacement reaction with the iron substrate or by the replacement reaction alone. In the combined process, at temperatures in the range 800 to 1100° C, the deposition occurs by at least 75% hydrogen reduction. At temperatures above 1100° C the rate of the replacement reaction increases more rapidly than that of the hydrogen reduction process, and so the replacement reaction accounts for more than 25% of the overall depostion. The growth morphologies of the layers have been studied as a function of deposition temperature by scanning electron microscopy. The morphologies obtained in the combined process are shown to agree with general predictions based on the effects of gas phase supersaturation on vapour growth morphologies. The deposits produced by replacement alone are shown to vary from having a vapour-etched crystalline morphology to having a flat porous morphology as the deposition temperature is increased.

1. Introduction

The production of silicide layers by the chemical vapour deposition of silicon followed by silicon–substrate diffusion interaction has been accomplished for a variety of different metallic substrates [1]. Titanium, zirconium, niobium, tantalum, chromium, molybdenum, tungsten, iron, nickel and various alloy steels have all been used as substrate materials. Molybdenum, iron and steel have received most attention because of their technological relevance [1–3]. Silicon may be deposited from the vapour phase by the hydrogen reduction of silicon tetrachloride or trichlorosilane. Silicon tetrachloride was used in many early patents on the coating of steel [4–6] and has also been used for many applications in the electrical and electronic industry since the pioneer work of Pring and Fielding [7].

In many processes utilising the hydrogen reduction of silicon tetrachloride, silicon deposition is also brought about, to a greater or lesser extent, by replacement reactions of the general type,



$$2M(s) + SiCl_4(g) \rightarrow Si(s) + 2MCl_2(g), \quad (1)$$

when the chloride of the substrate is significantly stable at the temperature and pressure used for deposition. The relative proportions of the hydrogen reduction and replacement reactions inevitably change as the deposition process continues. The former reaction is usually constant and gives a uniform rate of deposition, unless it is catalysed significantly by the substrate material [8, 9]. The latter reaction relies upon the diffusion of the deposited atoms to the reacting surface (or the diffusion of the deposited atoms into the substrate) for its continuance and thus decreases in rate as the deposition layers build-up. The dissolution of the deposited silicon in the substrate, or the formation of stable intermetallic compounds between the silicon and substrate, may reduce appreciably the activity of the silicon and hence allow an otherwise thermodynamically unfavourable reduction reaction to occur.

Silicon deposition on to iron proceeds by a combination of replacement and hydrogen reduction reactions. The relative amounts of each of the reactions have been shown to vary with deposition conditions from about 39 to 61% [1].

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However, the growth mechanisms and morphologies of the diffusion layers produced by the two reactions have received little attention. Consequently, the present study on the growth morphologies or iron silicide layers by the replacement reaction and by the combined reactions was carried out as part of a larger study of the effect of substrate reactivity on the growth morphologies of silicide coatings.

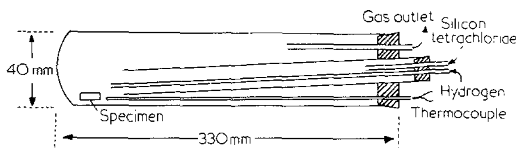


Figure 1 Schematic representation of vapour deposition reactor.

2. Experimental procedure

2.1. Vapour deposition system

A schematic representation of the closed-end tube deposition reactor used in this study is given in Fig. 1. This system allowed coated specimens to be either air-cooled (1273 to 473 K in 15 min) or furnace-cooled (1273 to 473 K in 6 h). Liquid silicon tetrachloride was contained in a glass reservoir at $-39 \pm 2^\circ$ C using a freezing mixture of trichloroethylene and solid carbon dioxide. Dried argon was passed through the reservoir at a constant flow rate of 45 ml min^{-1} as a carrier gas for the silicon tetrachloride vapour. This flow rate had been shown to give a maximum transfer of tetrachloride to the reactor in an earlier study on nickel silicide layers [9]. The low temperature of the tetrachloride reservoir was selected to ensure that gross deposits were not produced in the reactor. Hydrogen was passed through a catalytic purifier and drying system before being introduced into the deposition reactor at a point close to the iron substrate. A flow rate of 200 ml min^{-1} was used in all the hydrogen reduction experiments as this rate had previously been shown to be high enough to ensure that the supply of hydrogen was not rate-controlling in the deposition process. Deposition experiments were carried out at various temperatures in the range 800 to 1200° C with and without hydrogen as a reducing agent, such that deposition occurred by either a combination of the hydrogen reduction and replacement reactions or by the replacement reaction alone.

2.2. Specimen examination

Specimens of mild steel (0.09 wt% C, 0.09 wt% Si) 10mm × 1 mm were polished on emery paper, degreased in acetone and weighed prior to insertion in the deposition reactor. After deposition the samples were reweighed, to yield data on the kinetics of the deposition reactions, and were examined in a "Cambridge 180" scanning electron microscope to determine the morphologies of growth achieved under the various experimental deposition conditions. In certain cases optical microscopy was also used to study the growth mechanism of the layers.

3. Results and discussion

3.1. Growth kinetics

The relationships between weight change of samples (after 2 h) and temperature are shown in Fig. 2 for the replacement reaction alone and for the combined reduction and replacement reaction. A curve is also plotted for an estimated weight change that may be attributed to hydrogen reduction alone. This curve is only approximate because its estimation relied upon the assumption that the replacement reaction contribution was the

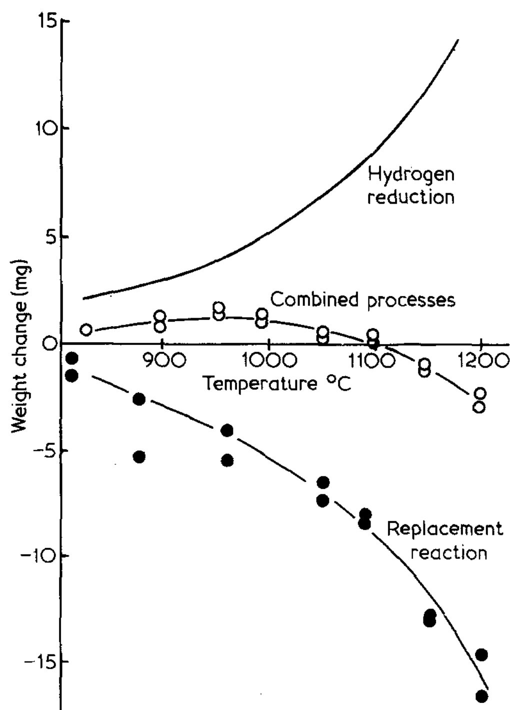
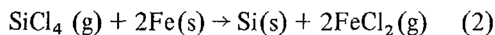


Figure 2 Relationships between weight change (after 2 h) and temperature for the combined reaction and the replacement reaction alone.

Figure 3 Surface morphology of layer produced by the combined reaction at: (a) 830° C; (b) 900° C; (c) 1000° C; (d) 1000° C edge of specimen; (e) 1100° C; (f) 1150° C.

same for the combined reaction and the replacement reaction alone. This is not completely valid because the deposition of extra silicon by the hydrogen reduction process will decrease the rate of the replacement reaction by creating a longer diffusion path for the replacement atoms. Consequently, the calculated curve will represent a minimum deposition that may have been achieved by the hydrogen reduction process.

The large weight loss of the specimens obtained in the replacement process occurred because, according to the stoichiometry of the deposition reaction,



$$SiCl_4\ (g) + 2Fe(s) \rightarrow Si(s) + 2FeCl_2(g) \quad (2)$$

an overall weight loss of 8.4 mg will be obtained for every 2.8 mg silicon deposited. The rates of deposition by both the replacement and combined

processes are both increased with increase in temperature. Fig. 2 shows that weight gains occur at temperatures in the range approximately 800 to 1100° C for the combined deposition process. This indicates that over the period of time investigated the average rate of deposition of silicon by hydrogen reduction was at least three times the rate of deposition by the replacement reaction. Consequently, it is evident that in this temperature range at least 75% of the silicon is deposited by the hydrogen reduction reaction with the remaining 25% being achieved by the replacement reaction. At temperatures above 1100° C, the samples lose weight as a result of an increase in the contribution of the replacement reaction to greater than 25% of the total silicon deposition. This demonstrates that the kinetics of the diffusion-controlled replacement reaction are increased more rapidly than those of the hydrogen reduction process over the temperature range 1100 to 1200° C.

3.2. Morphologies

3.2.1. Combined hydrogen reduction and replacement reaction.

Typical surface morphologies of the silicide layers produced at temperatures of 830, 900, 1000 and 1100° C in 2 h are shown in Figs. 3a to f. At 830° C smooth thin layers, which contain a few pores and show the grain boundaries and surface scratches of the original substrate, are produced. Such deposits are typical of low temperatures, low gas phase supersaturations and low growth rates. As the deposition temperature and the deposition rate increase, the growth morphologies become less smooth. Initially, at 900°C, significant disruption occurs at grain boundaries such that marked grooves can be seen on the surface layer. The most likely explanation for this type of surface disruption is the more rapid diffusion of the deposited silicon down the grain boundaries of the iron substrate. At 1000°C the growth morphology develops from that seen at 900°C such that a nodular dendritic growth occurs. Some of the grain boundary grooves that occurred at 900°C are still visible, however, the nodular growth can be seen to begin to form in regions between the grain boundary grooves (Fig. 3c). An interesting observation can be made in Fig. 3d which shows the edge of the specimen shown in Fig. 3c, and what had originally been the free space at the edge of the specimen. Large faceted silicon crystals have been produced by the hydrogen reduction reaction alone. These crystals are of the order of 60 μm in diameter compared to the 7 μm (approximate) diameter of the nodular growth from the iron substrate into the gas phase. The diffusion of silicon into the iron has apparently prevented the formation of compact faceted silicon crystals at these deposition rates. At the highest temperatures studied the nodular surface growths become more irregular (Fig. 3e) and eventually form large crystals of almost pure silicon on the surface of the growing layer (Fig. 3f).

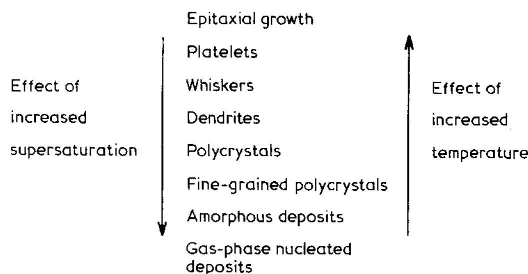


Figure 4 Effects of gas phase supersaturation and temperature on the surface morphologies produced by physical vapour deposition (after Blocher [10]).

This sequence of growth morphologies may be explained in terms of the effect of gas phase supersaturation upon the rate and growth of vapour-deposited layers. As outlined by Blocher [10] (Fig. 4) the effect of increasing the gas phase saturation and decreasing the substrate temperature in physical vapour deposition condensation growth is to move from expitaxial growth through platelets, dendrites, polycrystals to gas-phase nucleated powders. In the chemical deposition of silicon from silicon tetrachloride, increases in substrate temperature cause increasing gas phase supersaturation because the thermodynamics of both the hydrogen reduction and replacement reaction are favoured by increases in temperature. Consequently, the range of growth morphologies shown in Fig. 3 agree, in general terms, with predictions based on physical vapour deposition with a reversion of the substrate temperature effect and with certain slight changes in morphology brought about by the inter-diffusion of silicon and iron.

3.2.2. Replacement reaction

Figs. 5a to e show the range of surface growth morphologies obtained with the replacement deposition process at temperatures of 800, 860, 905, 980 and 1100°C. These morphologies are

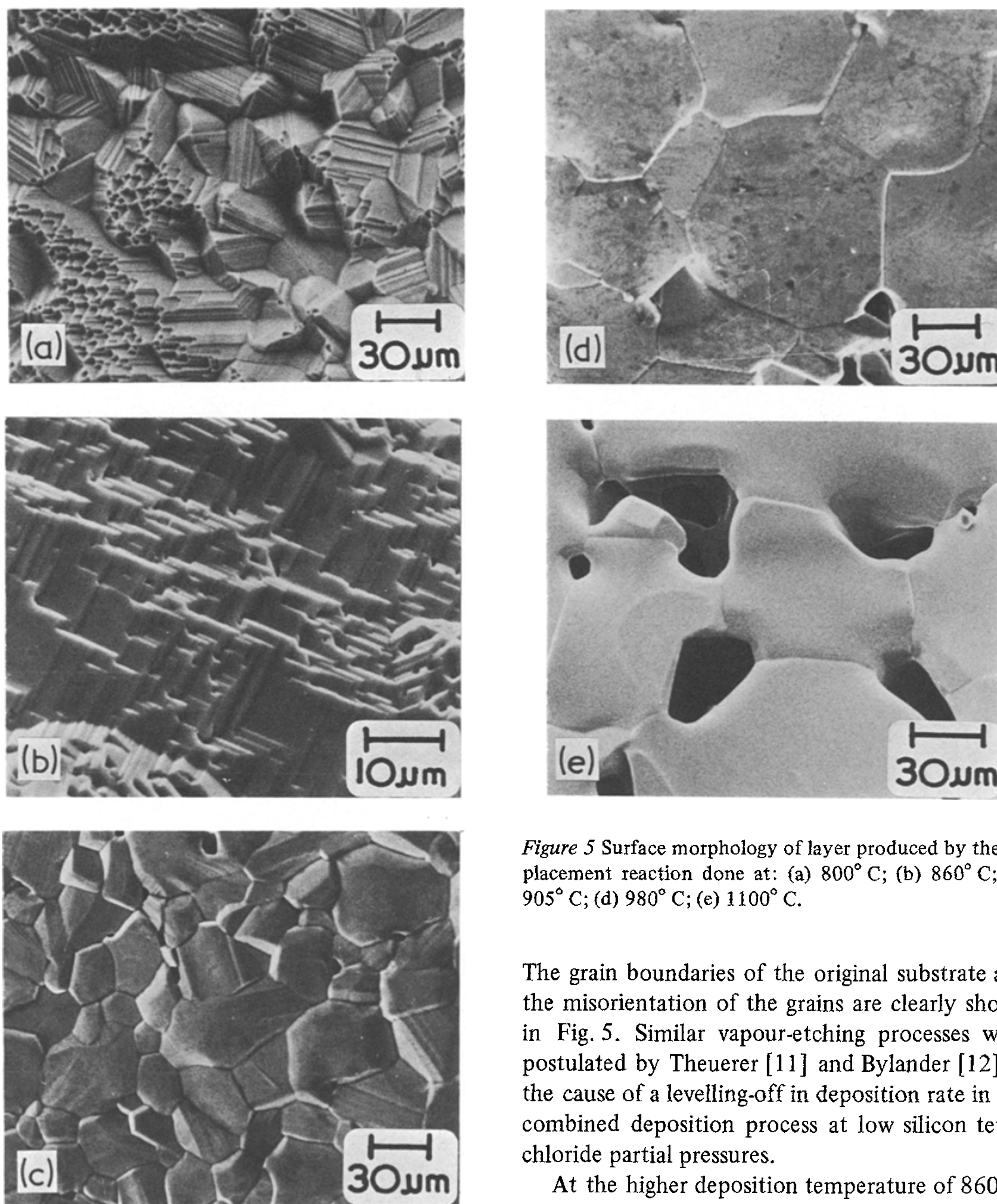
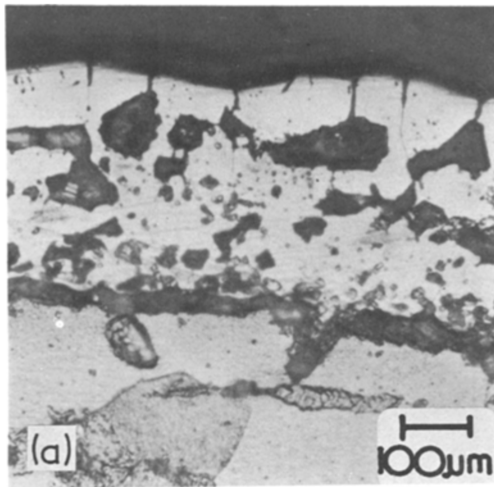


Figure 5 Surface morphology of layer produced by the replacement reaction done at: (a) 800° C; (b) 860° C; (c) 905° C; (d) 980° C; (e) 1100° C.

clearly very different from those obtained in the combined hydrogen reduction and replacement process. In general there is a reversal of the change in overall appearance of the layers with temperature when compared to the results of the combined process. The low temperature replacement layers are crystalline in appearance and are very similar to surfaces that have been thermally etched *in vacuo*. This morphology results from what is in effect a low temperature vapour etching process. The grain boundaries of the original substrate and the misorientation of the grains are clearly shown in Fig. 5. Similar vapour-etching processes were postulated by Theuerer [11] and Bylander [12] as the cause of a levelling-off in deposition rate in the combined deposition process at low silicon tetrachloride partial pressures.

At the higher deposition temperature of 860° C (Fig. 5b) the surface morphology still retains the etched appearance, however, many prism-shaped pores are apparent. At 905° C the grain boundaries are still visible, however, the increased rate of the replacement reaction at this temperature has produced a more general etching effect. Consequently, the reacted layer is flatter in appearance and is thus beginning to lose its characteristic three-dimensional grain, or crystal, morphology. The majority of the pores produced in the layers at 905° C are situated at grain boundary triple points and are apparently the result of preferential



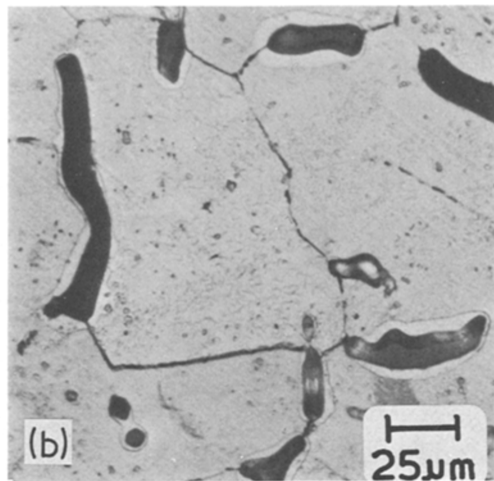


Figure 6 Cross-section of specimen produced by replacement reaction at 857° C (a) layer and substrate (b) centre of substrate.

reaction at grain boundaries and the higher grain boundary diffusion of the substrate atoms required for the continued deposition of silicon. At the upper temperatures studied, 980 and 1100° C, the silicide layers take on a flat appearance with an appreciable amount of surface porosity (Figs. 3d and e). Fig. 3e shows that the porosity extends into the layer and is very clearly a three-dimensional network of voids. It is apparent that at the higher temperatures and the higher rates of deposition the vapour-etched appearance of the low temperature deposits has been replaced by a flatter, much more porous growth which has resulted from the increased silicon–substrate diffusion interaction. This diffusion interaction, which requires the removal of two substrate atoms for each deposited silicon atom, produced extensive porosity in the silicide layer and throughout the substrate (Figs. 6a and 6b). The majority of the substrate porosity can be seen to be present at grain boundaries. The increased substrate porosity caused by the replacement deposits is evident on comparison of Fig. 6b with Fig. 7, which shows an equivalent point in a substrate that has been coated for the same period at the same temperature using the combined deposition reactions.

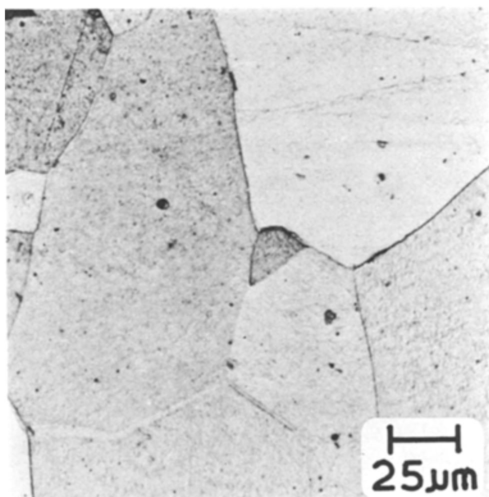


Figure 7 Cross-section of specimen produced by combined reaction at 830° C.

4. Conclusions

(1) At temperatures in the range 800 to 1100° C the overall deposition of silicon from silicon tetrachloride on to iron achieved by the combined hydrogen reduction and substrate replacement reactions in 2 h occurs by at least 75% hydrogen reduction. At higher temperatures of 1150 and 1200° C the rate of the replacement reaction increases more rapidly than that of the hydrogen reduction reaction and so the replacement reaction contributes to greater than 25% of the total deposition.

(2) The surface growth morphologies obtained by the deposition process are shown to vary with temperature in a manner that may be predicted from a consideration of the effects of gas phase supersaturation on growth morphologies in physical vapour deposition systems. As the deposition temperature is increased, the gas phase supersaturation increases and the growth mor-

phology changes from a smooth layer to a nodular dendritic layer and finally to a large-faceted nodule or crystal growth.

(3) The growth morphologies obtained with deposition by the replacement reaction alone are completely different from those obtained by the combined reaction. As the temperature is increased the surface morphologies of the deposits change from vapour-etched structures, showing grain boundaries and grain misorientation of the substrate, through a porous crystalline morphology to a very flat porous layer morphology. The extensive porosity obtained in both the deposit and the substrate results from the diffusion interaction of the iron and silicon that is required to maintain the deposition process.

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