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Effects of a silicon oxide layer on reactivity of silicon with copper(I) chloride

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The effect of an SiO_2 layer thermally grown or partially removed by standard cleaning treatment on the reaction between powder silicon or Si(100) wafer and solid or gaseous copper(I) chloride was studied. The rate of the reaction increases with decreasing oxide layer thickness, which is attributed to the formation of defects, such as pinholes, in the oxide layer, allowing the vapour transport of CuCl to the silicon surface. X-ray diffraction patterns indicate that the proportion of reaction products Cu_3Si, Cu_5Si and copper changes with thickness of SiO_2. In order to explain the presence of Cu_5Si and copper for thick layer and cavity formation inside Cu_3Si nuclei, it has been suggested that the reaction between Cu_3Si and CuCl is promoted.

1. Introduction

A clean silicon surface has a high affinity for oxygen and a silicon oxide layer about 2 nm thick (native oxide) quickly forms when the sample was exposed at room temperature in static air. Consequently, this thin oxide layer must be taken into account for all reactions between silicon and a gas or solid as recently suggested by Delarios *et al.* [1] for the effects of surface preparation on the kinetics of thermal oxidation of silicon. These authors related the properties of the cleaned surface to changes in the oxide growth mechanism and showed that (1 0 0) silicon wafers, given an HF final step prior oxidation (oxide thickness 0.5 to 0.9 nm), exhibit thicker oxides at a given time that the NH_4OH final clean (chemical oxide of approximately 1 to 1.5 nm). Liehr *et al.* [2] also investigated the effects of an oxide layer ($\leqslant 5$ nm) on chemical bonding and reaction at Pt/Si(1 1 1) and Ti/Si(1 1 1) interfaces. A comparative study has shown that the nature of the reaction with SiO_2 is very different for platinum and titanium and depends on the oxide layer thickness. Whereas titanium reduces the SiO_2 surface layer producing Ti–O bonds, platinum reacts with the silicon of the substrate through pinholes in the oxide layer to a thickness below 2.5 nm.

In our studies concerning the solid–solid reaction between silicon and CuCl, it was found that the reactivity of a freshly ground mixture is greater than that of the same mixture stored under static air for several days. This behaviour was believed to be due to the grinding which is effective in removing silicon dioxide from the silicon particles which results from Si–O bond cleavages [3] and generated clean crystallographic planes. In normal static air, the broken Si–O bonds react with the gaseous atmosphere generating oxygen-defect electron centres and decrease the reactivity with CuCl. In our work on the kinetics and mechanism of nucleation and growth of Cu_3Si compound from the reaction between powder or $Si_{(hkl)}$ wafers and solid, gaseous or molten copper(I) chloride [4, 5], we have undertaken a study of the effects of a silicon oxide layer on the reaction Si–CuCl where the oxide layer is purposefully increased by thermal oxidation of silicon or where the native oxide layer is thinner than about 0.6 nm, by chemical etching processes. The experiments were carried out using a powdered silicon–copper(I) chloride mixture in order to study the kinetic behaviour, and using a silicon wafer (Si(1 0 0) orientation) kept in a CuCl gaseous environment in order to investigate the influence of SiO_2 layer on nucleation and growth of Cu_3Si precipitates.

2. Materials and methods

The oxidation of powdered silicon proceeded in dry oxygen between 800 and 1000° C. Oxidation times ranged from 3 to 24 h giving oxide thickness between 51 and 282 nm (Table I) as calculated from the mass gain data, considering that the shape of the particles was close to spherical with an average diameter of 1.55 μm. The thickness of the native oxide on the silicon particle was supposed to be 2 nm, compared with that estimated in the case of wafers [1]. Silicon particles with about 1 nm SiO_2 thickness were

TABLE I Symbol and treatment procedures

Sample	SiO_2 layer thickness (nm)	Treatment conditions
Powder samples, mean diameter 1.55 μm		
1p	2	etching in 40% HF for 1 h
2p	2	native oxide
3p	51	thermal oxidation 800–1000° C
4p	100	
5p	195	
6p	382	
Si wafers, (1 0 0) orientation		
1w	0.6	etching in 40% HF for 150 min
2w	1.4	native oxide
3w	30	thermal oxidation at 900° C

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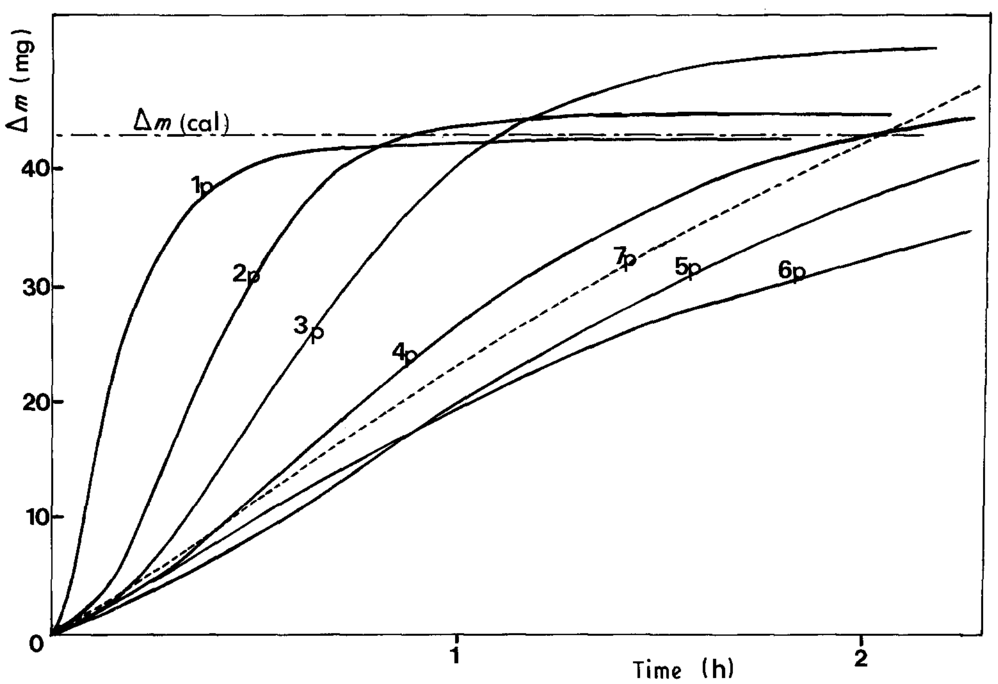

Figure 1 Effect of oxide thickness on kinetic behaviour. $\Delta m_{(\mathrm{cal})}$ represents the total consumption of CuCl by silicon.

prepared by dipping in 40% HF solution for 1 h to remove the oxide, rinsed in deionized water and then dried in vacuum (10^{-3} Pa). Wafers of n-type with Si(1 0 0) surface orientation were prepared as reported by Weber *et al.* [4]. The native oxide thickness determined from the AES intensity ratio $I_{\mathrm{O}kll}$ (51 eV)/$I_{\mathrm{Si}lmm}$ (92 eV) from Equation 1 of [6] is 1.4 nm. After dissolution of this native oxide in 40% HF for 150 min, the thickness was calculated to be 0.6 nm. A sample was also oxidized in dry oxygen at 900° C for 3 h giving an oxide thickness of about 30 nm. Table I gives the samples and treatment procedures of the oxide layers.

The mass changes for kinetic studies were measured using a McBain thermobalance with a sensitivity of 0.02 mg. 10 mg Si + CuCl mixture (Si/CuCl molar ratio of 1.76) were uniformly spread at the bottom of a scoop suspended from a quartz spring and placed in the reactor. The reactor was maintained under vacuum by pumping (1 Pa) at room temperature for 1 h, then preheated at 205° C for 30 min during which time no mass change occurred, and finally the temperature was raised to the reaction temperature of 257° C. The mass changes were calculated for 100 mg CuCl.

For the reaction between gaseous CuCl and Si(1 0 0) wafer the experimental apparatus used has been described elsewhere [4]. Briefly, it consisted of a glass tube placed in a horizontal tubular furnace which had a temperature gradient in the central zone. CuCl was evaporated at 250° C and a continuous flow was maintained by pumping (1 Pa) on a silicon wafer heated at 300° C. Chemically pure copper(I) chloride was used (puratronic 99.999%).

The reaction products were identified using conventional techniques such as X-ray diffraction, optical metallography, scanning electron microscopy and electron microprobe analysis.

3. Results

The effect of oxide layer thickness on kinetic behaviour was demonstrated directly by observing the loss mass, Δm, with time (curves 1p to 6p, Fig. 1) when the mixtures CuCl–Si were heated under vacuum at 257° C. Curve 7p corresponds to CuCl sublimation when it is placed alone in the scoop. As noted by previous investigators [7, 8] the mass change is associated

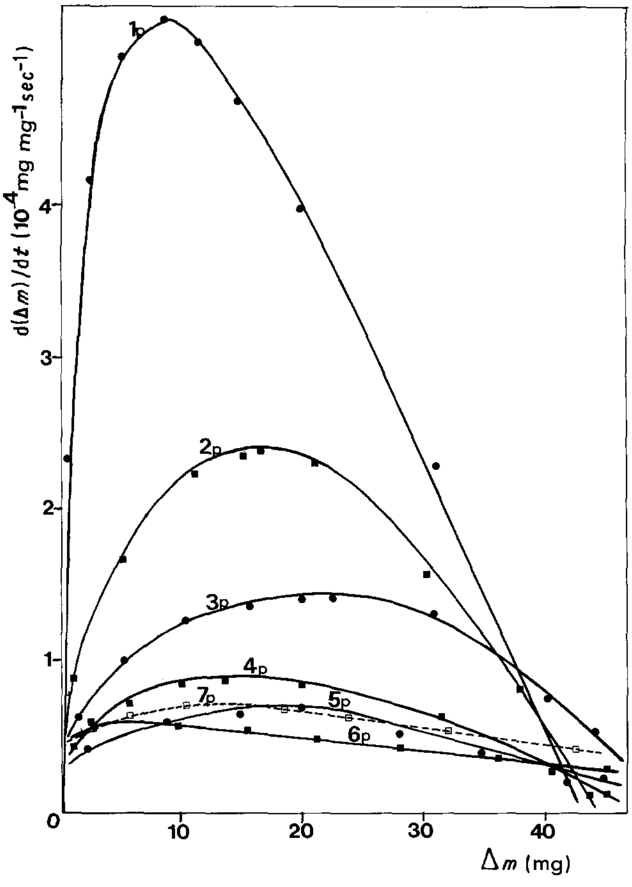

Figure 2 Effect of oxide thickness on the oxidation rate.

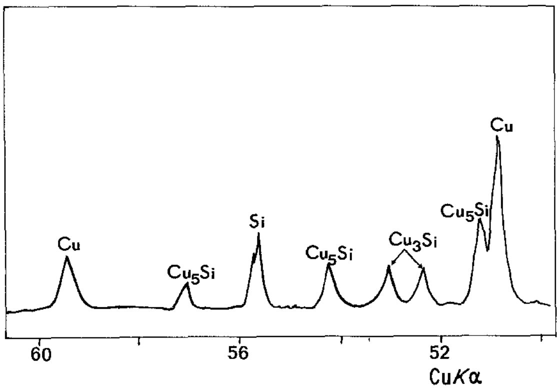

Figure 3 X-ray diffraction patterns obtained after reaction of powder silicon with CuCl (silicon covered by an SiO_2 layer of 100 nm).

with gas evolution ($SiCl_4$) occurring as a result of the reduction of CuCl by silicon. In our case (except for curve 1p and also curve 2p) the experimental loss mass (Δm_{exp}) for the thick oxide layers was different for each starting mixture, and was greater than that calculated (Δm_{cal}) on considering the total consumption of CuCl by silicon. The difference, $\Delta m_{exp} - \Delta m_{cal}$, was associated with the partial sublimation of CuCl which increased with the thickness.

The curves revealed the typical S-shape characteristic of a nucleation growth mechanism, i.e. the rate initially increased, reached a maximum and then decreased [5]. The $d(\Delta m)/dt = f(\Delta m)$ curves (Fig. 2) indicate that the reactivity of the mixture decreases with increasing oxide layer thickness, which also displaces the maximum rate $(d(\Delta m)/dt)_{max}$ towards high Δm values. In addition, these curves show that the rate associated with CuCl sublimation is predominant for thick oxides; the rate becomes a linear function of Δm from the low reaction times (curve 6p, Fig. 2) indicating that the reaction is inhibited and thus may be identified as CuCl sublimation (curve 7p, Fig. 2).

In the phases obtained after oxidation, X-ray diffraction patterns indicate the presence of copper, Cu_3Si and Cu_5Si compounds (Fig. 3). Fig. 4 shows the evolution of R_1, R_2 and R_3 ratios of the peak height corresponding to these phases with SiO_2 thickness where R_1, R_2 and R_3 are defined as

$$\begin{aligned} R_1 &= [Cu_{(0.208\,nm)} + Cu_{(0.180\,nm)}]/ \\ &\quad [Cu_3Si_{(0.203\,nm)} + Cu_3Si_{(0.200\,nm)}] \\ R_2 &= [Cu_{(0.208\,nm)} + Cu_{(0.180\,nm)}]/ \\ &\quad [Cu_5Si_{(0.196\,nm)} + Cu_5Si_{(0.187\,nm)}] \\ R_3 &= [Cu_5Si_{(0.196\,nm)} + Cu_5Si_{(0.187\,nm)}]/ \\ &\quad [Cu_3Si_{(0.203\,nm)} + Cu_3Si_{(0.200\,nm)}] \end{aligned}$$

According to the evolution of R_1 and R_2 ratios, we deduce that the proportion of the phase changes with thickness of SiO_2, copper and Cu_5Si being preferentially formed for thick layers. The curve in Fig. 4 relative to the R_3 ratio confirms the disappearance of Cu_3Si if the thickness of SiO_2 is increased.

When silicon wafers were reacted with $CuCl_{(g)}$ for 4 h at 300° C and after dissolution of copper in concentrated ammonia solution, we observed numerous precipitates crystallized epitaxially on the single-crystal substrate. Fig. 5 compares two reacted wafers. One wafer was given no pretreatment (Fig. 5a) and the other was etched in 40% HF (Fig. 5b). It is apparent that nearly the entire surface of the HF-etched wafer had reacted while the wafer covered with native oxide had discrete precipitates. Coating the wafer surface with 30 nm or more of SiO_2 partially or completely inhibited active site formation. In addition, wafers treated with HF acid revealed, in addition to Cu_3Si precipitates which were typically 5 to 10 μm in size, square pits about 5 μm in size aligned with the Si(1 0 0) planes [5] (Fig. 6). Fig. 6 also shows that the square pits contained patches of Cu_3Si.

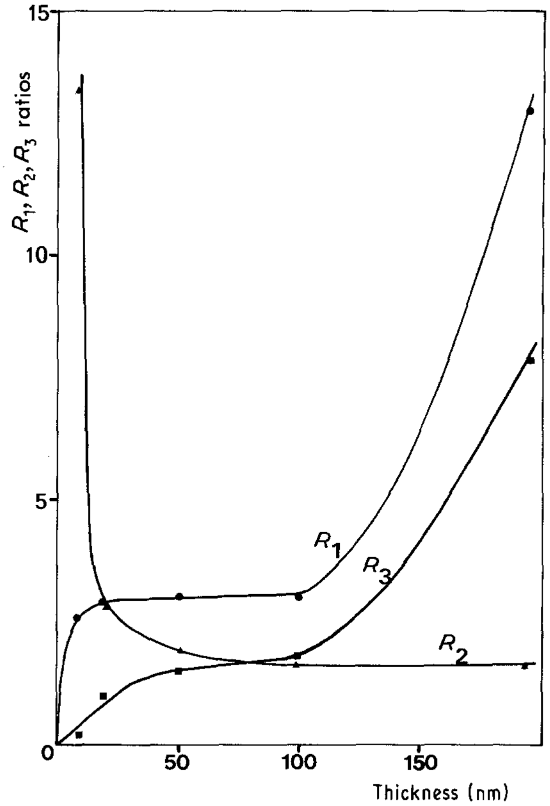

Figure 4 Evolution of R_1, R_2 and R_3 ratios as a function of oxide thickness.

4. Discussion and conclusion

These results clearly reveal that thermally grown SiO_2 passivated the silicon surface. As thermodynamically, SiO_2 does not react with gaseous or solid CuCl, this oxide layer is a barrier to CuCl–Si contact. Indeed, from work on thermal oxidation of silicon [9–11] and various silicides [12], the growth of an SiO_2 layer may be accomplished above 600° C by the transport of oxidant across the SiO_2 film and subsequent reaction of the oxidant with silicon at the Si–SiO_2 interface. It is thus unlikely that in our experiments, when the temperature is reported to be between 250 and 300° C, that the silicon atoms could diffuse through the SiO_2 layer and react with CuCl at the SiO_2–CuCl interface.

We shall rather consider the vapour transport of CuCl particles through defects such as pinholes always present in the SiO_2 oxide as recently suggested by Banholzer *et al.* [13]. In this hypothesis, the reactivity of the powder or silicon wafer with CuCl depends on

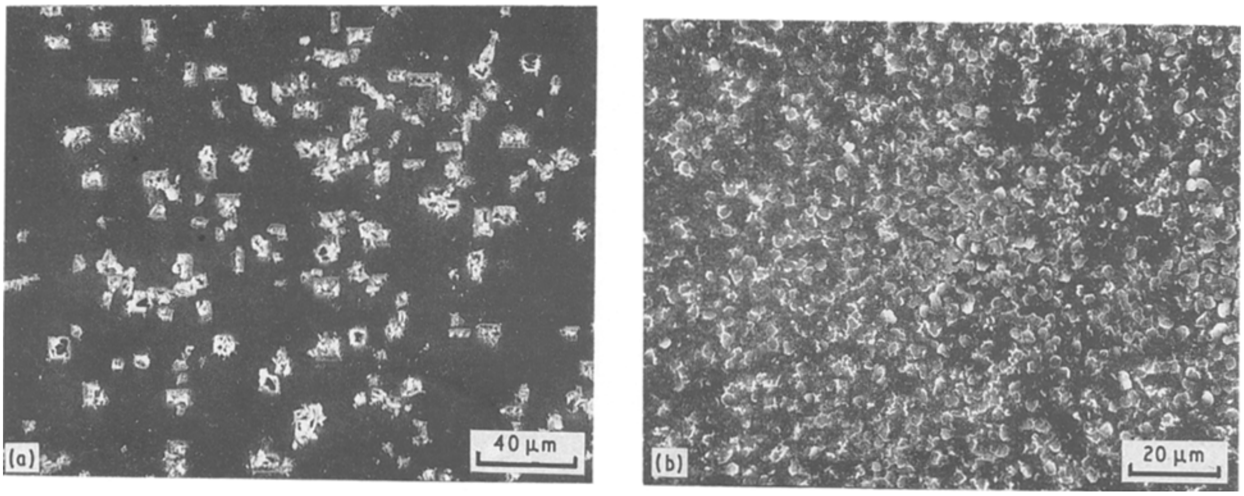

Figure 5 Scanning electron micrographs of two (1 0 0) wafers reacted under identical conditions but with different oxide thicknesses: (1) 1.4 nm, (b) 0.6 nm.

the defect density, which is a function of the SiO_2 thickness. When the defect density was increased by chemical etching with HF, the vapour transport of CuCl became easier, allowing the reaction of Si–CuCl to proceed. Additionally, when the defect density was decreased by the growth of a thicker SiO_2 layer which filled the pinholes, the reaction Si–CuCl proceeded at a reduced rate.

It is also necessary to consider that a thin reactive layer of the SiO_x ($x < 2$) type, which gradually increases the oxygen content, exists at the interface between silicon and SiO_2 whose composition and electronic properties differ from those of bulk silica, as postulated by many workers [14, 15]. This intermediate SiO_2 layer, about 0.5 nm thick, which is present in the early stages of oxidation or after etching with HF, might also modify the reactivity of CuCl with silicon. In particular, as the layer of reactive oxide persists between silicon and SiO_2 as oxidation proceeds, CuCl will react on the outside of the reactive layer (the boundary between amorphous silica and the reactive oxide) and not reach the silicon/oxide interface. Moreover, Hollinger [14] suggested that a 1.5 nm SiO_2 layer exists where the properties are different from that of the bulk oxide.

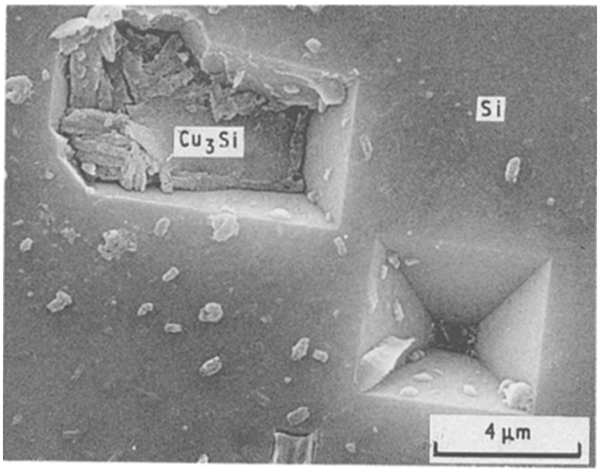

Figure 6 Scanning electron micrograph showing square pits and residual patches of Cu_3Si on Si(1 0 0) wafer treated with HF and after reaction with CuCl for 4 h at 300° C.

It should also be emphasized that the thickness of the oxide layer seriously changes the proportion of phases formed when the coexistence of various compounds (Cu_3Si and Cu_5Si) was demonstrated. Previous studies [5] have established that the reduction of CuCl by silicon leading to copper as the final phase may conceivably be explained if simultaneous and successive reactions are taken into account

$$7\,Si + 12\,CuCl \rightarrow 3\,SiCl_4 + 4\,Cu_3Si \quad (1)$$

$$9\,Cu_3Si + 8\,CuCl \rightarrow 2\,SiCl_4 + 7\,Cu_5Si \quad (2)$$

$$Cu_5Si + 4\,CuCl \rightarrow SiCl_4 + 9\,Cu \quad (3)$$

It is apparent from X-ray diffraction data that the intermediate Cu_3Si compound was preferentially consumed by CuCl when the reactivity of the mixtures decreased, i.e. for thicker layers and for reaction times greater than 4 h when in these conditions Cu_5Si and copper are present. Scanning electron micrographs of wafers etched in HF and after reaction with CuCl indicate the Cu_3Si consumption. Both observations, which seem contrary, can be explained by assuming that the copper precipitates were not formed by the same process in the case of mixtures or wafers. Indeed, in considering Equations 1 to 3, it appears that the easier the reaction of Cu_3Si formation, the greater the amount of copper produced from Cu_3Si consumption. This condition is realized for wafers etched in HF with a very small thickness of oxide when the amount of Cu_3Si increases and consequently so does the amount of copper. Important also in this mechanism is the large amount of Cu_3Si and copper produced on silicon wafers cleaned in HF, compared to that obtained for silicon particles covered with 10 nm or more of SiO_2. In this case, as SiO_2 was found to prevent the Si/CuCl reaction, the amount of Cu_3Si was slight and allowed Reaction 2 to proceed. Following Cu_5Si formation, the next step is the reaction of Cu_5Si and CuCl to produce copper as the final phase, as observed by X-ray diffraction.

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