

Active Site Formation in the Direct Process for Methylchlorosilanes

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The direct process for methylchlorosilane production was studied in a laboratory-scale fluidized bed reactor. The silicon was found to have discrete sites at which silanes were produced. The density of sites was controlled by the nature of the native oxide layer over the silicon. The active sites displayed regular geometry, indicating an anisotropic silicon reaction which preferentially leaves (111) planes exposed as the reaction proceeded. Carbon and SiO₂ layers 200 Å thick prevented active site formation. © 1986 Academic Press, Inc.

INTRODUCTION

A key step in the synthesis of silicone polymers is the reaction of silicon with methyl chloride to form methylchlorosilanes (1). This reaction, called the direct process, is accomplished without the formation of intermediate species. The reaction can be very selective when catalyzed by copper, producing up to 90 wt% dimethyldichlorosilane (1, 2). The direct process was discovered in 1939 by Rochow (3), and during the last 40 years there have been numerous related publications. Unfortunately, there is a lack of direct mechanistic information about the reaction. This paper describes a microscopic examination of the nature of reacting silicon.

EXPERIMENTAL METHODS

The reactor and operating procedures used in this investigation have been described previously (4). Reactions of Si powder with CH₃Cl were performed in a glass laboratory-scale fluidized bed reactor shown schematically in Fig. 1.

Metallurgical grade Si was used as bed material (for elemental analysis see Ref. (4)). Bed Si was prepared by grinding, aerodynamic classification, and reblending. The

final product had particles with sizes ranging from 300 to <1 μm. The BET surface area of the reblended Si was 0.55 m²/g. Copper was added as CuCl. Zinc and tin metal were added as promoters such that the overall composition was: 5 wt% Cu, 0.5 wt% Zn, and 75 ppm Sn. The product distribution of methylchlorosilanes was determined by GC analysis.

Single crystal Si wafers were also used as an ultrapure Si source. Boron-doped (20 ppb) wafers with (100) and (111) orientation were used in the experiments. Boron is believed to have no effect on the reaction when present at such low levels. The wafers were cut to 6 × 9 mm using a diamond saw. They were cleaned with CH₃OH + (CH₃)₂O + Cl₃CCH₃ (1:1:1), and freshly prepared Karos solution (Karos = 1:1 hot concd H₂SO₄ and 30% H₂O₂). A second procedure subjected the wafers to an additional etching step using aqueous 1% HF after the Karos to remove SiO₂. For reaction the wafers were mounted between glass fingers on the reactor stirrer blades (see Fig. 1). This exposed the wafers to the same reaction environment as the Si bed in the reactor.

The preparation of a Si charge prior to reaction was found to greatly influence the product distribution (1). This pretreatment is commonly called activation or contact mass formation. In the present work con-

¹ Member CRD Material Characterization Operation.

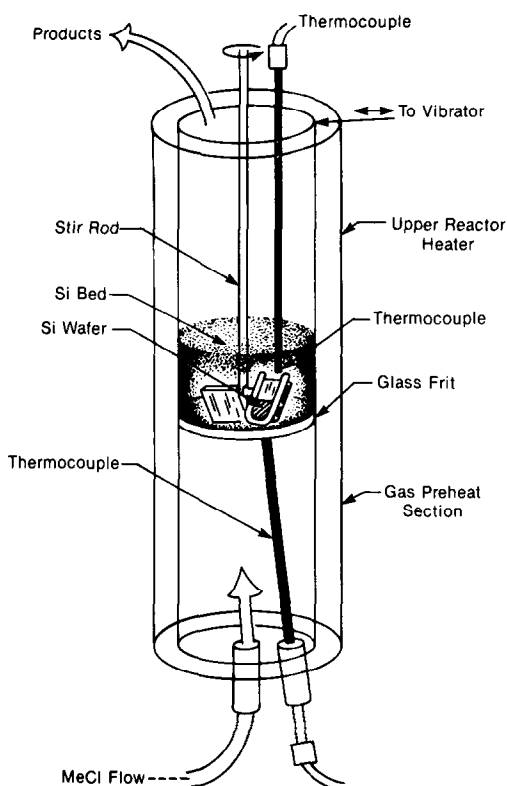


FIG. 1. Schematic of laboratory fluidized bed reactor.

tact mass preparation (including wafers) involved slurring ground CuCl with Si in hexane, evaporating the hexane, and heating to 380°C under Ar in a tube furnace for 1 h. Following heating the contact mass (and the wafers) was loaded into the reactor. Reactions were carried out at 300°C and stopped at various points (by replacing the MeCl with Ar) to determine the changes in the active regions with time.

To study the CuCl-Si reaction in detail, 2–50 μm CuCl particles were deposited on a Si wafer by dipping in a CuCl-hexane slurry. The coated wafers were then placed in a furnace at 380°C for a measured time (1 to 60 min), after which they were removed for examination. This treatment simulated processing the wafers received when they were mixed with bed powder, but allowed the wafer surfaces to remain free of Si particles. The hexane slurry process was used to disperse the CuCl particles.

The furnace experiments with wafers were supplemented using controlled atmosphere hot stage microscopy. In these experiments a CuCl particle and the surrounding Si surface was observed through an optical microscope as the temperature was increased, allowing real time observation of the CuCl-Si reaction.

RESULTS

CuCl-Si Reaction

Figure 2 shows CuCl-coated wafers before and after heating for 1 h at 380°C. The two cleaning procedures described above were used prior to coating with CuCl. Observation of wafers following heating to 380°C revealed the presence of new satellite particles which formed a halo around the original large CuCl particles. The satellite particles were typically 2 μm (see Fig. 2). Wafers treated with HF acid had more satellite particles than those wafers not treated with HF. Mechanical damage to the wafer surface caused particles to be preferentially deposited in the region of the damage. For example, scraping the wafer surface with a diamond scribe resulted in a large number of particles being deposited in the scratch.

To determine if particle deposition occurred via the gas phase, a Karos cleaned wafer which was not coated with CuCl was placed next to a wafer coated with CuCl. After heating small particles were found on both wafer halves. Analysis of the particles by Auger Electron Spectroscopy and Electron Microprobe revealed that the particles consisted primarily of Cu with a surface layer of Cu and Cl.

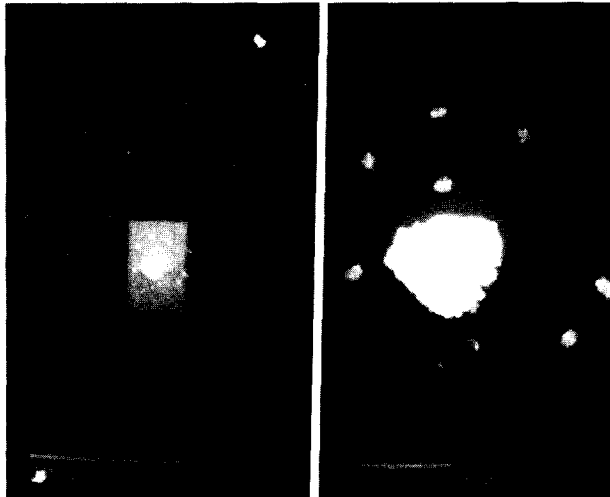
The formation of satellite particles around large CuCl particles was also studied with a controlled atmosphere hot stage using light microscopy. Satellite particle formation was found to occur within seconds at 300°C, while at lower temperatures (260–300°C) it proceeded at a reduced rate.

Heating a mixture of CuCl and Si produced a liquid condensate at the furnace outlet. The liquid was analyzed by GC-MS

**CuCl on
Silicon Wafer (100)**



**CuCl on
Silicon Cleaned in
 H_2SO_4/H_2O_2
Heated to 380 °C**



**CuCl on
Silicon Cleaned
in 1% HF,
Heated to 380 °C**

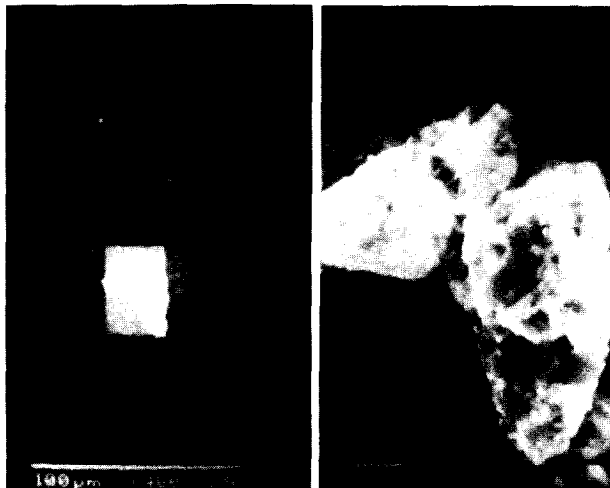


FIG. 2. SEM photos showing development of precipitates on a (100) wafer. Shown are CuCl particles on a Karos-cleaned (100) wafer before and after heating to 380°C in Ar for 1 h, and a (100) wafer heated to 380°C for 1 h which in addition to the Karos cleaning was etched in 1% HF.

to be SiCl_4 (90 wt%) and Si_2Cl_6 . Greater than 95% of the Cl from the CuCl reacted to form silanes.

Reaction with CH_3Cl

Figure 3 compares SEM micrographs of Si particles before reaction with CH_3Cl (Fig. 3a) and after 38% of the bed Si had reacted (Fig. 3b). Reaction of Si with CH_3Cl resulted in the formation of pits in the Si particles. The pits develop from the formation of volatile methylchlorosilanes which removes Si. The same phenomenon was seen on the Si wafers (Fig. 4). Pit size did not depend on the size of the initial CuCl particle. CuCl particles from 1 to 200 μm were used yet the pits were typically 5 to 10 μm in size.

The orientation of the exposed Si surface had a significant effect on the shape of the reaction sites. Square pits were observed when the (100) plane was exposed; hexagonal and/or irregular sites were observed when the (111) plane was exposed (see Fig. 4). The top edges of the square pits on the (100) wafers were aligned with the Si (110) planes. When viewed in cross section the sides of the pits in the (100) wafer were triangular producing a three-dimensional structure similar to an inverted square based pyramid. Figure 5 is a TEM bright field image, and corresponding electron diffraction pattern, showing a cross-sectional view of a reaction pit from a (100) oriented wafer. The diffraction pattern has been oriented with respect to the image utilizing a rotation calibration. Analysis of the diffraction pattern showed that the sides of the pit are (111) planes. In addition, Energy Dispersive X-Ray Spectroscopy showed that the dark spherical particles observed within the pit are Cu rich.

Figure 6 shows the change of active sites as the $\text{Si}-\text{CH}_3\text{Cl}$ reaction proceeded. The pits became deeper but only slightly wider on a (100) surface as the reaction proceeded. For reaction times less than 8 h (bed Si utilizations less than ca. 60%) active

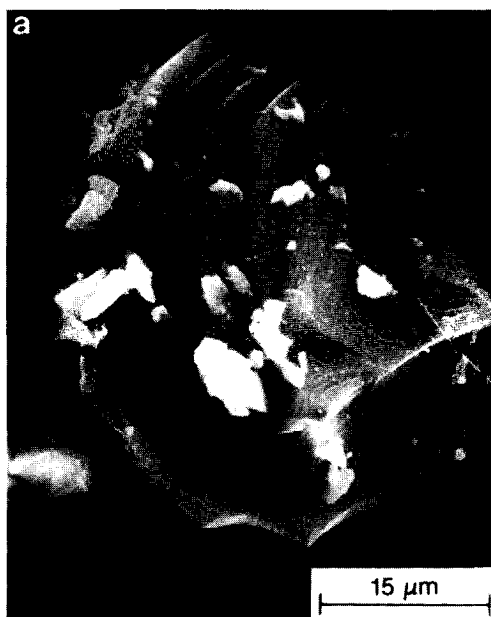
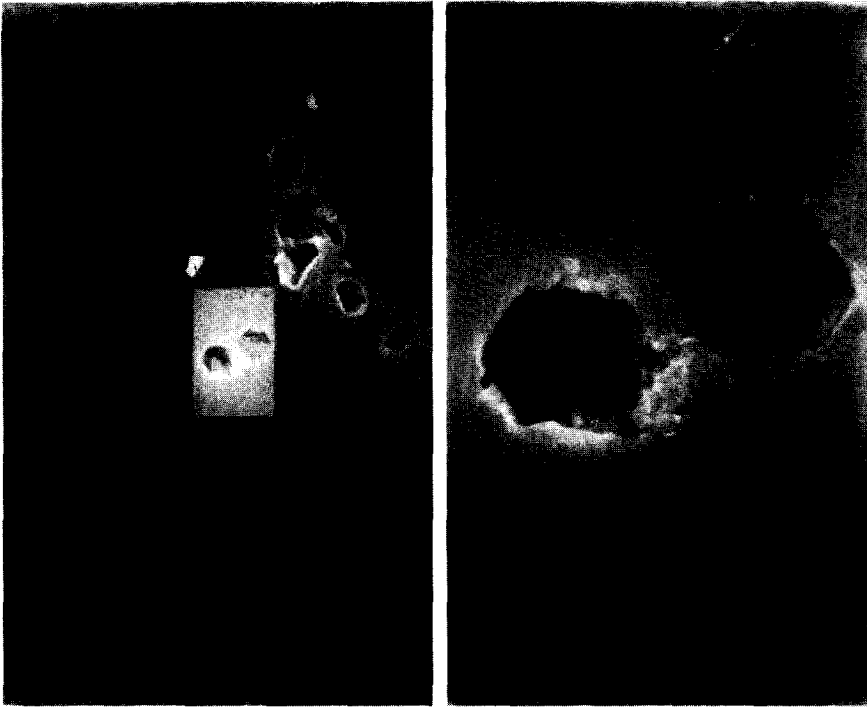


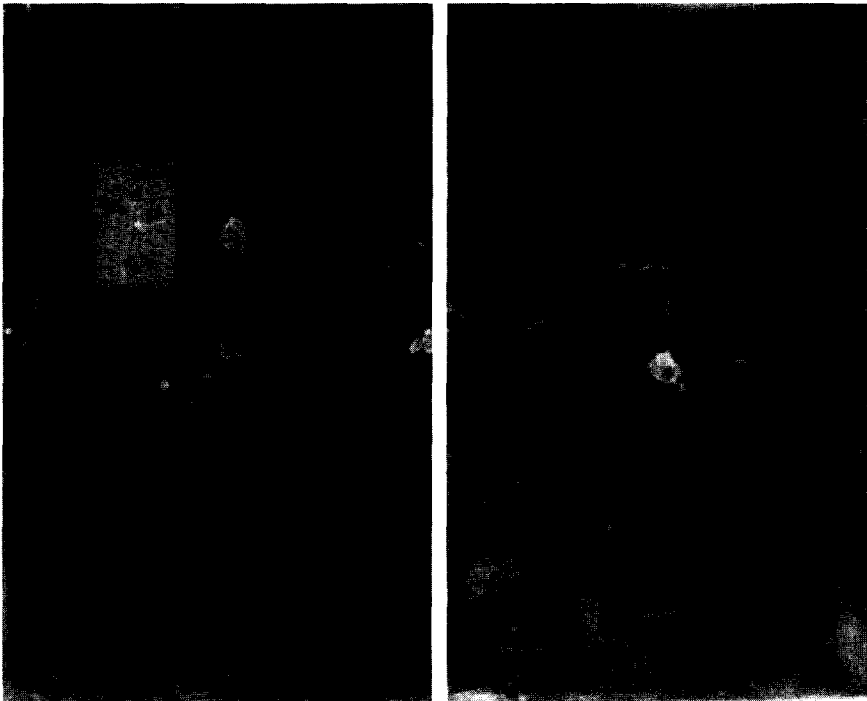
FIG. 3. SEM photo of Si particles before (a) and after (b) reaction with CH_3Cl in lab-scale fluidized bed for 4 h (Si utilizations 38%) using $\text{Cu}/\text{Zn}/\text{Sn}$ catalyst at 300°C .

regions on (100) wafers retained the square appearance when viewed from the top.

Figure 7 compares two reacted wafers. One wafer was given the standard cleaning



Si (111)



Si (100)

FIG. 4. SEM photo of (100) and (111) Si wafers cleaned with an organic and Karos wash (see text for details) after reaction with CH_3Cl in the fluidized bed for 4 h under same conditions as in Fig. 3.

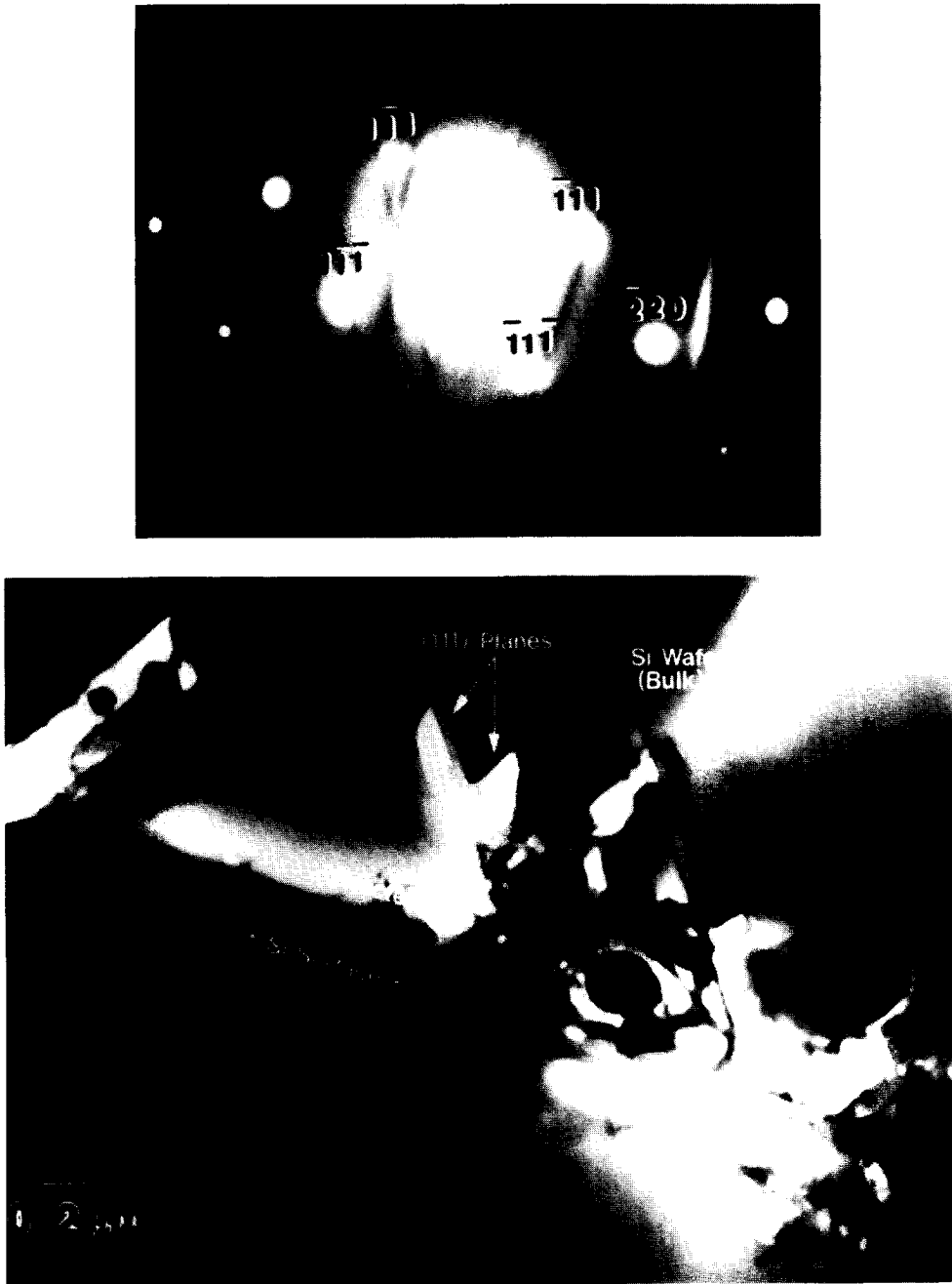


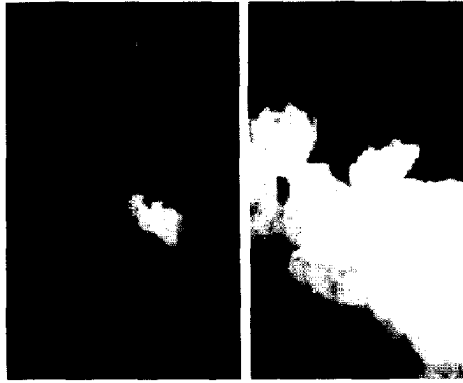
FIG. 5. TEM bright field image and corresponding electron diffraction pattern of a cross section through a reacted area on a (100) wafer.

treatment (organic wash + Karos cleaning) prior to coating with CuCl, and the other was etched in 1% HF in addition to the standard cleaning prior to CuCl coating. It

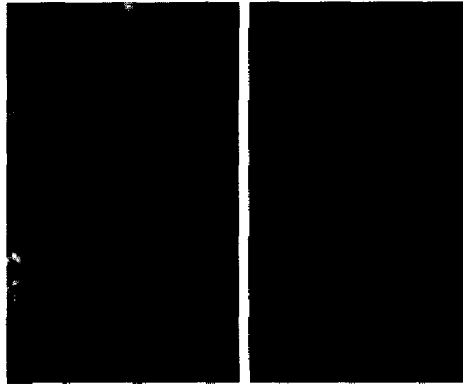
is apparent that nearly the entire surface of the HF etched wafer had reacted while the Karos-cleaned wafer had discrete pits.

Several wafer treatments were found to

CuCl on
<100> Silicon
Wafer Heated
to 380 °C
in Argon



CuCl on
<100> Si
Wafer Reacted
30 Minutes
with CH₃Cl



CuCl on
<100> Si
Wafer Reacted
90 Minutes
with CH₃Cl



CuCl on
<100> Si
Wafer Reacted
10 Hours
with CH₃Cl

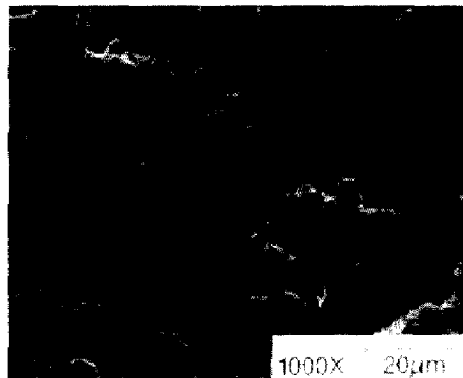


FIG. 6. Development with time of reacted areas on a (100) wafer.

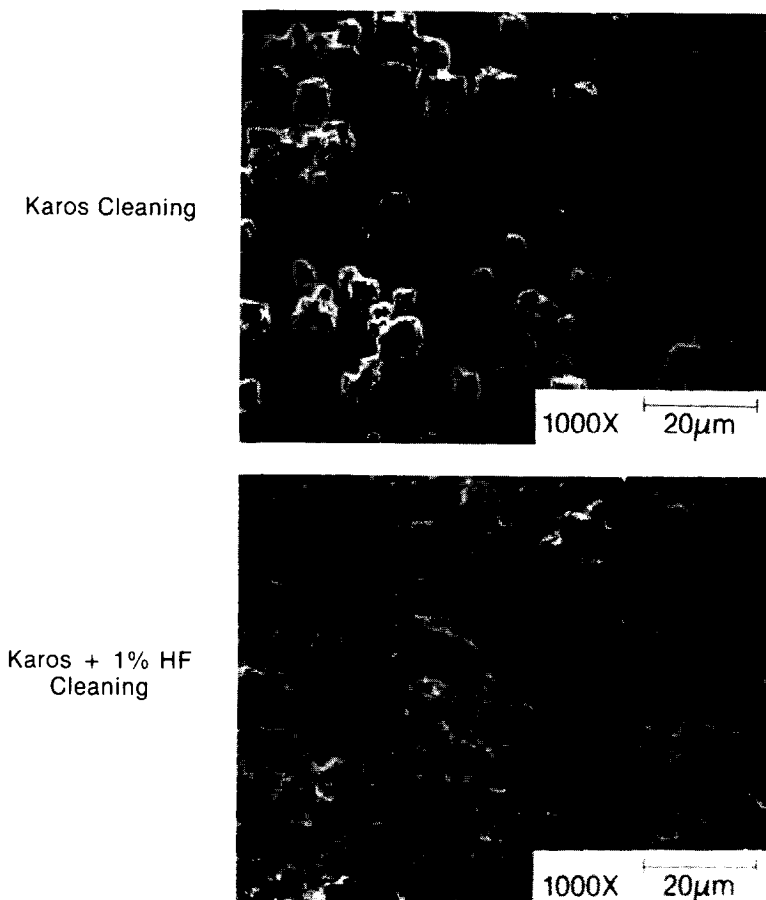


FIG. 7. SEM photos of two wafers reacted under identical conditions but cleaned by different procedures (see text for details).

prevent reaction. Coating the wafer surface with 200 Å or more of sputtered carbon prior to slurring with CuCl completely inhibited active site formation. Thermally grown SiO₂, 0.02 μ m thick, also passivated the surface.

DISCUSSION

Reactive Site Formation

It is generally accepted that the direct process occurs at the surface of Cu₃Si (η phase). Thus the pits seen in Figs. 3 and 4 may be patches of Cu₃Si. When CuCl is the source of Cu, the first step in the formation of these patches is gas phase transport of CuCl from CuCl particles to adjacent Si surfaces. Precipitate growth must occur via

gas phase transport, not surface diffusion, since in this study Cu precipitates were observed on wafers physically separated from CuCl-coated wafers during heating.

Silicon which has been exposed to air is covered by a layer of native SiO₂. This oxide layer is a barrier to Cu—Si contact. Native SiO₂ possesses defects, such as pinholes (5, 6). It is suggested that CuCl preferentially deposits at these defects. When the defect density was increased, by scratching or chemically etching with HF, the amount of Cu deposited and the amount of Si surface reacted was larger. Additionally when the defect density was decreased (i.e., by growing a thicker SiO₂ layer which will fill pinholes) the surface was unreacted.

Following vapor transport of CuCl the

next step is reaction of CuCl and Si to Cu and primarily SiCl₄:



When the first atomic layer of CuCl is deposited, intimate contact of CuCl and Si is established (through pinholes in the native oxide) allowing the above reaction to proceed. Cu and Si then combine by diffusion to form Cu₃Si. For the Cu₃Si to grow in thickness, additional CuCl deposits on it and reacts with the Si present again forming SiCl₄. Copper then diffuses away from the CuCl/Cu₃Si interface. The flux of Cu is toward the Cu₃Si/Si interface, at which new Cu₃Si forms. The alternative mechanism for the growth of the Cu₃Si layer involves Si diffusion from the Cu₃Si/Si interface to the CuCl/Cu₃Si interface. However, it has been established that Cu diffuses much more rapidly than Si in Cu₃Si (7). Thus, Cu diffusion is the dominate force in the formation of η phase.

Reaction Site Geometry

The square reacted areas with sides consisting of (111) planes observed on (100) oriented wafers, and hexagonal sites on (111) oriented wafers, indicates that one or more of the reaction steps are anisotropic. Analysis of the geometry of the active region must account for the orientation dependence of the reaction.

The anisotropic reaction exhibited in the MCS direct process has some similarities to crystallographic etches used by the electronics industry. Several solutions have been developed which dissolve Si preferentially in one or two crystallographic directions. These etches are generally slowest in the $\langle 111 \rangle$ direction exposing (111) planes as etching proceeds (8–12). The difference in etch rates for the low index planes has been correlated with the number of “free” bonds available at the surface (12). The larger the number of dangling bonds the faster the etch rate. The (111) planes of a diamond structure, such as Si,

have the smallest number of free bonds and thus etch the slowest.

Crystallographic etches remove Si in a two-step process. The first step is Si oxidation with an oxidizing agent (i.e., HNO₃, KOH, H₂O₂, Br) to form SiO₂. SiO₂ is relatively insoluble so a second step is required to dissolve the oxide and remove Si. The MCS process can be thought of in similar terms. Silicon is reacted (etched) with CH₃Cl to form a product (methylchlorosilanes) which is volatile thus removing Si. In order for the orientation dependent etches and the direct process to be anisotropic they must both be controlled by surface reactions and not diffusion.

When the (100) plane of Si covered with a native oxide is exposed to an orientation dependent etch, pits are formed shaped like inverted square based pyramids (8), very similar to the reaction sites observed in this work. The etch pits are believed to occur at pinholes in the native oxide substantiating the idea suggested above that the satellite Cu particles observed when CuCl on Si is heated are the results of nucleation at pinholes in the oxide.

Copper is required to catalyze the direct process. Any explanation of the anisotropic nature of the reaction must include the role of the catalysts. As stated above it is postulated that the active species in the Cu catalyzed direct process is Cu₃Si (η phase) (1). Recent experiments using pure η phase confirm its high selectivity for the production of dimethyldichlorosilane (13, 14). Weber and Gillot have studied the formation of η phase at 300°C from the gas phase deposition of CuCl (15). In their work CuCl was reacted with Si, forming precipitates at discrete sites on the wafers. Growth on a (100) plane resulted in square precipitates with a triangular cross section. These precipitates were very similar in shape to the pits observed in this work. Weber and Gillot suggested the geometry of the particles was the result of epitaxial growth of η phase over Si.

Weber and Gillot gave no evidence that

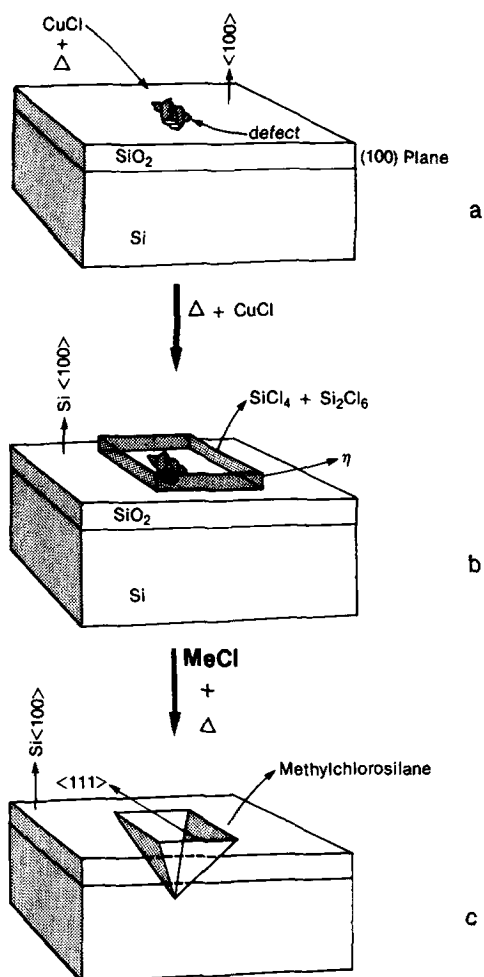


FIG. 8. Diagram illustrating proposed model for reaction site formation. (a) Vapor CuCl transport to defect in SiO₂, (b) reaction of CuCl with Si leaving Cu deposits, and Cu-Si alloying possibly to form η phase, (c) reaction of Si with CH₃Cl to form methylchlorosilanes.

the precipitates they observed were η phase and not simply Cu, or any reason why they had the shapes observed. Thus there is some question whether the precipitates observed for CuCl deposition of Cu on Si is actually η phase. However, it is clear that the orientation of the Si substrate was contributing to the shape of the precipitates formed. If similar structures are created in the preparation of contact mass from the reaction of CuCl and Si, the shape of these

precipitates may produce the geometry of the pits observed when the Cu-Si phase is reacted with CH₃Cl.

A possible explanation for the shape of the precipitates observed by Weber and Gillot is based on differing reaction rates (η phase formation) for Cu in the three primary lattice directions. If η phase is the active species in the direct process the Cu precipitates must combine with Si. Copper has been found to diffuse readily in η phase (16), however Cu reaction with Si at the η -Si interface may be anisotropic. The Si (111) planes are the most densely packed crystal planes. Crystal dissolution by alloying in Si is slower in the <111> direction than in either the <100> or <110> directions (17). Hindered reaction (alloying) in the <111> direction would result in slower η phase formation in the <111> direction. If η phase is the active form of Si this would result in less Si removal from the (111) planes than from other planes where η phase formation is faster.

A second explanation for the reaction leaving (111) planes exposed is that η phase is not the active form of Si and that the reaction mechanism favors atoms in planes other than the (111). The (110) and (100) planes are relatively open compared to the (111) and have more dangling bonds. Removal of an atom on the surface of a (100) or (110) plane requires breaking two Si-Si bonds, whereas removal from sequential (111) planes requires breaking alternatively three then one Si-Si bonds. Breaking three bonds requires more energy than breaking two. If the rate-limiting step involves Si-Si bond cleavage, reaction in the <111> direction will be slower causing (111) planes to be preferentially exposed. It is unclear how one would incorporate the role of Cu in this explanation and since Cu is essential to the reaction this mechanism seems less likely. More detailed mechanistic information is needed to pin down the reason for the exposure of (111) as the reaction proceeds.

SUMMARY

The CuCl catalyzed reaction of CH₃Cl with Si has been found to occur at discrete sites. Figure 8 summarizes the steps in the formation of active sites. The amount of Si surface reacted depends on the amount of damage in the native oxide layer. Increasing the defect density in the oxide increases the amount of Cu deposited and the number of active areas (Fig. 8a). The deposition of Cu from CuCl was found to occur by gas phase transport. The resulting Cu precipitates and subsequent reacted regions (pits) depend on the orientation of the underlying substrate (square for (100) planes and hexagonal for (111) planes) when viewed normal to the exposed surface (Fig. 8b). As the reaction proceeds (111) planes are exposed possibly due to hindered Cu reaction in the (111) direction in the Si lattice, and/or mechanistic details favoring reaction in the (100) and (110) directions (Fig. 8c). Once Si is removed from the surface, the excess Cu diffuses toward the Cu₃Si/Si interface exposing new η phase which continues the reaction.

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REFERENCES

1. Voorhoeve, R. J. H., "Organohalosilanes: Precursors to Silicones." Elsevier, Amsterdam, 1967, and references therein.
2. U.S. Patent 4,500,724 (Feb. 19, 1985).
3. Liebhafsky, H. A., "Silicones under the Monogram." Wiley, New York, 1978.
4. Ward, W. J., *et al.*, *J. Catal.* **100**, 240 (1986).
5. Liehr, M., LeGoues, F. K., Rubloff, G. W., and Ho, P. S., *J. Vac. Sci. Technol., A* **3**, 983 (1985).
6. Zaininger, K. H., *Proc. IEEE* **57**, 9 (1969).
7. Veer, F. A., Kolster, B. H., and Burgers, W. G., *Trans. Metall. Soc. AIME* **242**, 669 (1968).
8. Bean, K. E., *IEEE Trans. Electron. Devices ED-25* **10**, 1185 (1978).
9. Lee, D. B., *J. Electrochem. Soc.* **40**, 4560 (1969).
10. Tuck, Brian, *J. Mater. Sci.* **10**, 321 (1975).
11. Jenkins, M. W., *J. Electrochem. Soc.* **124**(5), 757 (1977).
12. Harvey, W. W., and Gatos, H. C., *J. Electrochem. Soc.* **105**, 654 (1958).
13. Frank, T. C., Kester, K. B., and Falconer, J. L., *J. Catal.* **91**, 44 (1985).
14. Frank, T. C., and Falconer, J. L., *Langmuir* **1**, 104 (1985).
15. Weber, G., and Gillot, B., in "Proceedings, 10th Intern. Symp. Reactivity of Solids." Dijon, 1984.
16. Ward, W. J., and Carrol, K. M., *J. Electrochem. Soc.* **129**(1), 227 (1982).
17. Ghandi, S. K., "VLSI Fabrication Principles," p. 10. Wiley, New York, 1983.