Chemistry of the direct synthesis of methylchlorosilanes from methyl + chlorine monolayers on a Cu_3Si surface

Dong-Hong Sun and Brian E. Bent *

Department of Chemistry and Columbia Radiation Laboratory, Columbia University, New York, NY 10027, USA

Antony P. Wright ‡ and Brian M. Naasz

Dow Corning Corporation, Midland, MI 48686, USA

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The direct process for synthesizing methylchlorosilanes from methyl chloride + silicon in the presence of catalytic amounts of copper has been studied in vacuum using a sample of Cu_3Si alloy, the bulk phase that is present in active regions of the catalytic direct process. From the melt containing 23% of excess silicon, a two-phase Cu_3Si + Si sample was prepared. Free silicon phase served both to replenish silicon reacted from Cu_3Si and to provide the grain boundaries found in an industrial process. Atomically clean surfaces of this material with varying Cu/Si atomic ratios were prepared by ion bombardment over a range of temperatures. While the dissociative adsorption of CH_3Cl was observed to be immeasurably slow on these surfaces under ultrahigh vacuum conditions, methyl + chlorine monolayers generated by the coadsorption of methyl radicals and Cl_2 led to selective formation of dimethyldichlorosilane. Adsorption of methyl groups alone produced trimethylsilane from two different active sites with very different kinetics. Adsorption of chlorine alone produced $SiCl_4$.

Keywords: direct process, methyl radical, Cu_3Si, alloy, methylchlorosilane, monolayer, ultra-high vacuum, surface

1. Introduction

Methylchlorosilanes, in particular dimethyldichlorosilane, are synthesized commercially by the direct process in which gaseous methyl chloride is reacted with metallurgical grade silicon powder in the presence of catalytic amounts of copper along with various promoters (e.g. zinc, tin and aluminum) [1,2]:

$$CH_3Cl + Si \xrightarrow{Cu} (CH_3)_xSiCl_{4-x}$$

While a consensus has yet to be reached on the mechanism(s) of the surface reactions and on the reasons for the remarkable selectivity of this process towards dimethyldichlorosilane, it is now generally agreed that the *bulk* solid phase presented at reacting surface regions of silicon particles is Cu_3Si [3–6]. It is also clear, however, that the composition of the surface phase of the alloy where catalysis occurs is probably not the same as that of the bulk [6–11].

A rigorous surface study of the direct process would ideally involve dissociative adsorption of a methyl chloride monolayer on Cu_3Si under ultra-high vacuum (UHV) conditions. Unfortunately such a study has been prevented by the "pressure gap" for this reaction. Specifically, it is found that methyl chloride dissociation is imperceptibly slow on Cu_3Si under the low flux conditions of UHV [12,13], and high pressures (which are less conducive to surface analysis) have been necessary to detect formation of methylchlorosilanes. For example, Falconer and co-workers investigated the direct process on low-surface-area samples which were transferred, without exposure to air, between an ultra-high vacuum chamber for preparation and characterization and an ambient pressure chamber for catalysis studies [12]. They exposed freshly sputtered Cu_3Si to CH_3Cl at atmospheric pressure and room temperature for 60 s. Subsequently a thermal desorption experiment on the cooled and evacuated sample detected desorbing methylchlorosilanes, but only above 500 K, indicating reaction limited kinetics, which in turn implies that tightly chemisorbed precursor intermediates were generated at the time of initial exposure to methyl chloride.

The objective of the present study was to investigate whether such a catalytically-active monolayer could be generated on Cu_3Si in UHV by separately adsorbing methyl radicals and chlorine on the surface. As shown in scheme 1, such an approach bypasses the C–Cl bond dissociation step, which is immeasurably slow under these low flux conditions. In a preliminary account of this work [14], it was shown that CH_3+ Cl monolayers do indeed react on Cu_3Si surfaces to produce methylchlorosilanes, and it was also demonstrated that the reactivity and selectivity for the desired dimethyldichlorosilane product was enhanced by the combined presence of excess silicon and trace amount of promoters (Zn, Sn

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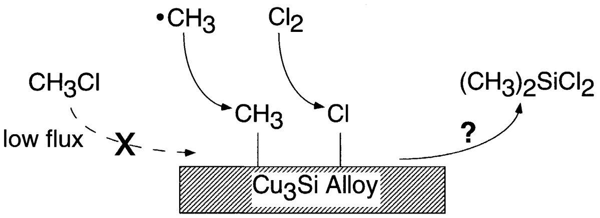
* Deceased.

‡ To whom correspondence should be addressed.



Scheme 1.

and Al). The present work investigates the role of excess silicon and/or the Cu_3Si/Si grain boundaries by studying the reactivity of CH_3+ Cl monolayers on Cu_3Si samples containing 15.88 wt% silicon (23% which is excess silicon and 77% which is contained in the Cu_3Si alloy phase) without additional promoters.

Prior to these monolayer reactivity studies, it was not obvious that simply generating CH_3 and Cl separately on the surface would lead to methylchlorosilanes analogous to what occurs from methyl chloride dissociation at high pressures. In fact, many of the mechanisms proposed for the direct process invoke the dissociation of CH_3Cl to CH_3 and Cl bonded at adjacent active sites and to specific surface atoms (either Cu or Si) [12]. Furthermore, it was not clear prior to this work that an atomically clean Cu_3Si surface would produce the catalytic products even if the proper adsorbates were generated on the surface, since there are significant and well-known induction periods required for the catalytic direct process, even when one initiates the process with Cu_3Si as opposed to a mixture of Cu + Si [15,16].

The results presented below confirm the preliminary studies of pure and promoter-doped Cu_3Si samples which showed that a catalytically active monolayer of CH_3 and Cl can be generated on low-surface-area Cu_3Si wafers in vacuum [14]. In the absence of Cl, methyl monolayers produce primarily trimethylsilane, and in the absence of methyl, Cl monolayers produce $SiCl_4$. The kinetics of the methyl reaction (but not of the Cl or CH_3+ Cl reactions) depend significantly on the surface structure and composition as demonstrated by studies in which the Cu/Si ratio at the surface is varied by ion bombardment and variable temperature annealing prior to adsorption. The results also demonstrate that excess silicon and Cu_3Si/Si grain boundaries do not enhance the activity or selectivity of dimethyldichlorosilane formation relative to pure Cu_3Si samples.

2. Experimental

Monolayer adsorption and reaction studies were performed in an ultra-high vacuum (UHV) chamber equipped with capabilities for Auger electron spectroscopy (AES) and temperature-programmed reaction (TPR) studies [17]. Cu_3Si alloy samples (15.88 wt% silicon, 77% of silicon in the alloy phase and 23% as excess silicon) were prepared at Dow Corning Corporation by heating a stoichiometric mixture of high-purity copper and semiconductor grade silicon to 1050°C in a quartz tube and then cooling the melt to form an alloy bar. The alloy bar was cut into 1 $cm^2 \times$ 4 mm wafers, and the wafers were then polished to a mirror finish. The Cu_3Si phase diagram [3] as well as SEM studies of similar samples [18] indicate that the surfaces of these samples contain Cu_3Si grains with regions of pure silicon between the grains. The samples were shipped in glass ampoules under high purity helium to Columbia University, where they were mounted on a molybdenum button heater and inserted into the UHV chamber. The samples could be resistively heated to 800 K and could be cooled with liquid nitrogen to 100 K. The surface temperature was measured by a chromel–alumel thermocouple junction that was spot-welded to a folded tantalum strip wedged into a slot cut into the side of the alloy. Compared with temperature measurement for wafers where the thermocouple was directly spot-welded on the sample (a presumably more accurate but fragile arrangement) the temperatures are reproducible to within 15 K at 200 K as evidenced by the reproducibility of the molecular desorption temperature for dimethyldichlorosilane. The surfaces were cleaned by argon ion bombardment (30 mA and 3 kV) at temperatures between 100 and 500 K and the Cu(60 eV)/Si(92 eV) Auger peak ratio was used to characterize the surface composition after sputtering.

Methyl radicals were generated in the gas phase by pyrolysis of azomethane [19] and adsorbed onto Cu_3Si surfaces held at 180 K. Previous studies have spectroscopically identified methyl groups on copper surfaces after dosing methyl radicals from a similar source [20]. Chlorine atoms were generated on the surface by the dissociative adsorption of Cl_2.

The surface reactions were investigated by a combination of AES and TPR studies, with authentic samples of the expected products being used to calibrate the signals from the two techniques. The Auger spectra were obtained with a single-pass cylindrical mirror analyzer operated with a modulation amplitude of 4 eV; the surface heating rate in the TPR studies was 2 K/s.

3. Results and discussion

The results are presented and discussed in the following order: (1) surface characterization by AES, (2) surface reactions of CH_3, (3) surface reactions of Cl, and (4) surface reactions of coadsorbed CH_3 and Cl.

3.1. Surface characterization

Surface characterization by AES showed: (1) that Cu_3Si was present at the surface of the wafer as evidenced by the split of the Si 92 eV transition to give peaks at 90 and 94 eV [6,21–25], (2) that the surfaces could be cleaned of all detectable oxygen and carbon by ion bombardment, and (3) that the near-surface ratio of copper/silicon was a strong function of temperature. For surfaces ion-bombarded below 250 K, the Cu(60 eV)/Si(94 eV) (92 eV at high temperature when the splitting disappears) Auger peak ratio was 1.4–1.6. This ratio decreased upon annealing to temperatures above 300 K, and by 400 K, was 0.6. Prior studies in the literature [6,11], for *temperatures above 300 K*, have reported that the Cu/Si Auger peak ratio for Cu_3Si decreases by a factor of two as surface temperatures increase from 300 K to above 700 K. On the basis of those results as well as ion scattering studies [11], it was concluded that the surfaces are enriched in silicon when annealed to 700 K. (These changes in the Cu/Si ratio are not reversible. Annealing to high temperature enriches the surface in silicon, but recooling does not enrich in copper.) Our results show that there are even more significant changes in surface composition for samples prepared below 300 K, and the factor of 2.5 decrease in the Cu/Si AES peak ratio at 400 K relative to 250 K implies significant surface enrichment with copper for samples prepared at 150 K. A more quantitative analysis of AES data is complicated by the line shape change of the surface-sensitive Si (90, 94 eV) peaks from alloy to pure silicon, and the poor surface-sensitivity of the Si (1619 eV) peak. The decrease in copper enrichment for temperatures > 300 K has a particularly significant effect on some of the surface reactions as will be discussed in the following paragraphs.

3.2. Methyl adsorption

Adsorption of a saturation coverage of methyl radicals onto Cu_3Si wafers at 150 K followed by heating of the surface, leads to the evolution of methylsilanes. The relative methylsilane yields are the same, to within experimental uncertainty, as those previously found [13] for samples of pure Cu_3Si, which are: $(7 \pm 7)\%$ SiH_3CH_3, $(18 \pm 7)\%$ $SiH_2(CH_3)_2$, $(73 \pm 7)\%$ $SiH(CH_3)_3$ and $(2 \pm 2)\%$ $Si(CH_3)_4$ on the basis of a comparison of the TPR peak areas of $m/e = 45$, 59, and 73 with literature values for the relative peak intensities for the major cracking fragments of the methylsilanes [26,27].

The kinetics of trimethylsilane evolution are a strong function of the surface preparation (composition) as indicated by the TPR curves in figure 1. As shown, when the Cu_3Si is sputtered at 140 K to produce a Cu-enriched surface, trimethylsilane (as monitored by $m/e = 59$, $SiH(CH_3)_2^+$) is evolved at 275 K. By contrast, Si-enriched surfaces obtained by sputtering at 330 K produce trimethylsilane at 555 K. This 280 K difference in the TPR peak temperature corresponds to a difference of more than five orders of magnitude in reaction rate if the rates were to be measured at a common temperature near 350 K.

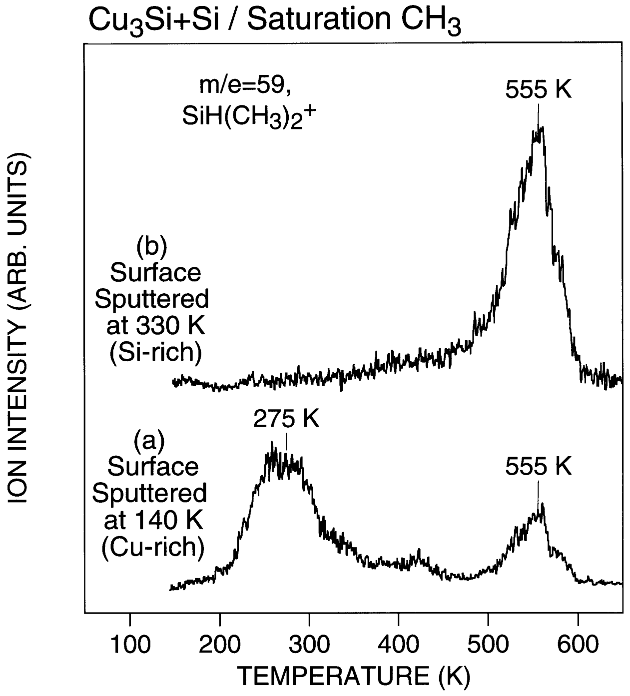


Figure 1. TPR spectra of $SiH(CH_3)_2^+$, a cracking fragment of $SiH(CH_3)_3$, after adsorbing a saturation coverage of methyl radicals onto Cu_3Si + Si surfaces at 150 K. The Cu_3Si + Si surfaces were ion bombarded at (a) 140 K and (b) 330 K prior to methyl radical dosing.

An interesting and important result (not shown in figure 1) is the finding that surfaces prepared with varying ratios of copper and silicon (as a result of ion bombardment at temperatures intermediate between 140 and 330 K) show trimethylsilane peaks centered at both 275 and 555 K but not at temperatures in between. In other words, the relative ratios of these two peaks vary with composition, but the peak temperatures are unchanged and no products are evolved at intermediate temperatures as the composition is varied. Also, when the surface CH_3 coverage is varied for samples where both the 280 and 580 K channels are observed, both reaction channels grow in at the same rate with increasing CH_3 coverage. These observations suggest the presence of two distinct types of surface sites for methylsilane formation which do not "communicate" with one another via surface diffusion of CH_3. On the basis of the correlation between the surface composition and the temperatures at which methylsilanes are evolved, we propose that the 555 K peak is associated with reaction at Si-rich sites while the 275 K peak is due to reaction at Cu-rich sites. Consistent with this interpretation, previous studies on pure Cu_3Si samples have shown that the 555 K peak due to Si-rich sites can be essentially eliminated by low-temperature sputtering. The presence of some intensity of this peak even after low-temperature sputtering in the present work presumably reflects the excess silicon in the sample. In the context of these Si-rich and Cu-rich active sites, it is interesting to note that the 580 K peak temperature for the Si-rich surface correlates with the temperature to which methyl groups are stable on a Si(100) surface [28,29]. Also the 280 K temperature for trimethylsilane evolution from a Cu-enriched surface is consistent with the finding the methyl groups are thermally stable to ~ 400 K on copper surfaces [20].

3.3. Chlorine adsorption

Chlorine readily dissociates on Cu_3Si surfaces at temperatures as low as 120 K. Unlike the case for CH_3 reaction on Cu_3Si, the surface sputtering temperature (i.e. the surface composition) does not have a significant effect on the reaction of Cl monolayers. AES studies show that chlorine leaves the surface at temperatures between 450 and 650 K, and TPR studies show that the gas phase product is $SiCl_4$. No $CuCl_x$ is detected. For reference, Cl_2 adsorption on Si(100) produces $SiCl_2$ at 850 K in TPR studies and only a very small amount of $SiCl_4$ evolution is detected at 500 K for a high surface Cl coverage [30]. High exposures of chlorine on copper surfaces results in the evolution of Cu_3Cl_3 at 450 K, but a Cl monolayer on Cu(111) [31–33], Cu(110) [32] and Cu(100) [34, 35] is stable to 800 K where it leaves the surface as CuCl.

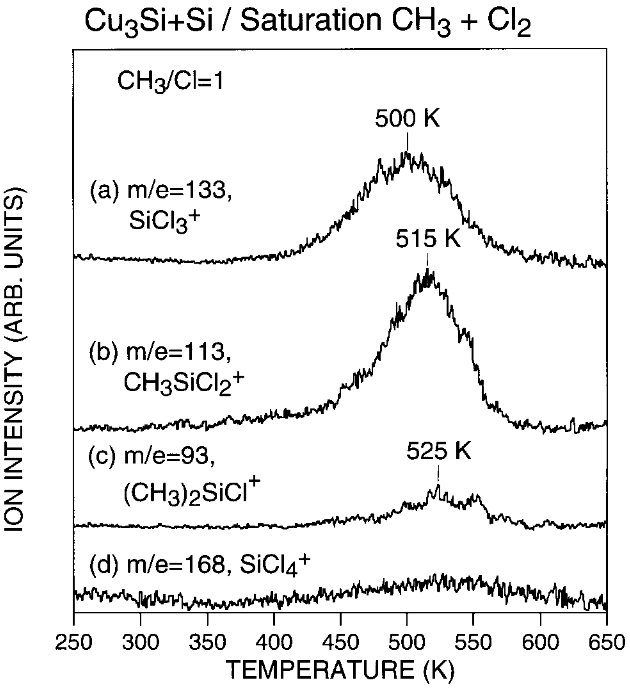


Figure 2. Methylchlorosilanes and tetrachlorosilane evolution from the reaction of a CH_3+ Cl (1 : 1 ratio) monolayer on a Cu_3Si + Si surface which had been prepared by ion bombardment at 330 K: TPR spectra monitoring (a) $SiCl_3^+$ (a major cracking fragment of CH_3SiCl_3), (b) $CH_3SiCl_2^+$ (a major cracking fragment of $(CH_3)_2SiCl_2$), (c) $(CH_3)_2SiCl^+$ (a major cracking fragment of $(CH_3)_3SiCl$) and (d) $SiCl_4^+$ (a cracking fragment of $SiCl_4$).

3.4. Methyl + chlorine co-adsorption

Coadsorption of methyl radicals and Cl_2 to form saturation monolayers with approximately a 1 : 1 stoichiometry of CH_3 and Cl (as determined by AES studies in which the relative sensitivities of C and Cl were determined using physisorbed monolayers of dimethyldichlorosilane) leads to the formation and evolution of methylchlorosilanes. The reaction products were identified by monitoring the characteristic ions of potential products including $SiCl_4^+$ ($m/e = 168$) for tetrachlorosilane, $CH_3SiCl_3^+$ ($m/e = 148$) and $SiCl_3^+$ ($m/e = 133$) for methyltrichlorosilane, $(CH_3)_2SiCl_2^+$ ($m/e = 128$) and $CH_3SiCl_2^+$ ($m/e = 113$) for dimethyldichlorosilane, $(CH_3)_3SiCl^+$ ($m/e = 108$) and $(CH_3)_2SiCl^+$ ($m/e = 93$) for trimethylchlorosilane. Small amounts of trimethylsilane ($(Si(CH_3)_3^+$, $m/e = 73$) are detected, but no CH_3Cl^+ or SiH_4^+ is observed.

Figure 2 shows TPR spectra for the major cracking fragments of the three methylchlorosilanes and tetrachlorosilane. These spectra were taken after adsorbing methyl groups and chlorine at 150 K onto a surface that was sputtered at 330 K. As shown, methylchlorosilanes are evolved from the surface around 500 K, which is a much higher temperature than the methylchlorosilane molecular desorption temperature (~ 200 K) from the same surface. This comparison indicates that the peak temperatures for methylchlorosilane evolution reflect the kinetics of product formation on the surface as opposed to the kinetics of product desorption from the surface. We note also that the methylchlorosilane product evolution temperature in these TPR studies is consistent with typical catalytic reaction temperatures of 550 to 600 K for the unpromoted direct process. The results here are similar to those reported by Lewis et al. [12] on active catalysts, with the exception that no desorption of CH_3Cl or $SiClCH_3$ (the suggested silylene intermediate, $m/e = 78$) was detected.

AES studies show that less than 50% of the adsorbed methyl groups (assuming that all the adsorbed carbon exists as methyl groups at 180 K adsorption temperature) form silane products in these TPR studies. The remaining methyl groups decompose to deposit carbon on the surface. It should be noted, however, that on the basis of the catalytic chemistry one would not necessarily expect a high efficiency of methyl conversion to silanes in a single monolayer experiment since in a steady-state catalytic process, the surface is continually replenished with methyl groups and chlorine to maintain a potentially large surface coverage while in a single monolayer TPR experiment, the coverage drops to zero. Although, by Auger, 20% of the chlorine remains on the surface after TPR, and some $SiCl_4$ is produced, a complete accounting for chlorine to balance lost methyl groups must await further study.

The relative yields of the methylchlorosilanes have been determined from the TPR peak areas of the major cracking fragments shown in figure 2. In this analysis, the relative mass spectrometer sensitivity factors (determined from mass spectrometric studies of authentic compounds [36]) and the contributions of cracking fragments have been taken into account. The yield of dimethyldichlorosilane relative to the total yield of methylchlorosilanes is $(62 \pm 7)\%$, while the yields of trimethylchlorosilane and methyltrichlorosilane are $(18 \pm 4)\%$ and $(20 \pm 6)\%$, respectively. To within the experimental uncertainty, this product distribution is the same as that found for pure Cu_3Si samples [14]. Furthermore, the product peak temperatures are the same to within 40 K. These results show that neither excess silicon nor Cu_3Si/Si grain boundaries have a significant effect on either the activity or selectivity of monolayer reactivity in the direct process in the absence of the promoters. On the other hand the selectivity of these equimolar CH_3/Cl monolayers to dimethyldichlorosilane can be increased to 85% by using Cu_3Si samples containing both excess silicon and the alloyed promoters Zn, Sn and Al [14]. We conclude that the promoter, not the excess silicon, was responsible for that improved selectivity. Studies are in progress to understand this effect and also to relate peak desorption temperatures of unpromoted and promoted alloys in more detail.

4. Summary

The results here show that methylchlorosilanes can be produced from $CH_3 + Cl$ monolayers that have been generated on Cu_3Si surfaces containing 23% excess silicon by directly introducing methyl radicals and chlorine in vacuum. Dimethyldichlorosilane, which is the dominant product of the catalytic direct process, is also selectively produced in these monolayer studies. The results also show that in the absence of methyl groups, surface Cl produces $SiCl_4$ while in the absence of Cl, surface methyl groups produce primarily trimethylsilane. It is shown that there are two different active sites (one Cu-rich and one Si-rich) with very different kinetics for the formation of trimethylsilane. There is no evidence that Cu_3Si/Si grain boundaries significantly affect this chemistry.

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