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Chemistry of the direct synthesis of methylchlorosilanes. UHV study of the chemisorbed fragments methyl and chlorine on copper silicide and their desorption pathways

Dong-Hong Sun [a], Brian E. Bent [a,1], Antony P. Wright [b,*], Brian M. Naasz [b]

[a] *Department of Chemistry and Columbia Radiation Laboratory, Columbia University, New York, NY 10027, USA*
[b] *Dow Corning, Midland, MI 48686, USA*

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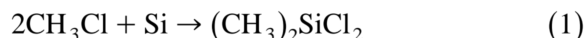
Abstract

The Direct Synthesis of methylchlorosilanes from methyl chloride and silicon, catalyzed by copper and minor promoter elements was reviewed with respect to use of ultra-high vacuum (UHV) surface reaction techniques to uncover the mechanism of the reaction. In particular, recent results were presented for sequentially adsorbing methyl radicals and chlorine on polycrystalline Cu_3Si alloy under ultra-high vacuum conditions. Methyl monolayers in the absence of chlorine produced primarily trimethylsilane, and chlorine monolayers in the absence of methyl produced $SiCl_4$. However, mixed monolayers of methyl groups with chlorine atoms abandoned these separate pathways and instead reacted at similar temperatures on the surface to produce methylchlorosilanes with selectivities to 85% Me_2SiCl_2 with Zn, Sn, and Al as promoters. © 1998 Elsevier Science B.V.

Keywords: Direct synthesis; Methyl radical; Cu_3Si; Alloy; Methylchlorosilane; Monolayer; Ultra-high vacuum; Surface

1. Introduction

Addition of elements including Mg, Zn, Cd, Al, Si, Ge, Sn, As, Sb, P, Zn, and Cd to organic halides can produce the corresponding organo element halides [1]. The Muller–Rochow process for Direct Synthesis of organochlorosilanes from elemental silicon and simple alkyl or aryl halides replaced indirect Grignard additions to $SiCl_4$ in the early 1940s. Commercial processes have been developed that react methyl chloride, ethyl chloride, or chlorobenzene to produce a mixture of products $R_xH_ySiCl_{(4-x-y)}$. The most important product, Me_2SiCl_2, is the key monomer of the silicones industry, and a sophisticated technology has evolved to maximize conversion of silicon, but control side products that include $MeSiCl_3$, Me_3SiCl, Me_2SiHCl, $MeSiHCl_2$, $Me_2ClSi–SiCl_2Me$, and hydrocarbons (Eq. (1)).



$$2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2 \quad (1)$$

On an industrial scale, ground metallurgical grade silicon, which naturally contains 0.5–1.0% of Fe, Al, Ca, Ti, V, Cr, Zr, Mn, and Ni, is

* Corresponding author. Fax: +1-517-496-6278.
[1] Deceased.

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reacted with gaseous methyl chloride at 250–350°C, 1–5 atmospheric pressure, in a fluidized bed reactor in the presence of copper and lesser amounts of various other elements as promoters [2,3]. The decomposition of methyl chloride, although normally minimal, is thermodynamically favored at reaction temperatures ($\Delta G_{573K} = -36$ kcal mol^{-1} for $CH_3Cl(g) \rightarrow HCl(g) + C + CH_4(g)$) [4]. The steady state chemical forms of the impurities and catalysts are influenced by thermodynamic factors. Almost all the metals commonly present in the direct synthesis in direct contact with CH_3Cl or HCl should react to form organometallic chlorides or element chlorides, respectively. With HCl, most of the element oxides, except Al_2O_3, TiO_2, SiO_2, and P_2O_3 should form chlorides. The resulting salts can be quite volatile, allowing contact with highly reducing silicon, and the equilibrium that eventually should dominate is $Si(s) + 4/n MCl_n \rightarrow 4/n\ M(s) + SiCl_4(g)$. Salts of elements giving negative free energies of reaction, e.g., ΔG_{573K}: Cu, -22 kcal mol^{-1} Sn, -21; P, -66 would be reduced by, and are observed to alloy with, silicon. Elements giving positive free energies of reaction, e.g., ΔG_{573K}: Al, 42 kcal mol^{-1}; Ti, 26, Zn, 17; would remain as salts, or if initially alloyed with silicon, would react, leaching out as salts.

About 1–5% copper is added as primary catalyst. Regardless of whether copper is introduced by alloying, sintering, or as powdered metal, oxide, or chloride, it is soon almost entirely alloyed onto the surface of silicon particles. The mechanism of transport and alloying when copper or copper compound is added separately as powder is probably predominantly as CuCl vapor. For example, a commonly practiced laboratory synthesis involves first heating silicon, CuCl powder, and co-catalysts to 300–350°C in inert gas, whereupon CuCl vapor is reduced by Si with $SiCl_4$ evolution. Inert gas is then replaced with a flow of CH_3Cl and the production of methylchlorosilanes begins [5]. The reduction stage has been studied in detail [6,7]. Certain intermetallic phases at silicon grain boundaries rich in Al or Ca are first to react with CuCl and methyl chloride [8]. The resulting $AlCl_3$ can complex with CuCl, increasing its volatility [9]. $AlCl_3$ vapor can penetrate the native oxide layer on silicon, chlorinating it to form $SiCl_4$ [10–12]. This is followed by reduction of CuCl or $CuAlCl_4$ vapor at exposed silicon sites [13]. X-ray diffraction studies have shown the bulk of the stable alloy initially formed is the intermetallic compound Cu_3Si, as one would expect from the phase diagram of the Cu/Si binary system [14]. It has been shown that Cu_3Si precipitates are formed epitaxially on single crystal silicon substrate in the reduction stage, resulting in square pyramidal and triangular pyramidal precipitates [6,15].

Microscopy has shown that during exposure to methyl chloride consumption of silicon begins in localized areas on the particle surface surrounding the Cu_3Si precipitates. Craters or pits are formed that expand outwards from the precipitates and deepen, leaving a historical record of site activity. In the expanding crater bottoms, where reaction is fastest, the Cu/Si ratio detected by SAM, XPS, and EDX is 0.1 or less [16,17]. If crystalline Cu_3Si is present in this region, dimensions are probably too small to obtain sharp XRD data [18]. If crystalline Cu_3Si is not present, it would seem from STM studies of clean Cu/Si(111) surfaces that only an atomic monolayer of copper could be present [19–21]. Cross-sectional TEM studies might resolve the issue. Pure Cu_3Si alloy, crushed, and used in the direct synthesis, easily produces methylchlorosilanes as well, but as reaction progresses rate slows as silicon builds up a layer of excess copper [14].

At some point in a commercial process, copper is transferred to freshly added silicon, and finally, over time, as carbon, metals, salts, oxides, and unalloyed copper build up in the bed, reaction terminates. Thus the processes that occur in the direct synthesis are complex, but can be broken down into component steps that relate in an interesting way to broadly diverse fields of chemistry, physics, and metallurgy.

At least four other classes of catalytic elements are simultaneously needed to achieve optimum performance in the direct synthesis. In principle, these may be effective in the different steps described above. Aluminum, naturally alloyed in the silicon, is beneficial, at least in the first step as described already (0.05–1%). Secondly, zinc is commonly added (0.05–1%). It has been proposed that zinc forms a molten chloride salt flux that might, for example, remove oxide from copper or copper silicide catalyst surface [17,22]. Zinc lowered the activation energy of the direct synthesis in laboratory kinetic studies with both catalyzed powders and Cu_3Si alloy wafers, and was called a ‘structural’ promoter by analogy to classifications used to describe supported catalysts [23–26].

Thirdly, an easily reducible promoter element such as tin, antimony, bismuth, or arsenic is added. Only a few parts per million of one of these elements was required to see a significant benefit [27]. Unlike zinc, tin apparently increases the number of active sites without lowering activation energy [23,25], and has been called a ‘textural’ promoter. It has been proposed that these promoters migrate to grain boundaries in Cu_3Si and cause interface decohesion and crack formation, resulting in additional active sites for reaction. The expected morphology has yet to be reported. Some corroborating evidence for this proposal is the report of a rapid accelerating effect on the 150°C air oxidation of Cu_3Si ingots by addition of 0.1–0.5% Sn, Sb, Bi, As, Ge, Pb. The fact that these were the only oxidation accelerators of 26 elements tested, and that the first four correspond to known promoters of the direct synthesis is intriguing [28,29]. Oddly, lead is a known direct synthesis poison! There may also be a direct role of tin in assisting the formation of product, suggested by the observation that tin can change the product composition. Zinc and tin were found only with copper in the pitted region of a CuCl activated silicon particle according to a scanning Auger characterization [30].

Lastly, phosphorous improves the selectivity of the direct synthesis towards Me_2SiCl_2 [31,32]. The mechanism of action may be its known accelerating effect on the rate of diffusion of copper through Cu_3Si, which would allow more rapid formation and spreading of Cu_3Si alloy on a silicon particle surface [33,34]. The rate of Cu_3Si intermetallic layer formation from heating a copper plated silicon wafer to 300°C is however, much faster than silicon consumption in the direct synthesis [35]. The presence of aluminum, zinc, tin and phosphorous as co-catalysts with copper are together in a complex interdependent way beneficial in achieving desirable direct synthesis performance [36].

A mechanism for the formation of Me_2SiCl_2 on active copper silicon alloy should describe both the molecular and metallurgical transformations that take place at the active site on the surface, as well as predict a potential energy diagram for reaction (Fig. 1) [37]. The direct synthesis is very exothermic ($\Delta H_{298K} = -37.7$ kcal/mol per CH_3Cl molecule reacted, A–G, Fig. 1) [38]. It is generally agreed that the direct synthesis follows Langmuir–Hinshelwood kinetics. Thus, a widely cited mechanism proposes activated dissociative chemisorption of methyl chloride at the silicon copper alloy surface (ABCD, Fig. 1). In a subsequent rate controlling step, proposed to occur with an activation energy of 26 kcal/mol (with only copper added as catalyst; DEF, Fig. 1) the adsorbed methyl and chlorine fragments reassemble on to silicon atoms in the alloy in a surface reaction that ultimately results in desorption of methylchlorosilanes (FG, Fig. 1) [39–43,14,25]. Because high partial pressure of product inhibits reaction, it is believed Me_2SiCl_2 and CH_3Cl compete for the same adsorption sites (D, F).

Enthalpies of adsorption of methylchlorosilanes on a catalytically active copper silicide surface, derived from constants in the observed pressure dependent rate equation, appear to lie close to 12 kcal/mol [25]. On the other hand, enthalpies of adsorption reported for CH_3Cl range widely from 4.7 to 21 kcal/mol, leading

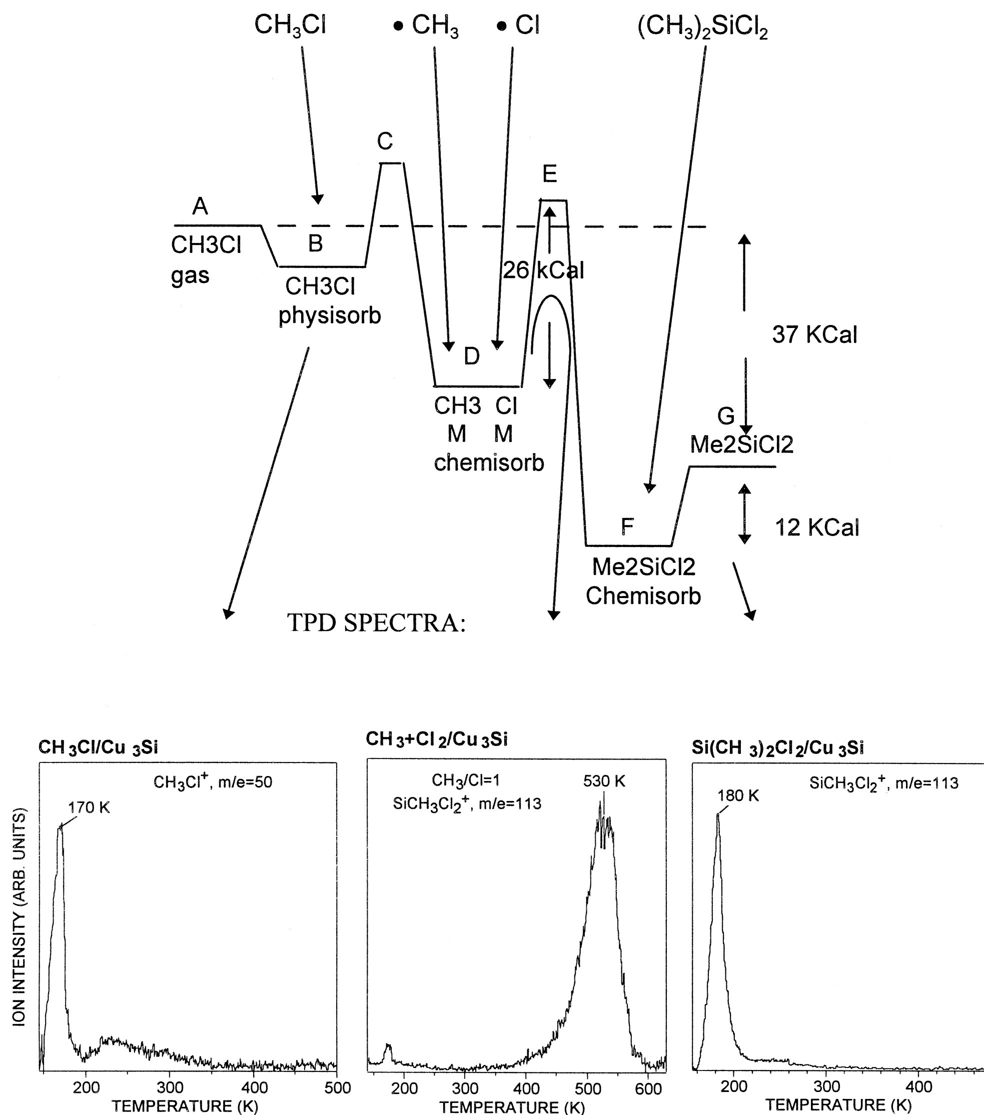

Fig. 1. Potential energy diagram for the direct synthesis.

to some disagreement as to whether the initial chemisorption is dissociative or not (B or D, Fig. 1). Voorhoeve [14], in his discussion, used the higher number to support the Klebanski–Vikhtengol'ts–Voorhoeve mechanism which proposed dissociative chemisorption with chlorine adsorbing on a copper site and methyl on a silicon site, followed by a rate limiting transfer that included chlorine moving from copper to silicon. Bond energy values applied by Voorhoeve to this mechanism predicted an adsorption energy of -23 kcal/mol. The heat of reaction for the related hypothetical reaction 0.25 Si + CH_3Cl + Cu = 0.25 Me_4Si + CuCl can be calculated as $\Delta H_{298K} = -29$ kcal/mole [4]. The possibility that CH_3 binds to a copper site and chlorine to a silicon site appears less probable given the low, 29 kcal/mol, Cu–CH_3 bond energy [44]. Recent attempts to extract a reasonable value for the enthalpy of adsorption of CH_3Cl from new kinetic data were inconclusive [42]. In a UHV study, TPD of CH_3Cl ph-

ysisorbed on copper indicated heats of adsorption of only 8–10 kcal/mol [45]. Kinetic data from recent bulk direct synthesis experiments with various co-catalyst combinations has been said to follow a compensation effect, whereby as activation energy decreased with co-catalyst addition, the preexponential factor decreased as well, resulting in an approximate isokinetic temperature of 320°C, a temperature at which co-catalysts should therefore have no effect [46]. The concept of 'structural' and 'textural' promoter mentioned earlier may not be congruent with a single compensation effect, and more accurate kinetic data are probably needed to resolve this issue. Clearly a fresh approach has been needed to independently determine energies of individual steps in the mechanism, and the structure and bonding of surface intermediates at the active site.

Recently studies have attempted to use surface science techniques to break down the direct synthesis into component steps. A surface study of the direct synthesis would be most rigorous if fractions of a monolayer of chemisorbed CH_3Cl dosed on a clean single crystal surface at low temperature were tightly bound under UHV conditions, as would be expected if dissociation to surface bound CH_3 and Cl fragments occurred. Ideally, surface reaction to form Me_xSiCl_{4-x} would only occur upon subsequent heating. In this way structural and bonding information, such as identification of CH_3 and Cl binding sites, might be deduced from surface characterization at low temperature without the complication of product or byproducts being present. Products would be detected by a mass spectrometer in a subsequent temperature programmed reaction (TPR) experiment which gives peak desorption temperatures, T_p, which can potentially be interpreted to give kinetic data, including approximate activation energies of product forming steps [47,48]. One should be able to conclude by such direct measurements whether chemisorption of CH_3Cl, or reaction of surface fragments is the rate determining step [49,50]. Studies like this have been approached by dissociatively chemisorbing alkyl halides on many surfaces to produce stable alkyl fragments and coadsorbed halogen atoms [50–52] [2] including methyl iodide on Cu(100) and methyl chloride on Si(111) [54,55].

Unfortunately, methyl chloride desorbs without dissociation from copper above 200 K [45] and as we show in this report, from Cu_3Si above 145 K [25]. This is an example of the 'pressure gap' separating many surface science studies from real catalytic processes. There is one consoling simplification, in that the direct synthesis proceeds at a low surface area well demarcated interface unlike many reactions on supported catalysts. Our approach to circumvent the pressure gap, illustrated in Fig. 1, has been to generate a catalytically-active monolayer on Cu_3Si in UHV by separately adsorbing methyl radicals and chlorine at low temperature. The approach has the added benefit of permitting control of CH_3/Cl stoichiometry, and of generating kinetic data directly on the proposed rate limiting step of the direct synthesis without the complication of CH_3Cl adsorption kinetics. Finally, experiments can be related to numerous related rigorous surface studies of CH_3 [50] and Cl [56–60] adsorbed on single crystal copper, and CH_3 [61–64] and Cl [65,66] adsorbed on single crystal silicon. Methyl radicals could be dosed by cracking of azomethane [67] and chlorine dosed directly from a gas reservoir. Until our recent studies, which have appeared as preliminary accounts [68,69], it had never been demonstrated that a copper silicide substrate could function to produce methylchlorosilanes while maintained continuously under UHV conditions.

Before presenting a summary of our results, we will selectively review other surface studies that preceded ours. One technique applied in recent years to circumvent the pressure gap has been to combine in a single apparatus the ability to measure kinetics at elevated pressure on cata-

[2] See for example Ref. [53] and Refs. 2–29 therein.

lytically active single crystals with capability to carry out surface analytical measurements before and after reaction under UHV conditions [70,71]. For example, starting in 1982, Falconer and co-workers investigated the direct synthesis on low-surface-area polycrystalline Cu_3Si and $Cu_3Si + 0.4\%$ Zn wafers 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 [72,73]. Their kinetic results showed the benefit of Cu and Zn in improving the fraction of product that was Me_2SiCl_2, but reaction rate was slower than that for uncatalyzed silicon alone. Auger analysis showed the presence of O, C, Cl, Si, Cu, and Zn, but since 500–1600 monolayers were reacted, it would be difficult to decide which elements were dynamically involved at the active site and which were spectator byproducts. Indeed on highly reacted surfaces, an Auger analysis vs. time of ion bombardment profile showed carbon and chlorine remained until the equivalent of 500 monolayers of silicon were removed, suggesting the presence of complex multilayers that may have contained copper chlorides or high boiling chlorosilane and carbonaceous residues. In more recent studies a freshly sputtered Cu_3Si wafer was exposed briefly to CH_3Cl at atmospheric pressure as it cooled from below 950 K to room temperature [25]. Subsequently, a thermal desorption experiment on the cooled and evacuated sample detected a desorbing mixture of methylchlorosilanes, similar in composition to those formed in the direct synthesis. Desorption occurred only above 500 K, indicating reaction limited kinetics, which in turn implied that tightly chemisorbed precursor intermediates, along with any product, were generated at the time of initial exposure to methyl chloride. The mass spectrometer also detected small amounts of mass 78, which the authors hypothesized was due to evaporation of some surface bound 'silylene' CH_3ClSi. More quantitative evidence is needed to determine if such an intermediate, if it exists, is a high energy adsorbed silylene or simply CH_3 and Cl adsorbed on the same surface silicon atom, and whether either is a significant participant in the mechanism. The observation that silacyclopent-3-enes are formed when butadiene is co-fed to the direct synthesis has been interpreted as due to surface alloyed silicon having silylene like reactivity [74].

In these and related studies, the surface of Cu_3Si was increasingly enriched in silicon after surface cleaning by argon ion bombardment, as post annealing temperature was increased above room temperature. We will show this enrichment is important because it can affect the surface chemistry. Quantification of the effect in the literature is confused by the different surface preparation and analysis methods applied by different authors. Preparation of a surface said to have the top layers composition approaching the bulk composition, evidenced by matrix corrected Auger peak ratios, involved surface etching with argon ions of 600 eV bombardment energy and ambient temperatures [75,76]. Higher temperatures gave a silicon enriched surface. A more surface sensitive synchrotron photoemission binding energy analysis of the Si 2p core level spectrum of a Cu_3Si surface prepared under these same conditions was interpreted to show silicon existed in two environments, one associated with bulk Cu_3Si, and the other silicon enriched, but with copper still present [76]. The proportion of the latter environment increase from $\sim 40\%$ to $\sim 70\%$ upon annealing the sample to 700 K. An adsorbate free Cu_3Si alloy wafer observed with LEIS and variable exit angle XPS indicated, after 3 keV argon ion bombardment without applied heating, a near surface silicon atomic fraction of 0.54, 0.56 (LEIS, XPS); increasing to 0.68, 0.74 after annealing to 700 K, respectively, indicating silicon enrichment at both temperatures relative to Cu_3Si (Si atomic fraction = 0.25) [77]. A Cu_3Si surface bombarded with argon ions of unspecified energy, then exposed to 1 atm CH_3Cl for 1 min at 300 K, showed by XPS an increase in silicon atomic fraction from 0.19 to

0.44 upon heating from 300 to 560 K [78]. A binding energy analysis of the Si 2p region showed an organometallic form of silicon was present at 102.8 eV as well as the element at 99.3 eV. The former, exhibiting the same binding energy as Me_2SiCl_2, was partially desorbed at 600 K. A Cl 2p 1/2 analysis gave a broad peak which the author interprets as at least partly due to a copper–chlorine interaction. This and earlier studies have been reviewed in detail [25].

All studies on Cu_3Si have had to work around the sensitivity of Cu/Si ratio to surface cleaning conditions and the unavailability of single crystal Cu_3Si (There is no liquidus boundary in the phase diagram). Above one monolayer, copper deposited on single crystal silicon forms very heterogeneous structures, discouraging investigation of this surface, despite its direct relationship to the real direct synthesis [21]. On the other hand, when silicon is deposited on copper (100) or copper (111) via a saturation exposure to SiH_4 at 420 K an incommensurate 5×3 structure is formed which is a two dimensional copper silicon alloy monolayer having large domains of near perfect hexagonal structure with Cu_2Si stoichiometry, as observed by STM and helium atom diffraction [79,80]. The deposition process and surface chemistry have been studied. The Cu/Si Auger ratio was said to be stable to 620 K [81–83]. No chemisorption was observed for CO, CO_2, H_2O, CH_3OH or atomic hydrogen on a fully formed surface. Only oxygen chemisorbed [84]. We will show CH_3 and Cl do chemisorb on this surface and that the chemistry on this substrate is related to that on Cu_3Si. The regular hexagonal structure of the surface should allow easier determination of CH_3 and Cl adsorption sites.

2. Experimental

Cu_3Si alloy samples were prepared at Dow Corning by heating a stoichiometric mixture of high purity copper, promoter elements, and semiconductor grade silicon to 1050°C in a quartz tube and then cooling the melt to form an alloy bar. Three compositions were prepared. These were pure Cu_3Si (12.23 wt.% Si); Cu_3Si + Si (15.88 wt.% silicon distributed 77% in alloy and 23% in a silicon second phase); and Cu_3Si + Si + promoters (15.88 wt.% silicon, 0.15% aluminum, 0.50% zinc, and 0.01% tin) [27]. The alloy bar was cut into $0.8\ cm^2 \times 3$ mm wafers, and the wafers then polished to a mirror finish. The Cu_3Si phase diagram [14] as well as SAM and SEM studies of similar samples [3] indicated that the surfaces of these samples contained ~ 100 μm Cu_3Si grains with inclusions of pure silicon between the grains in samples with excess silicon. Reactor studies on promoted samples, ground to < 200 mesh, showed they were catalytically active with a maximum selectivity of 84% dimethyldichlorosilane. 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 a UHV chamber. Cu(110) rather than Cu(100) was used as substrate for silane deposition, due to the crystal being on hand. Because of the known low interaction of Cu_2Si with copper substrate, we shall assume an identical structure on both surfaces [79]. Thus, Cu_2Si/Cu(110) samples were prepared in the UHV chamber at Columbia as follows. The Cu(110) crystal was sputtered 30 min at 300 K, 10 min at 950 K, then annealed 5 min at 980 K. Between dosing experiments, this procedure was repeated to remove silicon. The copper crystal was dosed with SiH_4 at 520 K. Under these conditions the silane decomposed on the surface giving surface silicide [82]. All exposures are given in units of Langmuir (L), where 1 L equals 10^{-6} Torr s, uncorrected for ion gauge sensitivity.

Monolayer adsorption and reaction studies were performed in an ultra-high vacuum (UHV)

[3] A.P. Wright, R. Durall, unpublished results, Dow Corning, 1994.

chamber equipped with capabilities for ion cleaning, Auger electron spectroscopy (AES) and temperature programmed reaction (TPR) studies [85]. The samples could be resistively heated to 800 K and cooled with liquid nitrogen to 100 K. The surface temperature was measured by a chromel–alumel thermocouple junction that was either spot-welded to a folded tantalum strip wedged into a slot cut into the side of the alloy wafer, or directly spot-welded to the alloy. The Cu_3Si surfaces were initially cleaned by argon ion bombardment for several hours to remove all the carbon and almost all oxygen. CH_3 was dosed below 180 K, Chlorine at 110 K. Sputtering between experiments was 10 min at 3 kV, 330 K, unless otherwise indicated. 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 [67]. Previous studies have spectroscopically identified methyl groups intact on copper surfaces after dosing methyl radicals from a similar source [86]. Some nitrogen was also detected by Auger on the surface after methyl radical dosing, but TPD studies of physisorbed azomethane showed total desorption occurred by 340 K. Methyl radical exposure was controlled by dose azomethane passed through the pyrolysis tube at temperature. 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. A 20 L dose of methyl radicals and 9.5 L dose of chlorine formed a saturation monolayer with approximately a 1:1 atomic ratio of C to Cl since the Cl(181 eV): C(272 eV) Auger peak ratio of 6.5 was then the same as that in physisorbed dimethyldichlorosilane. The surface heating rate in the TPR studies was 2 K/s. The Auger spectra were obtained with a single pass cylindrical mirror analyzer operated with a modulation amplitude of 1 or 4 eV. Mass spectrometry was used during TPR as described previously to identify and quantify desorbing products [68,69].

3. Results and discussion

The results are presented and discussed in the following order: (1) surface characterization by AES, (2) adsorption of molecules, (3) surface reactions of CH_3, (4) surface reactions of Cl, and (5) surface reactions of coadsorbed CH_3 and Cl.

3.1. Surface characterization

Surface characterization of Cu_3Si wafers 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 which coalesced to 92 eV above about 500 K, (2) that the surfaces could be cleaned of almost 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 pure Cu_3Si surfaces ion bombarded cryogenically below 250 K, the silicon surface atomic fraction estimated by correcting for matrix effects in Cu(60 eV) and Si(94 eV) Auger derivative spectrum peak heights was 0.17 [87,75,88]. Between 250 K and 400 K this ratio increased to 0.25, the value for bulk Cu_3Si, and then rapidly to 0.42 by 500 K; then 0.52 by 700 K. Auger data from Cu_3Si sputtered below room temperature has not previously been reported. Our data shows the low temperature resulted in a surface probably enriched in copper relative to Cu_3Si. Unexplained, is why silicon enrichment with increasing temperature occurred most rapidly between 300–450 K while that reported by Falconer occurred most rapidly between 550–650 K.

3.2. Adsorption of molecular reactants and products

Methyl chloride desorbed molecularly from Cu_3Si under all sputtering conditions tried. Peak

desorption temperature (T_p) was 145 K, evidenced by following mass 50 during temperature programmed desorption (TPD), corresponding very approximately to an Arrhenius activation energy of adsorption of 9 kcal/mol, were the surface reaction first order and the frequency factor 10^{13} s^{-1} [47,48]. This agrees with step A–B in the potential energy diagram of the reaction (Fig. 1). A 1000-L dose of CH_3Cl at 293 K gave no adsorbed chlorine or carbon by Auger. This agrees with the proposal that CH_3Cl chemisorption is activated, as depicted by steps B–C–D. Me_2SiCl_2 physisorbed on Cu_3Si gave a peak desorption temperature of 180 K, corresponding to an adsorption energy of 12 kcal/mol also shown in Fig. 1. The increased silicon surface atomic fraction on Cu_3Si with increased annealing temperature significantly affected surface chemistry. One indication of this was the observation that CH_3I, known to irreversibly chemisorb on copper, was completely desorbed molecularly from Cu_3Si at 190 K, if before dosing, the sample was annealed at 600 K. However when sputtered at 200 K and

Table 1
Summary of TPR experiments on argon sputtered Cu_3Si

Experiment			1	2	3	4	5	6	7
Promoters			No	No	No	No	Yes	Yes	Yes
Excess Si		% if all	0	0	23	23	23	23	23
Sputter	Temp.	K	180	330	140	330	120	350	600[a]
Adsorbate	Desorb	K TPD Peak Temperatures[b] (%) Chlorosilane distributions[c]							
CH_3Cl	CH_3Cl	K		145					
$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl_2$	K		180					
CH_3	$(CH_3)_3SiH$	K	280, 580	580	275, 555	555	290, 560	570	
		(Peak ratio)	(9:1)		(5:1)		(1:1)		
Cl_2	$SiCl_4$	K	350, 550	550	515	515			
		(Peak ratio)	(1:15)						
	$SiCl_3$	K					390[e]		
CH_3, Cl	$(CH_3)_3SiCl$	K		575		525	220, 327		
		(%-Trial 1)[d]		(17)		(18)	(4)		
		(%-Trial 2)		(10)		(15)			
		(%-Trial 3)				(18)			
	$(CH_3)_2SiCl_2$	K		550		515	240, 345	240, 385[f]	450
		(%-Trial 1)		(58)		(60)	(85)		
		(%-Trial 2)		(55)		(69)			
		(%-Trial 3)				(53)			
		K	370, 540	540	380, 540	530			
		(Peak ratio)	(1:14)		(1:16)				
	CH_3SiCl_3	K		500		500	255, 390		
		(%-Trial 1)		(23)		(14)	(11)		
		(%-Trial 2)		(34)		(14)			
		(%-Trial 3)				(27)			
	$SiCl_4$	(%-Trial 1)		(2)		(4)			
		(%-Trial 2)		(1)		(2)			
		(%-Trial 3)				(2)			

[a] Surface was annealed at 600 K.
[b] Where two temperatures are listed two peak desorption temperatures in the same desorption experiment are indicated.
[c] Percentage of each methyl and/or chlorinated silane relative to all the methyl and/or chlorinated silanes listed in same vertical column.
[d] Three duplicate trials show reproducibility of distributions.
[e] This temperature reading is from a thermocouple mounted differently on the sample relative to others in the table. This reading is at least 40 K higher than other readings for surfaces at the same temperature.
[f] Surface was annealed at 310 K for this experiment.

120 K without annealing, about 30% and 50% of CH_3I, respectively, could not be recovered from the surface. This result is consistent with the low temperature surface containing excess copper, as indicated by the Auger results.

3.3. Surface reactions of adsorbed CH_3

The dominant silane product from reaction of methyl radical alone with all surfaces tested was Me_3SiH, deduced from the presence of $m/e = 45$ (SiH_2CH_3+), $m/e = 59$ ($SiHMe_2+$), and $m/e = 73$ ($SiMe_3+$) in the same ratio as found in the cracking pattern of authentic Me_3SiH admitted to the same chamber. A quantitative comparison of ion intensities to those for reference compounds indicated a typical distribution Me_3SiH, 74%; Me_2SiH_2, 18%; and possibly small amounts of $MeSiH_3$ and Me_4Si. Reducing the sputtering temperature from 350 K to 140 K during surface cleaning prior to methyl dosing dramatically reduced the number of surface sites producing Me_3SiH ($m/e = 73$) at $T_p = 580$ K in a subsequent TPD experiment, replacing them with surface sites that produced Me_3SiH at only 280 K (Table 1). Activation energy was reduced from 33 to 16 kcal/mol. These sites appeared to be distinct, independent, and non-communicating, since increasing doses of CH_3 populated both sites in constant proportion, and peak temperatures did not shift with dose or sputtering temperature. By non-communicating is meant the adsorption chemistry at one site did not depend on the population of sites filled at the other. We propose, based on the Auger data, that the site that produces Me_3SiH at 580 K contains a greater proportion of silicon atoms relative to copper than the site that produces Me_3SiH at 280 K. For both sites, T_p is not significantly shifted by the formulation of excess silicon or promoters into the alloy.

A Cu_2Si/Cu(110) surface was prepared by dosing 5-L SiH_4 into a chamber containing a clean crystal of Cu(110) at 520 K [82]. This was a saturation coverage. Methyl radicals subsequently dosed on this surface at 120 K also

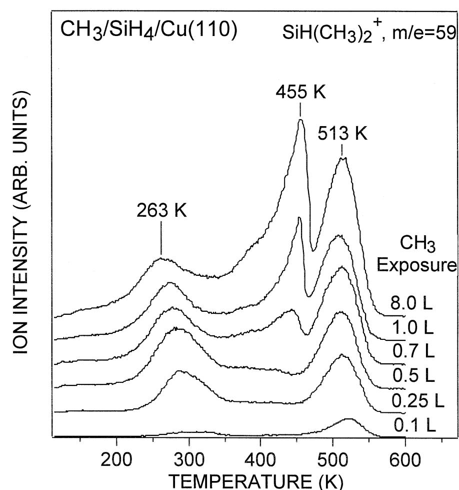

Fig. 2. Adsorption of methyl radicals on a Cu(110) surface dosed with a saturation coverage of silane at 520 K. TPR, following $m/e = 59$ ($SiHMe_2^+$), at increasing coverage of methyl.

produced Me_3SiH at two temperatures, T_p, one at 280 K and the other at 513 K, that are probably not significantly different from those with Cu_3Si alloy as substrate. These sites also appeared to be distinct, independent, and non-communicating (Fig. 2). The low temperature peak shape is symmetrical and shifts to lower temperatures at higher coverages, suggesting a reaction order > 1. The higher temperature peak does not shift, and sometimes appears asymmetric (not shown) suggesting a first order reaction [48]. Interestingly, however, at higher doses of CH_3, a third desorption peak, and thus third site, became occupied. This third site was never observed on Cu_3Si, indicating the surfaces differ form one another in some respects. In another experiment, as the dose of SiH_4 was increased from 0.2 to 10 L, the ratio of Me_3SiH desorbing at 280 K to that at higher temperature decreased from 100:0 to 30:70, again suggesting that the site exhibiting a high T_p is associated with a higher proportion of silicon atoms. T_p for the high temperature site first appeared at 335 K at low silane dose, and moved steadily towards 510 K as silane dose was increase to 5 L, above which it remained constant, suggesting the site structure depended on the surface silicon con-

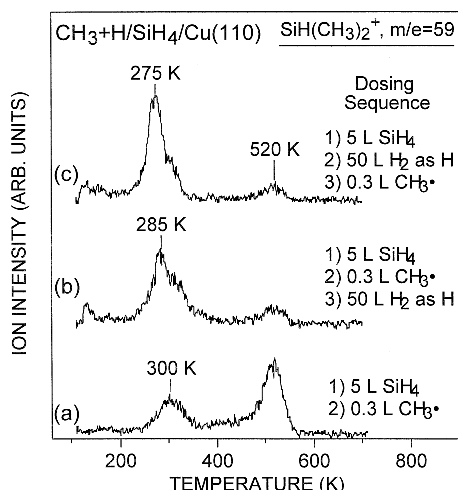

Fig. 3. Coadsorption of hydrogen atoms with methyl radicals on a Cu(110) surface dosed with a saturation coverage of silane at 520 K. TPR, following $m/e = 59$ ($SiHMe_2^+$).

tent, with the limit being a Cu_2Si monolayer, if surface structure follows that for Cu(100) substrate. Above 620 K, silicon diffuses into the bulk [82]. The low temperature peak obtained on Cu_2Si/Cu(100) is then due to a copper rich surface without a developed Cu_2Si monolayer.

Exposure of Cu_2Si/Cu(110) to hydrogen atoms at 120 K before or after dosing methyl at this temperature substantially reduced the amount of Me_3SiH desorbed at 520 K during TPR and increased the amount of $m/e = 59$, $HSi(Me)_2+$, desorbed at 300 K (Fig. 3). Because the low temperature peak was lowered 20 K with hydrogen adsorption, and because the ion $m/e = 73$ ($SiMe_3+$) was not observed for this peak, H_2SiMe_2 was suspected to be the major component. These observations suggested to us that the low temperature peak was due to reaction of surface bound hydrogen and surface bound methyl with silicon, agreeing with the observed higher order (> 1) properties of the desorption curve. It is then reasonable to propose that the surface bound intermediate formed upon methyl adsorption at low temperature is Me_2Si. We propose high temperature desorption only occurred if chemisorbed hydrogen was not already present at the related surface site. That is, when hydrogen atoms were not dosed, the Me_3SiH evolution temperature was controlled by the rate limiting decomposition of CH_3 at each surface site to produce hydrogen on the surface, which would then form Me_3SiH before it would diffuse from site to site, a mechanism agreeing with the observed first order properties of the desorption curve. A similar effect was observed in a TPR experiment in the system CH_3/Cu(110), CH_3I as CH_3 source, where T_p was 425 K for methane desorption resulting from methyl decomposition, but was 350 K if deuterium was coadsorbed with CH_3 at low temperature, CH_3D now being the product [85]. The observation that a surface low in silicon favors T_p for Me_3SiH desorption being 280 K, while a surface higher in silicon favors T_p being 513 K, agrees with the known lower decomposition temperature of CH_3 on Cu(110) (425 K) over that on Si (780 K) [85,61]. To accept the above argument, one must accept that it is reasonable for CH_3 to decompose at 300 K on Cu_2Si/Cu(110) but 425 K on copper.

An alternative explanation of the 300 K peak is that H atoms cogenerated in the hot azomethane source might selectively adsorb at active surface sites [67]. We did not, however, observe that the 300 K peak intensity depended on the radical source pyrolyzer temperature. Some hydrogen atoms were adsorbed on Pt(111) during exposure to azomethane sourced CH_3, however in this case T_p. For methane desorption was still shifted to lower temperature by presaturation with hydrogen, indicating the azomethane sourced cogenerated hydrogen was of minor importance [89]. On promoted Cu_3Si we found deuterium atoms dosed alone from D_2 over a hot tungsten wire, did chemisorb, but desorbed at 430 K during TPD, evidenced by following $m/e = 4$. Thus, H coadsorbed with CH_3 would not be available to generate Me_3SiH at 520 K at least, supporting the idea that at 520 K hydrogen comes from rate limiting CH_3 decomposition. Small amounts of $MeSiH_3$ have been observed to desorb at 600 K from CH_3 on Si(100) under certain conditions [90]. Clearly,

copper is a catalyst for the reaction of CH_3 with silicon to make Me_3SiH.

3.4. Surface reactions of adsorbed chlorine

For unpromoted samples exposed to 20-L chlorine at 110 K, equivalent to a saturated surface layer, the desorption product was $SiCl_4$ ($m/e = 168$ for $SiCl_4+$, $m/e = 133$ for $SiCl_3+$). Desorption occurred over a rather broad 150 range, centered at $T_p = 550$ K. Consistent with this, AES studies showed that chlorine left the surface between 450 K and 650 K. Neither the formulation of excess silicon into the alloy, nor changing surface sputtering temperature, hence Cu/Si ratio, had a significant effect on the peak desorption temperature for $SiCl_4$ (Table 1). Additionally, a small peak for $SiCl_4$, 5–10% of the total, occurred at 160 K, suggesting some $SiCl_4$ formed during the adsorption process itself. This has been observed in a prior study on Si(100) and might have been due to accidental photolytic generation of atomic chlorine during adsorption, followed by facile etching of the surface [91,92]. No $CuCl_x$ or elemental chlorine was detected by the mass spectrometer. For reference, chlorine adsorbed on Si(100) produced mainly $SiCl_2$ at 850 K and a very small amount of $SiCl_4$ ($m/e = 133$) at 500 K [66]. Chlorine adsorbed on Cu(100) evolved Cu_3Cl_3 at 450 K [60]. Thus, copper is a catalyst for the production of $SiCl_4$ from Si and Cl_2.

For the promoted sample, desorption of chlorosilanes after a 20 L exposure to chlorine occurred at $T_p = 390$ K rather than 500 K. Detection of $m/e = 133$ for $SiCl_3+$, with the correct isotope ratio for three chlorines, but not $m/e = 168$ for $SiCl_4$, forces us to suggest a $SiCl_3$ fragment desorbs directly. Observed in the same TPR experiment was a peak at 160 K, this showing signals at $m/e = 133$ and 168 K, indicating $SiCl_4$. Surface chlorine by Auger decreased at 160 K and again between 300 and 600 K. Further experiments are needed, preferably in the dark. Promoters thus lowered the temperature of reaction of chlorine with Cu_3Si, although they did not do so for the reaction of methyl and Cu_3Si. A single experiment with Cu_2Si/Cu(110) indicated a relatively larger amount of chlorosilanes desorbed at 160 K than at higher temperatures.

3.5. Surface reactions of adsorbed CH_3 + chlorine

Coadsorption of methyl radicals and Cl_2 to form a saturation monolayer of approximately 1:1 atomic ratio CH_3 and Cl on unpromoted Cu_3Si led to the formation and evolution of methylchlorosilanes in the TPR experiment at $T_p = \sim 550$ K (Table 1, Experiment 2), a temperature neither significantly affected by formulation of the alloy with excess silicon (Experiment 4), nor by changing sputtering conditions (Experiments 1 and 3). This temperature must be controlled by surface reaction kinetics, since it is much higher than the temperature of desorption of physisorbed Me_2SiCl_2 (Fig. 1). This is proof that the essential product forming step of the direct synthesis can proceed without reactions occurring in gas phase. This temperature is equivalent to an Arrhenius activation energy of reaction of 35 kcal/mol. This compares to the values of 26 kcal/mol for the unpromoted surface reaction, based on early studies of the direct synthesis that fit data to a Langmuir–Hinshelwood model [14,93]. That this activation barrier exists, would allow for the methyl chloride dissociation step in the direct synthesis to be not rate controlling. The heating rate during the TPR experiment would have to be ~ 1000 K/s, not the actual 2 K/s, to give a maximum silicon removal rate similar to that in the real direct synthesis, and this would boost T_p to 674 K [47]. If promoters were present, these temperatures were about 100 K less, typical of those found in the real direct synthesis (Experiments 5, 6, and 7). Repeated experiments consistently showed that T_p was also lowered further as a result of low temperature sputtering (Experiment 5), but only if promoters were present. The desorption curve was broad with two peaks

usually observed. We do not have an explanation for these observations at present. The range of T_p values (240–450 K, at 2 K/s heating rate) for the promoted sample is equivalent to Arrhenius activation energies of reaction of 15–28 kcal/mol (Line D–E, Fig. 1), assuming a first order surface reaction and frequency factor of 10^{13} s^{-1}. Apparent activation energies widely ranging from 10–25 kcal/mol for the promoted synthesis have been reported in recent years [46,94]. Apparent values might be expected to be less than the TPD derived values by only some small fraction of the rather high enthalpy of chemisorption of CH_3Cl due to high occupation of CH_3 and Cl sites [37,95]. Our results are similar to those reported by Lewis et al. [25] for CH_3Cl on active catalysts, with the exception that we detected no desorption of CH_3Cl or $SiClCH_3$ (the suggested silylene intermediate, $m/e = 78$). Because no CH_3Cl was desorbed, activation energy C–D was higher than energy D–E in Fig. 1. Because promoters lower T_p for products desorbed in experiments dosing Cl_2 or $Cl_2 + CH_3$, but not for products desorbed in experiments dosing CH_3 monolayer, it is suggested their mechanism of promotion relates to their interaction with the surface chlorine as opposed to their interaction with the surface methyl groups. Interestingly, the effect of low sputter temperature is opposite, lowering T_p for products desorbed in experiments dosing CH_3, but not from products desorbed in experiments dosing Cl_2 or, for unpromoted alloy, $Cl_2 + CH_3$.

Combining TPR and AES results, it was found 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 methylchlorosilane products in these TPR studies. The remaining methyl groups decompose to deposit carbon on the surface and 5% Me_3SiH. 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. It should be noted, however, that on the basis of the catalytic chemistry one would not necessarily expect a high efficiency of methyl and chlorine conversion to $Me_xSiCl_{(4-x)}$ 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, inefficiencies increase as the coverage drops toward zero. In one brief experiment on a CH_3 and Cl covered $Cu_2Si/Cu(110)$ surface, desorption of Me_2SiCl_2 was observed at 145 and 400 K, but the lower temperature peak was more intense, a finding perhaps related to etching by chlorine. Core level synchrotron based photoemission studies on this system are in progress (D.R. Strongin, data not shown).

The relative yields of the series of methylchlorosilanes $Me_xSiCl_{(4-x)}$ have been determined from the TPR peak areas of the major cracking fragments, and is shown in Table 1. The distributions are similar to those in a practical process, and reflect the beneficial effect of the promoters. For example, the 84% selectivity to $(CH_3)_2SiCl_2$ on promoted Cu_3Si is close to the reported values of ~90% while on pure Cu_3Si, the selectivity of 58% is typical for an unpromoted process [27].

4. Conclusions

The studies presented here show from TPR experiments that on an unpromoted copper silicide surface there are surface reaction controlled pathways occurring at 500–600 K for methyl monolayers in the absence of chlorine to produced primarily trimethylsilane, and chlorine monolayers in the absence of methyl to produced $SiCl_4$. However, mixed monolayers of methyl groups with chlorine atoms abandoned these separate pathways and instead reacted at similar temperatures on the surface to produce, with efficiencies under 50%, methylchlorosilanes, dimethyldichlorosilane being preferred (selectivity 58%). Thus, the rate controlling step

in the direct synthesis can occur in the complete absence of a gas phase and involves a surface reaction, and TPD derived activation energies remain consistent with a Langmuir–Hinshelwood model with an activated initial chemisorption step.

There is evidence that promoters may facilitate this surface reactivity. Thus, activation energy is lowered to ∼12 kcal/mol and the selectivity of the process towards dimethyldichlorsilane is increased to 85%, if the Cu_3Si samples contain Sn, Zn, and Al. Both approach values actually observed in the bulk direct synthesis. Results suggest that promoters have more effect on surface chlorine reactivity than surface methyl reactivity. By contrast, it was found that changes in the surface Cu/Si ratio have a significant effect on the reactivity of the surface methyl groups, but not on surface chlorine. Because increased Cu/Si ratio in a promoted sample, as well as the promoters themselves, seem to lower temperature of maximum desorption rate during TPR, further experiments are planned to prove both factors operate independently. Because the methodology used is that of a true UHV surface study, the way in which reactant fragments assemble at the active site should be revealed by low temperature adsorbate structural studies now in progress in other laboratories.

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References

[1] J.J. Zuckermann, Adv. Inorg. Chem. Radiochem. 6 (1964) 383.
[2] B. Kanner, K.M. Lewis, in: K. Lewis (Ed.), Catalyzed Direct Reactions of Silicon, Chap. 1, Elsevier, 1993.
[3] F.O. Stark, J.R. Falender, A.P. Wright, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Chap. 9.3, Pergamon, 1982.
[4] Thermodynamics Computer program 'HSC Chemistry 2.03', Outokumpu Research Oy, Pori, Finland.
[5] H.A. Oye, D.M. Gruen, Nat. Bur. Stand. Spec. Publ. (1979) 561, Proceedings of the 10th Mat. Res. Symp. on High Temperature Vapour and Gasses.
[6] G. Weber, B. Gillot, P. Barret, Phys. Status Solidi 75 (1983) 57.
[7] D. Viale, G. Weber, B. Gillot, J. Cryst. Growth 102 (1990) 269.
[8] H. Sorheim, H.A. Oye, in: H.A. Oye (Ed.), Silicon for the Chemical Industry II, Tapir Forlag, Trondheim, 1994 ISBN 82-519-144-2, p. 81.
[9] H.A. Oye, in: H.A. Oye (Ed.), Silicon for the Chemical Industry II, Tapir Forlag, Trondheim, 1994 ISBN 82-519-144-2, p. 129.
[10] H.M. Rong, H. Sorheim, in: H.A. Oye (Ed.), Silicon for the Chemical Industry III, Tapir Trykkeri, Trondheim, 1996 ISBN 82-90265-19-0, p. 199.
[11] H. Schafer, Z. Anorg. Allg. Chem. 445 (1978) 129–139.
[12] B. Guillot, H. Souha, D. Viale, J. Mater. Sci. 27 (1992) 1337.
[13] H. Souha, D. Viale, G. Weber, B. Guillot, J. Mater. Sci. 24 (1989) 1767.
[14] R.J.H. Voorhoeve, Organohalosilanes, Precursors to Silicones, Elsevier, 1967.
[15] W.F. Banholzer, N. Lewis, W. Ward, J. Catal. 101 (1986) 405.
[16] W.F. Banholzer, M.C. Burrell, J. Catal. 114 (1988) 259.
[17] H. Ehrich, D. Born, K. Richter, J. Richter-Mendau, H. Lieske, Appl. Organomet. Chem. 11 (1997) 237.
[18] H. Lieske, H. Fichtner, U. Kretzschmer, R. Zimmerman, Appl. Organomet. Chem. 9 (1995) 657.
[19] J.E. Demuth, U.K. Koehler, R.J. Hammers, P. Kaplan, Phys. Rev. Lett. 62 (1989) 641.
[20] R.J. Wilson, S. Chiang, F. Salvan, Phys. Rev. B 38 (1988) 12696.
[21] M. Mundschau, E. Bauer, W. Telieps, J. Appl. Phys. 65 (1989) 4747.
[22] R.A. Tutetskaya, K.A. Andrianov, I.V. Trofimova, E.A. Chernyshev, Usp. Khim. 44 (1975) 444, (Russ. Chem. Rev., 44 (1975) 212).
[23] H. Lieske, R. Zimmerman, Catal. Lett. 33 (1995) 413.
[24] J.P. Agarwala, J.L. Falconer, Int. J. Chem. Kin. 19 (1987) 519.
[25] K.M. Lewis, D. McLeod, B. Kanner, J.L. Falconer, T.C. Frank, in: K. Lewis, D.G. Rethwisch (Eds.), Catalyzed Direct Reactions of Silicon, Chap. 16, Elsevier, 1993.
[26] C.N. Satterfield, Heterogeneous Catalysis in Practice, McGraw-Hill, New York, 1980, pp. 95–97.
[27] W.J. Ward, A. Ritzer, K.M. Carroll, J.W. Flock, J. Catal. 100 (1986) 240.
[28] O. Heusler, Z. Metallk. 41 (1950) 261.
[29] F.O. Stark, J.R. Falender, A.P. Wright, in: G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Chap. 9.3, 1982.
[30] W.F. Banholzer, M.C. Burrell, J. Catal. 114 (1988) 259.
[31] R.L. Halm, O.K. Wilding Jr., R.H. Zapp, U.S. Patent 4,602,101 (1986).
[32] R.L. Halm, R.H. Zapp, R.D. Streu, U.S. Patent 4,965,388 (1990).

[33] F.J.J. van Loo, P.J.C. Vosters, J.G.M. Becht, R. Metselaar, Mater. Sci. Forum 29 (1988) 261.
[34] J.G.M. Becht, PhD Thesis, Technische Universiteit Eindhoven, Netherlands, 1987.
[35] W.J. Ward, K.M. Carroll, J. Electrochem. Soc. 129 (1982) 227.
[36] C.S. Kuivila, R.H. Zapp, O.K. Wilding, C.A. Hall, in: H.A. Oye (Ed.), Chemistry for the Chemical Industry II, Tapir Forlag, Trondheim, 1994 ISBN 82-519-144-2, p. 227.
[37] K.J. Laidler, Chemical Kinetics, McGraw-Hill, New York, 1987, Chap. 7.
[38] M.D. Allendorf, C.F. Melius, J. Phys. Chem. 97 (1993) 720.
[39] J. Joklik, M. Kraus, V. Bazant, Coll. Czech. Chem. Comm. 26 (1961) 427.
[40] M. Kadlec, M. Kraus, V. Bazant, Coll. Czech. Chem. Comm. 26 (1961) 436.
[41] J. Joklik, M. Kraus, V. Bazant, Coll. Czech. Chem. Comm. 27 (1962) 974.
[42] D.G. Rethwisch, T.J. Wessel, in: H.A. Oye (Ed.), Silicon for the Chemical Industry III, Tapir Trykkeri, Trondheim, 1996 ISBN 82-90265-19-0, p. 259.
[43] M.J. Van Dalen, PhD Thesis, Technical University, Delft, Netherlands, 1971.
[44] J.L. Lin, B.E. Bent, J. Phys. Chem. 97 (1993) 9713.
[45] K.A. Magrini, S.C. Gebhard, B.E. Koel, J.L. Falconer, Surf. Sci. 248 (1991) 93.
[46] H. Lieske, R. Zimmermann, Catal. Lett. 33 (1995) 413.
[47] P.A. Redhead, Vacuum 12 (1962) 203.
[48] R.J. Madix, Adv. Catal. 29 (1980) 1.
[49] F.M. Hoffman, D.J. Dwyer, in: D.J. Dwyer (Ed.), Surface Science of Catalysis, Chap. 1, ACS Symposium Series No. 482, 1992.
[50] B.E. Bent, Chem. Rev. 96 (1996) 1361.
[51] F. Zaera, Chem. Rev. 95 (1995) 2651.
[52] F. Zaera, Acct. Chem. Res. 25 (1992) 260.
[53] C.M. Chiang, T.H. Wentzhoff, B.E. Bent, J. Phys. Chem. 96 (1992) 1836.
[54] J.L. Lin, A.V. Teplyakov, B.E. Bent, J. Phys. Chem. 100 (1996) 10721.
[55] M.J. Bronikowski, R.J. Hamers, J. Vac. Sci. Technol. A 13 (1995) 777.
[56] P.J. Goddard, R.M. Lambert, Surf. Sci. 67 (1977) 180.
[57] G. Dagoury, D. Vigner, M.C. Paul, J. Rousseau, Proc. 7th Intern. Vac. Congr. and 3rd Intern. Conf. Solid Surf., Vienna, 1977, p. 1093.
[58] W. Sesselmann, T.J. Chuang, Surf. Sci. 176 (1986) 32.
[59] H.F. Winters, J. Vac. Sci. Technol. B 3 (1985) 9.
[60] H.F. Winters, J. Vac. Sci. Technol. A 3 (1985) 786.
[61] H. Gutleben, S.R. lucas, C.C. Cheng, W.J. Choyke, J.T. Yates Jr., Surf. Sci. 257 (1991) 146.
[62] H. Sinniah, M.G. Sherman, J.T. Yates Jr, K.C. Jandra, Proc. SPIE-Int. Soc. Opt. Eng. 63 (1990) 1208.
[63] C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke, J.T. Yates Jr., Surf. Sci. Lett. 273 (1992) L441.
[64] M.J. Kong, S.S. Lee, J. Lyubovitsky, S.F. Bent, Chem. Phys. Lett. 263 (1996) 1.
[65] H.N. Waltenburg, J.T. Yates Jr., Chem. Rev. 95 (1995) 1589.
[66] Q. Gao, C.C. Cheng, P.J. Chen, W.J. Choyke, J.T. Yates Jr., Thin Solid Films 225 (1993) 140.
[67] G.H. Smudde Jr., X.D. Peng, R. Viswanathan, P.C. Stair, J. Vac. Sci. Technol. A 9 (3) (1991) 1885.
[68] D.-H. Sun, A.B. Gurevich, L.J. Kaufman, B.E. Bent, A.P. Wright, B.M. Naasz, Proc. 11th Intern. Congr. Catal., Baltimore, MD, 1996, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), Elsevier, Amsterdam, p. 307.
[69] D.H. Sun, B.E. Bent, A.P. Wright, B.M. Naasz, Catal. Lett. 46 (1997) 127.
[70] D.W. Goodman, Chem. Rev. 95 (1995) 523.
[71] F. Zaera, A.J. Gellman, G.A. Somorjai, Acct. Chem. Res. 19 (1996) 24.
[72] T.C. Frank, K.B. Kester, J.L. Falconer, J. Catal. 91 (1985) 44.
[73] T.C. Frank, K.B. Kester, J.L. Falconer, J. Catal. 95 (1985) 396.
[74] M. Okamoto, S. Onodera, T. Okano, E. Suzuki, Y. Ono, J. Organomet. Chem. 531 (1997) 67.
[75] T.C. Frank, J.L. Falconer, Appl. Surf. Sci. 14 (1982) 359.
[76] Y. Samson, B. Tardy, J.C. Bertolini, G. Laroze, Surf. Sci. 339 (1995) 159.
[77] Y. Samson, J.L. Rousset, G. Bergeret, B. Tardy, J.G. Bertolini, Appl. Surf. Sci. 72 (1993) 373.
[78] K.M. Lewis, D. McLeod, B. Kanner, in: J.W. Ward (Ed.), Catalysis 1987, Elsevier, 1988.
[79] A.P. Graham, B.J. Hinch, G.P. Kochanski, E.M. McCash, W. Allison, Phys. Rev. B 50 (1994) 15304.
[80] T. Kanazawa, Y. Kitajima, T. Yokoyama, S. Yagi, A. Imanishi, T. Ohta, Surf. Sci. 357–358 (1996) 160.
[81] S.P. Lohokare, B.C. Wiegland, R. Nuzzo, Langmuir 11 (1995) 3902.
[82] B.C. Wiegand, S.P. Lohokare, R.G. Nuzzo, J. Phys. Chem. 97 (1993) 11553.
[83] L.H. Dubois, R.G. Nuzzo, Langmuir 1 (1985) 663.
[84] M.A. McCash, P. Chesters, P. Gardner, S.F. Parker, Surf. Sci. 225 (1990) 27382.
[85] C.M. Chiang, T.H. Wentzlaff, B.E. Bent, J. Phys. Chem. 96 (1992) 1836.
[86] C.M. Chiang, B.E. Bent, Surf. Sci. 279 (1992) 79.
[87] D.H. Sun, PhD Thesis, Columbia University (1997).
[88] P.M. Hall, J.M. Morabito, Surf. Sci. 83 (1979) 391.
[89] D.H. Fairbrother, X.D. Peng, M. Trenary, P.C. Stair, J. Chem. Soc., Faraday Trans. 91 (1995) 3619.
[90] C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke, J.T. Yates Jr., Surf. Sci. Lett. 273 (1992) L441.
[91] M.A. Mendicino, E.G. Seebauer, Appl. Surf. Sci. 68 (1993) 285.
[92] U. Streller, A. Krabbe, H.P. Krause, I. Twesten, N. Schwentner, J. Electron Spectrosc. Relat. Phenom. 80 (1996) 49.
[93] M. Kadlec, M. Kraus, V. Bazant, Coll. Czech. Chem. Comm. 26 (1961) 436.
[94] J.P. Kim, D.G. Rethwisch, J. Catal. 134 (1992) 168.
[95] G.C. Bond, A.D. Hooper, J.C. Slaa, A.O. Taylor, J. Catal. 163 (1996) 319.