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The Effect of Zn Promoter on Enhanced Diffusion during Catalytic Formation of Methylchlorosilanes

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The copper-catalyzed direct synthesis of methylchlorosilanes was carried out at atmospheric pressure and 550 K on four planar Cu_3Si alloy surfaces that contained <0.1 at% zinc and tin promoters. Kinetics were measured in a batch reactor attached to an ultrahigh vacuum chamber that allowed Auger surface analysis after reaction. Concentration depth profiles were obtained by ion sputtering and Auger analysis. These measurements showed that reaction almost completely depleted silicon in the subsurface regions of both unpromoted and tin-promoted Cu_3Si samples. The presence of zinc promoter in low concentrations (0.04–0.06 at%), however, dramatically increased silicon diffusion rates so that the subsurface regions of zinc-promoted Cu_3Si samples were *not* depleted of silicon. The increased diffusion rate is probably due to an increased rate of grain boundary diffusion. A synergistic interaction between zinc and tin further increased the subsurface concentrations of silicon. This dramatic increase in the silicon subsurface concentration in the presence of low concentrations of zinc indicates one important role of zinc promoters in the catalytic direct synthesis of methylchlorosilanes. © 1994 Academic Press, Inc.

INTRODUCTION

The copper-catalyzed direct synthesis reaction of solid silicon with gaseous methyl chloride to selectively form dimethyldichlorosilane ($(CH_3)_2SiCl_2$, DMD) is the basis of the silicone industry, in which DMD is reacted to form straight-chain silicone polymers (1). A secondary product of this reaction is methyltrichlorosilane (CH_3SiCl_3, MTC). Since MTC, which is difficult to separate from DMD, results in branched silicone polymers, much effort has been devoted to maximizing selectivity for DMD formation.

High-purity silicon alone does not react readily with CH_3Cl, and even after activation at high temperatures, selectivity for DMD formation is less than 1% (2). Commercially, the direct reaction is carried out on small particles of chemical-grade silicon, which contains Fe, Al, Ti, Mn, Ca, and Ni impurities (3). Reaction takes place at 1–4 atm pressure and 550–600 K in a fluidized bed, but a copper catalyst is necessary to obtain DMD selectivities of 70–90% (1). In addition to the copper catalyst, zinc and tin are added to the commercial reaction mixture as promoters. In laboratory-scale, fluidized bed studies with chemical grade silicon, Ward *et al.* (3, 4) found that both zinc and tin enhanced reaction rates and selectivities for DMD formation. Similar studies in packed-bed reactors with high-purity silicon also reported that zinc improved rates and selectivities for DMD formation, but tin had a deleterious effect on selectivity (5, 6). These promotion effects were sensitive to zinc and tin concentrations (3, 4), and a synergistic effect was observed when zinc and tin were used together (3, 6).

The objective of our study is to understand the effects of low concentrations of zinc and tin on the solid surfaces that take part in the direct reaction. To do so, model studies were carried out on a bulk Cu–Si stoichiometric alloy (Cu_3Si) so that the reacted surface could be characterized with Auger electron spectroscopy (AES). Previous studies have shown that Cu_3Si forms during the initial preparation and reaction of Cu–Si mixtures in fluidized-bed or stirred-bed reactors (1, 7, 8). Although these studies did not show that Cu_3Si is required for reaction, and Banholzer and Burrell (9) questioned whether Cu_3Si is needed, Frank *et al.* (10) showed that high-purity Cu_3Si reacts readily with CH_3Cl to form DMD with greater than 85% selectivity. Initial selectivities and apparent activation energies for methylchlorosilane formation were similar to those measured in particle-bed reaction studies. Thus, Cu_3Si appears to be a good model for studying the role of catalysts and promoters in the direct reaction to form methylchlorosilanes.

The presence of 0.4 at% zinc in Cu_3Si improved selectivity for DMD formation to greater than 95% (10). On Cu_3Si without promoters, the rate of DMD formation decreased with time, and it was concluded that silicon was not diffusing to the surface of bulk Cu_3Si fast enough to maintain the original reaction rate. The addition of 0.4 at% zinc apparently increased the rate of silicon diffusion because the rate of DMD formation on the zinc-promoted Cu_3Si was constant during the short reaction times used (<90 min). For a Cu_3Si sample containing 1.2 at% zinc

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(11), the rate of DMD formation was constant up to 300 min, but the selectivity was lower than that on unpromoted Cu_3Si.

In the current study, Cu_3Si with low concentrations of zinc and tin promoters (less than 0.1 at%) was used to study the direct reaction. High-purity materials were used to prepare the Cu_3Si samples in order to eliminate any promoting effects of impurities. Reaction was carried out in an atmospheric-pressure chamber attached to an ultrahigh vacuum chamber. This system allowed surface analysis before and after reaction without exposure to air. The segregation of silicon, zinc, and tin on the original Cu_3Si surfaces and the reaction kinetics on these surfaces will be reported elsewhere (12). The objective of this paper is to present the dramatic effect that zinc has on the location of silicon in reacted Cu_3Si samples, and thus elucidate one of the roles of the zinc promoter in this catalytic reaction. Thus, composition depth profiles of reacted samples were measured with ion sputtering and Auger spectroscopy. The subsurface regions of both zinc- and tin-promoted Cu_3Si alloys were analyzed.

EXPERIMENTAL METHODS

Four Cu_3Si samples were reacted with CH_3Cl in an atmospheric pressure reactor, which was attached to an ultrahigh vacuum (UHV) chamber. A bellows mechanism allowed the sample to move between the reactor and UHV without exposure to air. Surfaces were cleaned and characterized by Auger electron spectroscopy (AES) in UHV. The direct reaction was run in a recirculating batch reactor and products were identified by gas chromatography (GC). Details of the system are given elsewhere (10, 13).

The four Cu_3Si samples (22.7 ± 0.2 at% Si, 77.3 ± 0.2 at% Cu) were cut from ingots, which were prepared from the elements in a quartz tube furnace. A Si concentration of 25 at% was not used to make Cu_3Si because silicon precipitates form for concentrations higher than 23 at% (14). Formation of Cu_3Si (η-phase) was verified by polarized light microscopy (15). Reaction was carried out on one unpromoted Cu_3Si sample and on three samples containing the following promoter concentrations:

0.039 at% Zn (Cu_3Si–Zn)
0.014 at% Sn (Cu_3Si–Sn)
0.057 at% Zn and 0.013 at% Sn (Cu_3Si–Zn,Sn)

High-purity starting materials were used to prepare the alloys. The copper and tin were 99.999% and the silicon and zinc were 99.9999% (Alfa). Samples were cut from the ingots with a diamond saw and surfaces were polished with 0.3-μm Al_2O_3. Each sample was then mounted on a stainless-steel sample holder, which resistively heated the sample. The sample temperatures were monitored with a chromel–alumel thermocouple spotwelded to the back of each sample.

The samples were cleaned by Ar^+ sputtering and annealing at 550–675 K in UHV until the surface compositions did not change. Surface compositions were *estimated* from AES peak amplitudes and handbook sensitivity factors (16). The Cl (181 eV), C (273 eV), Sn (430 eV), O (507 eV), Cu (917 eV), Zn (994 eV), and Si (1620 eV) peaks were used. The low-energy Si (LVV) peak, although more surface sensitive than the Si (KLL) peak at 1620 eV, was not used to estimate compositions because its peak shape and intensity were both sensitive to the silicon chemical environment.

Clean surfaces were reacted in atmospheric-pressure CH_3Cl for 210–250 min at 550 K. After reaction, the sample was cooled, the reaction chamber was evacuated, and the sample was moved into the UHV chamber for AES analysis versus depth. The subsurface region of each reacted sample was analyzed by alternate Ar^+ sputtering and AES analysis. Surfaces were sputtered with 1 keV Ar ions (50–220 $\mu A/cm^2$) at 2–5° off normal incidence for 140–460 min and compositions of the exposed surfaces were obtained at 2–60 min intervals.

RESULTS

Figure 1 shows a representative Auger spectrum of the clean Cu_3Si–Zn surface after annealing at 575 K for 15 min. After reaction at 550 K, the surfaces contained silicon, copper, carbon, chlorine, and oxygen, as shown in Table 1. The Cu_3Si–Zn,Sn surface also contained 3% tin. Reaction with CH_3Cl changed the Si (LVV) peak shape and thus the silicon chemical environment. The location of the Si (LVV) peaks on reacted samples indicated the presence of Si–Cl (84 eV), Si–C (90 eV), and Si–Cu (90, 94 eV) bonds. On the two tin-containing surfaces, the Cu (MVV) peaks at 61 and 105 eV were absent after reaction.

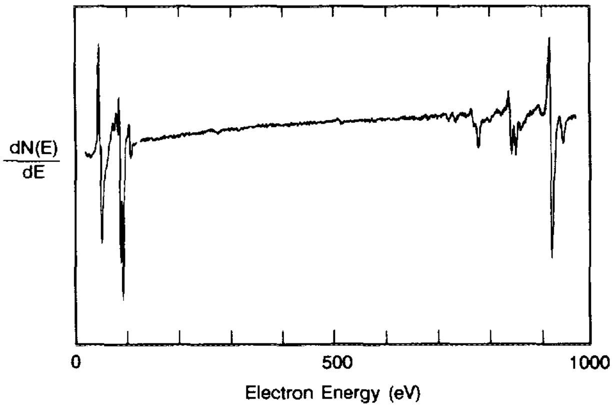

FIG. 1. Auger spectrum of clean Cu_3Si–Zn surface after annealing at 575 K.

TABLE 1

Surface Concentrations after Reaction at 550 K

Promoters	Reaction time (min)	Concentration (at%)					
		Si	Cu	C	Cl	O	Sn
Unpromoted	240	8	52	14	24	2	0
Sn	220	61	<0.5[a]	20	12	7	0
Zn	210	23	39	23	11	3	0
Zn,Sn	250	40	15	24	9	9	3

[a] Cu (917 eV) Auger peak not detected.

Thus, the top atomic layer contained very little Cu, although the high-energy Cu peak was observed on the reacted Cu_3Si–Zn,Sn sample.

Figure 2 shows the estimated concentrations versus ion dose for the unpromoted Cu_3Si sample. The ion dose is the product of sputtering time and ion current. The surface of the Cu_3Si sample after reaction contained copper, chlorine, oxygen, silicon, and carbon, as shown in Table 1, but Fig. 2 shows that the concentrations of carbon, oxygen, and silicon decreased rapidly with sputtering time. The 5–10 at% Cl measured during depth profiling may have resulted from chlorine diffusion from the bulk to the surface after the sputtering step. The dominant subsurface species was copper, which constituted 90% of the subsurface (note the scale on the right side of Fig. 2). That is, silicon reacted to form methylchlorosilanes faster than it was replenished by diffusion from the bulk so that silicon was depleted for a significant depth into the sample. Based on a rough estimate of the sputtering rate (17), approximately 1.1 μm were sputtered away in the 1.4 A · s ion dose represented in Fig. 2. This is an upper limit on the amount sputtered since the ion beam was near normal incidence.

The Cu_3Si–Sn surface had a higher concentration of silicon after reaction, and no copper was detected at the surface (Table 1). Although the composition of the top layers of the reacted Cu_3Si–Sn sample differed from the unpromoted Cu_3Si sample after reaction, the depth profile (Fig. 3) shows that copper was the dominant species (85%), and silicon was depleted in the subsurface region. When the sample was sputtered for a longer time than the unpromoted Cu_3Si sample, the silicon concentration slowly increased. In addition, when the tin promoter was present, the copper was depleted to a depth that was 6–7 times greater than that of the unpromoted Cu_3Si sample. This depleted copper region coincides approximately with the enhanced silicon concentration near the surface. That is, tin significantly increased the silicon concentration near the surface, but the subsurface of Cu_3Si–Sn was depleted of silicon, much like the unpromoted sample. Our sputtering estimates give an upper limit of 4.4 μm sputtered for a dose of 5.4 A · s. Since our reaction data indicate that approximately 1.8 μm was reacted away, these sputtering estimates are at least a factor of 2.5–3 high.

The most dramatic differences in subsurface compositions were observed for the two samples containing zinc, however. As shown in Figs. 4 and 5, the silicon was *not* depleted significantly in the subsurface region of either zinc-promoted Cu_3Si sample. The subsurface silicon concentration was approximately 7 times higher in Cu_3Si–Zn (Fig. 4) than in Cu_3Si (Fig. 2). Similarly, except in the immediate vicinity of the surface, the subsurface silicon concentration was 7–8 times higher in Cu_3Si–Zn,Sn (Fig. 5) than in Cu_3Si–Sn (Fig. 3). That is, the presence of zinc dramatically increased the silicon concentration in the subsurface region both in the absence and the presence of tin. When both zinc and tin were present and a higher zinc concentration was used, the silicon concentration was higher just below the surface than at the surface (Fig. 5). In the absence of zinc, however, the subsurface region of Cu_3Si was almost completely depleted of silicon after reaction, and except for very near the surface, the subsur-

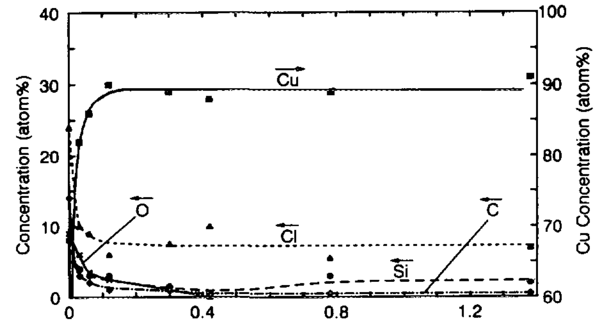

FIG. 2. AES compositions versus sputtering ion dose for Cu_3Si after reacting with CH_3Cl for 240 min at 550 K.

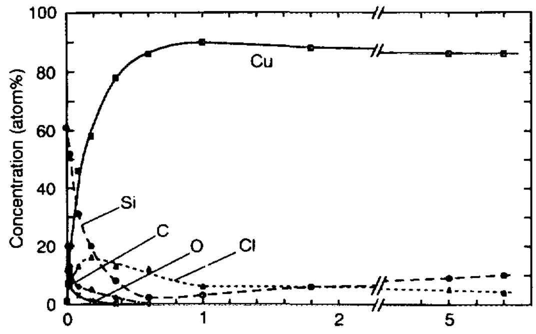

FIG. 3. AES compositions versus sputtering ion dose for Cu_3Si–Sn after reacting with CH_3Cl for 220 min at 550 K.

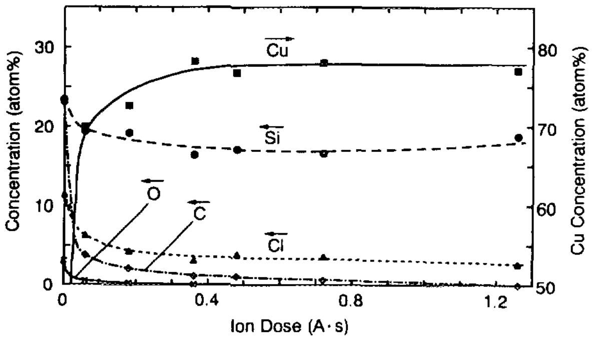

FIG. 4. AES compositions versus sputtering ion dose for Cu_3Si–Zn after reacting with CH_3Cl for 210 min at 550 K.

face region of the tin-promoted Cu_3Si was also depleted of silicon.

Concentration depth profiles were also measured for Cu_3Si and Cu_3Si–Zn,Sn after cleaning the samples and further reacting them at 600 K for 145 min. The reaction rates were higher at the higher temperatures, and more carbon was present on the Cu_3Si surface because of CH_3Cl decomposition. An ion dose of 0.6 A · s was required to sputter through the graphite layer, which we estimate had a maximum thickness of 350 nm. The silicon concentration was only 2–4% and the copper concentration was over 90% in the subsurface region of unpromoted Cu_3Si after reaction at 600 K. In contrast, on Cu_3Si–Zn, Sn the silicon concentration was almost 50% in the intermediate subsurface region and dropped to 30% by 0.4 A · s sputtering. These depth profiles are qualitatively similar to those obtained from the corresponding surface after reaction at 550 K. Zinc dramatically increased the concentration of silicon in the subsurface region. The Si (LVV) peak recorded during depth profiling of the Cu_3Si–Zn,Sn sample showed the 90–94 eV split peak that is characteristic of Cu–Si bonding.

The composition profiles for some elements show an exponential dependence on sputtering time, probably due to ion-induced mixing. Pitts *et al.* (18) showed that even films known to form well-defined interfaces display exponential concentration profiles due to sputter-induced mixing. Differences in sputtering yields of the various components also may have affected the depth profiles (17). Seah (19) predicted that the pure-element sputtering yield for oxygen is comparable to that of silicon. The sputtering yield of carbon is approximately half that of silicon, whereas the sputtering yield of chlorine is much higher. Although the pure-element sputtering yield of copper is twice that of silicon (19), previous studies (15, 20) have shown that copper and silicon have similar sputtering yields in Cu_3Si. Hence, the silicon-depleted regions of some samples were not due to preferential sputtering of silicon, and thus the measured concentration depth profiles are qualitative representations of the concentration profiles in the reacted alloys. The dramatic differences observed are due to the zinc promoter.

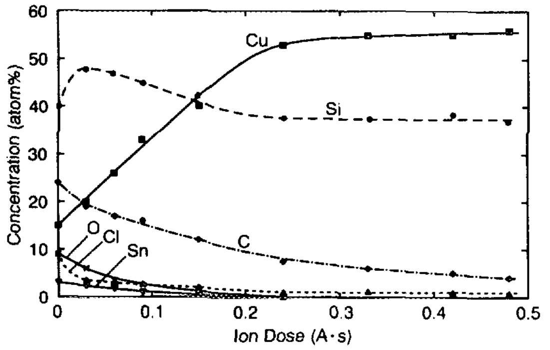

FIG. 5. AES composition versus sputtering ion dose for Cu_3Si–Zn,Sn after reacting with CH_3Cl for 250 min at 550 K.

DISCUSSION

What is surprising about our results is that zinc in such low concentrations (0.039–0.057 at%) can have such a dramatic effect on the subsurface silicon concentrations. In the absence of zinc promoters, the formation of methylchlorosilanes almost completely depleted the Cu_3Si subsurface region of silicon. Kinetics measurements showed that zinc increased rates and selectivities slightly, although silicon diffusion rates did not appear to limit methylchlorosilane formation on any of the Cu_3Si samples reacted for 210–240 min at 550 K (12).

X-ray photoelectron spectroscopy studies by Lewis *et al.* (22) also showed that zinc has a significant effect on the subsurface composition of unreacted Cu_3Si. An unpromoted Cu_3Si sample was enriched in silicon after heating, but sputtering away 4–5 nm restored the bulk composition (Cu/Si ratio of approximately 3). In contrast, for a Cu_3Si sample with 0.4% zinc, a Cu/Si ratio of 1.8 was maintained even after 600 nm were sputtered away. Addition of zinc was also observed to enhance silicon surface enrichment, especially above 675 K.

Since zinc dramatically increased the silicon concentration in the subsurface region, zinc apparently increases the rate that silicon diffuses in Cu_3Si. On Cu_3Si surfaces, as silicon is removed by reaction, silicon must move to the surface to react, and zinc increases the rate at which this occurs. In addition, zinc apparently increases copper dispersion on silicon particles. Gaspar-Galvin *et al.* (5) observed with SEM that copper was more dispersed on silicon when zinc and tin were present. They used high-purity silicon and CuCl and heated this mixture at 673 K in N_2. Since copper has a low melting point (1357 K) and surface mobility is significant above the Huttig temperature (407 K for Cu), copper catalysts usually must be supported or contain textural promoters to maintain high dispersions (21). Thus, zinc may act as a textural promoter in Cu–Si contact masses by enhancing silicon diffusion and copper dispersion. Zinc may cause more rapid formation of Cu–Si alloys in the fluidized bed reactors by enhancing copper–silicon interdiffusion.

In pure Cu_3Si, silicon is the segregating component, and both silicon and zinc segregate to the surface of Zn-promoted Cu_3Si annealed above 550 K (12, 13, 22). Frank *et al.* (13) proposed that this segregation behavior is due to the solid surface tensions (free energies) of zinc (0.10 N/m) and silicon (1.24 N/m), which are lower than that of copper (1.67 N/m). Our depth profiles show that zinc enhances silicon diffusion in Cu_3Si. An added solute can alter diffusion and segregation behavior in multicomponent systems (24–27), although the mechanisms of these effects are not well understood. Guttmann and McLean's (25) thermodynamic analysis showed that segregation of one component in a binary solid can be enhanced, hindered, or unaffected by the presence of additional species. Diffusion of both species, the added solute and the segregating component, will be enhanced if the solute is surface active (i.e., lowers surface free-energy) and the two species have a positive attraction interaction. An added species can also alter solubilities in solid solution or form precipitates, which change bulk composition. These effects can also influence segregation behavior.

Since the Cu_3Si samples used in our study and by Lewis *et al.* (22) were polycrystalline, silicon diffusion in grain boundaries may have been important. Grain-boundary diffusion usually exceeds bulk diffusion at temperatures less than 0.6 of the melting point (23). For Cu_3Si, this temperature is 653 K, so silicon diffusion in grain boundaries was significant during reactions at 550–600 K. However, Cu_3Si has a complex unit cell with a high concentration of vacancies and defects (14). Since bulk diffusion can occur via vacancies and lattice defects, bulk diffusion may also be important in Cu_3Si at 550–600 K.

Grain-boundary diffusion apparently occurs by site-jumping mechanisms (23, 28, 29). Kaur and Gust (23) proposed that grain-boundary diffusion rates are limited by the presence of high-energy sites. Since zinc segregates to the surface of zinc-promoted Cu_3Si to reduce surface free energy, it probably segregates to grain boundaries and reduces their free energy in polycrystalline Cu_3Si. Thus, zinc may enhance silicon diffusion in Cu_3Si by lowering grain-boundary free energy. Zinc may alter the bulk morphology of Cu_3Si, however, and thus affect silicon bulk diffusivity.

Since the depth profile of Cu_3Si–Zn,Sn showed higher concentrations of silicon than that of Cu_3Si–Zn, zinc and tin may act synergistically to enhance silicon diffusion. We feel it is unlikely that the difference in zinc concentration between the two samples (0.039 versus 0.057 at% zinc) is sufficient to cause the dramatic difference in silicon concentrations. Tin, like zinc, has a lower surface tension than silicon and copper, and tin segregates strongly to the free surface of Cu_3Si at 550–600 K (12). In the absence of zinc, however, tin does not enhance silicon diffusion.

CONCLUSIONS

Extremely low concentrations of zinc (0.039 mol%) dramatically increase subsurface silicon concentrations in reacted Cu_3Si alloys, apparently by increasing the rate of silicon diffusion. Low concentrations of tin do not alter silicon diffusion rates, although a synergistic affect appears to occur when both tin and zinc are present. Enhanced silicon diffusion may be due to enhanced grain boundary diffusion rates. This increase in the silicon diffusion rate may be one reason why zinc is an effective promoter in the direct synthesis of dimethyldichlorosilane.

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