Chemical Vapour Deposition of Transition-metal Silicides by Pyrolysis of Silyl Transition-metal Carbonyl Compounds

By **Bernard J. Aylett** * and **Howard M. Colquhoun**, Chemistry Department, Westfield College (University of London), London NW3 7ST

Pyrolysis of [Co(CO)$_4$(SiH$_3$)], [Fe(CO)$_4$(SiH$_3$)$_2$], and [Mn(CO)$_5$(SiH$_3$)] at 773 K in a flow system affords the transition-metal silicides CoSi, β-FeSi$_2$, and MnSi–Mn$_5$Si$_3$ respectively. Static pyrolysis of [Mn(CO)$_5$(SiH$_3$)] gives only amorphous solid products which contain, in addition to metal and silicon, appreciable quantities of carbon, hydrogen, and oxygen.

TRANSITION-METAL silicides are now of great interest [1] because of their high thermal stabilities, their resistance to corrosion, and their frequently novel electrical properties; V_3Si, for example, possesses one of the highest superconducting transition temperatures known,[2] and β-FeSi$_2$ is not only an intrinsic semiconductor [3] but also displays a remarkably high thermoelectric e.m.f. (up to 770 μV K^{-1}).[4] However, there have been few reports of methods for vapour-depositing the thin films of metal silicides needed for electronics applications or as protective coatings; such methods are limited to co-reduction of $SiCl_4$ and a volatile transition-metal halide (*e.g.* $TiCl_4$) with hydrogen,[5] and electron-beam evaporation of β-FeSi$_2$.[6]

It has previously been noted that the static pyrolysis of silyl transition-metal carbonyl compounds leads to dark solids of metallic appearance, containing both metal and silicon together with relatively large amounts of carbon, hydrogen, and oxygen.[7,8] We now report a more extensive study of the pyrolysis of these compounds, by both static and flow methods, to determine whether thin films of transition-metal silicides can in fact be obtained from such reactions.

EXPERIMENTAL

The volatile compounds [Co(CO)$_4$(SiH$_3$)],[7] [Fe(CO)$_4$(SiH$_3$)$_2$],[9] and [Mn(CO)$_5$(SiH$_3$)] [10] were prepared as previously described, and were purified by fractionation *in vacuo*. Pyrolysis under static conditions was examined by heating a known quantity of [Mn(CO)$_5$(SiH$_3$)] (50—100 mg) in a sealed tube *in vacuo* at 720 K for up to 1 h, and then quenching at room temperature. Analysis of the volatile products by volume (CO, H_2), by weight {unchanged [Mn(CO)$_5$(SiH$_3$)]}, or spectroscopically (SiH_4, CH_4) allowed the composition of the involatile residue to be determined by difference.

Flow pyrolyses were carried out using the borosilicate glass apparatus shown in Figure 1. The system was evacuated to a pressure of <0.01 mmHg,† and a mixture of helium carrier gas and silylmetal carbonyl vapour was then allowed to flow from a cooled inlet nozzle into the deposition zone, heated to 773 ± 5 K by a conventional resistance furnace. There solid decomposition products formed on the surface of a silica substrate, and also on the tip of the nozzle. Carrier-gas flow rates in the range 50—150 cm^3 s^{-1} at pressures of 0.5—1.0 mmHg, reaction times of 10—30 min, sample-vaporisation temperatures of 250—273 K, and sample weights of 50—100 mg were found to produce good, coherent, microcrystalline films. Typically, the mol ratio (helium : silylmetal carbonyl) of gases entering the hot zone was *ca.* 30 : 1.

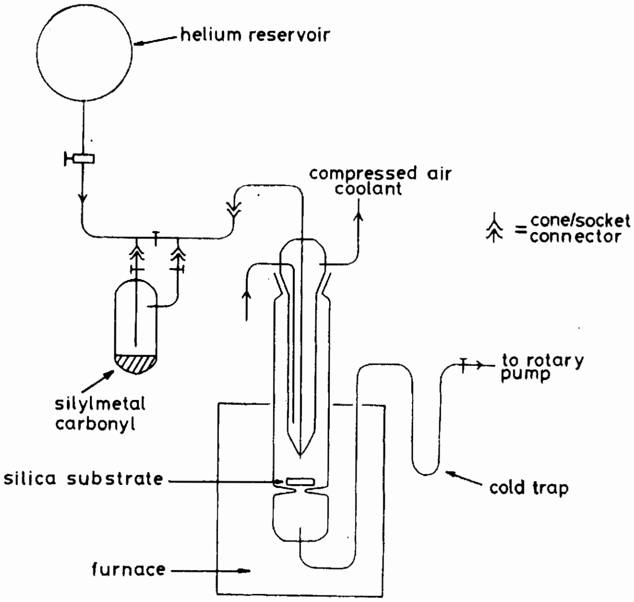

FIGURE 1 The flow pyrolysis system

The deposits were characterised by *X*-ray powder diffraction using a Philips PW 1130 instrument, and by scanning electron microscopy–electron-microprobe analysis using a Cambridge ' Stereoscan ' microscope fitted with an

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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EDAX energy-dispersive *X*-ray analyser. The microprobe results can be taken as only approximate guides to composition (probably ±10%), however, since films were invariably too thin to permit the extensive polishing required for accurate quantitative work.

RESULTS AND DISCUSSION

Static Pyrolysis.—The compound $[\mathrm{Mn(CO)_5(SiH_3)}]$ at 720 K gave CO, H_2, SiH_4, and CH_4 as volatile products; the residue consisted of an amorphous grey powder presumably produced by homogeneous gas-phase decomposition, together with an extremely thin 'metallic' film which covered the walls of the tube. An analysis of the volatile products for pyrolysis times of 1—60 min is shown in Figure 2, and the inferred residue compositions are given in the Table. Perhaps the most noteworthy features are the relatively high proportions of carbon and oxygen (*ca.* 30% of available CO) retained by the residue, suggesting that these elements are present not as residual carbonyl groups but as carbide and oxide respectively. Pyrolysis of $[\mathrm{Cr(CO)_6}]$ at 900 K has been reported to give up to 60% of Cr_2O_3–Cr_3C_2 with only 40% of Cr metal.[11] In the early stages of the reaction considerable monosilane was produced, but after 60 min at 720 K none remained. Hydrogen and methane were produced in increasing amounts as the reaction proceeded.

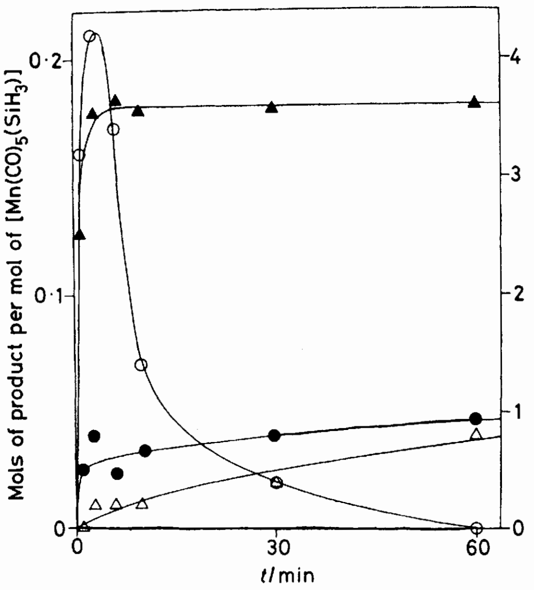

FIGURE 2 Analysis of volatile products from the static pyrolysis of $[\mathrm{Mn(CO)_5(SiH_3)}]$ as a function of time. The left-hand scale refers to SiH_4 (○) and CH_4 (△); the right-hand scale refers to H_2 (●) and CO (▲)

Compositions (atoms per atom of Mn) of residues from pyrolysis of $[\mathrm{Mn(CO)_5(SiH_3)}]$ at 720 K

	Composition				
t/min	Mn	Si	C	O	H
1	1.00	0.83	2.48	2.48	1.27
3	1.00	0.80	1.46	1.46	0.52
6	1.00	0.83	1.28	1.28	1.29
10	1.00	0.93	1.43	1.44	1.28
30	1.00	0.98	1.40	1.42	1.04
60	1.00	1.00	1.36	1.40	0.97

The following facts must be taken into account in any attempt to describe the course of this reaction. (*i*) Silylmetal carbonyls readily disproportionate, especially in the liquid phase, *e.g.* equation (1).[10] Silane thus

$$2[\mathrm{Mn(CO)_5(SiH_3)}] \xrightarrow{\text{Heat}} \mathrm{SiH_4} + [\{\mathrm{Mn(CO)_5}\}_2\mathrm{SiH_2}] \tag{1}$$

produced decomposes to silicon and hydrogen at temperatures above *ca.* 700 K.[12] (*ii*) Disiloxanes often result from the thermolysis of silylmetal carbonyls, *e.g.* equation (2) where R = H,[7] Me,[13] or Et.[14] Oxygen

$$[\mathrm{Co(CO)_4(SiR_3)}] \xrightarrow{\text{Heat}} \mathrm{O(SiR_3)_2} + ? \tag{2}$$

abstraction from metal-bonded CO groups *via* $\mathrm{M{-}CO}\!:\!\rightarrow\mathrm{Si}$ interaction is probably occurring [see (*iii*)]. In the present case, any $\mathrm{O(SiH_3)_2}$ produced will decompose rapidly to give SiH_4 and solids containing Si, O, and possibly H.[15] (*iii*) Under milder conditions, migration of silicon from the metal to oxygen may be observed, *e.g.* equation (3).[16] Isolation of these Si–O–

$$[\mathrm{Co(CO)_4(SiMe_3)}] \xrightarrow{105\,^{\circ}\mathrm{C}} [\mathrm{Co_3(CO)_9(COSiMe_3)}] + [\mathrm{Co_2(CO)_4(COSiMe_3)_4}] \tag{3}$$

C–M derivatives lends support to the proposed mechanism for disiloxane formation mentioned in (*ii*). (*iv*) Although reactions of ions in a mass spectrometer do not always parallel those of neutral species at higher pressures, it is known that the most important fragmentation pattern for silylmetal carbonyls involves 'stripping' of hydrogen and CO, leaving abundant $[\mathrm{M}_x\mathrm{Si}_y]^+$, and Si^+ ions (*e.g.* refs. 7, 9, and 10).

There is therefore ample precedent for a number of processes which collectively can yield solids with Si–O and M–C bonds and also silane, CO, and H_2 as volatile products. The slow formation of methane is accounted for by a subsequent Fischer–Tropsch reaction catalysed by the finely divided metal-containing residue,[17] *viz.* $\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}$.

Flow Pyrolysis.—In an attempt to overcome the disadvantages of static pyrolysis as a method of materials

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synthesis, including formation of ill defined amorphous solids and the occurrence of secondary reactions between by-products, the flow system illustrated in Figure 1 was designed. Flow pyrolysis of $[\mathrm{Co(CO)_4(SiH_3)}]$, $[\mathrm{Fe(CO)_4(SiH_3)_2}]$, or $[\mathrm{Mn(CO)_5(SiH_3)}]$ at 773 K, with helium as carrier gas, gave rise to a dark grey film on the surface of a silica substrate, and a ring of brittle material around the tip of the inlet nozzle. Both types of deposit were crystalline, the nozzle deposits in particular giving sharp X-ray powder-diffraction patterns which confirmed the presence of transition-metal silicides. X-Ray patterns from the substrate deposits were more diffuse, but showed that they contained the same phases as the corresponding nozzle deposits. The morphologies of the nozzle and substrate deposits were examined by scanning electron microscopy; this revealed extensive dendritic growth in the former (Figure 3) but a uniform blastular texture in the latter, characteristic of many materials formed by rapid vapour deposition (Figure 4).

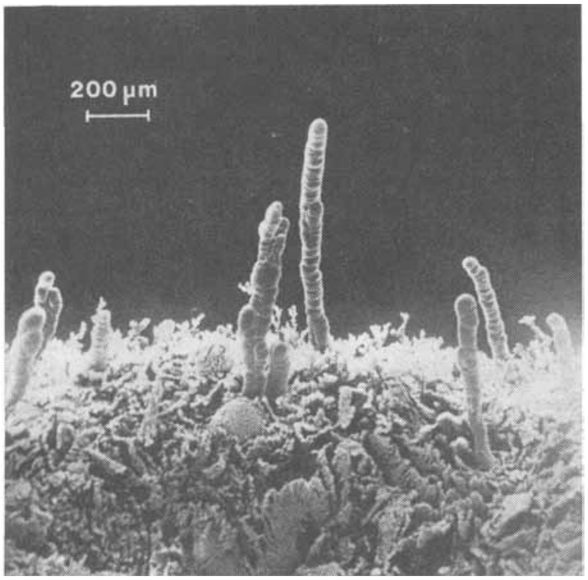

FIGURE 3 Dendritic growth in β-$\mathrm{FeSi_2}$ nozzle deposit

Flow pyrolysis of $[\mathrm{Co(CO)_4(SiH_3)}]$ produced deposits giving an X-ray powder pattern that corresponded to the single phase CoSi,[18a] and electron-microprobe analysis of the substrate deposit gave the approximate composition 50% Co and 30% Si (mol ratio Co : Si = 1 : 1.3). Decomposition of $[\mathrm{Fe(CO)_4(SiH_3)_2}]$ under similar conditions gave a material whose X-ray pattern showed β-$\mathrm{FeSi_2}$ [19] to be the only ordered phase present, and for which electron-microprobe analysis gave a composition 50% Fe and 45% Si (mol ratio Fe : Si = 1 : 1.8). On annealing this material at 1 270 K for 4 d, complete decomposition occurred, giving a mixture of α-$\mathrm{FeSi_2}$ [18b] (a metallic iron-deficient phase) and FeSi.[18c]

The iron disilicide system appears to have been a source of some confusion in the past. Some 40 years after its original synthesis by fusion of the elements,[20] α-$\mathrm{FeSi_2}$ was found to decompose on annealing at lower temperatures (*ca.* 1 200 K) giving β-$\mathrm{FeSi_2}$ and free silicon.[21] A second phase transition was later reported,[22] giving 'γ-$\mathrm{FeSi_2}$' at <920 K, but the existence of this phase has never been verified and the formation of β-$\mathrm{FeSi_2}$ at 773 K, reported here, would seem to rule it out altogether. More recently, Suchet [23] incorrectly attributed semiconducting properties to the iron-deficient α phase (referred to as $\mathrm{Fe_2Si_5}$), and Aronson *et al.*[24] suggested that $\mathrm{FeSi_2}$ (unspecified) does not obey Dudkin's criterion for semiconduction. This empirical criterion [25] can be expressed in the form that: 'a transition-metal binary compound should be semiconducting if $2R/D_{\mathrm{min.}}$ (= Δ) < 0.82, where R is the single-bond metallic radius of the transition element (Pauling value) and $D_{\mathrm{min.}}$ is the minimum metal–metal distance in the lattice of the compound being considered.' The structure of metallic α-$\mathrm{FeSi_2}$ has long been known [26] (R_{Fe} 117 pm, $D_{\mathrm{min.}}$ 268 pm, Δ 0.87), but that of semiconducting β-$\mathrm{FeSi_2}$ was determined only as recently as

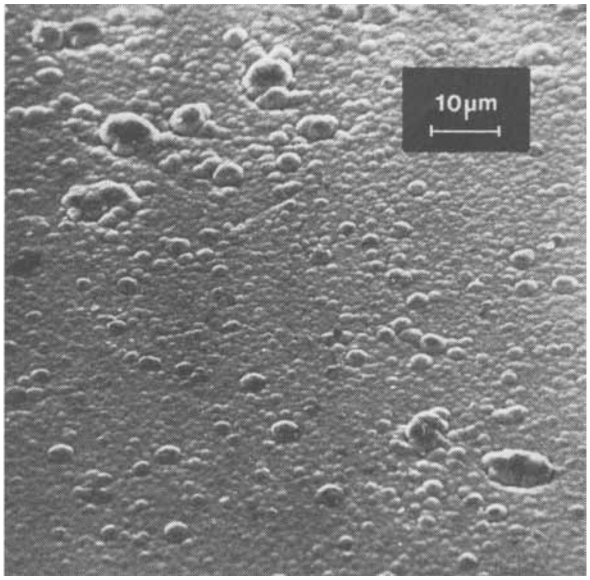

FIGURE 4 Surface of β-$\mathrm{FeSi_2}$ substrate deposit showing the blastular texture

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1971[19] (R_{Fe} 117 pm, $D_{min.}$ 297 pm, Δ 0.79), and it is now clear that Dudkin's criterion is in fact obeyed by both phases.

X-Ray powder photographs of the deposit from flow pyrolysis of $[Mn(CO)_5(SiH_3)]$ revealed a mixture of two phases, Mn_5Si_3[18d] and MnSi,[27] and electron-microprobe analysis gave the composition 65% Mn and 30% Si (mol ratio Mn : Si = 1 : 0.9). It might have been anticipated that only the single phase MnSi would be formed in this reaction since results for the iron and cobalt systems had suggested that the nature of the solid phase depended directly on the metal : silicon ratio in the molecular precursor. It has been found, however, that the phase having the *crystallographic* composition ' MnSi ' is invariably silicon-rich, and is in fact homogeneous at the composition Mn_4Si_5, so that equilibration of a 1 : 1 (atom : atom) mixture of Mn and Si gives, in addition to ' MnSi,' relatively large quantities of Mn_5Si_3.[28] The formation of two solid phases in the pyrolysis of $[Mn(CO)_5(SiH_3)]$ is thus readily accounted for.

The simple nature of the products formed under these conditions argues in favour of a ' stripping ' process like that mentioned earlier. The low partial pressure of silylmetal carbonyl ($<$0.5 mmHg) and the brief interval during which it is exposed to high temperature in passing from the nozzle to the substrate ($<$1 ms) combine to reduce the possibility of side reactions. As in many chemical vapour-deposition processes, the system is far from equilibrium and the products are not necessarily those most favoured thermodynamically.

Conclusions.—The flow pyrolysis of volatile silyl transition-metal carbonyl compounds offers a straightforward yet versatile method of depositing thin films of metal silicide at relatively low temperatures, using simple apparatus. The composition of the deposit is predetermined, and the technique is limited only by the availability of suitable volatile precursors. Extension of the method to other similar systems seems feasible; for example, pyrolysis of phosphinemetal complexes or metallaboranes might well yield transition-metal phosphides or borides.

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