

Cobalt deposition in porous silicon by chemical vapour infiltration and deposition; the effects of precursor instability¹

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Abstract

Cobalt has been deposited on and in porous silicon by chemical vapour infiltration and deposition using deuterated cobalt carbonyl hydride, $\text{DCo}(\text{CO})_4$. This precursor is unstable, and below about 22°C decomposes with an initial half-life of 10 min, probably forming $\text{DCo}_3(\text{CO})_6$. After a time which depends on the precursor concentration, the precursor decomposes more rapidly. This reaction increases the concentration of cobalt and the ratio of cobalt to hydrogen within the pores. At temperatures above about 22°C, a similar but smaller increase occurs in the concentration of cobalt, and $\text{Co}_2(\text{CO})_8$ is thought then to be the main decomposition product. Thermolysis preserves the increased levels of metal within the pores; it is inferred that each cobalt atom becomes linked to one silicon atom at the pore wall.

Keywords: Silicon; Cobalt; Chemical vapour infiltration and decomposition; Carbonyl; Porous; Metallising

1. Introduction

We have used chemical vapour infiltration and deposition (CVID) as a technique to metallise porous silicon (PS). The connected nature of the pores in this material makes it possible not only to metallise its external surfaces but also to deposit metal within the pores [1]. The CVID approach uses a volatile metal-containing precursor, which over a period of time can infiltrate into PS at room temperature. The precursor becomes sorbed on the pore walls and, when the PS is warmed, decomposes to deposit metal in situ. Such deposition is of great current interest, not only because it is a way of producing conducting regions in single-crystal silicon but also because it can modify the photo- and electroluminescent properties of highly porous PS wafers [2] and may stabilise them against atmospheric degradation.

For cobalt deposition using $\text{DCo}(\text{CO})_4$ (or its H analogue), different concentrations of metal occur at

different depths, depending on the conditions. Higher concentrations have been found in the pore regions near the surface (the "pore necks"), up to a plateau concentration which has been associated with complete closure of the pores by a plug of precursor molecules [3]. Rhenium depositions using $\text{HRe}(\text{CO})_5$ have shown that plugs of molecules form by capillary closing of open pores exposed to precursor vapour, a behaviour which is described by the Kelvin equation [4]. The thermal stability of $\text{HRe}(\text{CO})_5$ at room temperature has made it possible to measure the physical properties which determine this behaviour, but such measurements are much harder for the less stable $\text{HCo}(\text{CO})_4$. At room temperature, $\text{HCo}(\text{CO})_4$ decomposes particularly readily in a condensed phase, which will be present if any plugs form in the pores of PS; we report here the effects this produces.

2. Experimental

PS layers were produced from n^+ -type (0.015 Ωcm) (100) silicon substrates which were anodised in the dark for 15 min at 15 mA cm^{-1} in an electrolyte composed of 40% aqueous $\text{HF}:\text{H}_2\text{O}:\text{ethanol}$ (1:1:2). The poros-

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ity and thickness of the PS layers, as determined gravimetrically, were 65% and 4.5 μm respectively.

The CVID process and precursor synthesis are described in detail elsewhere [1]; the deuterated precursor $\text{DCo}(\text{CO})_4$ used in this work was maintained in a thermostatted bath at a temperature of -30°C during the deposition process. Precursor vapour entered the reaction chamber and was allowed to infiltrate the pores of the PS sample for periods ranging from 3 to 15 min, becoming sorbed on the pore walls. The sample was then heated to 150°C ; this decomposed the sorbed species in situ, while remaining precursor vapour decomposed at the hot PS surface to form a capping layer over the pores.

The gases in the reaction chamber were sampled by a quadrupole mass spectrometer (Spectramass Dataquad 200/DXM). Gas compositions both before and after heating the PS were determined and agreed with those found previously [3]. Since most of the added precursor in the reaction chamber was present as vapour, heating the sample produced gases derived from decomposition at the PS surface rather than within the pores. The gases produced by decomposition within the pores were studied by altering the reaction conditions: after infiltration, but before heating, the reaction chamber was briefly evacuated. This removed excess vapour, together with some of the molecules which had formed a plug in the pore necks by capillary condensation. The reaction chamber was then re-isolated, so that all gases present after subsequent heating must necessarily have derived from molecules trapped down the pores. Such molecules were at sufficiently low concentrations that they could not form multilayers of metal atoms and so must have reacted with the pore walls.

The metallised substrates were analysed by Rutherford back-scattering (RBS), nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA). The atomic concentrations of carbon, oxygen, silicon and cobalt as a function of depth were calculated from

the RBS and NRA results [5]. The absence of deuterium was confirmed by ERDA.

3. Results and discussion

Deuterated cobalt carbonyl hydride, $\text{DCo}(\text{CO})_4$, is a valuable precursor: it readily decomposes to give cobalt metal, and the presence of deuterium provides useful mechanistic information from mass spectral studies, since monitoring of H_2 , HD and D_2 concentrations makes it possible to separate the effects of precursor decomposition from reaction with Si–H groups on the pore walls. With it, samples of PS have been metallised using differing infiltration times, including longer times than those in previous studies. The depth profiles determined from the RBS and NRA results for these samples are shown in Fig. 1.

The sample with the shortest infiltration time (3 min) gives results very similar to those found previously [3] for times from 0.5 to 4 min, all of which showed a higher concentration of cobalt at the pore necks than further down the pores. The concentration at the pore necks always remained approximately constant for samples with a given porosity, indicating that the necks were saturated with a plug of precursor molecules. The profiles in Fig. 1, however, show a gradual increase in cobalt concentration at the pore necks for longer infiltration times, which suggests that the chemical nature of the plug must be changing.

Studies of $\text{HCo}(\text{CO})_4$ decomposition at higher pressures, with temperatures above about 22°C , have established that the products are hydrogen and $\text{Co}_2(\text{CO})_8$. At temperatures below about 22°C , however, the hydride is known [6] to give the trinuclear cluster $\text{HCo}_3(\text{CO})_9$. We have previously determined that the half-life of $\text{HCo}(\text{CO})_4$ vapour in the present reaction chamber is about 10 min [3]. Given the time-scale of the metallisations reported here, we believe that the precursor is

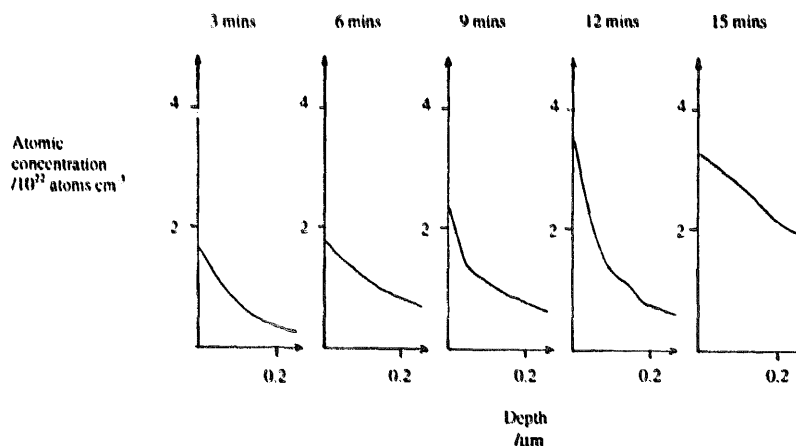


Fig. 1. Cobalt concentration vs. depth in samples metallised after different infiltration times.

decomposing within the pores to form these cobalt-rich compounds, especially since it is likely to be present as a condensed phase.

The resulting change in cobalt concentration can be estimated by considering the concentration in each of the compounds involved. This is easy when the crystal structures have been determined, because then accurate molecular densities are known. For $\text{DCo}(\text{CO})_4$, however, this density is not known experimentally, and we must proceed by analogy.

The molar volumes of $\text{DRe}(\text{CO})_5$ and $\text{Re}_2(\text{CO})_{10}$ are respectively 134 [4] and $112 \text{ cm}^3 (\text{mol Re})^{-1}$ [7]. On this basis, therefore, the change in molar volume on going from a metal–metal bonded dinuclear carbonyl to a metal carbonyl deuteride or hydride [8] is $22 \text{ cm}^3 (\text{mol D})^{-1}$. Adding this change to the molar volume of $\text{Co}_2(\text{CO})_8$, namely $91 \text{ cm}^3 (\text{mol Co})^{-1}$ [7], produces a calculated molar volume of $113 \text{ cm}^3 (\text{mol Co})^{-1}$ and hence a density of 1.52 g cm^{-3} for $\text{DCo}(\text{CO})_4$. The values for the relevant cobalt carbonyl species are listed in Table 1.

Considering first those experiments carried out below 22°C , the maximum concentration of cobalt present in the first sample (with an infiltration time of only 3 min) represents the concentration when pore necks are filled with almost pure $\text{DCo}(\text{CO})_4$. The maximum concentrations expected in other samples can therefore be predicted from the half-life of the precursor together with the density of the expected product ($\text{DCo}_3(\text{CO})_9$) relative to that of $\text{DCo}(\text{CO})_4$. The calculated curve based on a half-life of 10 min is compared with experimental data in Fig. 2. Initially there is good agreement, but the later deviations indicate that, after a few minutes, the reaction becomes more rapid than the vapour phase process. This is consistent with faster decomposition in a condensed phase as noted earlier, and suggests an autocatalytic process: the more packed a pore is with precursor, the more rapid will be its conversion. The cobalt concentrations for the pore necks therefore reach a new plateau (representing pores filled chiefly with $\text{DCo}_3(\text{CO})_9$) more rapidly than predicted.

Data for infiltration temperatures above 22°C show smaller increases in concentration. These correspond more nearly to formation of $\text{Co}_2(\text{CO})_8$, which will produce a lower plateau concentration of cobalt for a

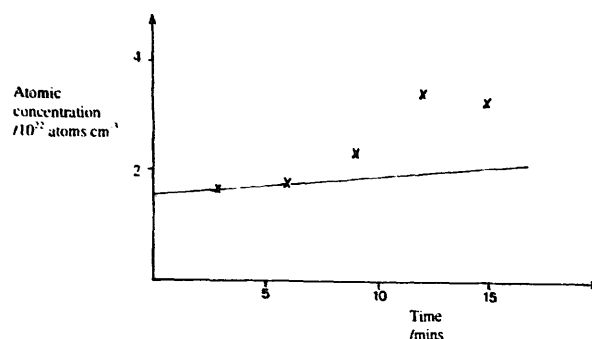


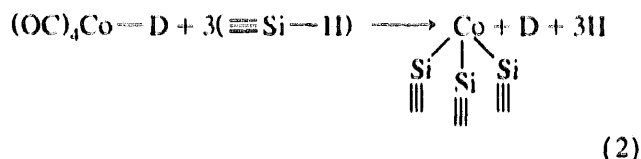
Fig. 2. Cobalt concentration at the pore neck vs. infiltration time. The curve represents calculated values assuming a half-life of 10 min for conversion of the precursor into $\text{DCo}_3(\text{CO})_9$.

packed pore than the trinuclear compound (see Table 1). They show that $\text{DCo}_3(\text{CO})_9$ is not a stable product in the pores above about 22°C , consistent with the previously-noted value for the bulk solid of 20°C .

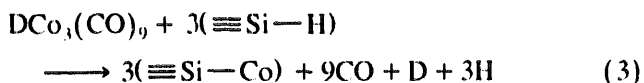
Formation of $\text{DCo}_3(\text{CO})_9$ involves loss of deuterium and carbon monoxide:



Clearly the D:Co ratio changes as this reaction proceeds. In previous work with $\text{DCo}(\text{CO})_4$, it had been assumed that the precursor remained unchanged in the pores of PS before thermolysis. The observed H:D ratio in the gases evolved on heating was 3, implying that three times as much hydrogen came from the pore walls as was produced from the cobalt compound; the process shown in Eq. (2) was therefore proposed, in which each Co bonds to three surface silicon atoms by displacing hydrogen from the Si–H bonds known to be present down the pore walls:



In the present study of this reaction by mass spectrometry, the infiltration time for the precursor was extended to about 40 min. After this time, the slow reaction (1) is expected to be essentially complete, so that thermolysis can now be represented by Eq. (3), again consistent with the observed H:D ratio of 3:



This product stoichiometry, with a metal atom bonded to just one silicon, has been found previously in the thermolysis of the more stable $\text{DRe}(\text{CO})_5$ within PS pores.

The slow decomposition of the deuterated precursor to form the trinuclear compound (Eq. (1)) results in deuterium evolution; the ratio of deuterium remaining in

Table 1
Physical parameters of cobalt carbonyls

Compound	Density (g cm^{-3})	Molar volume ($\text{cm}^3 (\text{mol Co})^{-1}$)	Cobalt concentration (mol Co m^{-3})
$\text{HCo}(\text{CO})_4$	1.52 ^a	113 ^a	8800 ^a
$\text{Co}_2(\text{CO})_8$	1.87 ^b	91 ^b	10900 ^a
$\text{HCo}_3(\text{CO})_9$	2.11 ^c	68 ^c	14700 ^a

^a This work; ^b Ref. [7]; ^c Ref. [6].

Table 2
The molar ratios of precursor deuterium to pore hydrogen found after different infiltration times of $\text{DCo}(\text{CO})_4$ into PS

Infiltration time (min)	Precursor deuterium	
	Pore hydrogen	
2	0.90	
6	0.78	
10	0.68	
15	0.52	
infinite ^a	0.33	

^a Ref. [3].

the pores to the amount of hydrogen displaced from pore walls by reaction with Co–D bonds will therefore change with time. This has been measured experimentally; results are presented in Table 2 and plotted in Fig. 3. Also included in the figure are a calculated curve based on a half-life of 10 min for the conversion of $\text{DCo}(\text{CO})_4$ into $\text{DCo}_3(\text{CO})_9$ and the expected level after infinite time.

Fig. 3 shows that the results agree well with this calculated curve. It was noted in connection with the results in Fig. 2 that some deviation from the calculated curve occurred at longer infiltration times, and a similar effect might be expected in connection with the mass spectrometry results. It will be less dramatic, however, since now the decomposing molecules are further down the pores and in lower concentrations. The slight deviation seen after 15 min infiltration may arise in this way.

4. Conclusion

The depth profiles show a variation in cobalt concentration that is in accord with the known decomposition products of $\text{HCo}(\text{CO})_4$. Within the pores of PS at temperatures below about 22°C, the deuterated precursor decomposes to give mainly $\text{DCo}_3(\text{CO})_9$, while above this temperature $\text{Co}_2(\text{CO})_8$ is chiefly produced. Both of these initial products decompose on heating and react

with the Si–H bonds on the pore walls to give Si–Co bonds; there is ample precedent for such reactions in molecular species [9].

The rate of initial decomposition is initially the same as that found in the precursor vapour, with a half-life of 10 min. After an induction period this is followed by a more rapid conversion of the precursor, so that experimental points deviate from the predicted curve. The induction period varies according to the proximity of the molecules being studied: depth profiles show that the deviation is significant for molecules at the necks of the pores where plugs of closely packed molecules form, while mass spectrometry results suggest that it is much less important deeper in the pores. Results from the latter technique support the production of $\text{DCo}_3(\text{CO})_9$ in the pores below about 22°C. The absence of deuterium and presence of hydrogen in the PS layer after thermolysis (shown by ERDA) correlates well with the concentrations of deuterium in the gas phase (present as HD and D_2) produced during pyrolysis; it seems clear that no H/D exchange involving the Si–H bonds on the pore walls has occurred. More tentatively, the measured concentrations of H_2 , HD and D_2 from reaction (2) suggest that some random redistribution process is taking place, possibly catalysed by the metal surface.

Precursor instability affects the metallisation process in several ways.

(i) Capillary condensation, which controls the formation of plugs of molecules within the pores, is facilitated; the larger, less volatile product molecules will quickly reach their saturated vapour pressure and plug the pores, even if the more volatile precursor is at too low a pressure to do this. This produces more metallisation at the top of the pores because capillary closing is an effective way of introducing large amounts of precursor.

(ii) When the intermediate decomposition product has a metal content higher than that of the precursor, this increases the metal concentration associated with a

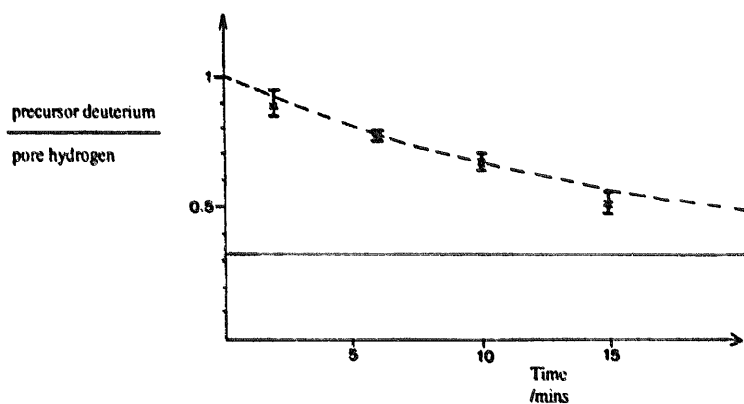


Fig. 3. Ratio of precursor deuterium to pore hydrogen vs. infiltration time. The curves represent calculated values assuming a half-life of 10 min for conversion of the precursor into $\text{DCo}_3(\text{CO})_9$ (dashed line) and the ratio expected after infinite time (solid line).

fully-packed pore and hence increases the degree of metallisation after thermolysis.

(iii) Since the decomposition of precursor molecules is faster in condensed plugs than in the vapour phase, a new plateau in metal concentration will be reached more rapidly than vapour-phase studies would predict.

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References and note

- [1] B.J. Aylett, L.G. Earwaker and J.M. Keen, *Mater. Res. Soc. Symp. Proc.*, 282 (1993) 281 and references cited therein.
- [2] P. Steiner, F. Kozłowski and W. Lang, *Thin Solid Films*, 255 (1995) 49; P. Steiner, F. Kozłowski, M. Wielunski and W. Lang, *Jpn J. Appl. Phys., Part 1*, 33 (1994) 6075; M. Jeske, J.W. Schultze, M. Thönissen and H. Münder, *Thin Solid Films*, 255 (1995) 63; M. Jeske, J.W. Schultze and H. Münder, *Electrochim. Acta*, 40 (1995) 1435; T. Ito, T. Yoneda, K. Furata, A. Hatta and A. Hiraki, *Jpn J. Appl. Phys., Part 2*, 34 (1995) L649.
- [3] B.J. Aylett, I.S. Harding, L.G. Earwaker, K. Forcey and T. Giaddui, *Thin Solid Films*, in press.
- [4] B.J. Aylett, I.S. Harding, L.G. Earwaker, K. Forcey and T. Giaddui, submitted to *J. Mater. Chem.*
- [5] D.G. Anderson, N. Anwar, B.J. Aylett, L.G. Earwaker, M.I. Nasir, J.P.G. Farr, K. Stiebahl and J.M. Keen, *J. Organomet. Chem.*, 437 (1992) C7.
- [6] G. Fachinetti, L. Balocchi, F. Secco and M. Venturini, *Angew. Chem., Int. Ed. Engl.*, 20 (1981) 204.
- [7] M.R. Churchill, K.N. Amoh and H.J. Wasserman, *Inorg. Chem.*, 20 (1981) 1609.
- [8] We assume that the molar volumes are essentially unchanged by H/D substitution.
- [9] B.J. Aylett, *Adv. Inorg. Chem. Radiochem.*, 25 (1982) 1; T.D. Tilley, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organosilicon Compounds*, Wiley, New York, 1989, Chapter 24.