

OMCVD of cobalt and cobalt silicide

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Cobalt and cobalt silicide layers were deposited by OMCVD using the Co precursors $\text{Co}(\text{C}_5\text{H}_5)_2$, $\text{Co}_2(\text{CO})_8$, $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$, and the Si precursors SiH_4 and Si_2H_6 . Strongly textured (111)- β Co layers were grown from $\text{Co}(\text{C}_5\text{H}_5)_2$, $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$ at temperatures above 300°C in H_2 at atmospheric pressure. Growth from $\text{Co}(\text{C}_5\text{H}_5)_2$ is inhibited on Si substrates. For temperatures $\geq 600^\circ\text{C}$ the Co layers deposited from $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ react with the Si(100) substrate to form $\text{CoSi}_2(001)$ aligned with the substrate orientation. $\text{Co}_2(\text{CO})_8$ gives amorphous Co between 200 and 300°C . The upper temperature is set by the occurrence of homogeneous gas-phase reactions at atmospheric reactor pressure. Cobalt silicide layers can be grown from $\text{Co}_2(\text{CO})_8$ and (di)silane at temperatures between 200 and 400°C . The Co/Si ratio in the layers decreases with increasing temperature and is independent of the gas-phase Co/Si ratio. Stoichiometric CoSi_2 is obtained at $\sim 300^\circ\text{C}$. Both $\text{Co}(\text{C}_5\text{H}_5)_2$ and $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ react with (di)silane, leading to the incorporation of carbon in the layer. The Co/Si ratio and the carbon content in the layers are practically independent of the deposition conditions. With $\text{CoCF}_3(\text{CO})_4$ no contamination-free silicide could be grown. The carbon incorporation with $\text{Co}(\text{C}_5\text{H}_5)_2$ and $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ can be avoided by a pulsed growth method in which the Co precursor and the Si precursor are introduced alternately into the reactor. With $\text{Co}(\text{C}_5\text{H}_5)_2$ the growth is then inhibited on Si substrates.

1. Introduction

Among the transition metal silicides applied in microelectronic devices as contacts, interconnects or gate electrodes, CoSi_2 is of special interest because of its good thermal and chemical stability and its low resistivity [1]. CoSi_2 has the cubic fluorite (CaF_2) structure which is closely related to the diamond structure of silicon. The lattice mismatch between CoSi_2 and Si is only 1.2% at room temperature, which enables the epitaxial growth of CoSi_2 on Si and vice versa. This makes the system Si/ CoSi_2 /Si of interest not only for the study of metal/semiconductor interactions but also for its use in new devices such as the (permeable) metal–base transistor [2].

Thin films of CoSi_2 are usually grown by sputtering or evaporating Co on Si, followed by an anneal at temperatures above 500°C (see, e.g., refs. [1,3]), molecular beam epitaxy (MBE) [4] or Co implantation [5,6].

The deposition of Co and CoSi_2 by chemical vapour deposition (CVD) offers several advantages, such as a uniform deposition over large

areas at a high growth rate, no substrate damage by energized atoms and the possibility for selective growth.

The number of reports on CVD of Co or CoSi_2 is limited [7–12]. This is mainly due to the absence of volatile halide precursors to transport Co to the reaction zone. Therefore, organometallics (OM) must be used as precursors to grow Co or CoSi_2 with CVD.

It is the aim of this work to evaluate the use of $\text{Co}_2(\text{CO})_8$ and $\text{Co}(\text{C}_5\text{H}_5)_2$ and of two new precursors, $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$, for the deposition of Co and CoSi_2 by OMCVD and to study the influence of precursor chemistry on growth behaviour.

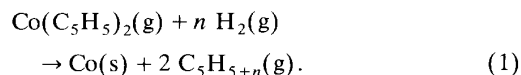
2. Cobalt precursors

Suitable precursors for use in OMCVD should have a high volatility, preferably a liquid, a low decomposition temperature, but well separated from the transport temperature to prevent premature decomposition, and a clean decomposi-

tion chemistry. Furthermore they should be easily accessible in high purity by chemical synthesis and be stable on prolonged storage. Based on these criteria, we examined two basic classes of Co precursors: cobaltocene ($\text{Co}(\text{C}_5\text{H}_5)_2 = \text{CoCp}_2$ and derivatives thereof) and cobalt carbonyl ($\text{Co}_2(\text{CO})_8$ and derivatives thereof).

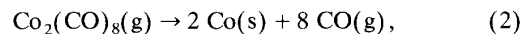
CoCp_2 is a solid at room temperature which is easy to handle and purify. It has a vapour pressure (fig. 1) of 57 mTorr at 50°C , which is high enough for use in OMCVD. If desirable, it can be further increased by substituting a hydrogen atom in the Cp group by a methyl group [13,14].

The Co–Cp bonds in CoCp_2 are through the d electrons of Co and the π electrons of the Cp rings. Because these bonds are weaker than the bonds in the Cp ring itself, the decomposition or reduction of CoCp_2 will primarily involve the breaking of the Co–Cp bonds. The formal valency of Co in CoCp_2 is +2. Therefore, a clean deposition of Co from CoCp_2 should be done in a reducing (H_2) atmosphere (eq. (1), $n = 1, 3, 5$):



For $n = 0$ this reaction represents the thermal decomposition in an inert gas. A thermodynamic evaluation of this equation (also for FeCp_2 and NiCp_2) has been given in a previous report [12].

Dicobalt octacarbonyl ($\text{Co}_2(\text{CO})_8$) is a solid with a vapour pressure of 60 mTorr at room temperature (fig. 1). The formal valency of Co in this molecule is 0. Therefore, the deposition of Co from $\text{Co}_2(\text{CO})_8$ is by pyrolysis, as expressed in eq. (2):



and no extra reductant is needed. It has been used for the deposition of Co [7–9] and CoSi_2 [9].

To our knowledge, no OMCVD using $\text{CoCp}(\text{CO})_2$ or $\text{CoCF}_3(\text{CO})_4$ has been described. Both compounds are liquids with high vapour pressures at room temperature (0.5 Torr for $\text{CoCp}(\text{CO})_2$ and even 15 Torr for $\text{CoCF}_3(\text{CO})_4$, fig. 1), which obviates the need for heating the bubbler and transport lines. Moreover, the decomposition temperatures ($\sim 140^\circ\text{C}$ for CoCp

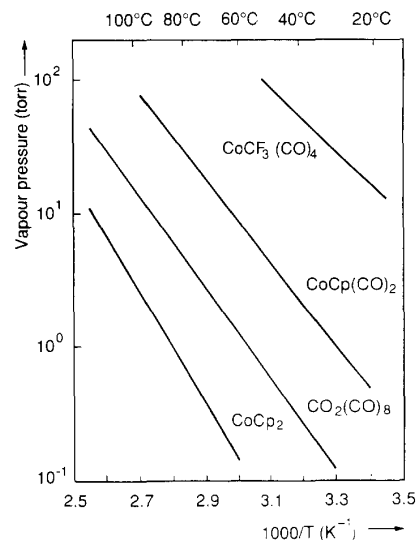


Fig. 1. Vapour pressures as a function of temperature for CoCp_2 [12], $\text{Co}_2(\text{CO})_8$ [18], $\text{CoCp}(\text{CO})_2$ (taken from the boiling point data as a function of distillation pressure [19]) and $\text{CoCF}_3(\text{CO})_4$ (determined by the vapour transport method [12]).

($\text{CO})_2$ and $\sim 200^\circ\text{C}$ for $\text{CoCF}_3(\text{CO})_4$) are higher than those of the other carbonyl compounds used for OMCVD: 50°C for $\text{Co}_2(\text{CO})_8$, -26°C (= melting point) for $\text{CoH}(\text{CO})_4$ [9] and 10°C for $\text{CoSiH}_3(\text{CO})_4$ [10,11]. Therefore, the risk of premature decomposition of these precursors before reaching the substrate is smaller.

The valency of Co in $\text{CoCp}(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$ is +1. Therefore, a clean deposition of Co from these precursors should be conducted in a reducing atmosphere.

3. Experimental

The depositions were performed in a horizontal water-cooled quartz reactor (inner diameter 50 mm). Substrates (maximum size $16 \times 60 \text{ mm}^2$) were placed on an inductively heated rectangular graphite susceptor coated with SiC. Carrier gases were Pd-diffused H_2 and Ti-gettered He. If not stated otherwise, the experiments were conducted at atmospheric pressure with a total flow

of 4 SLM (linear gas velocity $\sim 10 \text{ cm s}^{-1}$) or at a reduced pressure of 50 Torr with 1.8 SLM total flow ($\sim 70 \text{ cm s}^{-1}$). The Co precursors CoCp_2 , $\text{Co}_2(\text{CO})_8$ and $\text{CoCp}(\text{CO})_2$ (Strem Chemicals) were used without further purification. $\text{CoCF}_3(\text{CO})_4$ was synthesized by combining and adapting three published procedures [15–17] and purified by distillation.

CoCp_2 and $\text{Co}_2(\text{CO})_8$ were sublimed at 50 and 20°C , respectively, and $\text{CoCp}(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$ evaporated (both at 20°C) in a thermostated glass vessel (bubbler) with a fixed flow of carrier gas. The partial pressure of the precursor in the reactor was calculated from its vapour pressure (fig. 1) at the bubbler temperature, the flow through the bubbler and the total flow through the reactor, assuming that the total gas pressure in the bubbler equals the reactor pressure. Silane (100% or 1% in H_2 , Air Products) and disilane (99.9%, Air Products) were used as Si precursors for the growth of cobalt silicide.

Substrates used were Si(100) and Si covered with 400 nm Si_3N_4 or SiO_2 . These were all cleaned in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 5:1:1$, rinsed in de-ionized water ($> 18 \text{ M}\Omega$) and spin-dried. Si substrates were additionally dipped in HF (1%), rinsed in de-ionized water and immediately loaded into the reactor. Substrates were pre-baked in H_2 (30 min at 1000°C) to remove native oxide and then allowed to cool down to growth temperature.

Samples were characterized by Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Layer thicknesses were measured from SEM, AES sputter depth profiling or step-height profilometry. Resistivities were calculated from the layer thickness and the sheet resistivity as determined from 4-point probe resistant measurements.

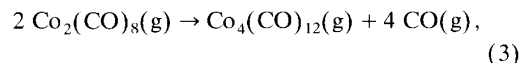
4. Results and discussion

4.1. Cobalt deposition

Experiments using CoCp_2 were performed in H_2 at temperatures between 300 and 700°C [12].

Under these conditions C-free (AES) Co can be deposited. The growth rate is first order in the partial pressure of CoCp_2 in the reactor (p_{CoCp_2}) and practically independent of temperature ($0.6 \text{ \AA/s}$ for $p_{\text{CoCp}_2} = 40 \text{ mTorr}$), indicative of a mass-transport-limited reaction. The crystal structure of the deposit, as revealed from XRD, is in all cases strongly (111) textured β -Co. When proper care is taken to remove native oxide from Si by HF dipping and an in-situ prebake in H_2 , no deposition of Co on Si is observed. This remarkable selectivity is specific to this type of precursor molecule [12]. In He no decomposition of the precursor is observed for temperatures up to 900°C .

Cobalt was also deposited from $\text{Co}_2(\text{CO})_8$ on Si and on Si covered with 400 nm Si nitride at temperatures between 150 and 400°C and with $p_{\text{Co}_2(\text{CO})_8} = 35 \text{ mTorr}$. In H_2 and He, identical results were obtained, both on Si and Si nitride. At 150°C the layers are black, due to an incomplete decomposition of the precursor at this temperature. At 200°C the amorphous layers are specular and metallic. The growth rate is $\sim 0.5 \text{ \AA/s}$. AES sputter depth profiling shows no incorporation of C and/or O at this temperature (detection limit $\sim 1 \text{ at\%}$). Above 200°C the growth rate decreases considerably with increasing temperature. Similar findings have already been reported for the deposition of Co from $\text{Co}_2(\text{CO})_8$ at atmospheric pressure [7,8]. We attribute this to increasing homogeneous gas-phase nucleation of the precursor molecules with increasing temperature. This nucleation is presumably caused by the dimerization of $\text{Co}_2(\text{CO})_8$ via the reaction



which is known to occur at temperatures above 50°C [20]. These dimers then polymerize to small particles which precipitate on the reactor wall [21].

Depositions with $\text{CoCp}(\text{CO})_2$ were conducted in H_2 and He at temperatures between 300 and 600°C . In contrast with CoCp_2 , the experiments in He now lead to deposition. This result implies

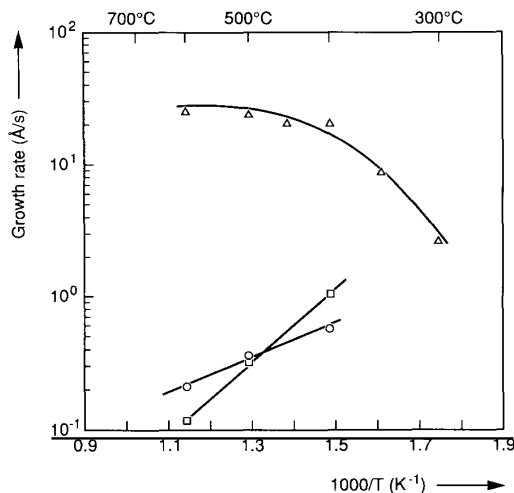


Fig. 2. Growth rate of Co from $\text{CoCp}(\text{CO})_2$ (30 mTorr) in H_2 (○) and He (□) at atmospheric reactor pressure and at 50 Torr in H_2 (Δ).

that for CoCp_2 the breaking of the first bond between the Co atom and one of the Cp rings must be the rate-limiting step for the decomposition. The growth rate at atmospheric pressure increases linearly with $p_{\text{CoCp}(\text{CO})_2}$. Again, it decreases with increasing substrate temperature, using He as well as H_2 as carrier gasses (fig. 2), due to homogeneous gas-phase nucleation. However, the upper temperature at which deposition is still possible at an acceptable growth rate is higher than for $\text{Co}_2(\text{CO})_8$.

The layers deposited in He are smooth and amorphous. AES sputter depth profiling reveals that they contain almost equal amounts of Co and C without any O, independent of temperature. The C incorporation must be attributed to the disproportionation of the Cp radical in the absence of H_2 . In contrast, no C incorporation above the Auger detection limit is observed in H_2 at atmospheric reactor pressure. The Cp group now reacts with H_2 to form stable and volatile hydrocarbons which are removed via the gas-phase:

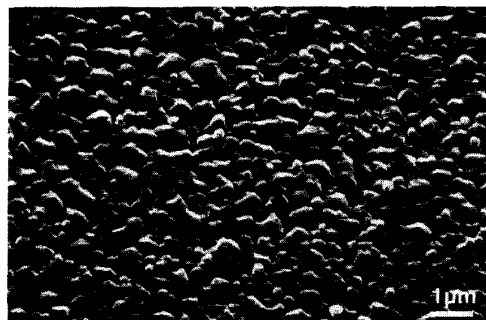
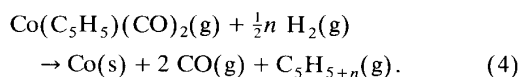


Fig. 3. SEM picture of a Co layer grown from $\text{CoCp}(\text{CO})_2$ on Si(100) at 600 °C in H_2 .

The Co films deposited in H_2 are rough (fig. 3) and crystalline. At 400 °C the layer on Si nitride is strongly (111) textured β -Co, similar to the Co deposited from CoCp_2 . On Si(100), additional small peaks associated with polycrystalline CoSi emerge, indicating that the Co film starts to react with the substrate at this temperature. For the layers deposited at 600 °C the (111) texture is lost and polycrystalline β -Co is formed. On Si(100) the only other detectable phase is CoSi_2 (001) (see fig. 4). This growth of CoSi_2 (001) aligned with Si(100) is most remarkable, as it is generally observed that cobalt silicide layers prepared by sputtering or evaporating Co onto Si(100) and

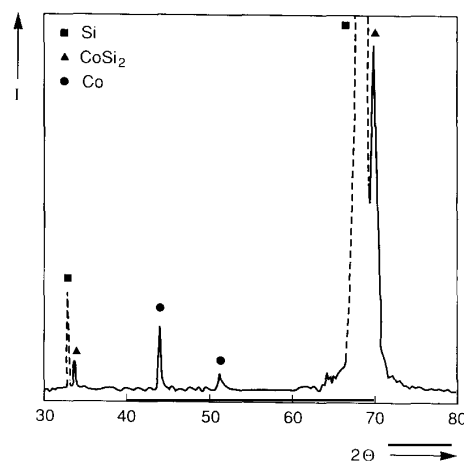


Fig. 4. XRD spectrum of the layer of fig. 3.

subsequent annealing lead to polycrystalline CoSi_2 [22], as opposed to $\text{Si}(111)$, for which epitaxial growth is observed. Evidently, OMCVD offers a way to produce also epitaxial CoSi_2 on $\text{Si}(100)$.

Experiments in H_2 at reduced reactor pressure and the same $p_{\text{CoCp}(\text{CO})_2}$ as in the atmospheric pressure experiments show a temperature dependence of the growth rate (fig. 2) which is commonly observed for CVD growth, i.e. a thermally activated reaction-limited growth at low temperatures and an almost temperature-independent mass-transport-limited growth at higher temperatures. The growth rate at 50 Torr is much higher than at atmospheric pressure. For the lower temperatures this growth enhancement is attributed to a suppression of homogeneous gas-phase reactions. At higher temperatures this enhancement can be partially explained by an increased diffusion coefficient of $\text{CoCp}(\text{CO})_2$ and a decreased thickness of the boundary layer.

Auger measurements for the layers grown at reduced hydrogen pressure show that they contain up to 50 at% C, similar to growth at atmospheric pressure in He. The C incorporation is attributed to the decomposition of $\text{CoCp}(\text{CO})_2$ (eq. (4)), which is no longer by reduction ($n \geq 1$) but by thermal disproportion ($n = 0$), leading to the unstable Cp radical.

For experiments using $\text{CoCF}_3(\text{CO})_4$ at atmospheric pressure in H_2 , decomposition starts at 200 °C. A maximum deposition rate of 0.03 Å/s

at $p_{\text{CoCF}_3(\text{CO})_4} = 220$ mTorr is reached at 300 °C. The deposition rate is proportional to $p_{\text{CoCF}_3(\text{CO})_4}$. From 300 °C upwards, the deposition rate decreases due to homogeneous gas-phase reactions that cause depletion of the precursor at the substrate. Metallic and specular layers, free from C, F and O contamination (AES), of (111) textured β -Co are obtained at 300 °C. At lower temperatures, up to 50 at% F is present due to incomplete decomposition of the precursor.

At reduced pressure, the deposition rate is much higher (0.4 Å/s at 300 °C and $p_{\text{CoCF}_3(\text{CO})_4} = 13$ mTorr) than at atmospheric pressure. However, in contrast with $\text{CoCp}(\text{CO})_2$, the deposition rate decreases with increasing temperature. None of our low-pressure experiments resulted in the formation of crystalline Co layers. AES shows that the layers grown at 300 °C are contaminated with 20 at% C and 50 at% F, again indicating incomplete decomposition of the precursor. At higher temperatures the main contaminant is C (up to 20 at%). The O content of the layers is below the AES detection limit at all deposition temperatures.

The results for the deposition of Co from the four precursors are summarized in table 1.

4.2. Cobalt silicide deposition

Cobalt silicide depositions with CoCp_2 and (di)silane were performed in H_2 and He between 500 and 900 °C with Co/Si gas-phase ratios rang-

Table 1
Summary of results for the deposition of cobalt

Precursor	Atmospheric pressure	Reduced pressure	Temperature (°C)	Composition (at%)
CoCp_2	H_2	H_2	300–700	$\geq 99\%$ Co ^{a)}
		H_2	300–700	No deposition
		He	300–900	No deposition
$\text{Co}_2(\text{CO})_8$	H_2, He		200–400	$\geq 99\%$ Co ^{b)}
$\text{CoCp}(\text{CO})_2$	H_2		300–600	$\geq 99\%$ Co ^{b)}
	He		300–600	50% Co, 50% C ^{b)}
		H_2	300–600	50% Co, 50% C
$\text{CoCF}_3(\text{CO})_4$	H_2		250–750	$\geq 99\%$ Co ^{b)}
		H_2	250–750	20% C, $\leq 50\%$ F, $\geq 30\%$ Co ^{b)}

^{a)} The growth is inhibited on Si.

^{b)} The growth rate decreases with increasing temperature due to homogeneous gas-phase reactions.

ing from 1/40 to 10 [12]. In contrast with the Co growth, deposition is now also found on Si areas. Above 600 °C the growth rate is thermally activated with an apparent activation energy of ~ 30 kcal/mol. It increases linearly with p_{CoCp_2} up to ~ 20 mTorr and then levels off, and is independent of (di)silane partial pressure (i.e. the Co/Si gas-phase ratio).

AES sputter depth profiling and RBS measurements reveal that the layers contain approximately 10 at% Co, 60 at% Si and 30 at% C (table 2), practically independent of deposition conditions. From these observations it is concluded that the growth proceeds via an intermediate reaction product of (di)silane and CoCp_2 . For layers grown on Si substrates there is always a thin layer of C-free CoSi_2 present at the Si interface, which is aligned with the Si(100) lattice [12].

The C incorporation can be fully suppressed by a pulsed growth method in which CoCp_2 and SiH_4 are alternately introduced into the reactor to prevent the adverse reaction between the precursors. The composition of the deposit at a given temperature can then be controlled by adjusting the partial pressures of the precursors and/or the pulse durations. As for the deposition of Co from CoCp_2 , the growth of cobalt silicide by this pulsed method is selective for non-Si substrates.

Cobalt silicide was deposited using $\text{Co}_2(\text{CO})_8$ (35 mTorr) and Si_2H_6 (140 mTorr) at atmospheric pressure in He between 200 and 400 °C. As for the growth of Co from $\text{Co}_2(\text{CO})_8$, the growth rate decreases with increasing tempera-

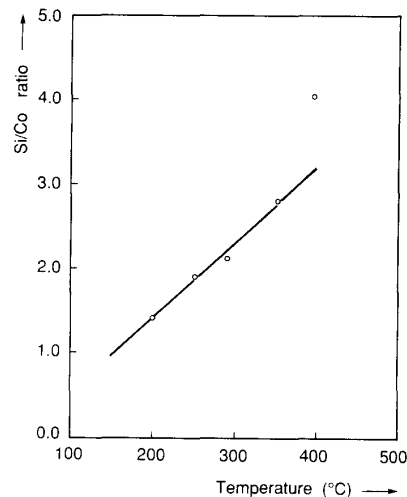


Fig. 5. Si/Co ratio (from AES) as a function of deposition temperature for layers grown from $\text{Co}_2(\text{CO})_8$ (35 mTorr) and Si_2H_6 (140 mTorr) at atmospheric pressure in He.

ture, from 0.7 Å/s at 200 °C to 0.05 Å/s at 400 °C. This decrease in deposition rate is not observed at reduced reactor pressure [9].

At all temperatures the C and O content in the layers is below the AES detection limit (~ 1 at%). The Co/Si ratio in the layers depends linearly on temperature (fig. 5) and reaches the stoichiometric composition just below 300 °C. These results compare well with the reduced reactor pressure experiments of West and Beeson using the same precursors [9]. Apparently, the composition not only is independent of the gas-

Table 2
Summary of results for the deposition of cobalt silicide

Co precursor	Si precursor	Carrier gas	Temperature (°C)	Composition (at%)
CoCp_2	SiH_4 , Si_2H_6	H_2 , He	500–900	10% Co, 60% Si, 30% C ^{b)}
$\text{Co}_2(\text{CO})_8$	Si_2H_6	He	200–400	CoSi_x , $x = f(T)$, C $\leq 1\%$, O $\leq 1\%$ ^{c)}
$\text{CoCp}(\text{CO})_2$	SiH_4	H_2	300–600	30% C, $\leq 30\%$ O ^{c)}
	SiH_4	H_2	600–700	35% Co, 45% Si, 20% C ^{b)}
$\text{CoCF}_3(\text{CO})_4$	SiH_4	H_2	300–750	10% C, 20% O, 2% F ^{c)}
	SiH_4 ^{a)}	H_2	300–750	$\leq 20\%$ O, $\leq 10\%$ F, 20% C ^{c)}

If not stated otherwise, the experiments were performed at atmospheric reactor pressure.

^{a)} At reduced reactor pressure (50 Torr).

^{b)} Contamination free cobalt silicide can be grown by alternate deposition (see text).

^{c)} The growth rate decreases with increasing temperature due to homogeneous gas phase reactions.

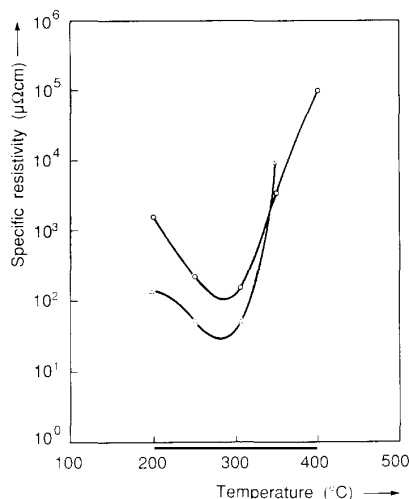


Fig. 6. Specific resistivity of layers grown from $\text{Co}_2(\text{CO})_8$ (35 mTorr) and Si_2H_6 (140 mTorr) at atmospheric pressure in He: (○) as-deposited; (△) after an anneal of 1 h at 800°C .

phase ratio, but also of reactor pressure. The resistivity of the as-deposited layers (fig. 6) reflects the dependence of composition on substrate temperature, i.e. the minimal resistivity ($130 \mu\Omega \text{ cm}$) is found at the temperature at which almost stoichiometric CoSi_2 is deposited (300°C). After an anneal of 1 h at 800°C it reduces further to $40 \mu\Omega \text{ cm}$, which is 2–3 times the minimum value reported for thin films of CoSi_2 .

The growth rate of cobalt silicide from $\text{CoCp}(\text{CO})_2$ (30 mTorr) and SiH_4 in H_2 at atmospheric reactor pressure decreases from $5 \text{ \AA/s}$ at 300°C to $0.3 \text{ \AA/s}$ at 600°C and is practically independent of p_{SiH_4} . The Co/Si ratio in the layers decreases with increasing temperature from 4 at 300°C to 1 at 600°C and is independent of the Co/Si gas-phase ratio. In this low temperature region, the results resemble those for $\text{Co}_2(\text{CO})_8$ with SiH_4 , although the growth rates and the Co/Si ratios are higher. However, where it was found that the layers grown from $\text{Co}_2(\text{CO})_8$ and SiH_4 are free of C and O, AES now reveals that at 300°C the layers contain $\sim 30 \text{ at\% C}$ and $\sim 30 \text{ at\% O}$. Obviously, CO is incorporated by an incomplete decomposition of $\text{CoCp}(\text{CO})_2$. The fact that this is not observed for $\text{Co}_2(\text{CO})_8$ under

similar growth conditions can be explained from the much higher growth rate using $\text{CoCp}(\text{CO})_2$, which gives rise to an enhanced trapping of CO. With increasing temperature the O content decreases, whereas the C content remains almost constant. Above 600°C , the layers do not contain any oxygen above the AES detection limit. This decrease in O content is due to a more complete breaking of the Co–CO bonds at higher temperatures, together with a decreasing growth rate. On the other hand, the C incorporation at increased temperature is caused by the disproportionation of the Cp ring upon reaction with SiH_4 , as was found for the reaction between CoCp_2 and SiH_4 [12].

Above 600°C , the results resemble those for CoCp_2 . The growth rate is independent of the Co/Si gas-phase ratio and increases with an apparent activation energy of $\sim 25 \text{ kcal/mol}$. For layers deposited on Si(100), XRD reveals the presence of CoSi_2 (001) as the only crystalline phase. However, just as for CoCp_2 , AES measurements show that this is associated with a thin layer of C-free CoSi_2 in between the Si substrate and a bulk layer of C-containing material. Obviously, this C incorporation observed for the reactions of CoCp_2 or $\text{CoCp}(\text{CO})_2$ with SiH_4 must be attributed to the specific nature of the Co–Cp moiety. From a comparison of the AES results for CoCp_2 or $\text{CoCp}(\text{CO})_2$ (table 2) it is seen that under equal conditions the use of $\text{CoCp}(\text{CO})_2$ leads to a larger Co/Si ratio and a smaller C contamination.

For CoCp_2 it was shown [12] that the C incorporation can be fully suppressed by introducing CoCp_2 and SiH_4 alternately into the reactor. However, no deposition is then found on Si substrates. This growth inhibition is specific to CoCp_2 and is not observed for $\text{CoCp}(\text{CO})_2$.

Experiments with a repeated ($45 \times$) sequence of $\text{CoCp}(\text{CO})_2$ (1 min, 100 mTorr) and SiH_4 (1 min, 1 Torr) were conducted in H_2 (760 Torr) at 600 and 650°C . Indeed, the layers now also grow on Si substrates. As expected for an independent growth of Co from $\text{CoCp}(\text{CO})_2$ and Si from SiH_4 under these conditions, the Co/Si ratio in the layer decreases with increasing substrate temperature ($1/2$ at 600°C and $1/5$ at 650°C). How-

ever, the layers are contaminated with ~ 5 at% C. This is probably incorporated by a reaction between the precursors, one of which was not yet fully removed from the reactor. These preliminary results indicate that it should be possible to grow C-free cobalt silicide on Si substrates if proper care is taken to purge the reactor in between the precursor pulses. In this pulsed growth method the composition of the silicide can be regulated at any temperature by adjusting the pulse durations or partial pressures of the precursors.

For $\text{CoCF}_3(\text{CO})_4$ the deposition of cobalt silicide was investigated in H_2 at atmospheric pressure and at 50 Torr. SiH_4 was used as an Si precursor. The Co/Si ratio in the gas-phase was varied from 1/10 to 1/2. The deposition rate is low at atmospheric pressure ($0.4 \text{ \AA/s}$ at 300°C , $p_{\text{CoCF}_3(\text{CO})_4} = 310 \text{ mTorr}$ and $p_{\text{SiH}_4} = 2 \text{ Torr}$). Under these conditions the Co/Si ratio in the deposit is around 1/2. The amorphous layers are contaminated with C, O and F (table 2). Increasing the substrate temperature leads to a decrease of the deposition rate and a decrease of the Co/Si ratio in the deposit.

At 50 Torr, the deposition rate is remarkably higher than at atmospheric pressure. The growth rate is now $0.1 \text{ \AA/s}$ at 300°C , with $p_{\text{CoCF}_3(\text{CO})_4} = 13 \text{ mTorr}$ and $p_{\text{SiH}_4} = 130 \text{ mTorr}$. Again, the growth rate and Co/Si ratio decrease with increasing temperature. At 300°C a Co/Si ratio of 1/2 was obtained, which decreased to a ratio of 1/10 in the range of 500 to 600°C . With increasing temperature the O content decreases from 20 at% at 300°C to 5 at% at 650°C , while that of F decreases from 10 at% to 1 at% in that range. The C content is almost constant at 20 at%. Pure cobalt silicide layers were not obtained.

The results for the deposition of cobalt silicide using the four precursors and the two silicon precursors under various conditions are summarized in table 2.

5. Conclusions

It is shown that cobalt and cobalt silicide can be grown by OMCVD, but that the kinetics of the

growth and the composition of the deposited layers strongly depend on the choice of the organometallic Co precursor.

All four Co precursors we investigated (CoCp_2 , $\text{Co}_2(\text{CO})_8$, $\text{CoCp}(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$) can be used to grow contamination-free Co. However, each precursor has its own merits and drawbacks. From a technological point of view the liquids $\text{CoCp}(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$ are preferred (high vapour pressure). To avoid C incorporation, the deposition has to be performed in a reducing H_2 ambient, except in the case of $\text{Co}_2(\text{CO})_8$. The three CO-containing precursors all show dominant homogeneous gas-phase reactions at atmospheric pressure, resulting in a sharp decrease in growth rate with increasing growth temperature. This can be suppressed by growing at reduced pressure. However, for $\text{CoCp}(\text{CO})_2$ and $\text{CoCF}_3(\text{CO})_4$ this leads to severe contamination of the deposit. The deposition of Co from CoCp_2 is inhibited on Si substrates.

Results change significantly in the presence of a Si precursor. Only $\text{Co}_2(\text{CO})_8$ and (di)silane yield contamination-free cobalt silicide at atmospheric pressure between 200 and 400°C . Unfortunately, the composition depends only on temperature and is stoichiometric at $\sim 300^\circ\text{C}$. A postanneal is needed to obtain (poly)crystalline CoSi_2 . The specific resistivity is then minimal ($40 \mu\Omega \text{ cm}$) at this temperature and composition.

With CoCp_2 and $\text{CoCp}(\text{CO})_2$, depositions can be performed at higher temperatures than with $\text{Co}_2(\text{CO})_8$, which obviates the need for post-annealing. However, both Cp-containing precursors react with SiH_4 and Si_2H_6 leading to disproportionation of the Cp ring and, consequently, to C incorporation. The composition of the layers depends on the combination of the precursors and is almost independent of process conditions. For depositions on Si substrates there is always a thin contamination-free layer present at the Si interface, consisting of single-crystalline CoSi_2 aligned with the Si(100) lattice.

No contamination free cobalt silicide can be grown with $\text{CoCF}_3(\text{CO})_4$.

The most promising technique to deposit contamination-free CoSi_2 is a pulsed growth method in which the Co precursor and the Si precursor

are introduced alternately into the reactor to avoid their mutual reaction. In contrast with the experiments in which the precursors are introduced simultaneously, the composition of the layer can now be controlled by adjusting either the pulse durations or the partial pressures of the precursors during these pulses. The ultimate mode for this method is atomic layer deposition. For the pulsed growth with CoCp_2 , the deposition is inhibited on Si substrates, similar to what is found for the Co deposition from this precursor. This selectivity is not observed for the pulsed growth of cobalt silicide with $\text{CoCp}(\text{CO})_2$.

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