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# Growth of Chromium Carbide in a Hot Wall DLICVD Reactor

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Chromium carbide coatings were grown at 748 K in a hot wall CVD reactor fed by sublimation of bis(benzene)chromium, BBC (MOCVD) and by direct liquid injection using a BBC/toluene solution (DLICVD). The two types of coatings exhibit an amorphous structure and the same C content (22 at.%). DLICVD permits delivering higher mass flow rate of precursors and consequently the growth rate is 3 times higher and the thickness uniformity is better than using MOCVD. Chromium metal deposition has also been investigated by DLICVD in this hot wall reactor using BBC/toluene/additive as precursor. The purpose of the additive is to block carbide formation. Two additives have been studied: (i) hexachlorobenzene ( $C_6Cl_6$ ) and (ii) thiophenol ( $C_6H_5SH$ ). The ratio additive/BBC required for Cr metal deposition is a few percent. In this process,  $C_6Cl_6$  is not decomposed and only traces of Cl (0.4 at.%) are found in the coatings. For a ratio  $C_6Cl_6$ /BBC > 27% the growth of any coating is blocked. The gas phase containing  $C_6H_5SH$  is more reactive since the onset of deposition occurs approximately 50 K before the temperature of the chlorinated compound. Furthermore, a sulfur contamination of 3 at.% has been analyzed in the coatings revealing a partial decomposition of the additive. The results are detailed and discussed in relation with previous works.

**Keywords:** DLICVD, Hot Wall CVD, Cr, S Doping.

## 1. INTRODUCTION

Industrial CVD processes frequently require (i) low deposition temperature and (ii) high flow rate of molecular precursor to maximize the growth rate and the process throughput. This is achieved using for instance (iii) continuous deposition on a conveyor belt set-up (atmospheric pressure is preferred) or (iv) a large scale isothermal reactor operating generally under low pressure. The first two criteria can be met using both metal organic compounds that significantly decrease the deposition temperature and direct liquid injection (DLI) coupled with a flash vaporization chamber which permits to deliver high flow rates of precursor.

Chromium based coatings deposition by CVD has been investigated for years. It has been demonstrated that chromium metal films (Cr) could be deposited using  $CrCl_2$  at 1323 K.<sup>1</sup> Chromium carbide coatings (CrC is used as general acronym) were deposited using MOCVD processes by our group<sup>2,3</sup> and others.<sup>4</sup>

On the other hand, DLICVD process has been used to deposit functional oxide films<sup>5</sup> and more rarely metal thin films.<sup>6,7</sup>

In previous works, chromium carbide coatings were deposited at low temperature by low pressure CVD using bis(benzene)chromium (BBC) as metal source either in a hot wall<sup>2</sup> or a cold wall CVD reactor.<sup>3</sup> Interestingly, it was demonstrated that addition of hexachlorobenzene ( $C_6Cl_6$ ) in the gas phase prevented the C incorporation into the films and, as a result, metal Cr coatings were formed.<sup>8</sup> If the trends were in agreement with thermodynamic simulations using BBC as sole reactant, the effect of  $C_6Cl_6$  was not predicted by thermodynamic modeling revealing a kinetic control of this process.<sup>9</sup> Deposition under atmospheric pressure of chromium carbide and Cr metal is also possible using a cold wall DLICVD reactor. A solution of BBC in toluene without and with addition of  $C_6Cl_6$  was used respectively.<sup>10</sup> In spite of the presence of a high amount of toluene in the reactive vapor phase, the inhibition effect of the chlorine derivative was always observed probably because in cold wall CVD reactor the chemical reactivity in homogeneous phase is significantly reduced.

The kinetics still played a major role as shown by the disagreement with thermodynamic simulation.<sup>11</sup>

A further step is presented in this paper, chromium carbide and Cr metal coatings were grown by DLICVD under low pressure in a hot wall reactor using respectively BBC/toluene and BBC/toluene/additive, where additives are  $C_6Cl_6$  and thiophenol ( $C_6H_5SH$ ). Here, gas phase chemistry is expected to be significant and consequently high carbon incorporation could occur according to thermodynamic calculations.<sup>11</sup>

## 2. EXPERIMENTAL DETAILS

Experimental conditions are reported in Table I. Si(100) wafers and thermally oxidized silicon were used as substrates ( $10 \times 15$  mm). They were degreased with ethanol in an ultra-sonic bath and placed along the longitudinal axis of reactor. The system was vacuum purged for 2 h using a turbo pump. The deposition chamber was a horizontal hot-wall CVD quartz reactor, 2.6 cm in diameter and 60 cm length for both processes (MOCVD and DLICVD). The reactor was heated by a one-zonal tubular furnace. It produces for instance an isothermal zone of about 20 cm at  $748 \text{ K} \pm 10 \text{ K}$ . The pressure was automatically monitored at 50 Torr during the experiments.

For the MOCVD process, commercial BBC was introduced into a glass saturator and sublimated at 378 K. The BBC vapour was transported using  $N_2$  as carrier gas and the pipes from saturator to reactor were heated at 393 K to avoid condensation. The BBC mass flow rate and consequently its mole fraction at the entrance of the reactor ( $X_{BBC}$ ) were calculated according to the procedure described elsewhere<sup>12</sup> and the vapour pressure of BBC.<sup>13</sup>

**Table I.** Experimental growth conditions of chromium and chromium carbide coatings.

Process	MOCVD CrC (#1)	DLICVD CrC (#2)	DLICVD Cr (#3)	DLICVD Cr (#4)
Furnace setpoint temperature (K)	748	748	748	748
Total pressure (Torr)	50	50	50	50
$N_2$ mass flow rate (sccm)	300	500	500	500
Toluene mass flow rate (sccm)	–	268	268	268
[BBC] in toluene (mol/L)	–	$3 \times 10^{-2}$	$3 \times 10^{-2}$	$3 \times 10^{-2}$
Mole fraction of BBC ( $X_{BBC}$ )	$10^{-3}$	$1.1 \times 10^{-3}$	$1.1 \times 10^{-3}$	$1.1 \times 10^{-3}$
$[C_6Cl_6]$ in toluene (mol/L)	0	0	0	$3 \times 10^{-3}$
[S] in toluene (mol/L)	0	0	$6 \times 10^{-3}$	0
Additive/BBC (%)	–	–	20	10
Duration (h)	3	2	2	2

For the DLICVD process, BBC was solubilised in toluene. When they are used, additives like  $C_6Cl_6$  or  $C_6H_5SH$  were solubilised directly in the BBC/toluene solution. This permits an easy control of the ratio additive/BBC. The container is maintained at room temperature and pressurised under 2 bars of  $N_2$  atmosphere. The solution was injected into a flash vaporisation chamber using a commercial system (Kemstream). The injected amount of solution is controlled by the injector parameters (opening time and frequency), which are monitored by a computer. The flash vaporisation of the pulsed spray occurred at 473 K. The reactive gas phase is transported to the reactor using an  $N_2$  stream through the vaporization chamber. From the total volume of liquid solution consumed in a run (ca.  $160 \text{ cm}^3$ ), the flow rate of liquid injected into the flash vaporization chamber is derived ( $1.3 \text{ cm}^3/\text{min}$ ). Then using the physical properties of the reactives (density, molecular weight) and assuming they behave like an ideal gas, the composition of the reactive gas phase delivered into the reactor has been determined. The total mass flow rate of the gas phase is 769 sccm ( $N_2$ , 500 sccm; toluene, 268 sccm; BBC, 0.85 sccm). Under the conditions of Table I the dwelling time of the species in the CVD reactor was 6 s.

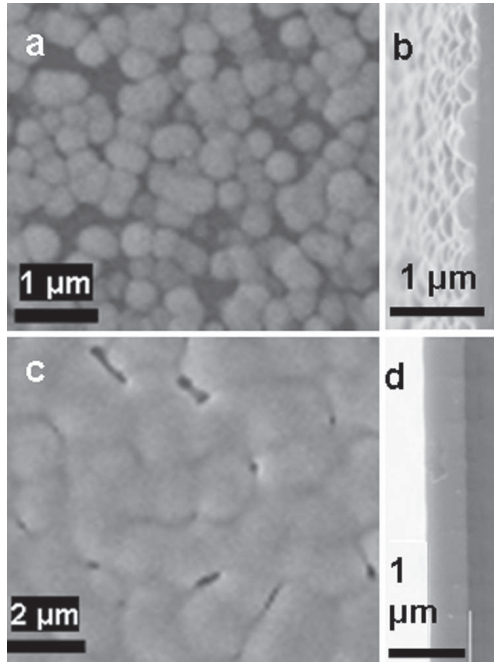
The coating structures were characterized by X-ray diffraction ( $Cu K\alpha$ ). The average crystallite size of the Cr metal coatings was determined using the Scherrer's formula from the FWHM of the (110) Cr peak. The morphology of the films has been investigated by SEM and the chemical composition has been analyzed by EDS, electron probe microanalysis (EPMA) and SIMS.

## 3. RESULTS AND DISCUSSION

### 3.1. Chromium Carbide Coatings: Comparison of MOCVD and DLICVD

Figure 1 shows SEM micrographs of samples from runs #1 and #2 (Table I). The surface morphology of the coating grown by MOCVD is heterogeneous (Fig. 1). It reveals a non continuous film and an equiaxed granular growth. Analyses of several samples along the reactor axis permits to determine a maximum growth rate of  $\sim 0.5 \mu\text{m}/\text{h}$ . The surface of the coating grown by DLICVD is smoother and the growth tends to be columnar type (Fig. 1). The films are very compact, excepted the samples at the outlet of the reactor which exhibit a low porosity due to the poor coalescence of the columnar grains. A maximum growth rate of  $1.5 \mu\text{m}/\text{h}$  has been measured for DLICVD.

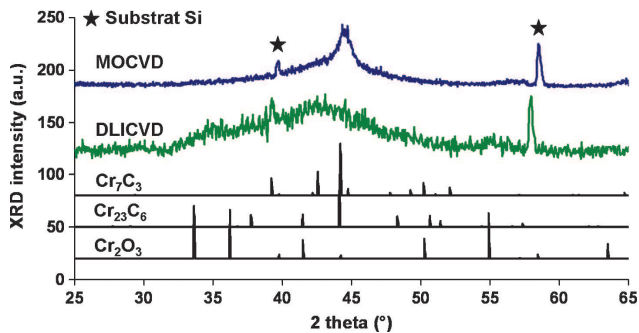
Figure 2 shows XRD diagrams of coatings grown by both processes. The coating grown by MOCVD exhibits a nanocrystalline structure while DLICVD films clearly leads to amorphous layers. The XRD patterns of both types of coatings show a broad diffraction peak centred on the main peaks of stable chromium carbides ( $43\text{--}44^\circ$ ). A broad shoulder around  $35^\circ$  could be due to traces of oxide. The



**Fig. 1.** SEM micrographs of chromium carbides films grown at 748 K by MOCVD (a, b) and DLICVD (c, d).

choice of  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$  XRD patterns in Figure 2 as reference structures for the carbide is in good agreement with the film composition reported in Table II. In fact, the C/Cr ratio of films grown by MOCVD (0.31), and the one grown by DLICVD (0.31) are between the values: 0.43 and 0.26 corresponding to the stable carbides  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$ , respectively. Moreover, despite a low contamination of oxygen, MOCVD and DLICVD CrC coatings have the same composition. This means that the toluene vapour in DLICVD does not increase the carbon content of the films as might be feared. This indicates the decomposition of toluene molecules is negligible under our conditions.

The growth rate of the layers is different in both cases. Despite the same initial mole fraction of BBC in both processes (Table I), the quantity of deposited material is two times more important in DLICVD (239 mg) than in MOCVD (121 mg), leading to a maximum growth rate of  $1.5 \mu\text{m/h}$  for DLICVD and  $0.5 \mu\text{m/h}$  for MOCVD. In fact



**Fig. 2.** Grazing-incidence ( $4^\circ$ ) XRD patterns of CrC films grown by MOCVD and DLICVD at 748 K on (100)Si substrate.

**Table II.** Composition of CrC coating deposited by MOCVD and DLICVD at 748 K compared to the stoichiometry of stable chromium carbides (EPMA data).

Sample	Cr (at.%)	C (at.%)	O (at.%)	C/Cr
DLICVD	71.4	21.8	6.8	0.31
MOCVD	70.2	21.7	8.1	0.31
$\text{Cr}_7\text{C}_3$	70.0	30.0	–	0.43
$\text{Cr}_{23}\text{C}_6$	79.3	20.7	–	0.26

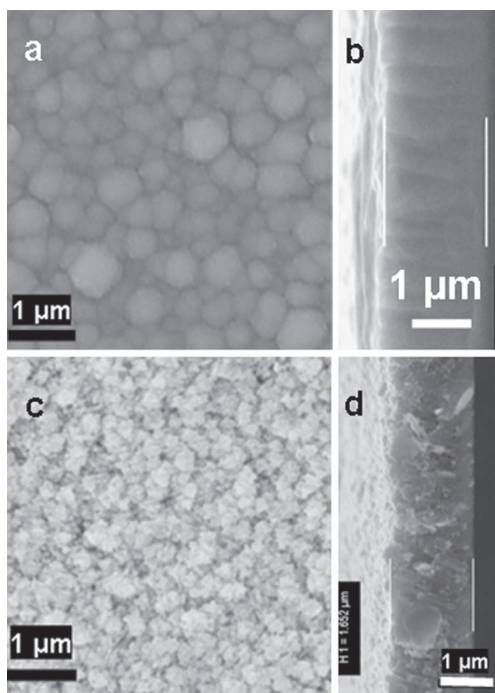
the key factor is the mass flow rate of BBC which was estimated to be two times higher in DLICVD compared to MOCVD. This is an interesting result because the BBC mass flow rate is close to its maximum using the sublimation technique (MOCVD) according to the previous models<sup>12</sup> while it can be increased by DLICVD above the values explored in this work for instance by increasing the liquid concentration or changing the injection parameters. This is an important flexibility of the DLICVD process to maximize the growth rate and to improve the thickness uniformity in the reactor axis.

### 3.2. DLICVD of Chromium Metal Coatings

Two routes have been investigated to deposit Cr metal coatings by DLICVD using a BBC/toluene solution as starting material: addition of two different chemical compounds that inhibit the heterogeneous decomposition of both the aromatic ligands of BBC and toluene molecules of the solvent. As reported in previous work,  $\text{C}_6\text{Cl}_6$  is known to have this effect and to be sufficiently stable at the deposition temperature to avoid chlorine contamination of the films<sup>8</sup> but it was not tested in a hot wall reactor or in presence of vapour of solvent. Another additive which has been investigated is  $\text{C}_6\text{H}_5\text{SH}$ . The molecular ratio additive/BBC were 10% and 20% for  $\text{C}_6\text{Cl}_6$  and  $\text{C}_6\text{H}_5\text{SH}$ , respectively (Table I).

The use of  $\text{C}_6\text{Cl}_6$  leads to the bcc cubic structure of metallic Cr as confirmed by XRD. In the range  $20$  to  $100^\circ$  ( $2\theta$ ), only peaks of Cr, with the main one at  $44.4^\circ$  corresponding to the (110) direction, have been observed. No other XRD peaks that could be due to carbides or oxide have been observed. EPMA analyses have confirmed that no contamination of oxygen is present in the films and the C content is typically 6 at.%. Moreover, the coatings did not exhibit preferential orientation of the growth whatever the local conditions, i.e., there is no structural change along the reactor axis.

Films are smooth and exhibit a metallic brightness. The layer morphology shown in Figure 3 reveals a columnar growth with a nodular aspect on the surface. The average grain size estimated by SEM from the surface morphology was found to increase in the reactor axis with the temperature (and BBC depletion) from 300 nm (693 K) to 600 nm (748 K).



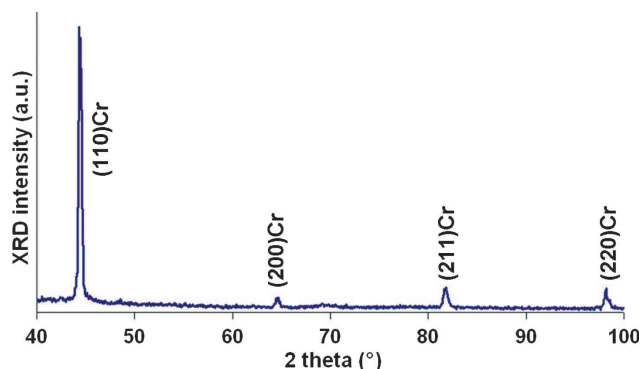
**Fig. 3.** SEM micrographs of chromium metal films grown by DLICVD using BBC/toluene/ $C_6Cl_6$  (a, b) and BBC/toluene/ $C_6H_5SH$  (c, d) at 748 K.

The maximum growth rate was  $1.4 \mu\text{m/h}$  but it decreases after the maximum due to the BBC depletion. The reactor was coated along  $\sim 35$  cm, i.e., only slightly more than half the length of reactor. Over this length the temperature increased from 543 to 753 K and the end of deposition was observed while the temperature was maximum. Calculations based on a mass balance showed that the end of the deposition was not due to the consumption of total BBC but to an excess of  $C_6Cl_6$  additive compared to the BBC. In fact, a critical ratio  $C_6Cl_6$ /BBC of approximately 27% seems to inhibit the heterogeneous decomposition of BBC and consequently the growth of any coating.

The coatings grown using thiophenol as additive exhibit also the Cr metal structure (Fig. 4). The samples at the entrance of the reactor were slightly textured in the [110] direction. This [110] preferential orientation of the growth changed to [200] direction along the reactor axis.

Figures 3(c) and (d) show a smooth surface morphology and a granular equiaxed growth. A slight porosity is observed on the cross section which could be related to the dark aspect of the film. Grains are clusters of crystallites, the mean size of which is approximately 420 nm and 62 nm, respectively.

The samples were slightly contaminated by sulphur but no change of the S/Cr ratio was observed along the reactor axis (EDS analysis). EPMA analysis has confirmed a S contamination of coatings of 3.3 at.% and a C content of 4 at.%. Moreover, SIMS analysis has shown the sulphur contamination is homogeneously distributed through the film thickness.



**Fig. 4.** XRD pattern of Cr metal films grown by DLICVD using BBC/toluene/ $C_6H_5SH$  at 748 K.

The maximum growth rate was  $1.9 \mu\text{m/h}$ . It reached about a quarter of the reactor then the growth rate decreased progressively due to BBC depletion up to the outlet of the reactor where the temperature sharply decreased so that no deposition occurred. It is noteworthy that the tube reactor as a whole has been covered. Using this sulfur additive, no critical ratio additive/BBC was observed. This gives a higher flexibility to the process to optimize the growth rate and the thickness uniformity in the reactor axis.

#### 4. CONCLUSION

Deposition of amorphous CrC coatings at 748 K by DLICVD from BBC/toluene was reported. In spite of the solvent vapour in the reactive gas phase, no excess of C incorporation was found in the films grown by DLICVD compared to those grown by MOCVD. Among the advantages of DLICVD, it was shown that DLI technique permits to deliver higher flow rates of precursor than MOCVD and consequently it is more adapted to feed hot wall CVD reactor. DLICVD of CrC coatings is more flexible to optimize the growth rate and the film thickness uniformity along the reactor axis as required for large scale reactor.

The deposition of polycrystalline Cr metal coatings in such hot wall DLICVD reactor has also been demonstrated at temperature as low as 500 K. Two routes have been investigated: the pulsed injection of a solution of (i) BBC/toluene/ $C_6Cl_6$  and of (ii) BBC/toluene/ $C_6H_5SH$  as precursors. The gas phase is slightly more reactive using  $C_6H_5SH$  compared to  $C_6Cl_6$  because the onset of deposition occurs at 478 K and 543 K respectively. Only traces of Cl ( $\sim 0.4$  at.%) were found in the coatings using  $C_6Cl_6$  while the S content is  $\sim 3$  at.% when thiophenol was used as additive indicating that this compound partially decomposed. Furthermore, with  $C_6H_5SH$ , the length of the coated zone in the tubular reactor was longer and the maximum growth rate was approximately 30% higher. A first remark for the chlorinated additive is that it leads to a better homogeneity of the coating structure along the reactor axis but, due to the BBC depletion, the thickness gradient toward

the outlet is sharper than using thiophenol. In fact, beyond a critical ratio  $C_6Cl_6/BBC = 27\%$  the growth of any coating is prevented. The second remark is that traces of Cl are redhibitory for corrosion protective coatings. For these two reasons, there is a greater interest to use  $C_6H_5SH$  instead of  $C_6Cl_6$  as additive for low temperature DLICVD of Cr metal coatings.

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