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Low Pressure CVD of Tungsten Carbides

P. Tägtström, H. Högborg, U. Jansson and J.-O. Carlsson

Thin Film and Surface Chemistry Group, Department of Inorganic Chemistry, University of Uppsala, Box 531, 751 21 Uppsala, Sweden

Abstract: Tungsten carbide films have been deposited by CVD from a $\text{WF}_6/\text{C}_3\text{H}_8/\text{H}_2$ gas mixture on several different substrate materials (Ta, Si, SiC and C). Single-phase WC films could easily be obtained on Ta substrates at 900 °C using a total pressure of 100 mTorr and a high linear gas flow velocity (7 m/s). It was found that the low pressures favoured the growth of carbon-rich films and made the deposition zone for WC longer. The phase composition of the films and deposition rates were also strongly affected by the substrate material. The substrate dependence was attributed to the chemical reactivity of WF_6 .

1 INTRODUCTION

Tungsten carbide films have many mechanical, electrical and chemical properties which make them interesting as thin film materials. One of the most likely applications for tungsten carbide films is as wear-resistant coatings, but they can also find use as e.g. high-temperature resistant materials and as active materials in heterogeneous catalysis. Both physical vapour deposition, PVD, and chemical vapour deposition, CVD have been used to grow tungsten carbide films (see e.g. ref. [1-8]). Hitherto, the most common tungsten sources in tungsten carbide CVD have been the halide compounds (i.e. WCl_6 and WF_6) while different hydrocarbons have usually been employed as carbon sources [4-8].

A problem in WC CVD is to deposit films consisting of only one phase and with uniform thickness. To the knowledge of the authors, tungsten-rich films containing several carbide phases have been obtained in most WC CVD studies [4-7]. An exception can be found in a paper by Takahashi and Itoh [8]. They were able to deposit single-phase WC films from a $\text{WCl}_6/\text{C}_3\text{H}_8/\text{H}_2$ mixture at temperatures above 1200 °C. However, this required a separation of WCl_6 from the main gas flow until the gases were mixed in the vicinity of the substrate surface. This was explained by the high reactivity of WCl_6 compared to C_3H_8 causing a preferential formation of metallic tungsten [8]. Mantle et al. deposited single-phase WC films provided that the substrates were pre-coated with W or W_2C [4]. Thermodynamic calculations in the $\text{WCl}_6/\text{CH}_4/\text{H}_2$ system by Teyssandier and Ducarroir indicate that the difficulties to deposit single-phase WC films may be due to a narrow deposition window [9].

In this study it is proposed that the problems with the preferential formation of tungsten-rich phases as well as the difficulties to deposit single-phase WC films can partly be reduced by carrying out the deposition process at very low total pressures and with high linear gas flow velocities. This can be

demonstrated e.g. by using WF_6 , C_3H_8 and H_2 as precursors. WF_6 is a highly reactive molecule compared to C_3H_8 and the halide will therefore react in the gas inlet region under the formation of metallic W and/or tungsten-rich phases such as W_2C . This leads to a subsequent depletion of the halide from the gas phase downstream in the reactor. One possibility to reduce this problem is to increase the reactivity of the hydrocarbon (e.g. use an aromatic compound) and/or to use a cold-wall CVD reactor. However, an alternative approach is to reduce the deposition pressure and increase the linear gas flow velocity of the reactants. This will increase the mean free path in the vapour and reduce the residence time of the molecules in the hot zone. Thus it is conceivable that the low pressure conditions significantly can reduce the reactions in the gas inlet region and increase the WF_6 concentration downstream in the reactor, thereby favouring WC CVD in the deposition zone.

The aim of this study was to demonstrate that single phase WC films can be deposited at temperatures below 1000°C from a $\text{WF}_6/\text{C}_3\text{H}_8/\text{H}_2$ mixture at very low pressures (and high linear gas flow velocities). The influence of the substrate material on the deposition process was also studied by thermodynamic calculations as well as experimental studies on four different substrates (Ta, Si, SiC and C).

2 EXPERIMENTAL

The deposition experiments were carried out in a hot-wall CVD system designed for film growth at very low total pressures (see Fig. 1).

Figure 1: Schematics of the low-pressure CVD system

The system consists of an 80 cm long quartz reactor with an inner diameter of 25mm, pumped by a diffusion pump with a capacity of 2000 l/s. In order to minimize back diffusion of oil, a liquid nitrogen trap is placed between the reactor and the pump. The gaseous reactants are supplied by a gas handling system, pumped with a standard roughing pump. From the gas handling system, the gases can be fed into the reactor, either through mass flow meters, or via a gas mixing vessel. Deposition pressures ranging from 100-500 mTorr can be obtained by throttling a gate valve. The base pressure of the system is in the 10^{-7}

Torr range and leak rates of approximately $5 \cdot 10^{-8}$ Torr-l/s can be achieved (this corresponds to a contamination level of 0.5 ppm in a typical experiment). The temperature gradient throughout the reactor is less than 25 °C at deposition temperatures of 900 °C.

The gaseous reactants H_2 , C_3H_8 and WF_6 had a purity better than 99.9999%, 99.95% and 99.98%, respectively. Prior to deposition, the internal walls of the gas mixing vessel were passivated by backfilling with WF_6 . The desired gas mixture was obtained by filling the vessel with one gas at a time and measuring the pressure with a capacitance manometer. Most experiments were performed with a $p(C_3H_8)/p(WF_6)$ ratio of 19 and an $p(H_2)/p(C_3H_8+WF_6)$ ratio of 1. To reduce oxidation of the samples during heating and cooling of the reactor, a small hydrogen flow at a pressure of 25 mTorr was applied. Upon charging the reactor with samples, an argon flow through the reactor was used to reduce contamination from air. In most experiments, the substrates were placed perpendicularly to the gas flow. However, in the pressure experiments (section 3.1), the substrates were placed in parallel to the flow.

The substrates used in this study were Ta, Si, α -SiC and amorphous C. The polycrystalline Ta substrates were cut from commercially available cold-rolled foils with a claimed purity of 99.9% while the Si and SiC substrates were cut from wafers of single-crystalline Si(100) (B-doped, resistivity 6.8-7.2 Ω cm) and α -SiC(0001), respectively. The C substrates were prepared by depositing a thin continuous film of amorphous carbon on Si(100) by CVD. The details for the C CVD process have been presented elsewhere [10]. Prior to an experiment, the substrates were degreased and rinsed in methanol. The Si and SiC substrates were also etched in a 1:10 HF:H₂O solution to remove surface oxides.

The deposited WC films were characterised by X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRFS), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and atomic force microscopy (AFM). The amount of deposited W-atoms per cm² was measured by XRFS. Carbon and silicon have a negligible absorbance and the result from the XRFS analysis can therefore be converted into a film thickness, assuming that the film has an ideal density and uniform thickness. Phase identification with XRD was made with a Siemens D5000 powder diffractometer using $CuK\alpha$ radiation ($\lambda=1.5418\text{\AA}$) in a normal θ -2 θ arrangement. The topography was studied with a Topometrix TMX 1200 AFM. Finally, the surface composition of the deposited films as well as of the substrates was analysed by XPS, using a PHI 5500 multitechnique instrument.

3 RESULTS AND DISCUSSION

3.1 Influence of total pressure and linear gas flow velocity

As discussed above, WF_6 is a highly reactive molecule compared to most hydrocarbons. This difference may lead to a fast deposition of W (or W-rich carbides) and a subsequent depletion of WF_6 in the vapour when the reactants are transported through the CVD reactor. The depletion effect was investigated by depositing tungsten carbides at two different total pressures on a large number of Ta substrates, placed horizontally at equidistant positions in the reactor. It was found that the higher pressure (500 mTorr) and the lower gas flow velocity (2.7 m/s) yielded a high deposition rate of W-rich phases (β -WC_{1-x}, metallic W...) at the entrance of the reactor (Fig.2). The film deposited at the gas inlet consisted mainly of metallic W while simultaneous deposition of WC and β -WC_{1-x} was observed approximately 9 cm into the furnace.

The β -WC_{1-x} phase is a metastable carbide phase which is isostructural with TiC [11]. This phase is frequently obtained in PVD of tungsten carbide films (see e.g. ref. [1, 2]) but usually not in CVD. The deposition rate of the tungsten-containing films decreased strongly downstream in the reactor. No tungsten or tungsten containing deposit was observed at distances larger than 22 cm into the reactor.

Figure 2: Thickness profile of tungsten carbide films on Ta at a total pressure of a) 500 mTorr and b) 100 mTorr. Temperature in the centre of the reactor: 900 °C. Deposition time: 30 min. Vapour composition: 50% H₂, 47.5% C₃H₈ and 2.5% WF₆.

In contrast, the lower pressure (100 mTorr) and higher gas flow velocity (7.4 m/s) resulted in a much more uniform deposition profile (Fig. 2). The deposition rate of the W-rich phases was reduced and no traces of the β -WC_{1-x} phase were observed. In addition, a rather broad zone for the deposition of single-phase WC was obtained in the centre of the reactor. The results show the importance of a low total pressure and a high linear gas flow velocity in CVD of WC from C₃H₈/WF₆/H₂.

3. 2 Influence of substrate material on WC CVD

A series of preliminary low-pressure CVD experiments showed that the WC CVD process was strongly influenced by the substrate material. This effect was studied in a series of deposition experiments as well as by thermodynamic calculations for four different substrate materials (Ta, C, SiC and Si) which may be of interest for future applications. The thermodynamic calculations were carried out by using a free-energy minimization technique [12].

The thermodynamic calculations show that the Si substrate is highly reactive towards WF₆ at the high temperatures used in the deposition process (see Table I). This is in agreement with the behaviour observed in W CVD on Si substrates (see e.g. ref. [13]).

Table I. Summary of thermodynamic calculations and experimental results (deposition conditions: see Fig. 2).

Substrate	Thermodynamic calculations			Experimental results	
	Gaseous products	Solid products	Driving force $-\Delta G$ (kJ/mole)	Film composition	Film thickness (W atoms/cm ²)
Si	SiF ₃ , SiF ₂ , SiF ₄	WSi ₂ , SiC	350.7	WSi ₂ , W ₂ C, WC, β -WC _{1-x}	$2.51 \cdot 10^{18}$
SiC	SiF ₃ , SiF ₂ , SiF ₄ , HF	C, WC	255.2	WC, β -WC _{1-x}	$4.30 \cdot 10^{17}$
C	HF	WC	251.8	none	0
Ta	HF, TaF ₅ , H	Ta ₂ C, WC	533.0	WC	$6.14 \cdot 10^{17}$

The calculations suggest that Si should react with the reaction gas mixture under the formation of volatile silicon fluorides and solid WSi₂ and SiC. This reaction is substrate-driven with a rather high driving force ($-\Delta G = 350.7$ kJ/mole). The predicted reactivity of Si was confirmed in deposition experiments where severe substrate etching and deposition of a mixture of WSi₂, W₂C, WC and WC_{1-x} were obtained. The deposition rate was relatively high (approximately $4 \cdot 10^{16}$ W atoms /cm²·min). Moreover, the films exhibited a poor morphology and a poor adhesion. Consequently, Si must be considered as a highly unsuitable substrate material for the experimental conditions used in this study.

In contrast, thermodynamics suggest that carbon (graphite) should be completely inert towards the reaction gas mixture (see Table I). This means that only WC (or other tungsten carbide phases) should be deposited and that no substrate etching should occur. The experiments, however, showed that no tungsten-containing films could be deposited on amorphous carbon substrates. Furthermore, XPS analyses of the carbon substrates showed no signal from any tungsten-containing species on the surface. This suggests that some reaction step(s) in the CVD of tungsten carbides on carbon is strongly suppressed or inhibited. For this reason, we have carried out preliminary experiments in a UHV system to study the adsorption and surface reactions of WF₆ on different carbon substrates (for a description of the UHV system, see ref. [14]). The experiments show that the sticking coefficient for WF₆ adsorption on graphite and amorphous carbon is very low [15]. Hence, it is conceivable that the difficulties to deposit WC on amorphous carbon is due to a low adsorption rate of WF₆ on this substrate material. It is likely that carbide deposition could be obtained at higher deposition pressures where more reactive subhalides can easily be formed by homogeneous reactions in the vapour.

The thermodynamic calculations also show that SiC should be reactive towards the reaction gas mixture (see Table I). WF₆ can react with SiC under the formation of volatile silicon fluorides, solid WC and solid C. However, the driving force ($-\Delta G$) for this process is only slightly higher than for the homogeneous reaction (cf. the C and SiC substrates in Table I) indicating that SiC should be rather inert towards WF₆. The experimental results also confirmed that WC can be deposited on SiC together with small amounts of the cubic β -WC_{1-x} phase (see Fig. 3). The deposition rate on SiC was fairly low (approximately $7 \cdot 10^{15}$ W

atoms/cm²·min). Furthermore, the films were smooth and exhibited good adhesion to the substrate material (see Fig. 4).

Figure 3. X-ray diffractograms of a) a single-phase WC film deposited on Ta and b) WC/WC_{1-x} film deposited on SiC at 900°C. Deposition pressure: 100 mTorr. ■ Ta₂C, □ TaC, ● Ta.

Finally, the best film quality in this study was obtained with Ta as substrate material. However, the thermodynamic calculations show that Ta is also a highly reactive substrate. The most important substrate reaction is a reduction of WF₆ by Ta according to the reaction:

This reaction has recently been confirmed in UHV adsorption experiments by Högberg et al. [16]. Furthermore, Ta exhibits a strong affinity to carbon and easily forms TaC and/or Ta₂C in the presence of carbon-containing gases.

The experimental results showed that WC films could easily be deposited on Ta in a broad temperature and vapour composition range. At 900 °C, single-phase WC films were deposited with p(C₃H₈)/p(WF₆) ratios ranging from 10 to 39. Metallic W and/or W₂C could be obtained with p(C₃H₈)/p(WF₆) ratios below 10. No free carbon could be detected in the films by Raman spectroscopy or XRD. Moreover, the diffractograms confirmed that TaC and Ta₂C are formed during the deposition process. The film thicknesses were typically 2.5·10¹⁷-1.0·10¹⁸ W atoms/cm² after a deposition time of 60 minutes. This corresponds to a film thickness of about 500-2000 Å assuming ideal film density. Finally, it was found that the WC films deposited on Ta exhibited a smooth nodular morphology and a good adhesion (see Fig. 4).

Figure 4. AFM micrographs of WC/WC_{1-x} film deposited on SiC (left) and a single-phase WC film deposited on Ta at 900°C (right). Deposition pressure: 100 mTorr.

4 CONCLUDING REMARKS

Thin films of single-phase WC have been deposited in a hot-wall CVD reactor using very low pressures (100 mTorr) and high gas flow velocities. It was demonstrated that lower total pressures and higher gas flow velocities reduced the WF₆ depletion in the vapour, increased the carbon content in the films and increased the length of the WC deposition zone. Single phase WC films could easily be obtained on Ta substrates. The deposition rates of the WC films obtained in this study were rather low (max. 0.2 µm/h). However, no attempts have been made to optimize the deposition process with respect to deposition rate. It is likely that considerably higher deposition rates can be obtained by a careful tuning of the process.

The deposition rate and phase composition of the carbide films were strongly affected by the substrate material. The high deposition rate on Si was explained by the chemical reactivity of this substrate towards WF₆. This also resulted in a mixture of different phases including WSi₂. The fact that single phase WC films were obtained on Ta, while a phase mixture of WC and WC_{1-x} was deposited on SiC suggests that the WC_{1-x} phase is stabilized by Si. Moreover, no deposition was observed on clean carbon substrates. This was probably due to a low adsorption rate of WF₆ on carbon surfaces.

The results in this study clearly demonstrate that well-characterized WC films can be deposited on certain substrate materials. However, lower deposition temperatures and higher deposition rates are desirable for the deposition of e.g. wear-resistant coatings. It is likely that this can be accomplished with more reactive carbon precursors. Further investigations with unsaturated and aromatic carbon precursors will therefore be carried out in our laboratory.

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