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Chemical vapor deposition of hafnium carbide and hafnium nitride

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Abstract

The paper describes alternative high- temperature coatings for carbon fiber reinforced carbon (CFC) and carbon fiber reinforced silicon carbide (C/SiC) comparing CVD of hafnium carbide and hafnium nitride. Hafnium carbide and hafnium nitride layers were obtained in a thermally- stimulated CVD reactor by reaction of hafnium tetrachloride, methane and addition of hydrogen. Thermodynamic modeling of the reactions

shows the possibility of depositing a nearly carbon- free hafnium carbide layer, but HfN should be deposited at lower temperatures without any solid byproduct. These theoretical calculations could be proved experimentally in a thermally activated CVD process.

Introduction

CFC and C/SiC provide outstanding opportunities for future high temperature applications. Due to their instability in air at higher temperatures, they need protective coatings. Up to now, silicon dioxide is a widely used coating, despite its low melting point. Silicon carbide provides a far better protection, but reacts with its oxidation product silicon dioxide yielding the volatile monoxide. This reaction starts at approximately 1400°C and thus destroys the protective layer. Hafnium carbide and hafnium nitride exhibit extremely high melting points of 3887°C¹ and 3310°C², and no volatile monoxides are known. Thermogravimetric determination of the mass change of pure HfC and HfN powders (≈ 300 mesh) obtained from Johnson Matthey, Alfa Products, in oxygen (75 ccm/min.) at a heating rate of 10K/min show a about 200°C higher oxidation resistance for HfN than HfC, Fig. 1. Compared with SiC, the oxidation resistance of both compounds appears poor. Nevertheless, HfC is believed to

Fig. 1 Mass change of pure HfC and HfN- powders compared to SiC

be an interesting candidate as a part of high-temperature protective coatings for CFC and C/SiC-Composites³ due to the refractory, thermally insulating dioxide and the formation of an oxide interlayer $\text{HfO}_{2-x}\text{C}_Y$ ⁴.

Thermodynamic Calculations

Thermodynamic calculations based on minimization of the Gibbs free energies were performed with a PC program⁵ using the well-known Solgasmix- algorithms and a thermodynamic database⁶ as well as calculated⁷ and experimentally determined values⁸. Although hafnium monohalide is a well-known solid⁹, experimental results neglect its existence. This compound, different HfCl_{1-x} species as well as a possible Hf_2N phase were not taken into account.

Calculation results in the System HfCl_4 - CH_4 - H_2

Starting with equivalent concentrations of 1 mol HfCl_4 and CH_4 in the temperature range from 800 to 1200°C, a total pressure of 50 mbar and a surplus of hydrogen from 10 to 100 mol, calculations showed that HfCl_3 and carbon are always present. The HfCl_2 -content, which is not shown in the table, is neglectable small (<0,01 mol). Values are summarized in table 1 for a total pressure of 50 mbar.

	800 °C			1000°C			1200°C		
	$\text{H}_2 : \text{CH}_4$ - ratio			$\text{H}_2 : \text{CH}_4$ - ratio			$\text{H}_2 : \text{CH}_4$ - ratio		
	1:100	1:50	1:10	1:100	1:50	1:10	1:100	1:50	1:10
H_2	100,8	51,08	11,56	100,5	50,76	11,24	100,4	50,54	11,01
CH_4	0,12	0,07	0,02	0,02	0,01	< 0,01	< 0,01	< 0,01	< 0,01
HCl	1,99	1,54	0,79	2,87	2,43	1,5	3,29	2,92	1,98
HfCl_3	0,37	0,37	0,29	0,34	0,45	0,6	0,23	0,35	0,62
HfCl_4	0,22	0,34	0,58	0,02	0,05	0,18	< 0,01	0,01	0,04
C	0,48	0,63	0,86	0,35	0,49	0,77	0,23	0,36	0,66
HfC	0,4	0,29	0,12	0,63	0,49	0,23	0,76	0,64	0,34

Table 1 Calculated results in the system HfCl_4 - CH_4 - H_2 in mol, total pressure 50 mbar

1:100 leads to the conclusion that the deposition of carbon can be minimized by a HfCl_4 surplus ratio between 2,5 and 4,5. This effect is even more important at higher temperatures as shown in figure 2.

Figure 2 $\text{HfC}:\text{C}$ -ratio as a function of the $\text{HfCl}_4 : \text{CH}_4$ -ratio in the vapor phase

carbon are always present. The HfCl_2 -content, which is not shown in the table, is neglectable small (<0,01 mol). Values are summarized in table 1 for a total pressure of 50 mbar.

Varying the HfCl_4 to CH_4 ratio at different temperatures, a total pressure of 50 mbar and a HfCl_4 surplus ratio of hydrogen ratio of

It is mentioned¹⁰ that higher deposition rates should be obtained by means of in-situ chlorinating of metallic hafnium with a surplus of hydrogen, thus leading to the formation of hafnium subchlorides. Although it is true that the reaction of methane with hafnium subchlorides is less endothermic than with HfCl_4 ¹¹, their sublimation temperatures are quite higher¹². The exothermic

chlorination of hafnium thus leads to the readily volatile, white HfCl_4 , to distinguish from the intense colored hafnium subchlorides ¹³.

Calculation results in the System $\text{HfCl}_4\text{--N}_2\text{--H}_2$

Figure 3 Calculation results in the system $\text{HfCl}_4\text{--N}_2\text{--H}_2$. used values :
 Influence of temperature: $\text{HfCl}_4 : \text{N}_2 : \text{H}_2$ according 1:100:100, 50 mbar
 Influence of pressure: $\text{HfCl}_4 : \text{N}_2 : \text{H}_2$ according 1:100:100, 1000°C
 Influence of hydrogen surplus $\text{HfCl}_4 : \text{N}_2$ according 1:100, 1000°C, 50 mbar
 Influence of nitrogen surplus $\text{HfCl}_4 : \text{H}_2$ according 1:100, 1000°C, 50 mbar

In HfC- CVD, rising CH_4 - content lead to an increase of carbon deposition, whereas in HfN- CVD a surplus of nitrogen increases deposition of HfN. The reaction temperature reaches a shallow optimum and dependence of pressure is quite neglectable. According to these findings shown in figure 3, optimum deposition conditions are about 1000°C with high nitrogen and hydrogen ratio towards HfCl_4 , depending from experimental setup.

Experimental Section

Abb. 4 Apparatus

CVD layers were obtained in a thermally- stimulated CVD- equipment as shown in figure 4. As substrates, platelets made of glasslike (i. e. nonporous) carbon and quartz were used. Gases were obtained from Messer- Griebheim, Germany (H_2 5.0, CH_4 2.5, N_2 5.0) and purified further with Oxyorb cartridges (Cr^{2+} - complex and molecular sieve) from Messer- Griebheim). Gas mixtures were obtained by metering desired quantities

of each gas through calibrated mass flow meters (Bronkhorst Hi- Tec, The Netherlands). HfCl_4 from Johnson Mathew, GmbH Alfa Products was handled in an argon box and filled into the sublimator. The partial pressure of HfCl_4 was taken as the vapor pressure at the temperature of the sublimator ¹⁴.

Chemical Vapor Deposition of HfC and SNMS Analysis of HfC Layers

HfC- layers with a typical thickness of about $2,5 \mu\text{m}$ were prepared on platelets made of SiO_2 and glassy carbon. Depth- resolved distributions of the elements C, O, Si, Hf and as a possible contaminant chlorine were measured with Plasma- SNMS (Secondary Neutral Mass Spectrometry). Analysis was performed with the INA3- system (SPECS, Berlin, Germany). The sample surface is sputtered by ions of a low pressure Argon rf plasma with kinetic energies of 400 eV and a current density of 0.7 mA/cm^2 . A cooling system kept the temperature of the sample below 10°C . The emitted neutral surface atoms are ionized by plasma electrons, mass separated in a quadruple filter, and further detected by a secondary electron multiplier ¹⁵.

The atomic SNMS signals of the relevant elements have been recorded versus sputter time. With known erosion rates, these time profiles were converted into depth profiles. To prevent charging, the samples are covered by a tantalum grid (100 mesh, transmission 60%). Conversion of atomic intensities into relative concentrations was performed using detection factors obtained from measurements of pure HfC, HfO_2 and HfN. The powdered pure compounds were pressed into indium foil as carrier. An erosion rate of 1 nm/s was calculated taking into account the thickness of the HfC layers of about $2 \mu\text{m}$, obtained from SEM images of fracture edges, and the sputter time necessary to reach the interface between HfC and the substrate.

Due to several experimental problems with the highly hygroscopic HfCl_4 , the determination of kinetic parameters of HfCl_4 - CVD must still be continued. Up to now, experimental results confirm the above described thermodynamic calculations. However, SNMS analysis of deposited layers ¹⁶ clearly showed oxygen contamination in some layers, thus leading to deposition of hafnium dioxide.

As shown in figure 5, the ratio of carbon to hafnium concentration roughly agrees with the stoichiometry of HfC .

Figure 5 Element distribution obtained by SNMS-analysis of a sample prepared at 1060°C , $\text{HfCl}_4 : \text{CH}_4 : \text{H}_2$ according to 0,6:1:11 and 50 mbar

The concentration of carbon was determined to be at least 30% more than hafnium for a depth $> 1\mu\text{m}$. Near to the surface, the carbon concentration exceeds the HfC - stoichiometry more than in deeper regions. The extremely high C/Hf intensity ratios at the very surface (10 nm) are due to sputter relaxation phenomena. The interface region extends into both phases by $0.3\mu\text{m}$, probably due to interdiffusion. The depth resolution of the instrument under the given experimental conditions was checked to be much lower, namely 10 nm. Silicon and oxygen signals in the low depth region should not be explained as an incoherent HfC layer but as uncovered borders of the SiO_2 substrate. A nearly constant contamination of chlorine over the whole investigated area was found.

Chemical Vapor Deposition of HfN

Hafnium nitride could be deposited in the thermodynamically predicted region. Measurable deposition started at 700°C . In the temperature region from 700 to 900°C , a golden layer like the similar TiN was found. At higher temperatures, the layers grow more grayish. Deposition rates as a function of inverse temperature are shown in figure 6.

Figure 6 Arrhenius plot of $\ln(\text{layer growth rate})$ versus $1/\text{temperature}$ of HfN .
Experimental parameters : $\text{HfCl}_4 : \text{N}_2 : \text{H}_2$ according 1:100:100, 50 mbar, $\text{Re} \approx 1,5$

Summary

Thermodynamic calculations are useful in predicting optimal temperature and concentrations for CVD of HfC and HfN. SNMS as a new analysis tool in CVD was successfully employed in analyzing deposited thin film layers of hafnium carbide. The important carbon content in the HfC layers as well as chlorine contamination could be obtained as a function of the layer depth. HfN, a possible oxidation protective coating as an alternative to HfC, could be deposited according to the shown thermodynamic calculations at lower temperatures.

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