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# THE CHEMICAL VAPOR DEPOSITION OF ZIRCONIUM CARBIDE ONTO CERAMIC SUBSTRATES

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## ABSTRACT

Zirconium carbide is an attractive ceramic material due to its unique properties such as high melting point, good thermal conductivity, and chemical resistance. The controlled preparation of zirconium carbide films of superstoichiometric, stoichiometric, and substoichiometric compositions has been achieved utilizing zirconium tetrachloride and methane precursor gases in an atmospheric pressure high temperature chemical vapor deposition system. Laminar and equiaxial microcrystalline morphologies were obtained for superstoichiometric and substoichiometric zirconium carbide; respectively, allowing cursory metallographic identification of composition. Observed reductions in film density associated with zirconium carbide films that contain additional free carbon or excess zirconium are reported. These changes in film density were found to be consistent with compositional changes. An apparently linear relationship (correlation of 0.99) between methane flow in this chemical vapor deposition system and zirconium carbide stoichiometry in the substoichiometric range deposited above  $ZrC_{0.61}$  has been observed.

## INTRODUCTION

Substoichiometric zirconium carbide continues to be an attractive material for a wide number of applications [1-3]. Substoichiometric zirconium carbide has a very high melting point ( $3540^{\circ}C$ ), good thermal conductivity, and is resistant to chemical attack. Unfortunately, the deposition of zirconium carbide continues to be difficult due to the low vapor pressure of zirconium tetrachloride [4], the hazards associated with generating zirconium tetrachloride *in-situ*, and the lack of alternative precursors which yield substoichiometric zirconium carbide [5]. In this paper, a summary of efforts to understand and control deposition of substoichiometric, stoichiometric, and superstoichiometric zirconium carbide from zirconium tetrachloride and methane gaseous precursors and a discussion of how physical properties such as morphology, and density, change with zirconium carbide stoichiometry are presented.

## EXPERIMENTAL

Pure zirconium tetrachloride, ( $ZrCl_4$ , Strem 99.6%), methane ( $CH_4$ , Matheson 99.99%), hydrogen ( $H_2$ , Baker, 99.999%), and argon (Ar, Baker 99.999%), were used in the deposition of zirconium carbide. Sodium hydroxide (Aldrich -50% solution in water) was used for titration/destruction of byproducts produced in the zirconium carbide deposition. The films were deposited on  $ZrO_2$  based materials.

The depositions were performed in the atmospheric pressure high temperature chemical vapor deposition (HTCVD) system shown in Figure 1. The main features of this HTCVD system are the gas delivery system, the resistively heated  $ZrO_2$  based substrate, the inert atmosphere chamber, and the exhaust/titration system. Controlled heating of the substrate using feedback from a type C thermocouple was achieved electronically with a

Barber-Coleman digital temperature controller and a custom-built power supply. The gas delivery system separately feeds hydrogen/methane and zirconium tetrachloride/argon flows to the hot substrate. MKS mass flow controllers were used to control the flows of all gases. After zirconium carbide deposition onto the hot substrate, reaction byproducts are feed into an exhaust system for titration and/or decomposition by bubbling the exhaust gas through a sodium hydroxide aqueous solution. A natural gas burn-off is used to combust excess

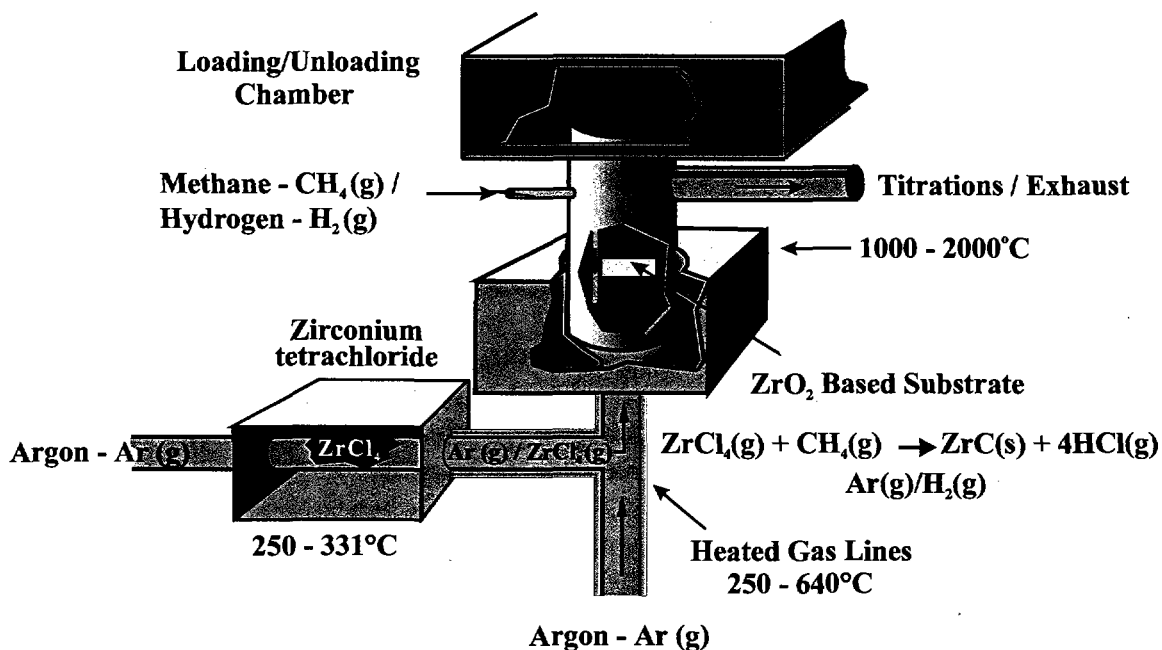


Figure 1. Atmospheric Pressure High Temperature Chemical Vapor Deposition System.

hydrogen and methane. Once the substrate is cooled back to room temperature, it was removed from the chamber via the inert atmosphere chamber for further analysis. Heating of the zirconium tetrachloride was necessary in order to generate sufficient flow of zirconium tetrachloride into the argon gas flowing through the vaporizer. Heated gas lines were used to maintain the zirconium tetrachloride vapor stream and prevent clogging of the gas lines via zirconium tetrachloride condensation.

Analysis of the zirconium carbide films involved film thickness determination, morphology, density, chlorine content, and stoichiometry. Scanning Electron Microscopy (SEM) samples were prepared by cross sectioning the samples and mounting them onto double-sided carbon tape. Samples were then analyzed on a R.J. Lee Personal SEM at 15keV. Density determinations were completed using mercury porosimetry (Stem Penetrometer Aminco #JS-7113). Chlorine content was determined by dissolving in water and titrating using mercury nitrate and bromophenol blue.

The film stoichiometry was determined using three different methods. In the first method, a comparison was made between the sample X-ray lattice parameter and both literature and standards lattice parameters. The diffraction data used to determine the zirconium carbide lattice parameter were obtained using a Scintag PAD-V x-ray diffractometer by measuring the intensity of diffracted copper  $K\alpha$  radiation over a range of  $5^\circ \leq 2\theta \leq 148^\circ$  in steps of  $0.03^\circ$  at a rate of 15 steps/minute.

The second method used to determine film stoichiometry was Auger Electron Spectroscopy (AES). The AES data was collected on a Physical Electronics 595 spectrometer using 10 kV electrons and a 4 kV argon ion beam for sputtering. Relative sensitivity factors were determined from  $ZrC_{0.83}$  and  $ZrC_{0.97}$  zirconium carbide standards provided by Aptech, Inc.

The third method used to determine film stoichiometry involved the direct determination of carbon content by measuring weight percent of carbon in the film using a LECO<sup>®</sup> IR-412 carbon determinator.

## RESULTS AND DISCUSSION

Zirconium carbide films (10 – 39  $\mu\text{m}$ ) of superstoichiometric, stoichiometric and substoichiometric composition were deposited onto a number of zirconium oxide based ceramic materials at a rate of 1.98 – 4.43  $\mu\text{m/hr}$  in a atmospheric pressure high temperature chemical vapor deposition system. Results from nine representative zirconium carbide deposition runs, which resulted in the fabrication of superstoichiometric to substoichiometric zirconium carbide films, are provided in Table 1.

Table I. Experimental data for the deposition of zirconium carbide films from zirconium tetrachloride ( $ZrCl_4$ ) and methane ( $CH_4$ ) precursor gases.

Item	Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Film 7	Film 8	Film 9
Deposition Temperature [°C]	1600	1600	1700	1700	1700	1700	1600	1600	1600
$ZrCl_4$ Source Temperature [°C]	288	280	290	300	300	300	300	300	300
$ZrCl_4$ Carrier Gas Flow [Ar - slpm]	0.094	0.064	0.120	0.125	0.125	0.125	0.125	0.125	0.125
$CH_4$ Flow [slpm]	0.201	0.250	0.020	0.010	0.0008	0.008	0.0072	0.008	0.0078
Film Thickness [ $\mu\text{m}$ ]	39.07	24.50	17.58	10.12	8.96	14.38	18.58	15.11	36.80
Deposition Rate [ $\mu\text{m/hr}$ ]	3.10	4.43	2.30	3.36	1.98	3.23	2.99	2.16	2.95
Chlorine [ppm]	219	70	Not Obtained	56	29	20	Not Obtained	Not Obtained	20
Film Density [ $\text{g/cm}^3$ ]	3.7	3.3	6.2	6.6	6.0	6.7	6.6	6.7	6.6
XRD Lattice Parameter [ $\text{\AA}$ ]	Not Obtained	4.70074	Not Obtained	Not Obtained	4.69695	4.69861	Not Obtained	Not Obtained	4.69967
C/Zr Ratio	$ZrC_{1.0}$ 1.10 C	$ZrC_{1.0}$ 3.90 C	$ZrC_{1.0}$ 0.14 C	$ZrC_{1.0}$ 0.06 C	$ZrC_{1.0}$ 0.79 Zr	$ZrC_{0.92}$	$ZrC_{0.61}$	$ZrC_{0.92}$	$ZrC_{0.84}$
C/Zr Ratio Method	AES	AES	AES	AES	LECO	LECO	LECO	LECO	LECO

The superstoichiometric (above  $ZrC_{1.0}$ ) and substoichiometric (below  $ZrC_{0.61}$ ) zirconium carbide films (Films 1, 2, 3, and 5) having compositions in the two-phase field have significantly lower density than expected. This is consistent with the film composition analysis results which reveal the presence of free carbon (Films 1, 2, and 3) and free zirconium (Film 5), respectively. Alternatively, films (Films 4, 6, 7, 8, 9) having compositions in the single phase field have a uniform high density very close to the density of zirconium carbide.

An analysis of films 7, 8, and 9 revealed an apparently linear relationship between methane flow and stoichiometry for substoichiometric zirconium carbide (Figure 2) provided a constant zirconium tetrachloride temperature and carrier flow is maintained. This very good correlation shows that the system delivers a uniform amount of zirconium tetrachloride to the substrate and that a controlled stoichiometry may be achieved for zirconium carbide depositions.

Morphology differences between superstoichiometric and substoichiometric zirconium carbide are best reflected in Figure 3 (Film 2) and Figure 4 (Film 9) where superstoichiometric zirconium carbide has a lamellar structure whereas the substoichiometric zirconium carbide film has an equiaxial microcrystalline structure with no indication of lamination. In addition, it was noted that higher deposition temperatures (Film 4 – Not shown) resulted in significant grain growth within the layer.

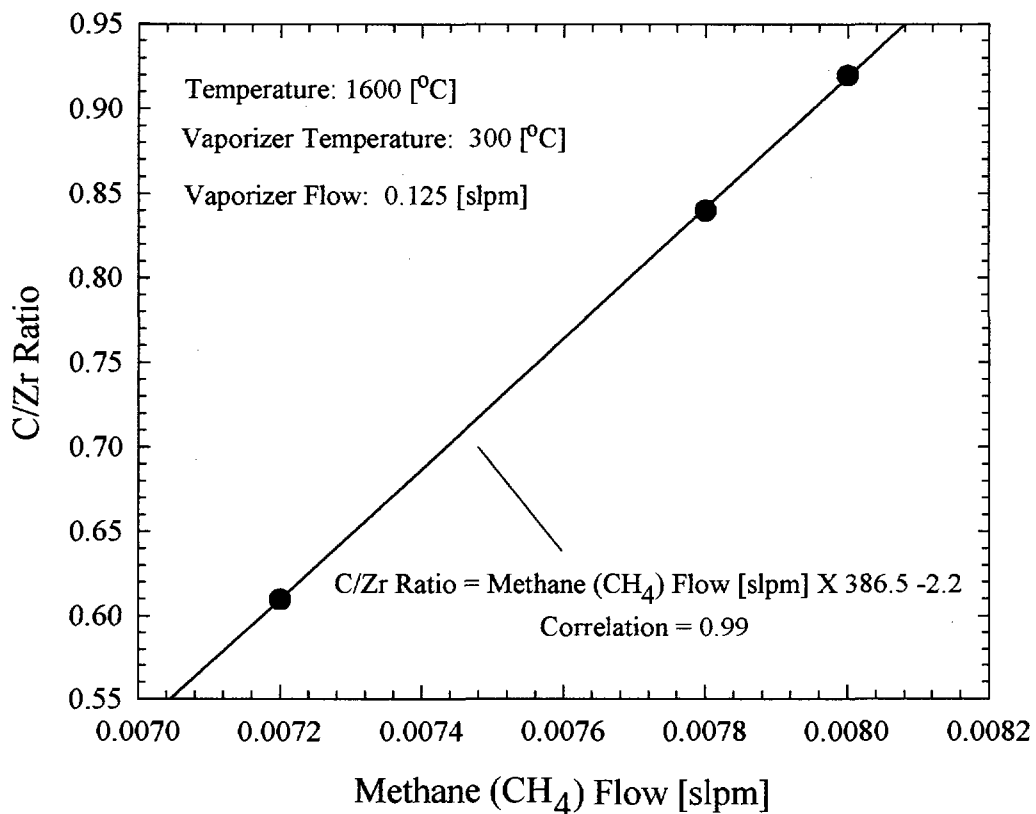
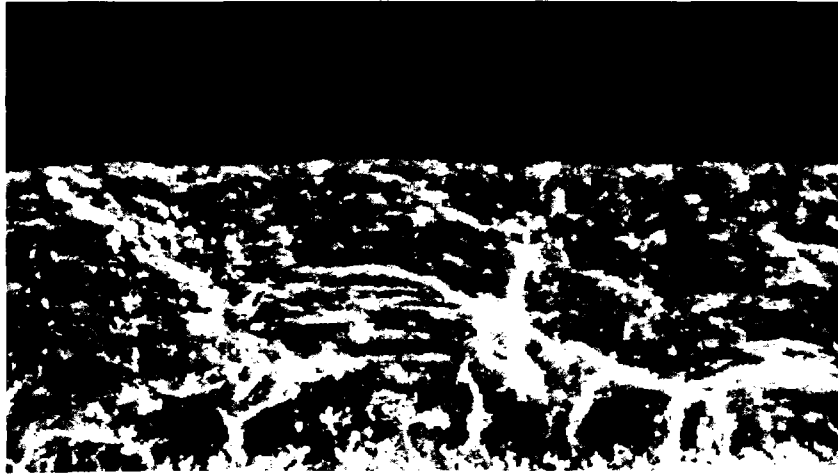
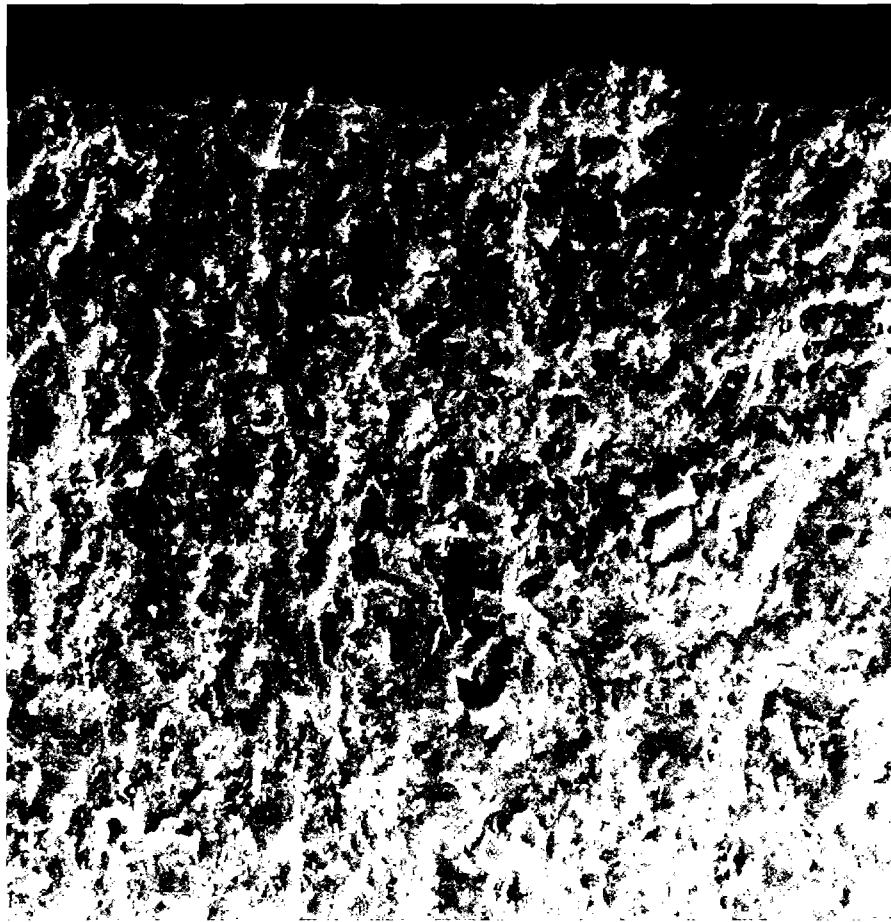


Figure 2. Plot of C/Zr Ratio (LECO Determined) and Methane Flow for substoichiometric zirconium carbide depositions (Films 7, 8, 9)



10  $\mu$

Figure 3. Cross-Section of  $\text{ZrC}_{1.0} + 3.9 \text{ C}$  (Superstoichiometric) Zirconium Carbide Film.



5  $\mu$

Figure 4. Cross-Section of  $\text{ZrC}_{0.84}$  (Substoichiometric) Zirconium Carbide Film.



## CONCLUSIONS

The following has been observed when depositing zirconium carbide films using zirconium tetrachloride and methane gaseous precursors:

1. Zirconium tetrachloride vapor flow control can be achieved with careful design of the chemical vapor deposition system. Specifically, it is important to control temperature, surface area, and carrier flow of the vaporizer to provide constant and controllable zirconium tetrachloride delivery.
2. Deposition of superstoichiometric, stoichiometric, and substoichiometric zirconium carbide may be obtained by control of methane flow at constant zirconium tetrachloride flow conditions.
3. Film density correlates with stoichiometry, particularly for highly superstoichiometric (excess carbon) films.
4. An apparently linear relationship between the C/Zr ratio and the methane flow rate for substoichiometric zirconium carbide and a constant zirconium tetrachloride flow rate has been observed.
5. Superstoichiometric and substoichiometric zirconium carbide exhibit distinct morphological differences.

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