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Thermodynamic calculation for the chemical vapor deposition of silicon carbonitride

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Abstract

In order to tailor the phase composition of silicon carbonitride (SiCN) by chemical vapor deposition or chemical vapor infiltration (CVD/CVI), it is necessary to set up a series of phase diagrams at a larger temperature range from 800 K to 1800 K using $SiCl_4$, NH_3, CH_4/C_3H_6 and H_2 as precursors. The equilibrium conditions of thermodynamic calculation were determined by temperatures, total pressures, dilute gas H_2 and molar ratios of reactants. CVD phase diagrams provide a qualitative description of phase composition, while the deposition efficiencies directly give the conversion extent from precursors to condensed phases. The low temperature phases (Si_3N_4, C) and high temperature phase (SiC) are also proved by thermodynamic calculation of CVD SiCN, which gives a clear way to conduct the experiments.

Keywords: Thermodynamic calculation; Chemical vapor deposition; SiCN ceramic; Phase diagram; Theoretical deposition efficiency

1. Introduction

Silicon carbonitride (SiCN) ceramic is a promising material with adjustable composition and excellent properties such as attractive mechanical properties, superior microwave absorption performance and good erosion resistances.[1–4] Therefore, many works have focused on SiCN ceramic preparation for various applications.[5] At present, the common preparation methods are CVD, PIP and sintering, but the strict parameters for CVD SiCN films, and poor density of PIP and sintering methods limit their applications. Therefore, it is desire to obtain a kind of dense and homogeneous SiCN substrates. Thermodynamic calculation helps one understand the influence factors and deposition mechanism of CVD process, and get the desired preparation methods of SiCN ceramics.

Before setting up a CVD process, it is particularly useful to characterize the system by using a suitable computer program to calculate the equilibrium of gaseous species, liquids and condensed phases.[7,8] Most of thermodynamic calculations have focused on PIP SiCN ceramics utilizing polymer precursors.[9,10] However, thermodynamic calculations of CVD SiCN ceramics using $SiCl_4/NH_3/CH_4/H_2$ and $SiCl_4/NH_3/C_3H_6/H_2$ initial gases have focused on SiC–Si_3N_4 co-deposition,[6,11] and only a few temperatures and dilution ratios of $H_2/SiCl_4$ have been studied by using CVD phase diagrams.

Until now, experiments are mainly on CVD SiCN films, which were prepared at low temperature and atmosphere.[12,13] Kouakou et al.[14] studied the role of silicon on the growth of SiCN film by using N_2/CH_4 gas mixture. Swain et al.[15] showed that H_2 had an important influence on the structure and the forming of chemical bonding in SiCN film. It is obvious that the crucial conditions for CVD SiCN films are the deposition temperature, total pressure and molar ratio of the gas mixture. In order to obtain CVD SiCN ceramics with the expected phase composition and content, it is urgent to study both CVD phase diagrams and

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Table 1
The overall reactions in Si-C-N-H-Cl system.

Chemical reaction equations
(1)$3SiCl_4(l) + 4NH_3(g) \rightleftharpoons Si_3N_4(s) + 12HCl(g)$
(2)$SiCl_4(l) + CH_4(g) \rightleftharpoons SiC(s) + 4HCl(g)$
(3)$3SiCl_4(l) + C_3H_6(g) + 3H_2(g) \rightleftharpoons 3SiC(s) + 12HCl(g)$
(4)$CH_4(g) \rightarrow [C] + H_2(g) \rightleftharpoons C(s) + 2H_2(g)$
(5)$C_3H_6(g) \rightarrow [C] + H_2(g) \rightleftharpoons 3\,C(s) + 3H_2(g)$
(6)$SiCl_4(g) \rightarrow [SiClx] + [Cl] \rightleftharpoons Si(s) + 2Cl_2(g)$

theoretical deposition efficiencies of condensed phases. Here, the deposition efficiency is more objective and straightforward for the experimental design.

In the present work, thermodynamic calculation of SiCN using Si-C-N-H-Cl system includes CVD phase diagrams as well as deposition efficiency diagrams, which is based on deep understanding of the relations among CVD parameters, thermochemistry properties of components, gas diffusion and mass transport theory.[16,17] The purpose is to get the deposition mechanism of CVD process and preparation conditions of CVD SiCN substrate.

2. Method of calculation

Thermodynamic calculation is performed by using FactSage (Thermfact/CRCT and GTT-Technologies, Montreal, Canada and Herzogenrath, Germany). The input of the program requires atomic composition of the species, concentration of the initial species, the total pressure and temperature. The distribution of equilibrium species and their concentrations are based on the Gibbs free energy minimum principle. It was assumed that the reactions among the gas species come to a rapid equilibrium, forming molecules which represent the most stable distribution. This would be also suitable for metastable conditions where only the gas phase exists before deposition as well as for the more stable multiphase situations.[18] The thermochemical data like standard enthalpy and standard entropy as a function of temperature was consist with the value of JANAF which has been reviewed.[19–22] Hence, the overall chemical reactions and the possible products in Si-C-N-H-Cl system are listed in Tables 1 and 2, respectively, which are the basic principle of CVD process and are used to deduce the CVD mechanism.

Generally, the results are presented as CVD phase diagrams and deposition efficiencies diagrams as a function of temperatures and the molar ratios of input gases. The molar ratios of reactants are defined as $\delta = [CH_4]_0/[CH_4 + NH_3]_0$ (or $\delta = [C_3H_6]_0/[C_3H_6 + NH_3]_0$), $\gamma = [SiCl_4]_0/[CH_4 + NH_3]_0$ (or $\gamma = [SiCl_4]_0/[C_3H_6 + NH_3]_0$), here the amount of $CH_4 + NH_3$ (or $C_3H_6 + NH_3$) is fixed. The values of γ, the system pressure, and the concentration of dilute gas are variable in Si-C-N-H-Cl system. Because of interest in the atmospheric pressure CVD and lower pressure CVD (LPCVD), a wide range of total pressures was studied. Argon used as dilution gas is presented in constant abundance to the rest of the input gases.

Table 2
Species considered in Si-C-N-H-Cl system.

			Equilibrium gas phases			
H_2	HCl	$SiCl_4$	SiH_2Cl_2	$SiHCl_3$	$SiCl_3$	$SiCl_2$
SiH_3Cl	$SiCH_3Cl_3$	SiCl	CH_4	HCN	CH_3Cl	C_2H_2
C_2H_4	CH_3Cl	C_2H_6	CH_2Cl	ClCN	CH_3	NH_3
H	Cl	N_2	NH_2	Cl_2	SiH_4	SiH
Si	Si_2	Si_2N	Si_2C	SiC_2	SiN	
			Equilibrium condensed phases			
SiC	Si_3N_4	C				

3. Experimental

The SiCN ceramic was prepared by CVD on the porous Si_3N_4 ceramic. Porous Si_3N_4 ceramics with porosity of 42% and density of 1.9 g/cm^3 were used as precursors. The fabrication detail of porous Si_3N_4 ceramic was given elsewhere.[24] The porous Si_3N_4 ceramic was machined into specimens and then ultrasonically cleaned in ethanol absolute and dried in air. The specimens were made available for CVD reactor to deposit SiCN ceramic from silicon tetrachloride ($SiCl_4 \geq 99.99$ wt.%), ammonia ($NH_3 \geq 99.99\%$) propylene ($C_3H_6 \geq 99.99\%$) and methane ($CH_4 \geq 99.99\%$). $SiCl_4$ was carried into the reaction chamber by bubbling hydrogen ($H_2 \geq 99.999\%$) gas. Argon ($Ar \geq 99.9\%$) was used as dilution gas to keep the total pressure. A typical processing parameter was chose according to the thermodynamic diagram, in which T=1273 K, $\gamma = 1.5$, $\delta = 0.6$ and the dilution ratio of 10 for 7 h at 0.01 atm were used for ternary co-deposition ceramics. Morphology of CVD SiCN ceramic was examined by SEM (S-4700, Hitachi, Tokyo, Japan). The element of the local area in the SiCN ceramic was analyzed by EDS (Genesis XM2, EDAX, USA). The as-prepared SiCN–Si_3N_4 ceramics were then annealed at 1773 K in N_2 for 2 h. Phase distribution was identified by TEM (G-20, FEI-Tecnai, Hillsboro, USA) and phase crystallization analysis were conducted by XRD (X'Pert Pro, Philips, Netherlands).

4. Results and discussions

4.1. The CVD phase diagrams in the Si-C-N-H-Cl system with various γ

The previous experiments and thermodynamic calculations[6,11,14] show that the concentration of $SiCl_4$ in the system has an important influence on the deposition of both SiC and Si_3N_4, since Si atom is the main component of SiCN ceramics.

CVD phase diagrams of the Si-C-N-H-Cl system at 0.01 atm with variable γ are shown in Figs. 1 and 2. A small Si + SiC co-deposition region appears at higher temperature, when insufficient $SiCl_4$ is added to the system. Fischman et al. and Kingon et al.[18–23] studied the phase diagrams of SiC, in which C + SiC phase is deposited with excessive carbon amount, while Si + SiC phase is deposited with abundant silicon content. This seems to be inconsistent with the phase diagrams in this paper, because the phase compositions in this paper are more complicated, and the maximum deposition temperature of all the phases regions decreases with the increase of γ. Thermodynamic calculations of