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Thermodynamic calculations and kinetic verifications on the chemical vapor deposition process of Si–C–N ceramic from the $SiCl_3CH_3$–NH_3–H_2–Ar precursors

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Received 30 May 2014; received in revised form 21 July 2014; accepted 22 July 2014

Abstract

Based on the Gibbs principle of minimum free energy and Factsage software, the thermodynamic phase diagram and three-dimensional yield map were firstly calculated from the $SiCl_3CH_3$–NH_3–H_2–Ar system. The effects of temperature, total pressure, reactant ratios of $3[NH_3]/[SiCl_3CH_3]$ and $[H_2]/[SiCl_3CH_3]$ on the formation and yield of condensed phases were discussed. Predominant condensed phases at equilibrium were SiC, Si_3N_4 and graphite phases. The concentration of condensed phase products was used to confirm the composition of Si–C–N. Through the kinetic verification at 1173.15 K, it could be demonstrated that Si–C–N ceramics are obtained by chemical vapor deposition from the $SiCl_3CH_3$–NH_3–H_2–Ar system. The deposits were amorphous and mainly constituted by C–C, Si–N and Si–C bonds from XPS analysis, which were well consistent with the results of thermodynamic calculation. The real part and the imaginary part of permittivity were approximately 4 and 0, respectively, which indicated the amorphous deposits possess the low dielectric constant and loss.

Keywords; Dielectric properties; Thermodynamic calculation; Experimental verifications; Chemical vapor deposition; Si-C-N ceramic

1. Introduction

In recent years, materials absorbing electromagnetic wave (EMW) have attracted worldwide attention as a result of the development of radar-absorbing technology [1]. Silicon carbide (SiC) ceramic is a good selection to fabricate EMW absorption materials because of its wide band gap and practical applications in severe environments. However, it has been demonstrated that the low electrical conductivity of pure SiC results in low dielectric loss [2], such as SiC powders [3], SiC foams [4], and SiC matrix composites [5]. In our previous work [6], porous Si_3N_4–SiC composite ceramics with 11 vol% SiC was fabricated, which achieved a minimum reflection loss of -6.7 dB at 12.2 GHz. Nonetheless, the dielectric properties of CVI SiC also need to be improved.

Changing the conductivity of SiC by doping is an effective way to improve its dielectric properties [7]. It was reported that doping of SiC with N (p-type) or B (p-type) or mental (Ti, Ni and Al) had better microwave dielectric loss in the X-band than that obtained pure SiC [8–12]. Silicon carbonitride (Si–C–N) ceramic is a promising material [13] for its attractive properties, such as corrosion resistance, high temperature oxidation resistance, hardness and wide band gap [14–16]. Besides, the electronic band gap of 3.8 eV indicates the wide band-gap dielectric of this material [17]. Si–C–N ceramics or Si–B–C–N ceramics fabricated by polymer derived ceramics (PDCs) had shown good EMW absorbing properties after high-temperature treatment [10,18,19]. However, such a high heat-treatment temperature could influence the application of PDCs-Si(B)CN in CMC considering the performance degradation of fibers and other reinforcing phases at higher temperatures. Simultaneously, main focus of Si–C–N ceramic made by CVD is on the thin films, and it is necessary to develop this high performance Si–C–N matrix.

Low-pressure chemical vapor deposition/infiltration (LPCVD/CVI) plays an important role in preparing the composites [20–22]. As widely accepted, $SiCl_3CH_3$–H_2–Ar is the general precursor system to produce SiC matrix. Therefore, it is

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http://dx.doi.org/10.1016/j.ceramint.2014.07.110

Please cite this article as: Y. Liu, et al., Thermodynamic calculations and kinetic verifications on the chemical vapor deposition process of Si–C–N ceramic from the $SiCl_3CH_3$–NH_3–H_2–Ar precursors, Ceramics International (2014), http://dx.doi.org/10.1016/j.ceramint.2014.07.110

necessary to confirm whether the suitable dielectric properties could be obtained after N being introduced into SiC matrix. Thus the $SiCl_3CH_3$–NH_3–H_2–Ar system was explored. Though the thermodynamic and dynamics of $SiCl_4$–NH_3–C_3H_6–H_2–Ar [23] system and $SiCl_4$–NH_3–CH_4–H_2–Ar [24] system had been studied, three effective precursors makes the process of deposition more complicated than two effective precursors of this system. Nevertheless, the process of LPCVD is very complicated, so thermodynamic calculation of Si–C–N ceramic to direct the kinetic experiment is necessary. Since thermodynamic calculation can not only provide information about the influencing factors of the system, but also help to predict the extent of reaction and understand the influence of reaction parameters on the CVD process. From the analysis of the thermodynamic calculation, the optimization of deposition parameters could be well studied. Currently, the researches about the thermodynamic calculation and kinetic experiment of $SiCl_3CH_3$–NH_3–H_2–Ar system are still scarce.

In this paper, the thermodynamic phase diagram and three-dimensional yield map of the CVD process from $SiCl_3CH_3$–NH_3–H_2–Ar system were calculated within wide ranges of process parameters. The proper parameters were determined. Meanwhile, the principles and mechanisms of the effect of process parameters were discussed. Finally, the dielectric properties of Si–C–N ceramics were tested using Si–C–N/Si_3N_4 composite ceramics.

2. Calculation method

The calculation method is based on the Gibbs principle of minimum free energy. First of all, the initial conditions are confirmed, such as system temperature and system total pressure. The temperature range in this work was from 973.15 K to 1473.15 K; the system total pressure was 0.01 atm.; the moles of $SiCl_3CH_3$ was 3; define $\alpha=[H_2]/[SiCl_3CH_3]$, $\beta=3[NH_3]/[SiCl_3CH_3]$, ([X] stands for original molar quantity of material X) and α ranges from 5 to 20, while β ranges from 0 to 45. Secondly, all of the thermodynamic calculation data is from the data base of Factsage software.

The thermodynamic phase diagram and three-dimensional yield map were drawn using the Factsage calculation results which determined the relationship between reaction parameters and condensed product.

3. Results and discussion

3.1. Effect of temperature on the thermodynamic phase diagram and reaction product

Fig. 1 shows the thermodynamic phase diagram with different temperatures from 973.15 K to 1473.15 K. The detailed discussions are as follows:

For C+Si_3N_4, the double phase field of C+Si_3N_4 appears from 973.15 K to 1173.15 K and this area decreases with the rising temperature because of the increasing of SiC phase and the decreasing of Si_3N_4 phase. Above 1273.15 K, there is no C+Si_3N_4 double phase filed.

For SiC+C+Si_3N_4, the three phase field of SiC+C+Si_3N_4 also appears from 973.15 K to 1173.15 K and its proportion increases firstly and then remains almost the same because of the increasing of SiC and the decreasing of Si_3N_4 at higher temperature. Above 1273.15 K, the three phase field of SiC+C+Si_3N_4 disappeared.

For SiC+Si_3N_4, the double phase field of SiC+Si_3N_4 only appears at 1273.15 K. Higher temperature hinders the generation of Si_3N_4 and the phase of C disappears at specific condition.

For C+SiC, the double phase field of C+SiC appears from 1173.15 K to 1473.15 K and this area increases dramatically and then decreases slightly with the rising temperature. The maximum value obtains at 1273.15 K.

For SiC, the single phase field of SiC appears from 1273.15 K to 1473.15 K and the area increases with the rising temperature. This system is appropriate for the deposition of SiC, and the product is carbon-rich SiC or SiC above 1373.15 K.

The position and proportion of the phase field differ with that of $3[NH_3]/[SiCl_3CH_3]$ slightly when the temperature changes, because lower temperature makes for the generation of Si_3N_4. Also it was demonstrated that Si_3N_4 does not emerge and the deposition product is SiC or carbon-rich SiC above 1373.15 K.

The effect of $[H_2]/[SiCl_3CH_3]$ is tremendous, where the proportion of SiC phase increases and C phase decreases with the increase of $[H_2]/[SiCl_3CH_3]$.

Fig. 2 shows the three-dimensional yield map of C–SiC–Si_3N_4 from 973.15 K to 1473.15 K. Fig. 2a–c shows that moles of condensed phases of C and Si_3N_4 present a rising trend while the phase of SiC was opposite trend under 1173.15 K. When the molar ratio of $3[NH_3]/[SiCl_3CH_3]$ is big enough, the condensed phases are C and Si_3N_4 under 1273.15 K and the saturation concentration of $3[NH_3]/[SiCl_3CH_3]$ increases with the increasing temperature. As shown in Fig. 2d–f shows the main condensed phases are SiC and there is also a small amount of C phase above 1273.15 K. This consequence is not fit for the phase diagram if taking into consideration of Si_3N_4 phase in 1273.15 K. This is because of the appearance of Si_3N_4 when $3[NH_3]/[SiCl_3CH_3]$ reaches 30 and its yield too low to be ignored. High molar ratio of $[H_2]/[SiCl_3CH_3]$ is in favor of the generation of SiC and goes against the production of C and Si_3N_4. Molar ratio of $[H_2]/[SiCl_3CH_3]$ has no effect on the yield map of SiC and C above 1273.15 K, while temperature plays a key role in both the formation and product yield of C–SiC–Si_3N_4.

In conclusion, Si–C–N with different molar ratio of SiC, Si_3N_4 and C could be obtained by changing the parameter of precursor ratio under 1173.15 K.

3.2. Effect of total pressure on the thermodynamic phase diagram and reaction product at 1173.15 K

The thermodynamic phase diagram and three-dimensional yield map of C–SiC–Si_3N_4 at 1173.15 K with total pressure of 0.05 atm and 0.1 atm are shown in Figs. 3 and 4. There are

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