Study on thermodynamics and kinetics of chemical vapor deposition of silicon nitride

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Abstract

The thermodynamics and kinetics methods had been applied to study the effects of the deposition temperature, the reaction gas ratio and the dilution gas on Si3N4 formation in the SiCl4-NH3-H2 system. The studies revealed that raising the deposition temperature would accelerate the chemical reaction and increase Si3N4 yield below 1400 K, higher temperature prompted the side reactions. With the increase of NH3 concentration, the content of Si3N4 in the reaction products also increased. As the diluent gas, H2 could accelerate the reaction and the deposition of Si3N4. However, the excess dilution gas would carry away the reaction gas and inhibit the reaction. The comprehensive effect of temperature and gas ratio on Si3N4 deposition were also analyzed by the three-dimensional figures. Finally, the optimal conditions for Si3N4 preparation were suggested.

1. Introduction

As an important ceramic material, silicon nitride (Si3N4) is widely used in industrial and defense fields due to its excellent high temperature strength and creep resistance, good wear resistance and corrosion resistance properties, and high specific modulus (modulus of elasticity/density) [1–3]. Si3N4 can be used as the high temperature structure materials in the engine, transmission device and other high temperature fields to replace nickel, chromium and other resource-poor metal materials [4, 5]. At the same time, Si3N4 is also the main candidate material for high-temperature wave-absorbing and wave-passing materials, cutting tools, wear-resistant parts and semiconductor MOS circuit [6, 7]. Therefore, the research about Si3N4 has always been the research focus for scholars in the last few decades and on and on.

At present, the preparation processes of Si3N4 mainly refer to the hot-press sintering, pressure-free sintering, reactive sintering, chemical vapor deposition, physical vapor deposition, and so on [8–10]. During those preparation processes, chemical vapor deposition (CVD) is the main process for preparing silicon nitride thin films and Si3N4-based matrix composite materials [11]. In chemical vapor deposition, solid phase products form on the substrate through chemical reactions with gas phase as the precursor. Because of involving the decomposition of gas, the transformation from gaseous state to solid state and so on, the CVD process is extremely complex [12]. There are many reactants and accompanying chemical reactions in CVD process, as well as the changes in the concentration and the composition of substances. In preparation of Si3N4 by CVD, the gaseous precursors containing Si and N elements (such as NH3, SiCl4, SiHCl3, SiH2Cl2, SiH4, etc.) are introduced into the deposition furnace. Those gaseous precursors decompose and react with each other under high temperature. Then the solid products deposit on the substrate to obtain Si3N4. At present, the main gaseous precursor systems for chemical vapor deposition of silicon nitride are SiCl4-NH3 [13, 14], SiH4-NH3 [15], SiH2Cl2-NH3 [16], SiHCl2-NH3 [17], SiHCl3-NH3 [18]. Some scholars also have studied the other gaseous precursor systems according to the application requirements, such as SiH2[NHC(CH3)3]-NH3 [19],

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(C₂H₅)₃SiH₂-NH₃ [20], C₂H₆Cl₂Si [21]. In all the gaseous precursor systems, SiCl₄-NH₃ system is one of the widely used. Currently, the study on SiCl₄-NH₃ system mainly focuses on the characterization of deposition process, product microstructure and properties. The thermodynamics and dynamics involved in the deposition process are rarely studied. By analysis the thermodynamic of CVD process, the main material and key process parameters controlling the reaction could be identified, which could guide the actual preparation process and improve the preparation efficient.

In this paper, FactSage software was applied to study the thermodynamics and kinetics of SiCl₄-NH₃ system. The influences of deposition temperatures, partial pressure of gas, and dilution gas species on reaction products and deposition rate were also discussed. Finally, the optimal process parameters for depositing Si₃N₄ were suggested.

2. Thermodynamics and kinetics calculation method

In an equilibrium system, the chemical reactions follow minimizing the total chemical potential Gibbs free energy of the system. The gas compositions and gas concentration at the given conditions could be obtained according to the chemical equilibrium principle. In this paper, the chemical reactions of SiCl₄-NH₃-H₂ system were studied according to Gibbs free energy minimum principle by using the thermodynamical data of more than 15,000 kinds of inorganic substances and the multi-phase equilibrium formula. Based on the system equilibrium, the generated phases in the system were obtained by analysis the thermodynamical parameters of each phase in the system. The influences of process parameters such as deposition temperature, NH₃/SiCl₄ ratio and dilution gas species on the equilibrium gas and solid phase compositions during the vapor deposition process were also studied.

3. Results and discussion

3.1. Phase selection

Within the temperature range studied (600–2000 K), SiCl₄-NH₃-H₂ system would generate more than 40 substances. In those substances, the amount of some is very small in the whole temperature range, and the molar content of some changed little in the deposition process (such as H₂, HCl). Therefore, the effects of the two kinds substances on the deposition process and the result were limited, and they could be ignored in the successive thermodynamic analysis. In the subsequent discussion, the following main products were selected: SiCl₄, SiCl₃, SiCl₂, SiHCl₃, Si₃N₄, NH₃, and then the reaction thermodynamics of the system was calculated.

3.2. The effect of temperature on the equilibrium system

In this study, Si₃N₄ was prepared by using SiCl₄-NH₃ system through CVD method. The chemical reaction was as follows:

\[3\text{SiCl}_4 + 4\text{NH}_3 = \text{Si}_3\text{N}_4 + 12\text{HCl}\]

The Gibbs free energy (ΔG) and the reaction rate (K) of the chemical reaction at different temperatures were calculated, as shown in figure 1. As the deposition temperature rising, ΔG decreased and K increased. The opposite change in these two parameters indicated that increasing the deposition temperature was beneficial to the Si₃N₄ formation. With the increasing deposition temperatures, the motion rate and motion frequency of molecules and atoms were enhanced in the deposition process. On the one hand, those changes in the motion of substance particles accelerated the decomposition of gaseous precursors. On the other hand, the collision frequency between the new substance particles raised, which was helpful for the formation of new substances. In addition, it could also be seen from the figure that ΔG was less than 0 when the deposition temperature was higher than 500 K. In other words, the chemical reaction occurred spontaneously as the temperature was greater than 500 K from the thermodynamic point of view. However, the reaction rate of the chemical reaction also should be considered. In generally, raising the temperature would accelerate the chemical reactions.

When the gaseous precursors were introduced into the deposition furnace, they decomposed firstly, involving the following reactions.

\[\text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl} \]  \hspace{1cm} (2)
\[\text{SiCl}_4 \rightarrow \text{SiCl}_2 + 2\text{Cl} \]  \hspace{1cm} (3)
\[\text{SiCl}_4 \rightarrow \text{SiCl} + 3\text{Cl} \]  \hspace{1cm} (4)
\[\text{NH}_3 \rightarrow \text{NH}_2 + \text{H} \]  \hspace{1cm} (5)
\[\text{NH}_3 \rightarrow \text{NH} + 2\text{H} \]  \hspace{1cm} (6)
Figures 2 and 3 present the changes of $\Delta G$ and $K$ in the decomposition process of SiCl$_4$ and NH$_3$ with the deposition temperatures. From the chemical reaction (2) to (4) and (5) to (6), $\Delta G$ increased and $K$ decreased at the same temperature. The differences in $\Delta G$ and $K$ of the decomposition reactions indicated that the formation process of decomposition products from SiCl$_3$ to SiCl and from NH$_2$ to NH became difficult. The differences in decomposition changed the gas components and the gas ratio in the reaction system. Increasing the deposition temperature would narrow the gap in $\Delta G$ and $K$, and promoted all the chemical reactions.

As an important factor in the chemical reaction, the deposition temperature affected not only the chemical reactions, but also the product yield. The molar yield of the main substances in the equilibrium composition with temperature was calculated under the given conditions (SiCl$_4$: NH$_3$: H$_2$: Ar = 30: 60: 20: 100,
P = 0.1 MPa), as shown in figure 4. As can be seen from the figure, the molar yield of most substances in the system had a great relationship with the deposition temperatures.

Theoretically, when the deposition temperature was in the range of 1000–2000 K, the deposition reaction of Si$_3$N$_4$ was an endothermic reaction. Therefore, increasing the deposition temperature was conducive to the development of chemical vapor deposition. However, the deposition rate of Si$_3$N$_4$ in the SiCl$_4$-NH$_3$-H$_2$ system was not increased linearly with the deposition temperature as shown in the figure. When the deposition temperature was below 1300 K, the product yield of Si$_3$N$_4$ gradually increased with the increasing deposition temperature and reached the maximum value at about 1400 K. Further increasing the deposition temperature, the product yield of Si$_3$N$_4$ decreased rapidly. Those seemingly abnormal changes happened in the system mainly due to the competing reactions in CVD process. There were two kinds of chemical reactions in CVD process, one kind was the reaction between SiCl$_4$ and NH$_3$ forming Si$_3$N$_4$, and the other one was the thermal decomposition reaction of reactant molecules (SiCl$_4$, NH$_3$). Those two kinds of reactions competed and influenced each other. When the deposition temperature was below 1300 K, the deposition reaction between SiCl$_4$ and NH$_3$ forming Si$_3$N$_4$ was the main reaction. Therefore, $\Delta G$ of the reaction decreased and the reaction rate $K$ increased as the temperature increasing, which improved the yield of Si$_3$N$_4$. However, as the deposition temperature increasing, the decomposition rate of the main reactants (SiCl$_4$, NH$_3$) accelerated. On the one hand, the decomposition of the gas precursor consumed the effective gas contents involved in the formation of Si$_3$N$_4$, resulting in the reduction of Si$_3$N$_4$ production. On the other hand, the by-products formed by the decomposition of the reactants would cause the increase of side reactions, generating more by-products such as SiCl$_{10}$, SiH$_4$, Cl$_2$, SiH, Si and Si$_2$. Those side reactions consumed the sources of Si and N elements and inhibited the Si$_3$N$_4$ formation, which reduced the deposition amount of Si$_3$N$_4$. In addition, the activity of the reaction gas enhanced with the increasing deposition temperatures, which improved the probability of homogeneous gas reaction. Solid powder generated in the gas and was taken away by the constantly flowing stream, reducing the deposition probability of Si$_3$N$_4$ on the matrix. Therefore, increasing temperature was beneficial to the production of Si$_3$N$_4$ according to the thermodynamics. Nevertheless, considering other by-products and side reactions in the system, the deposition rate of presented not linear relationship with the temperatures. In the actual deposition process, in order to obtain a high deposition rate and ensure the chemical composition of products, the reaction temperatures of the system were set in the range of 1200–1400 K.

3.3. Effect of reactant concentrations on the equilibrium compositions

In the chemical reactions, the relative content of reactants, in other words, the partial pressure of reaction gas in the system had great influence on the types and formation rates of the products. In CVD process, the reaction gases were in a state of continuous flow. The gas flow state was different from the equilibrium state of the general chemical reaction under the relatively static state. The flowing of the gas reactants made it difficult to analyze the reaction equilibrium. However, the reaction gas could also be considered in a relatively static state under the condition of infinitesimal time, so the analysis of phase diagram was still useful for guiding the CVD process.

The influence of the reaction gas ratio $R = \text{NH}_3/(\text{NH}_3 + \text{SiCl}_4)$ on the products at 0.1 MPa, 300 K–2000 K was illustrated in figure 5. With the increasing $R$ (the increasing NH$_3$ concentration), the boundary temperatures between the solid phase and the gas phase of Si$_3$N$_4$ were promoted, expanding the generation area of silicon nitride. Those changes in the phase diagram meant that the increasing in NH$_3$ concentration was conducive to
the Si$_3$N$_4$ deposition. It could also be seen in the phase diagram that Si$_3$N$_4$ solid phase formed when the deposition temperatures at about 600 K. As mentioned before, $\Delta G$ at 600 K was less than zero, which meant that the reactions of generating Si$_3$N$_4$ could occur spontaneously. In the actual reaction process, in order to get faster deposition rate, the temperature was generally adjusted in 1200–1400 K.

In order to study the influence of the reaction gas ratio $R$ on the molar yield of Si$_3$N$_4$, the flow rate of SiCl$_4$ was set at 30 ml min$^{-1}$ and the pressure was 0.1 MPa, the $R$ was changed by adjusting the flow rate of NH$_3$. The molar yield changes of Si$_3$N$_4$ with the reaction gas ratio of $R = \text{NH}_3/(\text{NH}_3 + \text{SiCl}_4)$ were calculated at 1000 K, 1200 K and 1400 K respectively, as shown in figure 6. As seen in the figure, the molar yield of Si$_3$N$_4$ increased almost linearly with $R$. The small values of $R$ meant the low partial pressure of NH$_3$ and the high partial pressure of SiCl$_4$ in the reaction system. In this case, the chemical reaction rate in the system was controlled by the concentration of NH$_3$. As the partial pressure of NH$_3$ increasing (the increase of $R$ in figure 6), the chemical reaction controlled by the NH$_3$ increased and improved the deposition rate of Si$_3$N$_4$. When the value of $R$ increased to a certain extent, the partial pressure of NH$_3$ in the system was high enough. The reaction rate in turn was controlled by the concentration of SiCl$_4$ because of the fixed flow rate of SiCl$_4$. The deposition rate of Si$_3$N$_4$ didn’t increase continually with the value of $R$. Moreover, the collision probability between SiCl$_4$, NH$_3$ and other reactants particles in the reaction system increased with the increase concentration of NH$_3$, which reduced the probability of solid phase products adhering to the matrix surface and resulted in the decrease in the mole yield of Si$_3$N$_4$. Under the same proportion of reaction gas, the mole yield of Si$_3$N$_4$ changed little as the deposition temperature raising from 1000 K to 1200 K. As the deposition temperature further raised to 1400 K, the probability of adverse reactions in the gas phase increased, which inhibited the formation of Si$_3$N$_4$ and decreased the mole yield of Si$_3$N$_4$.
3.4. The effect of dilution gas on the main products

In CVD process, the diluted gases didn’t participate in the chemical reaction process directly, but they could affect the chemical reaction process by adjusting the collision and the partial pressure of the gas in the reaction system. For the given concentration of the reaction gas (SiCl₄:NH₃ = 30:60), the yield of Si₃N₄ at the different temperatures was plotted in figure 7. Obviously, H₂ and Ar promoted the deposition reaction compared to N₂ at the same temperatures and gas pressure.

For further understanding the influence of dilution gas on the products, the molar yield of several main products at T = 1100 K, P = 0.1 MPa and different dilution gas ratios was listed in table 1. As seen in the table, the molar amount of the chief gas compounds containing Si element (such as SiCl₄, SiHCl₃, SiCl₃, SiCl₂) decreased with the increase of H₂ content in the diluted gas system. However, the content of the solid product Si₃N₄ increased. The totally different trend in the products was mainly relationship with the molecular weight of the diluted gas. At the same temperature and pressure, the diluted gas of Ar and H₂ had the same kinetic energy. Since the molecular weight of H₂ was smaller than that of Ar, the motion speed of H₂ was higher, which increased the collision between the reaction gas molecules. Therefore, the increasing content of H₂ promoted the chemical reaction and benefited the formation of Si₃N₄.

Figure 8 showed the mole yield of Si₃N₄ with H₂ content. As seen in the figure, the production of Si₃N₄ increased almost linearly with H₂ content in the diluted gas. In the low-pressure chemical vapor deposition process, more than 60% of the raw materials entering the deposition chamber were taken away by diluted gas and didn’t take part in the actual reactions. The introduction of diluted gas would reduce the loss of the reaction gas and increase the retention time of reaction gas in the deposition area. According to le chatellet’s principle, those changes in the reaction gas would promote the chemical reaction to the forward reaction and increase the deposition rate of solid phase products. However, the introduction of diluted gas reduced the concentration of reaction gas in the system and was of no advantage to the reactions, which was in contradiction to the results in figure 8. There were two main factors contributing to this contradiction result. The one factor was that the introduction of H₂ into the gas system would reduce the concentration of reaction gas and inhibit the homogeneous gas reaction. At the same time, those changes in the gas system accelerated the homogeneous gas-solid reaction and increased the deposition rate of Si₃N₄. Further increasing the H₂ flow, the concentration of the reaction gas decreased rapidly and the deposition of the solid phase decreased. The second factor was that increasing H₂ concentration would reduce the total pressure of the reaction system. Since the total reaction was a

Figure 7. The effect of the dilution gas type on the mole yield of Si₃N₄. N₂-black line; Ar-blue line; H₂-red line.

| Table 1. The influence of dilution gas ratio on the molar yield of main products. |
|---------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| 100H₂ + 200Ar                  | 150H₂ + 150Ar                | 200H₂ + 100Ar                | 250H₂ + 50Ar                  | 300H₂ + 0Ar                   |
| Si₃N₄                         | 8.3112                       | 8.7591                       | 9.0540                       | 9.2365                       | 9.4005                       |
| SiCl₄                         | 0.89993E-2                   | 0.64007E-2                   | 0.47275E-2                   | 0.36033E-2                   | 0.28202E-2                   |
| SiCl₃                         | 0.90418E-3                   | 0.70851E-3                   | 0.56910E-3                   | 0.46695E-3                   | 0.39022E-3                   |
| SiCl₂                         | 0.79711E-3                   | 0.68813E-3                   | 0.60111E-3                   | 0.53094E-3                   | 0.47375E-3                   |
| SiHCl₃                        | 0.33862E-3                   | 0.30706E-3                   | 0.27663E-3                   | 0.24941E-3                   | 0.22573E-3                   |
| SiH₂Cl₂                       | 0.16689E-5                   | 0.19293E-5                   | 0.21202E-5                   | 0.22611E-5                   | 0.23664E-5                   |
volume increase reaction, reducing the total pressure in system would promote the reaction and increased the conversion rate of the material. Therefore, the use of H₂ as a dilution gas was conducive to the deposition of Si₃N₄.

3.5. The comprehensive effect of temperature and gas ratio on Si₃N₄ deposition
As the previous analysis, the deposition temperature and the reaction gas ratio both had important influence on the reaction process. However, the two-dimensional figure was difficult to present the comprehensive influence of these two factors on the reaction. Therefore, the three-dimensional figure had been established to explain the comprehensive effect. Figure 9 illustrated the changes of SiCl₄ concentration with the deposition temperature and the reaction gas ratio. As seen from the figure, the concentration of SiCl₄ in the system decreased with the increasing deposition temperature. As the initial concentration of SiCl₄ increased in the system, the decrease trend of SiCl₄ became more significant. It also could be seen in the figure that when the deposition temperature was higher than 1000 K, the concentration of SiCl₄ drops rapidly, indicating that the reaction starts rapidly from 1000 K. As the deposition temperature continued to rise, SiCl₄ was rapidly consumed. At about 1300 K, almost
all SiCl$_4$ in the reaction system had been consumed. Figure 10 shown the variation of Si$_3$N$_4$ mole yield with the deposition temperatures and the reaction gas ratio. As seen in the figure, the mole yield of Si$_3$N$_4$ increased firstly and then decreased with the deposition temperature in the whole changes of the reaction gas ratio. The mole yield of Si$_3$N$_4$ reached the maximum value near $R = 0.4$–0.5 and 1300 K.

4. Conclusion

In this paper, the influences of deposition temperature, reaction gas ratio and dilution gas on Si$_3$N$_4$ formation in the SiCl$_4$-NH$_3$-H$_2$ system had been studied through the thermodynamic method. The deposition temperature had great influence on Si$_3$N$_4$ deposition. As the temperature increases, the Si$_3$N$_4$ output increased firstly and reached the maximum at about 1300 K. Later, due to the accelerated decomposition of reaction gas and side reaction, Si and N sources are consumed, resulting in the decrease in the Si$_3$N$_4$ output. Increasing the NH$_3$ concentration was beneficial to the Si$_3$N$_4$ formation and increased the mole yield in the reaction system. When the reaction gas ratio $R$ was higher than 0.5, the collision probability between SiCl$_4$ and NH$_3$ raised, and the yield of Si$_3$N$_4$ did not continue to increase significantly with the NH$_3$ concentration. Compared with Ar and N$_2$, H$_2$ could promote the reaction due to its small molecular weight and high molecular movement speed. With the increase of H$_2$ content in the reaction system, the production of Si$_3$N$_4$ will increase. When the amount of diluted gas was too large, the accelerated flow of the gas will take away the reaction substance, inhibit the reaction, and reduce the production of Si$_3$N$_4$. Comprehensive considering the influence of the deposition temperature, the reaction gas ratio, and the diluted gas, the optimal conditions for Si$_3$N$_4$ preparation in SiCl$_4$-NH$_3$-H$_2$ system were $R = 0.4$–0.5, 1300 K and H$_2$ serviced as the diluted gas.

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References

[1] Krstic Z and Krstic V D 2012 Silicon nitride: the engineering material of the future J. Mater. Sci. 47 533–52
[2] Wang L et al 2019 High tough W-added silicon nitride ceramics Ceram. Int. 45 19055–9
[3] I.R.F 2000 Silicon nitride and related materials J. Am. Ceram. Soc. 2 245–65
[4] Iyas K et al 2020 Characterization of a silicon nitride ceramic material for ceramic springs J. Eur. Ceram. Soc. 40 3541–54
[5] Inagaki Y, Kondo N and Ohji T 2002 High performance porous silicon nitrides J. Eur. Ceram. Soc. 22 2499–94
[6] Wu C, Chang C and Duh J 2016 Silicon nitride coated silicon thin film on three dimensions current collector for lithium ion battery anode J. Power Sources 325 64–70
[7] Li Y et al 2019 Enhanced thermal conductivity in Si₃N₄ ceramic by addition of a small amount of carbon J. Eur. Ceram. Soc. 39 157–64
[8] Qin X et al 2020 Silicon nitride ceramics consolidated by oscillatory pressure sintering Ceram. Int. 46 14235–40
[9] Suchaneck G, Norkus V and Gerlach G 2001 Low-temperature PECVD-deposited silicon nitride thin films for sensor applications Surf. & Coatings Technology 142-144 (none) 808–12
[10] Yuan B et al 2009 Silicon nitride/boron nitride ceramic composites fabricated by reactive pressureless sintering Ceram. Int. 35 2155–9
[11] Liao C et al 2019 Deposition temperature and heat treatment on silicon nitride coating deposited by LPCVD Journal of Inorganic Materials 34 1231–7
[12] Allendorf M D and Melius C F 1998 Understanding gas-phase reactions in the thermal CVD of hard coatings using computational methods Surf. Coat. Technol. 108-109 191–9
[13] Liu Y L et al 2007 Fabrication and characterization of SiO₂/Si₃N₄ composites Journal of University of Science & Technology Beijing Mineral Metallurgy Material 14 454–9
[14] Ren H et al 2015 Thermodynamic study on the chemical vapor deposition of silicon nitride from the SiCl₄-NH₃-H₂ system Computational and Theoretical Chemistry 1051 93–103
[15] Britta L et al 1996 Chemical vapour deposition of silicon nitride filaments from silicon subhydrides and ammonia J. Eur. Ceram. Soc. 16 15–23
[16] Olson J M 2002 Analysis of LPCVD process conditions for the deposition of low stress silicon nitride. Part I: preliminary LPCVD experiments Mater. Sci. Semicond. Process. 5 51–60
[17] Kenjirou W and Shouji W 1982 Electric conduction in nitrogen-rich silicon nitride films produced by SiH₄Cl₂ and NH₃ J. Appl. Phys. 53 568–75
[18] Liu X J et al 2004 Growth and properties of silicon nitride films prepared by low pressure chemical vapor deposition using trichlorosilane and ammonia Thin Solid Films 460 72–7
[19] J G et al 2004 Characterization of low-temperature silicon nitride LPCVD from Bis(tertiary-butylamino)silane and ammonia J. Electrochem. Soc. 5 G353–9
[20] Grow J M et al 1995 Growth kinetics and characterization of low pressure chemically vapor deposited Si₃N₄ films from (C₃H₇)₂SiH₂ and NH₃ Mater. Lett. 23 187–93
[21] Patil L S et al 2005 Effect of deposition temperature on the chemical properties of thermally deposited silicon nitride films Opt. Mater. 27 663–70